Twisted Donor-Acceptor Fluorescent Molecular Rotors and Conjugates for Sensing, Photocatalytic and Electroluminescence Applications

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Dedications

Dedicated to my beloved parents and brother

Declaration

The work presented in this thesis has been carried out by me under the guidance of Dr. Sanchita Sengupta at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgment of collaborative research and discussions. This thesis is a bona fide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's thesis work, I certify that the above statements by the candidate are true to the best of my knowledge.

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Never stop dreaming, never stop believing, never give up, never stop trying, and never stop learning - Roy Bennett

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List of abbreviations

A	Acceptor
ACN	Acetonitrile
ACQ	Aggregate-caused quenching
AI	Aminoindole
AIE	Aggregate induced emission
BDT	Benzodithiophene
BET	Back electron transfer
BODIPY	4,4-difluoro-4-bora-3a,4a-diaza-s-indacene
CBZ	Carbazole
CHCl ₃	Chloroform
CV	Cyclic voltammetry
D	Donor
DAPI	4',6-diamidino-2-phenylindole
DCM	Dichloromethane
DE	Delayed emission
DFT	Density functional theory
DI	10,15-Dihydro-5H-diindolocarbazaole
DMF	N,N-Dimethylformamide
DMSO	Dimethyl sulfoxide
EAS	Evolution-associated spectra
EET	Excited energy transfer
EIL	Electron injecting layer
EML	Emissive layer
EQE	External quantum efficiency
ESA	Excited state absorption
ETE	Energy transfer efficiency
ETL	Electron transporting layer
FLIM	Fluorescence lifetime imaging

FMO	Frontier molecular orbital
FMR	Fluorescent molecular rotors
FRET	Förster resonance energy transfer
FWHM	Full width half maxima
HIL	Hole injecting layer
НОМО	Highest occupied molecular orbital
HRMS	High resolution mass spectrometry
HTL	Hole transporting layer
IC	Internal conversion
ICT	Intramolecular charge transfer
IQ	Indoloquinoxaline
IQE	Internal quantum efficiency
IRF	Instrument response factor
ISC	Inter-system crossing
ITO	Indium tin oxide
LE	local emission
LUMO	Lowest unoccupied molecular orbital
МСН	Methylcyclohexane
MTT	(3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide)
NBS	N-bromosuccinimide
NIR	Near infrared
NMP	N-methyl-2-pyrrolidone
NP	4-bromo-1,8-naphthalic anhydride
OLEDs	Organic light-emitting diodes
OPVs	Organic photovoltaics
PC	Photocatalyst
PEnT	Photoinduced energy transfer
PET	Photoinduced electron transfer
PF	Prompt fluorescence
PI	Phenanthroimidazole

PLICT	Planarized intramolecular charge transfer
PLQY	Photoluminescence quantum yield
RISC	Reverse intersystem crossing
RIR	Restricted intramolecular rotation
SET	Single electron transfer
SOCT	Spin orbit charge transfer
TADF	Thermally activated delayed fluorescence
TAS	Transient absorption spectroscopy
TBAF	Tetra-n-butylammonium fluoride
TBAHFP	Tetrabutylammonium hexafluorophosphate
TCSPC	Time-correlated single photon counting
TEA	Triethylamine
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
TFA	Trifluoroacetic acid
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TICT	Twisted intramolecular charge transfer
TLC	Thin layer chromatography
TMS	Trimethyl silane
Tol	Toluene
TRPL	Time resolved photoluminescence
TTA	Triplet-triplet annihilation

Abstract

Twisted organic donor-acceptor (D-A) fluorescent molecular rotors (FMRs) are of great importance because of their photophysical properties that are tunable by variations in solvent polarity, temperature, viscosity, and pH. Accordingly, FMRs have found extensive applications as probes for sensing, bio-imaging, as well as in organic electronics and photocatalysis. In cellular microenvironment, an abnormality in viscosity, temperature and pH can lead to cellular malfunctions and various diseases. Fluorescent molecular rotors exhibit twisted intramolecular charge transfer (TICT) process resulting in multi-stimuli responsive dual emission and serve as efficient ratiometric sensors to detect the abnormalities in cellular microenvironment. Another class of twisted D-A molecules are characterized by their small singlet-triplet energy gaps that facilitate reverse intersystem crossing (RISC). Such molecules as a result of RISC can exhibit long-lived delayed fluorescence (DF) components and show thermally activated delayed fluorescence (TADF) process. Accordingly, TADF conjugates have found profound utilization as emitters in electroluminescence applications such as in organic light-emitting diodes (OLEDs). Owing to their long-lived DF components and suitable excited state redox potentials, TADF conjugates serve as photocatalysts for various organic transformations.

This thesis intends to address the design, synthesis, and investigation of photophysical properties of twisted organic (1) D-A FMRs with TICT properties, and (2) D-A conjugates with TADF properties, and their utilization for sensing, bio-imaging, photocatalysis and OLEDs. The first chapter describes the design and synthesis of TICT-based three D- π -A rotors based on BODIPY and benzodithiophene chromophores utilized for ratiometric temperature sensing and viscosity sensing. Furthermore, the triplet states of regioisomeric BODIPYs and a triad rotor are populated via spin-orbit coupling ISC and CT-mediated ISC respectively as delineated by steady state and transient absorption spectroscopy. Accordingly, these rotors showed high singlet oxygen quantum yields and could catalyze the aerobic photooxidation of thioanisole to methyl phenyl sulfoxide with 99% selectivity. The second chapter discusses the synthesis of three D-A rotors functionalized with aminoindole and naphthalimide and their utilization for pH sensing and live cell imaging of A549 (lung cancer) and L929 (fibroblast) cell lines, thereby differentiating healthy and diseased cells using these rotors. In the third and fourth chapters, diindolocarbazole-based D-A conjugates with TADF properties are designed and synthesized for photocatalytic organic transformations and OLED applications. The photocatalytic transformations include energy transfer mediated isomerization of E-stilbene to Z-stilbene with up to 90% conversion and electron transfer mediated C-H arylation of heteroarenes with up to 86% yield. The thesis concludes with the major findings of all chapters and future perspectives of twisted D-A TICT rotors and TADF conjugates towards development of multifunctional sensors, imaging probes and broadening their scope as organic photocatalysts.

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Introduction

1.1. Features of Donor-Acceptor Chromophores

Donor-acceptor (D-A) molecules are an important class of organic conjugated systems where D and A are separated by a π -spacer. The interaction between D and A and the occurrence of intramolecular charge transfer (ICT) between them leads to the formation of new low-energy molecular orbitals and a charge transfer state. The optical, electronic and electrochemical properties of D-A systems can be tuned easily by adjusting the electron donating ability of D and electron accepting ability of A chromophores and/or by varying their spacer type and length.¹⁻⁴ In other words, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) levels and singlet-triplet energy (ΔE_{ST}) levels in D-A systems are adjustable to achieve the desired properties that are required for specific applications. Therefore, these D-A systems are advantageous over single molecules. For example, the impact of D-A system on photophysical properties can be demonstrated by the UV/Vis absorption spectra of aniline, nitrobenzene and 4-nitroaniline. Since, 4-nitroaniline is a D-A system, it shows an intense bathochromically shifted absorption band at ~ 350 nm while aniline and nitroaniline absorb in lower UV region around ~ 250 nm.³

Generally, polyaromatic organic chromophores without heavy atoms or atoms that can enhance intersystem crossing (ISC) upon photoexcitation have an electron promoted to a higher singlet excited state (S_1 or S_2 or S_n) and after internal conversion (IC) reach the lowest singlet excited state (S_1), eventually emits to the ground state (fluorescence) along with the dissipation of heat or energy. The rate of fluorescence in such molecules is significantly faster than the rate of ISC and there is also a wide energy gap between the singlet state and the triplet state (ΔE_{ST}).⁵ Therefore, the possibility of populating the triplet state is very less in such organic dyes (Figure 1.1 a). However, in case of D-A chromophores, due to the formation of ICT state, the energy gap between CT state and triplet state decreases and hence, the possibility of populating the triplet state increases. This triplet state can be populated through various photophysical processes such as radical pair ISC, or spin-orbit charge transfer (SOCT)-ISC^{6,7} (which will be discussed in photocatalysis part vide infra) that allows the emission from triplet state called phosphorescence. Therefore, D-A systems could be utilized as a photosensitizer or as photoredox catalysts based on their triplet energy levels and long-lived triplet states as well as suitable redox potentials (Figure 1.1b).⁸ When the ΔE_{ST} gap in twisted D-A molecules slightly decreases (< 0.1 eV), the possibility of reverse intersystem crossing (RISC) is also increased which is responsible for molecules to emit from singlet state called delayed fluorescence along with prompt fluorescence. This overall process is called thermally activated delayed fluorescence (TADF) (Figure 1.1c).^{9,10} Due to TADF process, these systems are efficiently utilized in organic light-emitting diodes (OLEDs) and in photocatalysis.^{5,11–13} Another class of D-A compounds where the π -spacer present between the D and A in D-A systems can cause the rotation across the spacer are known as the fluorescent molecular rotor (FMR).^{14,15} Such FMRs are extremely sensitive to minor changes in their surroundings such as viscosity, temperature, solvent polarity and pH.^{15–17} Thus, D-A molecules have advantages over single chromophores and can be utilized in various applications such as sensing, photocatalysis, solar cell, OLEDs, bio-imaging and non-linear optical materials.^{18,19}



Figure 1.1. Jablonski diagram of (a) polyaromatic organic chromophore; D-A chromophore with possibility of (b) ISC and (c) RISC. S = singlet state; T = triplet state; F = fluorescence; ISC = intersystem crossing; ΔE_{ST} = singlet-triplet energy gap; LE state = local excited state; ICT = intramolecular charge transfer; TICT = twisted intramolecular charge transfer; P = phosphorescence; PF = prompt fluorescence; DF = delayed fluorescence.

1.2. Light-Induced Processes in Chromophores

1.2.1. Photoinduced Energy Transfer (PEnT)

Upon photoexcitation of D-A molecules, either energy transfer (PEnT) or intramolecular charge transfer (ICT) from D to A can occur. In D-A systems, the excited energy can be transferred non-radiatively via two dominant pathways: (1) Förster resonance energy transfer (FRET)^{20–23} and (2) Dexter energy transfer (DET)^{21,24} as shown in Figure 1.2. FRET can occur through space via dipole-dipole interactions between D-A over large distances (1-10 nm) between D and A. In FRET,

the rate of energy transfer depends upon the factors such as the spectral overlap of donor emission and acceptor absorption, the relative orientation of the transition dipoles of D and A and the fluorescence quantum yield of D.



Figure 1.2. Jablonski diagrams of D–A systems having (a) Förster Resonance Energy Transfer (FRET). θ : angle between vectors of the donor emission and the acceptor absorption; (b) Dexter Energy Transfer (DET). Reproduced from reference 19 with permission from the Royal Society of Chemistry.

The rates constant of energy transfer (k_{ET}) is given by Förster theory^{21,23} represented by equation1.1:

$$k_{ET} = \frac{1}{\tau_D} \left(\frac{R_0}{r}\right)^6 \tag{1.1}$$

where, τ_D is the lifetime of the donor chromophore in the absence of donor, R_0 is the Förster radius and the r is the center-to-center distance between D and A. The energy transfer efficiency can be calculated using any of the following equation no. 1.2-1.4:

$$E = 1 - \frac{F_{DA}}{F_D} \tag{1.2}$$

$$E = 1 - \frac{\tau_{DA}}{\tau_D} \tag{1.3}$$

$$E = 1 - \frac{\phi_{DA}}{\phi_D} \tag{1.4}$$

where F_D is the intensity of donor in the absence of acceptor and F_{DA} is the emission intensity of donor in the presence of acceptor. Similarly, τ_{DA} is the lifetime of donor in presence of acceptor and τ_D is the lifetime of donor and Φ_D is the fluorescence quantum yield of donor and Φ_{DA} is the quantum yield of donor in presence of acceptor.

Dexter energy transfer (DET) is another process where the non-radiative energy transfer occurs over shorter distances (1 nm) from photoexcited donor to acceptor where D and A exchange their electrons and it is a through-bond phenomenon (Figure 1.2). Dexter transfer can be observed even if the spectral overlap of donor emission and acceptor emission is small. In DET, the rate constant of energy transfer depends on the orbital interactions and Van der Waals radii (R) of donor and acceptor with a dependence of DET rate dependence of e^{-R} .¹⁹

1.2.2. Photoinduced Electron Transfer (PET)

In D-A systems connected through π -spacer, photoexcited electron transfer can occur either through intramolecular electron transfer (within the system from D to A) or intermolecular electron transfer processes (from D of one system to A of another system) and formed a charge transfer (CT) state. If, however, the CT is not facilitated through the π -spacer, it could occur through space due to the favourable overlap of D and A orbitals and such process is called through space charge transfer.^{25,26} The frontier molecular orbital (FMO) description of photoinduced electron transfer (PET) in D-A chromophores upon photoexcitation of D as well as A is presented in Figure 1.3.¹⁸

If donor is excited,



If the acceptor is excited,



Figure 1.3. Schematic representation of the photoinduced electron transfer (PET) between D and A on excitation of either D or A. BET = back electron transfer.

In the excited state, D-A molecules become more reactive toward electron transfer. Upon photoexcitation, either donor or acceptor gets photoexcited and after PET, and a charge-separated species D.+...A⁻ is formed (Figures 1.3). The extra electron on the acceptor returns to the ground state after electron transfer to the donor (charge recombination or back electron transfer (BET). The direction of CT depends on the oxidation and reduction potentials of the ground state and excited state of the D-A system.^{5,8} The total energy of the CT-complex decreases due to change in the ability to donate and accept electrons in the excited state. The Gibbs free energy of charge separation (ΔG_{cs}^0) for D-A chromophore is given by the following equation 1.5:

$$\Delta G_{cs}^{0} = e[E_{ox}(D) - E_{red}(A)] - E_{00} + \Delta G_{s}$$
(1.5)

where, e is the electronic charge, E_{ox} (D) is the first oxidation potential of D and E_{red} (A) is the first reduction potential of A, E_{00} is the energy of the S₀ \rightarrow S₁ transition (calculated by taking the intersection point of normalized absorption and emission spectra) and ΔG_S is the static Coulombic energy, given by the following equation 1.6:

$$\Delta G_S = \frac{e^2}{4\pi\varepsilon_S\,\varepsilon_0\,R_{cc}} - \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{R_D} + \frac{1}{R_A}\right) \left(\frac{1}{\varepsilon_{ref}} - \frac{1}{\varepsilon_S}\right) \quad (1.6)$$

where, ε_{S} is the dielectric constant of the solvent, ε_{Ref} is the dielectric constant of the solvent used for experiment, ε_{0} is the permittivity of free space. R_{D} and R_{A} refer to the effective radii of donor and acceptor obtained from geometry optimized structure using density functional theory (DFT) calculations and R_{cc} is the distance between the centers of the D and A.

Furthermore, Gibbs free energy of charge recombination (ΔG_{CR}) can also be calculated using the following equation 1.7:

$$\Delta G^0{}_{CR} = -(\Delta G_{CS} + E_{00}) \tag{1.7}$$

Using the above relations, the driving force for both photoinduced charge separation and charge recombination processes between donor and acceptor can be calculated. If the values of ΔG^0_{CS} and ΔG^0_{CR} are negative, it indicates that both photoinduced forward and backward electron transfer processes are exergonic and thermodynamically feasible.

The ICT state of D-A molecule differs in electronic structure and molecular geometry from the ground state. Since the electron transfer occurs in CT state, generally, the dipole moment in the excited state increases as compared to the ground state dipole moment. Upon photoexcitation, the solvent dipoles reorient themselves around the ICT state and hence lower the energy of the excited state. With the further increase in solvent polarity, solvent reorganization stabilizes the ICT state and therefore, emission occurs at lower energy or higher wavelength, this process is termed as positive solvatochromism. In few cases such as betaine-30, the dipole moment of excited state



Figure 1.4. (a) Chemical structure of DNS; (b) absorption and emission spectra of DNS in different polarity of solvent and (c) image of DNS in solvents of increasing polarity in UV-chamber. H = hexane; CH = cyclohexane; T = toluene; EA = ethyl acetate; Bu = n-butanol. Reproduced from reference 21 with permission from Springer eBook.

quantum yield of ICT state decreases due to the rapid non-radiative deactivation or due to the fast charge recombination rate and smaller energy gap between CT state and ground state. Figure 1.4 shows effect of polarity of solvent on emission (CT band) of 4-dimethylamino-4'-nitrostilbene (DNS) indicate positive solvatochromism.²¹

1.2.3. Twisted intramolecular charge transfer (TICT)

Twisted intramolecular charge transfer (TICT) compounds are characterized by showing a rotation around a single bond of D and A system where both chromophores are connected through a π spacer. Grabowski et. al., proposed the first model of TICT in 1973 and explained the phenomenon using the example of p-N,N-dimethyl amino-benzonitrile (DMABN).²⁸ Upon photoexcitation, DMABN showed dual fluorescence bands (LE emission band and TICT emission band) which is strongly dependent on temperature and solvent polarity.¹⁸ In non-polar solvent, only single fluorescence band was observed from LE state where it adopted coplanar conformation which is stabilized by electronic conjugation and gives a sharp emission. However, in polar solvents, DMABN showed fast intramolecular charge transfer from donor to acceptor and produced a relaxed perpendicular structure i.e., TICT state. Due to the equilibrium between coplanar conformer and perpendicular conformer, dual fluorescence bands were observed i.e., high energy band from the LE state and low energy band from TICT state and the intensity of these bands were dependent on the polarity of the solvent (Figure 1.5). Also, the emission intensity of TICT-active molecules is sensitive towards the temperature of the systems. With the rise in temperature, the emission intensity increases with hypsochromic shift because the excited electron crosses the activation barrier from CT state to local excited state (LE) and hence LE state gets more populated and emission occurs from LE state. Although TICT active molecules enable red shifted emission or near-IR emission, their emission intensities weaken due to the various non-radiative deactivation.²⁹ The relaxation pathways i.e., LE emission or TICT emission, of TICT-active molecules could be easily modulated by steric restrictions, substituents, temperature and polarity of the solvent. Hence, TICT process opens various possibilities to design and synthesize rotor molecules that can be utilized for various applications such as temperature-viscosity sensor, biomedical imaging and electronic applications such as in organic light emitting diodes (OLEDs).¹⁹

There are other modifications of TICT in structures such as in A-D-D', where D and D' are two donors that are joined through a single bond and planarization could occur at excited state instead

of TICT. Upon photoexcitation, charge transfer may occur from D to A, which immediately leads to planarization in excited state by rotation around D and D' to stabilize D^{+} by D'. Consequently, a new state known as the planarized intramolecular charge transfer (PLICT) state is formed.³⁰ The emission from PLICT state to ground state is overlap allowed, therefore large quantum yield can be observed in such compound compared to less emissive TICT compound.



Figure 1.5. TICT behaviour of DMABN through intramolecular rotation of D and A part at excited state and its transitions from LE state and TICT state.

1.2.4. Thermally Activated Delayed Fluorescence

Thermally activated delayed fluorescence (TADF) materials have emerged as efficient emitters for organic light-emitting diodes (OLEDs) and in addition serve as promising photocatalysts for various organic transformations. This field started around 2011 after the seminal work of Adachi and co-workers where they reported a D-A compound, 2-biphenyl-4,6-bis(12-phenylindolo[2,3a]carbazole-11-yl)-1,3,5-triazine (PIC-TRZ) with indolocarbazole as donor unit and triazine as acceptor unit (Figure 1.6).⁹ The emitter PIC-TRZ was utilized as emitting layer in the fabrication of OLED device and the external quantum efficiency (EQE) reached upto the theoretical limit (discussed later in section 1.6) of fluorescence compounds. DFT calculations showed that there is limited overlap between HOMO and LUMO levels which helps in smaller singlet-triplet energy gap (ΔE_{ST}). Fluorescence and phosphorescence studies at 5 K indicated a very small ΔE_{ST} of 0.11 eV for this compound. Transient photoluminescence of PIC-TRZ showed prompt component with decay time of ~ 10 ns and a longer delayed component with decay time of 230 µs. Furthermore, photoluminescence quantum yield (PLQY) was calculated in degassed toluene (Tol) by nitrogen gas and without degassed Tol solution. The degassed solution showed PLQY of ~ 35% with an intense delayed component and without degassed solution showed PLQY of only ~ 10% where the delayed component was completely absent. With all these calculations and measurements, the first ever TADF material was confirmed and utilized for OLEDs. The fabricated OLED device using PIC-TRZ as emitting layer showed an efficiency of ~ 5.3% at low current density. From this work, it was concluded that TADF led to very high EQE reaching almost the theoretical limit (EQE ~ 5-7.5%) of fluorescence compound.³¹ Followed by the first report on TADF, a large body of work had been carried out with development of newer molecules, rapid and exponential progress in the performances of OLEDs with the current state of the art TADF OLEDs reaching up to 42% presently.³²



Figure 1.6. Chemical structure of PIC-TRZ and its energy diagram with various processes indicated. PF= prompt fluorescence, DF = delayed fluorescence, P = phosphorescence.

1.3. Aggregate Induced Emission (AIE)

The fluorescence quantum efficiencies of organic fluorophores such as perylene may reach unity in solution in the molecularly dissolved form but it decreases dramatically in condensed phase or solid state³³ (Figure 1.7). This decrease in emission in solid state is due to intramolecular π - π stacking interactions which further decrease the possibility of applications of such organic fluorophores in solid state. This effect is known as aggregation caused quenching (ACQ). In 2001, Tang and co-workers coined the concept of aggregate induced emission (AIE) for propeller shaped molecules where the fluorophores showed enhancement in emission intensity in condensed and solid state due to restricted intramolecular rotation (RIR).³⁴ In solution form, these molecules were non-emissive due to freely rotatable junctions and hence rapid non-radiative deactivation. In binary mixture of good and bad solvent as well as condensed phase and solid state, they became highly emissive due RIR or due to the formation of aggregates. Tang and co-workers explained AIE mechanism using hexaphenylsilole (HPS) which is very weak emissive or non-emissive in organic solvent such as tetrahydrofuran (THF) and becomes highly emissive in THF/water mixture due to the formation of aggregates of HPS molecule in aqueous medium (Figure 1.7). Hence, AIE is a widely applicable phenomenon and in contrary to ACQ effect, leads to emission enhancement. Therefore, AIE-active chromophores can further be utilized in various applications such as sensing, bio-imaging and optoelectronics. Numerous varieties of AIE-active molecules have been developed, studied and explored in various applications over the last two decades.^{33,35–38}



Figure 1.7. Fluorescence image of solutions of (left) perylene and (right) HPS in different factions of THF/ water mixtures with perylene and HPS showing typical ACQ and AIE effects, respectively. Reproduced from reference 33 with permission from American Chemical Society.

1.4. Organic Chromophores used in this Thesis

To observe D-A behaviour in photophysical properties and redox properties for various applications, we have utilized few chromophores such as 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY), benzodithiophene (BDT), 4-Bromo-1,8-naphthalic Anhydride (NP), diindolocarbazole (DI), substituted phenanthrene (PF) and indoloquinoxaline (IQ). Few important structural features and characteristics of these chromophores are highlighted below:

4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY)



Figure 1.8. General chemical structure of 4,4'-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) dye.

Organic D-A chromophores based on BODIPY dyes are employed in various applications such as sensing,^{39,40} biolabeling,⁴¹ bio-imaging,⁴² photodynamic therapy,⁴³ organic photocatalysis,⁴⁴ dyesensitized solar cells, organic photovoltaics (OPVs)^{45,46} and organic light emitting diodes (OLEDs)⁴⁷ in recent years because of its outstanding thermal, photochemical stabilities, strong visible light absorption, high fluorescence quantum yields and good solubility and facile accessibility of their triplet excited states.^{44,48–50} The BODIPY dye was first reported in 1968 by Treibs and Kreuz.⁵¹ The basic skeleton of BODIPY contains 8 positions such as meso-position (8position), α -position (3 and 5 positions), β -position (1, 2, 6 and 7) and boron center position (4 and 4') that could be used for modulating the photophysical properties (Figure 1.8). The functionalization at the meso-position and boron center position does not alter the optical properties drastically while functionalization at α and β -positions can extend the conjugation which further alters the optical properties. BODIPY dyes can be easily synthesized by condensation reaction between carbonyl compounds and pyrrole, followed by oxidation either with p-chloranil or dichloro-dicyano-benzoquinone (DDQ) and finally addition of boron trifluoride diethyl etherate (BF₃·OEt₂) and base (triethyl amine) leading to formation of BODIPY chromophores at moderate to good yields.^{45,52}

Benzo[1,2-b:4,3-b'] dithiophene (BDT)



Figure 1.9. General chemical structure of Benzo[1,2-b:4,3-b']dithiophene (BDT) dye.

Benzodithiophene (BDT) is a rigid and planar conjugated structure with two thiophene rings across one benzene ring (Figure 1.9) and this chromophore has found significant applications in OPVs, organic field effect transistors and as excellent building blocks for conjugated polymers.^{53–56} Fine-tuning of energy levels is possible through facile functionalization of the BDT cores at various positions. Suitable functionalization of the core also enhances solubility, effectively increases the thermal stabilities and lowers HOMO energy levels and thus promotes high charge transport properties and high exciton mobilities.⁵⁷ The BDT core is widely used as an electron donor in D-A copolymers and small molecules for optoelectronic applications.⁵⁸

4-Bromo-1,8-naphthalic Anhydride (NP)



Figure 1.10. General chemical structure of 4-Bromo-1,8-naphthalic anhydride dye.

1, 8-naphthalimide (NP) derivatives play a crucial role in the design of fluorescent materials and are an appealing class of electron-deficient chromophores.⁵⁹ The structure of naphthalimide is inherently of D- π -A nature that incorporates naphthalene as a π bridge, electron-donating substituent at 4-position as the D and dicarboximide as an electron A (Figure 1.10).⁶⁰ The most effective synthetic strategies of NP derivatives focus on the functionalization of the N-imide site or functionalization at 4-position and thus possess outstanding chemical stability, high fluorescent
quantum yields, photo- and thermal stabilities, high electron affinity and tunable emission behaviour depending on substituents.⁶¹ Owing to these optical characteristics, naphthalimide has found widespread applications in the development of optoelectronic materials, bio-imaging probes, laser dyes, metal sensors, pH sensors, fluorescent dyes and organic field-effect transistors.^{62–64}

10,15-Dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole or Diindolocarbazole(DI)



Figure 1.11. General chemical structure of diindolocarbazole (DI) dye.

Diindolocarbazole (DI) is a rigid, planar and conjugated structure with three indole rings fused with one central benzene ring (Figure 1.11) and extensively utilized for the fabrication of OLEDs with a very high EQE of ~ 38% reported till now.^{65–67} Diindolocarbazole could be functionalized by any acceptor from the N-site and utilized as an efficient donor for D-A emitters in OLEDs. Diindolocarbazole provides larger spatial HOMO volume to the emitter thus delivers a larger photoluminescence quantum yield. Due to the steric hindrance of adjacent hydrogens of donor and acceptor, large dihedral angles can be obtained which decrease the overlap between HOMO and LUMO that further reduces ΔE_{ST} and as a result enhance the RISC and therefore promotes TADF behaviour and eventually facilitates high EQE in OLED devices.^{65–67}

Phenanthrene Derivatives

Difluorodibenzophenazine (PF)



Figure 1.12. General chemical structure of difluorodibenzophenazine (PF) dye.

Difluorodibenzophenazine (PF) is a large and rigid π -conjugated planar acceptor (Figure 1.12) with deep LUMO level and shows excellent photo- and thermal-stabilities.⁶⁸ The two sp² hybridized N-atoms and fluorine atom make it a strong electron-deficient chromophore⁶⁹ and could be utilized in OLEDs, host materials, electron and hole transport materials.^{70,71} The fused aromatic system could be synthesized by condensation reaction between phenanthrenedione and difluoro substituted phenylenediamine in good yield and further easily could be functionalized by donor part at phenanthrene core for D-A system with long wavelength emission.

Phenanthroimidazole (**PI**)



Figure 1.13. General chemical structure of phenanthroimidazole (PI) dye.

Phenanthroimidazole (PI) is a large and rigid block that consists of phenanthrene moiety and phenyl-substituted electron-deficient imidazole ring which make PI electron deficient in nature

(Figure 1.13) and could be utilized efficiently in emitting layer, electron-transporting layer and hole-blocking layer in OLEDs.^{72,73} Substitution with electron-withdrawing such as -CN, -CF₃ at the imidazole ring could improve electron withdrawing tendency of PI.⁷⁴ Furthermore, suitable donor moieties could be substituted at phenanthrene core to make it D-A chromophore for various applications.

Carbazole (CBZ)



Figure 1.14. General chemical structure of carbazole (CBZ) dye.

Carbazole (CBZ) is an electron-rich unit that exhibits good charge transport properties, high photoconductivity and high thermal stabilities and are widely used in OPVs and OLEDs as host materials and emitter materials in form of D-A co-polymers.^{75–79} Carbazole is a tricyclic system of fused pyrrole rings with two benzene rings (Figure 1.14) and they can be easily converted in D-A system by functionalization at N-atom or fused phenyl core. Functionalization of electron-donating group at the phenyl core can increase the donating tendency of CBZ.^{80,81}

Indoloquinoxaline (IQ)



Figure 1.15. General chemical structures of indoloquinoxaline (IQ) derivatives.

Indoloquinoxaline (IQ) and difluoro-substituted IQ (2F-IQ) are fused systems of alkylated indole and quinoxaline or difluoro-substituted quinoxaline having a planar structure with strong electronwithdrawing characteristics (Figure 1.15). Indoloquinoxaline derivatives have been utilized extensively in biochemistry and medicinal chemistry^{82,83} and have significant applications in host materials of OLEDs.^{84,85} Fluoro-substituted IQ revealed anticancer activity against numerous human tumor cell lines.⁸⁶ IQ and 2F-IQ can be synthesized in a facile manner by condensation reaction between bromoisatin and phenylenediamine or difluoro-substituted phenylenediamine and further, converted in D-A system by connecting D chromophore at the bromine sites.

1.5. Fluorescent molecular rotors (FMR)

Fluorescent molecular rotors (FMR) are an emerging class of fluorophores, generally made up of donor (D) and acceptor (A) chromophores where D and A are either connected through π -spacer or without spacer. These rotors serve as potential analytical probes for the detection of subtle changes in microenvironmental parameters such as temperature, viscosity, polarity, and pressure. Therefore, they were employed as microenvironment sensors for biological systems and in materials science. Generally, FMR shows rotation either from planar ground state to twisted excited state which is called twisted intramolecular charge transfer (TICT) or from twisted ground state to planar excited state which is called planarized intramolecular charge transfer (PLICT). Due to this rotation, the emission intensity of FMR can show responsiveness towards various stimuli such as viscosity, temperature, different polarity of solvents, pH, in few cases water or poor solvents (which is further responsible for the enhancement of emission intensity due to the formation of aggregate induced emission (AIE)) etc. Accordingly, such FMR have been developed and utilized in various applications as represented in the next section.

1.6. Applications of Organic D-A FMRs

As discussed earlier, the emission of organic D-A rotor is sensitive towards various stimuli such as solvent polarity, pH, viscosity, and temperature of the system. Hence, FMRs can be utilized as optical probes for sensing polarity, pH, viscosity, and temperature of biological or materials science relevant microenvironments.



Figure 1.16. Applications of fluorescent D-A rotors.

1.6.1. Temperature and Viscosity Sensor

Temperature and viscosity of surroundings are fundamental physical parameters that influence the activity of chemical and biological systems. Cellular membrane with abnormal viscosity and temperature can lead to various diseases such as Alzheimer, atherosclerosis, diabetes and malfunction of living cells.¹⁶ Hence, it is of paramount importance to develop methods that can accurately determine temperature and viscosity at the microscopic levels. Ratiometric temperature and viscosity sensing using monitoring emission of organic FMRs is a more convenient method compared to other methods such as fluorescence lifetime imaging microscopy, dual fluorophore ratiometric sensing,⁸⁷ single emission based fluorescent molecular rotors etc.⁸⁸ In ratiometric sensing, a fluorophore with dual emission at a specific wavelength has excellent spatio-temporal resolution and accuracy and low sensitivity to external variables. Molecular probes with ratiometric temperature and viscosity are essential for precise (bio)molecular detection, sensing, imaging, and theranostic applications.

Temperature Sensor

The emission band of organic D-A molecule shows responsiveness towards changes in temperature and viscosity of the medium. In most cases, the rise in temperature affects the rates of radiative and non-radiative deactivation of organic D-A rotors and, as a result, alters the intensity of their emission bands.⁸⁹ Generally, with the rise in temperature in polar solvents, the emission

intensity of CT band increases with hypsochromic shift. Thermal energy assists the excited electron in the crossing of the activation barrier from CT state to LE state that populates the LE state causing hypsochromic shift in the emission with increased intensity. In non-polar solvents such as methyl cyclohexane (MCH), Tol, the LE emission however decreases with rise in temperature due to non-radiative deactivation. Recently, Kuimova and co-workers reported cyclopropyl substituted BODIPY molecular rotors (Figure 1.17) and utilized those for temperature sensing in living cells. They showed that due to the substitution of groups at α -and β -position of BODIPY with cyclopropyl groups (BODIPY 2, 3), a fluorescent lifetime-based viscosity sensor (BODIPY-C₁₀) could be transformed into temperature sensor.⁹⁰ Marti and co-workers reported polyethylene glycol substituted BODIPY (PEG-BODIPY) for temperature sensing and live cell imaging. The fluorescence lifetime of this compound varied with temperature change and therefore, it was utilized for temperature monitoring in vitro and in cells with the help of fluorescence lifetime imaging (FLIM) technique.⁹¹ Hence the variation in microenvironment's or macroenvironment temperature could be measured using such rotors as sensors.



Figure 1.17. BODIPY based temperature sensors utilized for temperature monitoring in various cells.

Viscosity Sensor

The emission band of organic D-A molecule shows responsiveness towards change in viscosity of the medium. In case of rise in viscosity, the emission intensity of molecular rotors is enhanced due to the restriction of molecular rotations which leads to the exclusion of non-radiative deactivation pathway. Quantitatively, the viscosity sensitivity of molecular rotors could be calculated using Förster-Hoffmann theory^{16,92} (equation 1.8):

$$\log (I/I_0) = C + x \log \eta$$
 (1.8)

where, I_0 and I are the emission intensities at the initial viscosity and intensity at different viscosities respectively. The viscosity of the medium is given by η^{69} , C is the experimental temperature- and concentration-dependent constant and x is the viscosity sensitivity of the molecular rotors. Kuimova and co-workers reported BODIPY based molecular rotors for viscosity sensing and temperature sensing.⁹³ They reported that the dynamic range of viscosity could be increased by varying the substituents on meso-phenyl ring from electron donating ether group to weakly electron accepting Bromine atom or ester groups (Figure 1.18). Furthermore, they employed these rotors in live cells to measure the viscosity of cellular environment.⁹³



Figure 1.18. BODIPY based viscosity sensors utilized for viscosity and temperature monitoring in live cell.

Gryczynski and co-workers reported BODIPY and triazine based trimers (Figure 1.19) for their utilization as molecular viscometers. They concluded that triazine based BODIPY trimer with a very high molar absorption coefficient can sense subtle viscosity changes in various environments depending upon molecular solvents, lipid vesicles and several Cancer cell lines.⁹⁴ The substitutions at 1- and 7-positions of BODIPY hinder the intramolecular rotation (2, BODIPY-triad non-rotor), therefore, unable to detect the viscosity change. Kim and co-workers reported BODIPY and coumarin based viscosity sensor (C-BODIPY) and utilized it for quantifying the viscosity of mitochondria in living HeLa cell line and justified the result with FLIM experiment. Xu and co-

workers reported the design and synthesis of two naphthalimide based thermoresponsive molecular rotor (BNAP) that showed positive solvatochromism, AIE effect and utilized those for viscosity sensing and viscosity related temperature sensing.⁹⁵



Figure 1.19. BODIPY and naphthalimide-based viscosity sensors utilized for viscosity monitoring in various cell lines.

1.6.2. pH sensor and Bio-imaging

In biological processes, the intracellular pH has substantial role in regulating an organelle's functions, various enzymatic activities, protein degradation and several other cellular behavior. Abnormal intracellular pH is an indication of malfunction of cellular processes and serious diseases, such as cancer, Alzheimer's disease, or other neurodegenerative diseases.^{81,96} Cancerous cells are known to show slightly acidic behavior^{97,98} and hence, it is important to develop pH sensors that can identify abnormal pH behavior or a cancerous cell based on pH. In this regard, D-A fluorescence rotor-based sensing and imaging probes have received significant attention owing to their excellent sensitivity and spatio-temporal resolution ability.^{99–103} A variety of fluorescent probes have been synthesized and utilized for intracellular pH sensing.^{104,105}

Recently, Tang and co-workers reported TICT and AIE active D-A molecule 4-(dimethylamino)styryl)quinoxalin-2(1H)-one (ASQ) which showed response towards multiple stimuli such as pH, polarity and aggregation and utilized it for albumin protein sensing, ratiometric pH sensing, and biogenic amine gas sensing.¹⁰⁶ Upon trifluoracetic acid (TFA) addition in the solution of ASQ in dichloromethane (DCM), the main emission band started to decrease and a new hypsochromically shifted band formed and started to increase due to the protonation of D site. With further addition of TFA, the main band again started to increase and hypsochromic band start to decrease due to protonation of A. Reversible effect was also observed with the addition of triethylamine (TEA) in acidic solution of ASQ. In D-A rotors, upon addition of acid, either donor or acceptor can be protonated. If donor gets protonated, it weakens the electron donating capability and hence CT character reduces leading to decrease in emission intensity accompanied by a hypsochromic shift. While if acceptor gets protonated, it strengthens the CT character and hence enhancement of emission intensity.¹⁰⁶ Zhao and co-workers reported rhodamine and naphthalimide based fluorescent probe (RNL) and utilized for staining lysosome in HeLa cells (Figure 1.20). To confirm the localization of RNL in lysosome, HeLa cell line were incubated with lysosome staining probe Green DND-189 and the excellent co-localization (Figure 1.21) indicates RNL probe selectively stains the lysosome. Furthermore, the fluorescent probe was utilized for detection of lysosomal pH changes.¹⁰⁷



Figure 1.20. Quinoxaline and naphthalimide-based pH sensors utilized for ratiometric pH sensing and detection of lysosomal pH change.



Figure 1.21. Fluorescence microscopy images of living HeLa cells co-stained with RNL (5 mM) and LysoSensors Green DND-189 (1 mM). (a) Red emission of RNL (560–700 nm), (b) green emission of LysoSensors Green DND-189, (c) overlay of (a) and (b), and (d) a bright field image. Excitation wavelength of RNL and LysoSensors Green DND-189 was 405 nm and 488 nm, respectively. Reproduced from reference 107 with permission from the Royal Society of Chemistry.

Jin and co-workers reported the identification of cancer cells based on UV/Vis microspectroscopy and common pH-indicators such as bromothymol blue and bromocresol green (Figure 1.22). The cancer cells are known to have slightly acidic extracellular and intracellular pH values.⁹⁷ Upon incubating the cancereous and healthy mammalian cell line with pH-indicators, the cancer cells exhibited yellow and bright colour under UV/Vis microspectroscopy while the healthy cells displayed blue and green colour due to the neutral intracellular pH of cell.¹⁰⁸



Figure 1.22. Visual identification and screening of cancer cells from normal cells and cytotoxicity assays. (a) Bright-field optical microscope images of cancerous HepG2, HeLa, A549, 4T1, normal cells HL7702 and L929 before and after 5min incubation with 1mg mL⁻¹ of bromothymol blue, respectively; All scale bars: 20µm. (b) Cytotoxicity assays for the A549, HeLa, HL7702, and L929 cells after the incubation with bromothymol blue or bromocresol green. A, B, C, D under the X-coordinate represent A549, HeLa, HL7702, and L929 cells, respectively. (c) Bright-field microscopy images of co-cultured cancerous 4T1 and normal HL7702 cells before (left, scale bar: 50µm) and after (right, scale bar: 15µm) the treatment with bromocresol green. The cells within the white dotted line are identified as HL7702 cell. (d) chemical structure of bromothymol blue and bromocresol green. Reproduced from reference 108 with permission from the Springer Nature.

1.7. TADF compounds for Organic Light-emitting Diodes (OLEDs)

The development of organic light-emitting diodes (OLEDs) has attracted great attention of researchers for their utilization in displays of smartphones, TV screen and in panels for lighting applications.¹⁰⁹ For display applications, the main requirement is high efficiency and emission color purity, which depend on the emitting (organic material) layer of OLEDs.¹¹⁰

Basic structure and working principle of OLEDs

Organic light-emitting diodes (OLEDs) are thin multilayer devices (Figure 1.23) that consist of cathode as an electron source, an electron injecting layer (EIL), an electron transporting layer (ETL), an emissive layer (EML) composed of organic molecules, hole transporting layer (HTL), hole injecting layer (HIL) and anode. Anode is made up of indium-tin oxide (ITO) which is transparent and allows light to pass through it.¹¹¹



Figure 1.23. Schematic representation of multilayer OLEDs and light emission mechanism in the EML of OLEDs. Reproduced from reference 111 with permission from The Chemical Record.

The electrons and holes start to move towards each other upon applying an external electric field. The electrons are transported to the EML through EIL followed by ETL and likewise holes are transported to the EML through HIL and HTL. At the EML, electrons and holes recombine to create excitons which subsequently emit light via radiative transitions, resulting in an emission. The colour of OLEDs is determined by the organic materials that are utilized in the emissive layer and the external quantum efficiency (EQE) of OLED is given by the following equation 1.9¹¹²:

$$\eta_{EQE} = \gamma \times \varphi_{PL} \times \eta_r \times \eta_{out} = \eta_{IQE} \times \eta_{out}$$
(1.9)

whereby, γ represent the charge carrier recombination efficiency, φ_{PL} represents the photoluminescence quantum yield of organic material, η_r represents radiative exciton utilization efficiency of the materials, η_{IQE} represents internal quantum efficiency and η_{out} represents the optical coupling output efficiency which is around 20% when using conventional glass substrate which could be further enhanced using horizontal molecular orientation of the dipoles of the

emitting molecules.³¹ Upon electrical excitation, 25% of singlet excitons and 75% of triplet excitons are generated and hence, conventional fluorescence can harvest only singlet excitons while the triplet excitons are non-radiatively deactivated. Therefore, the EQEs reach upto maximum of 5-7.5% using fluorescent molecules as emitting layers.¹¹³ Phosphorescent molecules can harvest both excitons and hence 100% (IQE) is theoretically achievable and relatively higher device EQEs can be observed than fluorescent OLEDs.^{114,115} Generally, the emissive layer in phosphorescent OLEDs is composed of organic materials that include transition metals such as Ruthenium (Ru), Iridium (Ir), Platinum (Pt) etc. Since there are several constraints of transition metals such as high cost, toxicity, non-abundance, it is desirable to utilize low cost, earth-abundant and non-toxic materials excluding metals in the emissive layers.

Since TADF active materials can harvest both excitons due to fast RISC, their IQE can theoretically reach up to 100%. Adachi and co-workers in their breakthrough work reported the first example of TADF, PIC-TRZ which showed emission at 506 nm with small ΔE_{ST} of 0.11 eV and the EQE of OLED device using PIC-TRZ was 5.3%.⁹ A maximum IQE can be achieved either by decreasing ΔE_{ST} or by increasing the photoluminescence quantum yield (PLQY) of TADF molecules. In twisted D-A molecules (with large dihedral angle), lower ΔE_{ST} can be achieved by reducing the overlap integral of HOMO and LUMO.¹¹⁶ However, small overlap integrals lead to a decrease in transition dipole moments between the ground state and excited state and therefore, lower oscillator strength that significantly decrease PLQY and limit performance of OLED devices.¹¹⁷ Therefore, a trade-off between the ΔE_{ST} and PLQY of D-A CT molecules is necessary for optimal EQE in OLED devices. Insertion of a phenyl ring between donor and acceptor in a twisted D-A TADF molecule leads to high PLQY and smaller ΔE_{ST} , which results in high EQE.¹¹⁸ Bulky and rigid structure of D-A leads to smaller ΔE_{ST} due to high steric hindrance and hence the spatial separation of frontier molecular orbitals, high PLQY due to reduced vibronic coupling leading to higher EQE. Recently, Kwon and co-workers reported the synthesis of highly efficient green TADF emitters using a new rigid donor called diindolocarbazole (DI) and reported high EQE of 31.4% without any out-coupling and a very low-efficiency roll-off characteristics (Figure 1.24).¹¹⁹ In 2019, Kwon and co-workers reported the synthesis of blue TADF emitters based on DI donor and symmetric, rigid oxygen-bridged boron acceptor, with narrow-band blue emission, high PLQY and smaller ΔE_{ST} in Tol. The fabricated OLED device showed a maximum EQE of 38.1% with low roll-off characteristics of 25.2% at high luminance of up to 5,000 cd m^{-2.66} In

2017, Yang and co-workers reported phenanthrene derivatives based TADF emitters and due to the rigid and strong electron withdrawing character of phenanthrene derivatives provide yellow to deep red emitting OLED device with a maximum EQE of 16.9%.¹²⁰



Figure 1.24. Diindolocarbazole and phenanthrene based TADF molecules utilized for highly efficient OLEDs.

1.8. Photocatalysis

Photocatalysis offers a powerful strategy to activate organic molecules and achieve organic transformations by transferring electron (photoredox catalysis) or energy (photoinduced energy transfer (PEnT)) between excited photocatalyst and substrates. Development of metal-free photocatalysts (PCs) have attracted tremendous attention in the area of small molecule activated photocatalytic reactions due to their sustainability and cost-effectiveness compared to conventional transition metal-based PCs.^{5,121} In case of fluorescent organic PC, if the lifetime of PC is less than 1 ns, it cannot participate in photoinduced electron transfer (PET) and PEnT processes due to the very rapid decay of the excited state (~ 2×10^{10} s⁻¹).⁸ In phosphorescent molecules, the phosphorescence lifetime varies from microseconds to milliseconds and T₁ to S₀ being spin-forbidden transition, the rate of PET or PEnT is much faster compared to rate of phosphorescence.⁸ In fluorophores, the rate of ISC can be enhanced by attaching heavy atom (I, Br) to the core of chromophores and therefore, spin-orbit coupling (SOC) is enhanced which

results in population of triplet state.^{6,44} In case of D-A chromophore (without heavy atoms), ISC can occur either due to RP-ISC or SOCT- ISC.^{6,44,50} If the D-A molecules are directly linked in orthogonal orientation without any spacer, then photoinduced electron transfer from D to A leads to change in the spin multiplicity as a result of the sufficient torque generated by change in orbital angular momentum. As a result, ISC occurs due to the SOCT-ISC in such systems.⁶ If the D-A systems however, are connected by a spacer (i.e., spatial overlap between D-A is minimized), the value of exchange interaction decreases and hence the energy gap between ¹CT and ³CT is reduced that facilitates their efficient mixing. Upon photoexcitation, electron transfer from D to A generates a radical pair ¹CT state which is subsequently transferred to ³CT because of efficient mixing of ¹CT and ³CT states.



Figure 1.25. Possible pathways of populating of triplet state and deactivation of excited PC via energy transfer or electron transfer to the substrate.

Therefore, ³CT state becomes populated by triplet radical pairs and charge recombination populates the lowest triplet state through RP-ISC.^{6,44,50} Upon photoexcitation and subsequent population of triplet state of photocatalyst, it could be effectively utilized for PEnT and PET. In case of PEnT mechanism, the energy of triplet state (E_T) of photocatalyst should be close to the triplet energy of substrate for effective transformation. In case of photoredox catalysis, the mechanism could either be reductive quenching or oxidative quenching of the photocatalyst depending on the redox potentials of the photocatalyst and substrate (Figure 1.25). For a photocatalyst to be an effective oxidant, the excited state reduction potential (E_{red}^{*PC}) of

photocatalyst must be more positive than oxidation potential (E_{ox}) of the substrate. Likewise, for the photocatalyst to be an efficient reductant for thermodynamically favourable PET, the excited state oxidation potential (E_{ox}^{*PC}) of the photocatalyst must be more negative than the reduction potential (E_{red}) of the substrate.⁵

Recently, Huang and co-workers reported iodine-substituted aza-boron-dipyrromethene (2I-BODIPY) photosensitizer (Figure 1.26) with high ISC rate ($\varphi_{ISC} = 91\%$) and ~ 88% singlet oxygen quantum yield and utilized for photodynamic therapy.¹²² Due to heavy atom attached to the core, an efficient ISC was observed revealed by ultrafast femtosecond transient absorption spectroscopy and theoretical calculations. Recently, Mazzone and co-workers reported the synthesis of triplet photosensitizers meso-thienyl borondipyrromethene (BODIPY) derivatives and utilized for triplet-triplet annihilation (TTA) upconversion. Based on femtosecond/nanosecond transient absorption spectroscopy as well as DFT computations, fast ISC was revealed to be occurring due to SOCT-ISC.¹²³ Donato and co-workers reported the synthesis of D-A systems based on phenothiazine as donor and BODIPY as acceptor and utilized for TTA upconversion and an efficient triplet state was achieved due to SOCT-ISC as indicated by pico/nanosecond transient absorption spectroscopy and DFT calculations.¹²⁴



Figure 1.26. BODIPY-based photocatalysts populating the triplet state via various processes and utilized in TTA and photocatalytic reactions.

Due to the smaller ΔE_{ST} of TADF compounds, RISC is possible at ambient temperature, therefore longer lifetime of few microseconds can be observed similar to phosphorescent compounds.⁵ Thus, TADF compounds are capable of acting as efficient photocatalysts. In 2016, Luo and Zhang reported 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN), a well-known TADF molecule from the seminal work of Adachi and co-workers¹⁰, as photocatalyst for dual catalyzed cross-coupling reaction for the first time (Scheme 1.1).¹²⁵ The molecule 4CzIPN has been extensively studied in photocatalysis due to its long-lived triplet state (1.3 µs), suitable redox potentials and the similar properties as Ir based photocatalysts.^{12,126,127} Thereafter, several TADF molecules have been reported in various photocatalysis reactions through PEnT and PET based on the energy levels and redox potentials of PC and substrate.^{5,12,128–130}



Scheme 1.1. Cross-coupling reactions using 4CzIPN (TADF materials) as photocatalyst. The E to Z isomerization of stilbene (triplet state energy (E_T) of E-stilbene = 2.2 eV and E_T of Z-stilbene= 2.5 eV) was utilized as the most fundamental example of PEnT reaction to evaluate the



Scheme 1.2. Isomerization of stilbene using immobilized 4CzIPN molecules as photocatalyst.

effectiveness of TADF molecules as photocatalyst.^{5,11,12,131} In 2018, Zhang and co-workers reported the effectiveness of TADF molecules in PEnT with the utilization of E to Z isomerization of stilbene and found a conversion of upto ~ 90% after 24 h (Scheme 1.2). They further utilized these molecules in PEnT-mediated cross-coupling of various carboxylic acids and aryl halides with excellent yields.¹² Bergens and co-workers reported functionalized 4CzIPN, immobilized on carbon indium-doped tin oxide (ITO) electrodes for E to Z isomerization of stilbene with ~ 84% conversion to product after 48 h.¹³²

TADF materials have also been utilized as PC in variety of photoredox catalysis reactions where the PC can undergo either reductive quenching or oxidative quenching based on the excited state



Scheme 1.3. Photocatalysis reactions such as oxidative quenching, reductive quenching, energy transfer and dual Ni(II) catalysis using pDTCz-DPmS as photocatalyst.

redox potentials of PC and substrate. Recently, Colman and co-workers reported TADF compound 9,9'-(sulfonylbis(pyrimidine-5,2-diyl))bis(3,6-di-tert-butyl-9H-carbazole) (pDTCz-DPmS) as PC and utilized in various reactions such as reductive quenching, oxidative quenching, energy transfer and dual catalysis using Ni (II) as co-catalyst (Scheme 1.3).¹¹

Synthesis of arylated heteroarenes by photocatalytic method is most well studied among other reaction methods such as C-H activation and transition metal catalyzed cross-coupling reaction.¹³³ König and co-workers reported the arylation of heteroarenes by photocatalyzed single electron transfer process using aryl diazonium salts as aryl source and Eosin Y as the photocatalyst (Scheme 1.4) and observed 80% yield in dimethyl sulfoxide (DMSO) and ~ 12% yield in acetonitrile (ACN).¹³⁴ The reduction potential of aryl diazonium salts are close to - 0.2 V^{127,135} therefore, aryl diazonium salts are well-known for radical formation and are utilized as oxidative quenchers in photocatalytic C-H arylation reactions.



Scheme 1.4. The C-H arylation of heteroarenes using Eosin Y as photocatalyst.

1.9. Aim of the thesis

Twisted organic donor-acceptor (D-A) fluorescent molecular rotors (FMRs) are of great importance because of their photophysical properties that are tunable by variations in solvent polarity, temperature, viscosity and pH. Another class of twisted D-A molecules are characterized by their small singlet-triplet energy gaps that facilitate reverse intersystem crossing (RISC). Such molecules as a result of RISC can exhibit long-lived delayed fluorescence components and show thermally activated delayed fluorescence (TADF) process. This thesis titled "*Twisted Donor*-

Acceptor Fluorescent Molecular Rotors and Conjugates for Sensing, Photocatalytic and *Electroluminescence Applications*" involves the design, synthesis and photophysical studies of organic D-A rotor molecules with twisted intramolecular charge transfer (TICT) and conjugates with TADF properties. The key findings of this thesis are in the following directions:

- Design and synthesis of twisted D-A TICT rotors based on BODIPY and benzodithiophene (BDT) chromophores and TADF conjugates based on diindolocarbazole (DI) electron donors with various acceptors such difluorodibenzophenazine (PF), phenanthroimidazole (PI) and indoloquinoxaline (IQ).
- Photophysical and electrochemical characterization of D-A rotors and conjugates using various steady-state spectroscopic techniques, transient absorption spectroscopy and validation of the results using density functional theory (DFT) and time-dependent DFT calculations.
- Investigation of ratiometric temperature and viscosity sensing, pH sensing, bio-imaging and photocatalysis reactions of the synthesized D-A rotor molecules.
- Utilization of DI based TADF conjugates in energy and electron transfer photocatalysis and in organic light-emitting diodes (OLEDs).

The thesis is divided into seven chapters and the details of each chapter are as follows:

Chapter 1 presents a discussion on the importance and advantages of D-A rotor molecules over heavy atom-free organic chromophores and the different excited state processes involved in such molecules upon photoexcitation. The mechanisms of various photophysical processes such as TICT, aggregate-induced emission (AIE) and TADF have been discussed. Subsequently, structural, and optical features of the chromophores that have been used in this thesis are presented. Lastly, literature examples based on some of these chromophores in the areas of sensing, imaging, photocatalysis and OLED applications are discussed.

Chapter 2 provides information on materials used for the synthesis and characterization techniques with the details of these methods used for the characterization of all molecules in this work.

Chapter 3a describes the design and synthesis of three D- π -A molecular rotors/non-rotors, *pp*-AD and *pp*-ADA, Me-*pp*-ADA based on BDT donor and BODIPY acceptor and a biphenyl spacer and explored the influence of π -spacer length and methyl substituents at specific positions in the

acceptor backbone on TICT behaviour of these molecules. TICT rotors pp-AD and pp-ADA showed near-infrared (NIR) emission (~ 712 nm, ~ 725 nm respectively) with considerably high (pseudo) Stokes shift of upto ~ 208 nm and ~ 221 nm respectively, these values being the highest known for any BODIPY-based compound so far. However, compound Me-*pp*-ADA with methyl substituents did not show TICT due to the impeded free rotation of the meso-phenyl group of the BODIPY and instead exhibited excitation energy transfer with a transfer efficiency of ~ 88% as revealed by steady-state emission and transient absorption spectroscopy. Furthermore, the ratiometric temperature and viscosity sensing and rigidochromic behaviour of these rotors were also analyzed.

Chapter 3b describes the synthesis of biphenyl functionalized regioisomeric BODIPYs such as *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY and T-BODIPY (thiophene at meso-position) and a triad rotor T-ADA (BDT as donor and BODIPY as acceptor. Subsequently, photophysical studies and investigation of these rotors as organic photosensitizers (PSs) were performed. Among all PSs, T-ADA showed charge transfer (CT) band at ~ 650 nm and exhibited AIE phenomenon. The singlet oxygen quantum yields (SOQY) for all molecules were calculated and T-BODIPY showed SOQY of ~ 77% due to the presence of heavy atom (Br atom at thiophene ring) and CT mediated intersystem crossing (ISC). However, rotor T-ADA showed SOQY of ~ 35.1% due to CT-mediated ISC and such observations were substantiated by transient absorption spectroscopic studies. Due to the efficient generation of ${}^{1}O_{2}$ for all compounds, *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, *mm*-BODIPY and T-ADA were utilized as photocatalysts in the aerobic photooxidation of thioanisole to methyl phenyl sulfoxide with high selectivity of 99%.

Chapter 4 describes the synthesis and investigation of three rotor molecules **AIN**, **AINP** and **F**-**AINP** based on aminoindole (AI) donor and naphthalimide acceptor. Photophysical and solvatochromic studies for all compounds indicated the formation of a longer wavelength emission band attributed to charge transfer (CT) from AI to naphthalimide. The emission of all rotors was highly sensitive to temperature and viscosity of the solvent and their ratiometric temperature sensing and viscosity sensing properties were analyzed. All rotors were AIE active except **F**-**AINP** due to intramolecular hydrogen bonding between NH- and F at the 7-position of the indole that led to restricted intramolecular rotation and hence distinct photophysical properties. Furthermore, all rotors serve as colorimetric pH sensors where upon lowering of pH (protonation), the intensity of

CT band decreased indicating the weakening of CT interactions due to protonation on donor and the spectral changes could be reverted by base addition. Accordingly, rotors **AINP** and **F-AINP** were utilized for live cell imaging on A549 (lung cancer) and L929 (fibroblast) cell lines. The live cell fluorescence microscopic studies therefore revealed the localization of **AINP** and **F-AINP** dyes in the cytoplasmic space of A549 cell.

Chapter 5 describes the synthesis and investigation of two new twisted D-A TADF conjugates **DI-PF** and **DI-PI** based on DI donor and PF and PI derivatives as acceptors. Triads **DI-PF** and **DI-PI** showed CT bands at ~ 590 nm and at 519 nm with a large Stokes shift of 196 nm and 126 nm respectively. Fluorescence and phosphorescence studies at 77 K for **DI-PF** and **DI-PI** revealed very small to modest ΔE_{ST} values of 0.01 eV and 0.34 eV respectively. Transient photoluminescence decay profiles of **DI-PF** and **DI-PI** showed shorter prompt components of 40 ns and 13.38 ns and longer delayed components of 6.15 µs and 2.05 µs respectively confirming the TADF nature for **DI-PF** and **DI-PI**. These combined properties of **DI-PF** and **DI-PI** make them suitable photocatalysts in reactions involving energy transfer and electron transfer pathways. Accordingly, these compounds were employed as photocatalysts in E to Z isomerization of stilbene with a maximum of 66% conversion based on their triplet energy levels and in arylation of various heteroarenes with excellent isolated yields of up to 86% in acetonitrile (ACN).

Chapter 6 describes the synthesis of four twisted D-A TADF conjugates CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ based on phenyl carbazole (Ph-CBZ) and DI donor and IQ and difluorosubstituted indoloquinoxaline (2FIQ) act as an acceptor. The molecules CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ showed CT bands at ~ 512 nm, 527 nm, 523 nm and 546 nm respectively. Fluorescence and phosphorescence studies at 77 K for CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ revealed ΔE_{ST} values of 0.17 eV, 0.26 eV, 0.17 eV and 0.20 eV respectively. Transient photoluminescence decay profiles of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ showed shorter prompt components (11.4 ns to 31 ns) and longer delayed components (36.4 ns to 1.5 µs) confirming the TADF nature of all molecules. Compounds CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ were employed as photocatalysts in E to Z isomerization of stilbene with up to 90% yield of products and in arylation of various heteroarenes with excellent substrate scope and isolated yields of ~ 80% in ACN. Additionally, solution-processable OLEDs were fabricated using green emitters CBZ-IQ, DI-IQ and DI-2FIQ. **Chapter 7** discusses the conclusion of this thesis with the major findings from all the chapters as well as a brief discussion on present and future perspectives of these rotors and TADF conjugates in development of multifunctional sensors, imaging probes, OLEDs and in broadening their scope as photocatalysts.

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Materials and Methods

2.1. Materials

Toluene (Tol) and tetrahydrofuran (THF) were dried over sodium/benzophenone and distilled prior to use. N, N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) were dried over calcium hydride and distilled prior to use. Dichloromethane (DCM) and chloroform (CHCl₃) were dried by refluxing over phosphorous pentoxide (P_2O_5) and distilled before use. Methanol (CH₃OH) and acetone were dried by stirring over potassium carbonate (K₂CO₃) followed by distillation. Triethylamine and diisopropylamine were dried by stirring over KOH pellets and distilled before use. All chemicals and solvents were purchased from commercial suppliers (Sigma Aldrich, SD Fine Chemicals) and used without further purification. Acetic acid (CH₃COOH, Rankem), ammonium acetate (97%, GLR), ammonium chloride (NH₄Cl, Rankem), 1-bromohexane (>98%, Spectrochem), 4-bromo-1,8-naphthalic anhydride (95%, Sigma Aldrich), benzaldehyde (98%, Avra), boron trifluoride-diethyl etherate (BF3.OEt2, Sigma Aldrich), diethylamine (98%, Avra), N-ethyldiisopropylamine (DIPEA, 98%, Avra), 2,4-dimethylpyrrole and pyrrole (97%, Sigma Aldrich), hydrochloric acid (HCl, 99%, Rankem), N-bromosuccinimide (NBS, 95%, Sigma Aldrich), iodine (99%, GLR) NMP (98%, GLR), piperidine (spectrochem), potassium carbonate (K₂CO₃, 99%, Rankem), potassium hydroxide (KOH, Rankem), sodium bicarbonate (NaHCO₃, 99%, Rankem), sodium sulphate (Na₂SO₄, 99%, Rankem), sodium chloride (NaCl, 99%, Rankem), tetrabutylammonium hexafluorophosphate (TBAHFP, 98%, Alfa Aesar), t-butanol (Rankem), tetrachloro-1,4-benzoquinone (chloranil, 99%, Sigma Aldrich), triethylamine (99%, Rankem), trifluoroacetic acid (TFA, ≥99%, Sigma Aldrich), 5-bromoisatin (95%, GLR), phenylenediamine (98%, GLR), difluoro substituted phenylenediamine (98%, GLR), 2-oxoindole (98%, GLR), (98%. (98%. phosphorus oxychloride GLR). tert-butyl benzene GLR), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, Sigma Aldrich), tri-tert-butylphosphine tetrafluoroborate (97%, Sigma Aldrich), indole (98%, Avra), 7-fluoroindole (99%, GLR), hydroxylamine o-sulfonic acid (98%, GLR) 2,6-diisopropylaniline (97%, GLR), 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 98%, Sigma Aldrich), lithium chloride (LiCl, 98%, GLR) and Potassium tert-butoxide (t-BuOK, 99.99%, Sigma Aldrich), thiophene-3-carboxylic acid (99 %, Sigma Aldrich), 4-formylphenylboronic acid (95%, Sigma Aldrich) and 1-bromo-4-iodobenzene (99%, Sigma Aldrich).

2.2. Methods for Compound Purification

Thin layer chromatography (TLC) was performed using aluminium sheets pre-coated with silica gel (Merck, DC Kieselgel 60 F254). For the purification of compounds, column chromatography separations were performed using silica gel of mesh size 60-120.

2.3. Methods for Characterization

NMR Spectroscopy: ¹H, ¹³C, ¹¹B, and ¹⁹F NMR spectra were recorded on Bruker Biospin Avance III FT-NMR 400 MHz spectrometer and Avance Neo (Bruker) 500 MHz spectrometer at room temperature. Tetramethyl silane (TMS) was used as an internal standard.

Mass Spectroscopy: High-resolution mass spectra were recorded with Waters QTOF mass spectrometer. The software used for acquiring mass spectra was Flex Control, Bruker (USA) and software used for analyzing mass spectra was Flex Analysis 3.1.

UV/Vis absorption spectroscopy: UV/Vis and near-infrared (NIR) spectral measurements were carried out with Carey 5000 and Cary 60 UV/Vis spectrophotometer using a quartz cuvette with 10 mm path length.

Fluorescence spectroscopy: Steady-state emission and excitation studies were carried out with Hitachi F7000 fluorescence spectrophotometer equipped with R928F photomultiplier expandable up to 900 nm.

Temperature-dependent UV/Vis: Temperature-dependent absorption spectra of samples were measured using Agilent Cary 60 UV/Vis spectrophotometer equipped with single cell Peltier accessory.

Temperature-dependent fluorescence spectroscopy: Temperature-dependent fluorescence of samples were measured using temperature-controlled cuvette holder for Hitachi F7000 spectrophotometer (Luma 40) from Quantum Northwest. Luma 40 temperature controller was used for measurements in the temperature range of -10 °C to 100 °C.

Time-resolved fluorescence spectra: Time-resolved fluorescence spectra were measured using time-correlated single photon counting (TCSPC) spectrometer from Fluorocube, Horiba Jobin Yvon, NJ equipped with picosecond laser diodes as an excitation source. The 375 nm, 510 nm and

590 nm laser diodes were used as a light source for the excitation of different samples and the instrument response function (IRF) was collected using Ludox 47 (colloidal silica) solution. The full-width half maximum (FWHM) of IRF was ~ 250 ps. The optical pulse durations from < 70 ps were used. Highly integrated picosecond PMT modules as well as micro channel plate PMTs were used for the time resolution.

Cyclic voltammetry: The electrochemical measurements were performed using CHI-610 electrochemical workstation from CH Instruments (USA), with a conventional three-electrode single-compartment cell consisting of glassy carbon as the working electrode, Ag/AgCl containing 1 M KCl solution as the reference electrode, and Pt wire as the counter electrode. Cyclic voltammetry measurements were performed at a scan rate of 100 mV/s. Tetrabutylammonium hexafluorophosphate (TBAHFP) (Alfa Aesar) (0.1M) dissolved in pre-dried DCM was used as a supporting electrolyte. The solutions were purged with nitrogen prior to measurement. The electrochemical potential was internally calibrated against the standard ferrocene/ferrocenium (Fc/Fc⁺) redox couple prior to each measurement. Based on the first oxidation potential onset (E_{onset}^{ox}) and first reduction potential (E_{onset}^{red}), the HOMO and LUMO were calculated¹ using equations 2.1 and 2.2 as follows:

HOMO =
$$-(E_{onset}^{ox} + 4.76) \text{ eV}$$
 (2.1)
LUMO = $-(E_{onset}^{red} + 4.76) \text{ eV}$ (2.2)

Spectroelectrochemistry: Spectroelectrochemical measurements were performed using a cell assembly (SEC-C) supplied by BAS Inc (Japan) and the assembly comprised of a Pt counter electrode, a Pt gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The absorption spectra were measured using an ocean optics set up connected in absorbance mode and using the FLAME spectrometer. Voltages were swept in the range of -2 V to +2 V, pre-dried DCM was used as solvent and TBAHFP was used as the supporting electrolyte. The solutions were purged with nitrogen for 10 min prior to spectroelectrochemical measurements.

Fluorescence Quantum Yields: Fluorescence quantum yield was measured by relative method using Rhodamine B ($\Phi_R = 0.5$ in ethanol (EtOH)) and 4',6-diamidino-2-phenylindole (DAPI, $\Phi_R = 0.58$ in DMSO) as reference dyes and using the following equation 2.3:²

$$\Phi = \Phi_{\rm R} \left(I/I_{\rm R} \right) \left(A_{\rm R}/A \right) \left(\lambda_{\rm exR}/\lambda_{\rm ex} \right) \left(n^2/n^2_{\rm R} \right)$$
(2.3)

where Φ_R is the quantum yield of reference dyes, I and I_R are integrated fluorescence intensities of compounds and reference dye respectively, A and A_R are the absorbance of the compounds and reference dye respectively, and n and n_R are the refractive indices of solvent (s) used for compounds and reference respectively.

DFT Calculations: Quantum chemical density functional theory (DFT) calculations were performed in the ground state using Gaussian 09 program suite.³ The side chains in all molecules were replaced with methyl groups in order to account for the electron-donating effect of the alkyl chain and at the same time reduce the computational time and cost. The studied molecules were optimized using global hybrid B3LYP functional and 6–31G (d, p) basis set in the gas phase together with frequency calculations. The frontier molecular orbital (FMO) energy levels and FMO distribution were obtained from geometry optimization of the neutral ground-state geometries. In order to achieve theoretical ΔE_{ST} , time-dependent DFT (TD-DFT) calculations were performed in chloroform (CHCl₃) using the polarization continuum model (PCM), B3LYP functional and 6–31G (d, p) basis set to determine the singlet and triplet energy levels. The frontier molecular orbital (FMO) electronic levels and FMO distribution were obtained to be singlet and triplet energy levels. The frontier molecular orbital (FMO) electronic levels and FMO distribution were obtained from geometries.

Thermogravimetric analysis (TGA) was carried out from 25 to 800 °C (at a heating rate of 10 $^{\circ}$ C min⁻¹) under a nitrogen atmosphere on a Shimadzu DTG-60 instrument.

pH measurements: pH was measured with a LAB INDIA pH cum conductivity meter (Sr. No. PC14360507) instrument.

Cell Viability Assay: MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-tetrazolium bromide) (TC191, Himedia) assay was performed to measure the viability of A549 cells treated with compounds **AINP** and **FAINP** described in Chapter 4.⁴ The assays were performed in triplicates with the cells seeded on a 96-well plate. The media was discarded from the cells, and 50 μ l of MTT stock solution (5 mg/mL) was added to each well containing 50 μ L of Opti-MEM media. After incubating the plate at 37 °C for 3 hours, 150 μ L of DMSO (MTT solvent) was added to each well and shaken for 15 minutes. The absorbance of the reaction mixture was measured at 590 nm using a microplate reader and analyzed the results.

Dye treatment to cells: The adherent lung cancer cell line A549 and the fibroblast cell line L929 were obtained from NCCS, Pune. The cells were cultured in high glucose DMEM media (D1152, Sigma-Aldrich) supplemented with 10% Fetal Bovine Serum (FBS) and maintained at 37 °C and 5% CO₂. The cells grown for 50% confluency were treated with 0.005 mg/mL of compounds **AINP** and **FAINP** in Chapter 4⁴ diluted in DMEM and incubated for 10 min at 37 °C. Following the incubation, the media was removed, washed twice with 1X PBS solution, and added the fresh media. Wheat Germ Agglutinin (WGA) (5 µg/ml), Hoechst (1 µg/ml), and Lysotracker reagents (50 nM) were used to stain the membrane, nucleus, and lysozymes, respectively. The stained cells were imaged using a super-resolution microscope (Zeiss LSM980 Airyscan 2) at 63X magnification and an inverted microscope (Leica Dmi8) at 40X magnification. The fluorescence excitation/emission wavelength of dyes are as follows: $\lambda_{ex}/\lambda_{em} = 488/510$ nm; WGA $\lambda_{ex}/\lambda_{em} = 595/615$ nm; Hoechst $\lambda_{ex}/\lambda_{em} = 360/460$ nm; Lysotracker $\lambda_{ex}/\lambda_{em} = 595/615$ nm.

Transient Absorption Spectroscopy: A customized broadband femtosecond transient absorption spectrometer (TAS, Newport Corp.) was used to investigate the excited state charge transfer dynamics.^{5,6} Briefly, the light source is output from a commercial Ti: sapphire laser (Libra, Coherent Inc.) with a central wavelength of 800 nm, the repetition rate of 1 kHz, and pulse duration of 50 fs. The incident pulse is split into pump and probe pulses. One part of the pulse was guided into a commercial non-collinear optical parametric amplifier (NOPA, Topas White, Light conversion), which was used to tune the wavelength of the pump pulse to electronically excite the sample, the other part of the output from the amplifier is focused onto a CaF₂ crystal to generate a broadband white-light probe pulse. The transient absorption data are collected at the pump magic angle (54.7°) with respect to the vertically polarized probe to negate the anisotropic effects of the sample. The spectrally-dispersed differential signal (ΔOD) is generated by using a mechanical chopper to block every alternate pump pulse. The data is analyzed using open-source global analysis software (Glotaran, version 50 1.5.1) to obtain evolution-associated spectra (EAS) assuming a three-state kinetic model. The absorbance of the sample used for the TA measurements was about 0.3 at the excitation wavelength. The absorbance was recorded after the experiment to rule out any effect of photobleaching in the sample.

Photocatalysis: The oxidation of thioanisole was performed in presence of O_2 and irradiated by green LED light and E to Z isomerization of stilbene and C-H arylation of heteroarenes were

performed in presence of Ar under blue light (Kessil PR160L-456 nm) irradiation at room temperature. The singlet oxygen quantum yields were calculated by irradiating the solution mixture with monochromatic light source using KiloArc 1000W Xenon UV lamp at specific wavelengths.

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Structure–Property Relationships in Multi-stimuli Responsive BODIPY-Biphenyl-Benzodithiophene TICT Rigidochromic Rotors Exhibiting Stokes Shift Up to 221 nm

Abstract: Structure–property relationships of donor– π –acceptor (D– π –A) type molecular dyad (*pp*-AD) and triads (*pp*-ADA and Me-*pp*-ADA) based on benzodithiophene and BODIPY with biphenyl spacers have been reported. Rotors *pp*-AD and *pp*-ADA showed efficient twisted intramolecular charge transfer (TICT) with near infrared (NIR) emission at ~ 712 nm and ~ 725 nm with (pseudo-)Stokes shifts of ~ 208 nm and ~ 221 nm, respectively, and prominent solvatochromism. A structurally similar triad, Me-*pp*-ADA, with tetramethyl substituents on the BODIPY core instead was TICT inactive and exhibited excitation energy transfer with a transfer efficiency of ~ 88% as revealed using steady state emission and transient absorption measurements. Rotors *pp*-AD and *pp*-ADA showed NIR emission with an enhancement in intensity with the addition of water in THF solution as well as a pronounced change in emission intensity with temperature and viscosity variations, which justify their utility as temperature and viscosity sensors. Furthermore, a linear correlation of lifetime with fluorescence intensity ratios of the donor and acceptor justifies the rigidochromic behaviour of these rotors.



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3.1. Introduction

The development of organic fluorescent rotor molecules has been a rapidly emerging research area in recent years due to their versatile and tunable luminescent properties and have found extensive applications in the areas of (bio)sensors, bio-imaging, theranostics and many more.^{1,2} In this context, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene³ (BODIPY) dyes are an interesting class of chromophores due to their efficient and tunable absorption in the visible region, high fluorescence quantum yields and remarkable thermal and photochemical stabilities.⁴⁻⁶ Usually, BODIPY dyes exhibit a small Stokes shift and emission in green region owing to their straightforward excited state relaxation.^{4,5} However, structural variations such as donor- π -acceptor (D- π -A) design with rotatable junctions lead to modification of the excited state where an adiabatic relaxation mechanism such as twisted intramolecular charge transfer (TICT) causes dual emission originating from local excited (LE) state and TICT state.^{7,9} TICT emissions are red-shifted, resulting in a large (pseudo) Stokes shift^{10,11,12} and thus are advantageous for bio-imaging¹³ due to deeper tissue penetration and non-interference from tissue autofluorescence.^{14,15} TICT rotors are sensitive to multiple external stimuli (i.e., environmental parameters) such as solvent polarity, temperature and viscosity and can therefore serve as powerful optical probes for sensing temperature and viscosity in biological or material science relevant microenvironments.^{8,16,17} TICT rotors are mechanosensitive probes and the surrounding viscosity affects fluorescence lifetime, thereby leading to rigidochromism with a ratiometric response.¹⁸ Such rigidochromic rotors allow noninvasive mechanical imaging of (bio)materials.¹⁸ Although a large class of TICT molecular rotors of D- π -A type have been reported, examples of rotors with red^{19,20} or near infrared (NIR) emission^{21,22} with large Stokes shift (> 200 nm) are extremely rare. Di-alkynyl spacer linked porphyrin dimers (red em. ~ 780 nm) is one such example used for viscosity sensing by ratiometric and lifetime-based methods.²³ Maillard and co-workers reported glycoconjugated porphyrin dimers (red em. ~ 740-800 nm) for ratiometric temperature sensing.²⁴ Cao and co-workers reported a TICT based dye (N,N-dimethyl-4-((2-methylquinolin-6-yl)ethynyl)aniline) with a positive temperature coefficient and a mega Stokes shift of ~ 210 nm (although em. was at 550 nm).²⁵ Tang and co-workers reported a TICT dyad of triphenylamine and benzylidene imidazolone (TPA-BI) with a Stokes shift of ~ 202 nm and aggregate induced emission (AIE) suitable for efficient twophoton imaging.¹² Generally, TICT rotors also show AIE phenomenon where these molecules (AIE-gens) are weakly emissive in a "favourable" solvent (e.g. tetrahydrofuran) due to rapid non-

radiative deactivation of excited state by intramolecular rotations. However, they form (nano)aggregates in anti-solvent such as water leading to restricted intramolecular rotation and enhanced luminescence.²⁶⁻²⁸ AIE-gens have been used in chemosensing, light emitting, in-vitro and in-vivo imaging, image-guided therapy and theranostic applications.^{29,30} However, AIE-gens that emit at wavelengths longer than 700 nm are rare but are advantageous for bio-imaging and sensing due to effective tissue penetration and the predominant solvent being water that is wellsuited for cellular uptake of these rotor molecules.³⁰ Recently, our group reported regioisomeric rotor dyads and triads, in which BODIPY (A) and benzodithiophene (BDT) (D) were connected by either para-phenylene (*p*-AD, *p*-ADA) or meta-phenylene (*m*-AD, *m*-ADA) spacers.³¹ While the para-regioisomers showed efficient TICT with a maximum Stokes shift of ~ 194 nm (red em. upto 700 nm) for *p*-ADA,³² meta-regioisomers instead showed pronounced aggregation properties. In this work, we have investigated the effect of spacer length as well as tetramethyl groups on the photophysical properties of TICT rotors. The biphenyl spacer has been introduced with BODIPY and BDT as A and D respectively (*pp*-AD, *pp*-ADA, and Me-*pp*-ADA in Figure 3.1) which can increase the dipole length and lead to a modified excited state that might lead to larger Stokes shift than the earlier reported rotors.³¹ Accordingly, an unprecedented (pseudo) Stokes shift of ~ 221 nm for a BODIPY triad pp-ADA with NIR emission was achieved. Moreover, pp-AD and pp-ADA also exhibits efficient AIE with NIR response and prominent rigidochromic behaviour. On the other hand, tetramethyl substituents (at 1-, 3-, 5-, 7- positions) have been incorporated in the BODIPY core in Me-pp-ADA which shows significantly altered photophysical features compared



Figure 3.1. Chemical structures of dyad *pp*-AD and triads *pp*-ADA and Me-*pp*-ADA investigated in this work.

to the other two rotors. As a result of the tetramethyl substituents, the intramolecular meso-phenyl rotation is significantly impeded and thus **Me-pp-ADA** was TICT inactive non-rotor. However, it exhibited excitation energy transfer (EET) from BDT to BODIPY with a transfer efficiency of ~ 88% thus serving as a promising energy transfer cassette.

3.2. Result and Discussion

3.2.1. Synthesis

The syntheses of dyad *pp*-AD, triads *pp*-ADA and Me-*pp*-ADA were performed as detailed in Scheme 3.1. For the synthesis of *pp*-AD, *pp*-ADA and Me-*pp*-ADA, D precursor was synthesized starting from thiophene-3-carboxylic acid.^{34,35} For the acceptor precursor, bromo functionalized biphenyl was first synthesized by Suzuki coupling of 4-formylphenylboronic acid and 1-bromo-4iodobenzene³⁶ followed by condensation with pyrrole and 2,4-dimethyl pyrrole to obtain BODIPY^{37,38} acceptors *pp*-BODIPY and Me-*pp*-BODIPY respectively. Finally, dyad and triads were synthesized by Stille coupling reaction³² of corresponding BODIPY and di-stannylated BDT (D₂) for *pp*-ADA and Me-*pp*-ADA and mixture of mono- and di-stannylated BDT (D₁+D₂) for *pp*-AD. All compounds were purified by column chromatography as well as preparative thin layer chromatography (TLC) and were characterized by ¹H NMR, ¹³C NMR and high-resolution mass spectrometry (HRMS).



Scheme 3.1. Synthesis of *pp*-AD, *pp*-ADA and Me-*pp*-ADA.

3.2.2. UV/Vis Absorption and Emission

Steady state UV/Vis absorption and emission spectra of dyad pp-AD and triads pp-ADA, Me-pp-**ADA** were measured in chloroform (CHCl₃) at $c \sim 10^{-6}$ M. Three major absorption peaks were obtained for all dyad and triads corresponding to BODIPY S₀-S₁ transition (~ 504 nm), BDT π - π * transition (~ 312-322 nm), and a broad peak around ~ 360-390 nm corresponding to transitions arising due to electronic interactions of BDT and biphenyl which are conjugated (Figure 3.2). In case of *pp*-AD, donor excitation at 391 nm led to strong emission at 430 nm (originating from D) and a very weak emission at 524 nm (originating from A) and red-shifted peak at 712 nm corresponding to TICT. Acceptor excitation at 504 nm led to a significant emission band at 524 nm and a broad, red shifted peak at 712 nm with a (pseudo) Stokes shift of ~ 208 nm. Similarly, in *pp*-ADA, upon donor excitation at 391 nm and acceptor excitation at 504 nm, apart from the emission peaks at 430 and 524 nm, a broad TICT peak at 725 nm with a (pseudo) Stokes shift of ~ 221 nm was observed. However, in case of Me-pp-ADA, upon donor excitation at 391 nm, emission only from the acceptor at 516 nm was observed and BDT emission was completely quenched. This observation is attributed to EET from BDT to BODIPY that led to quantitative quenching of donor fluorescence (vide infra). Additionally, no red-shifted emission band was observed for Me-pp-ADA which indicates that this compound was TICT inactive. The molar absorption coefficients (ε) of *pp*-AD and *pp*-ADA, Me-*pp*-ADA were 27370 M⁻¹cm⁻¹, 36280 M⁻¹ ¹cm⁻¹, and 31758 M⁻¹cm⁻¹ respectively.



Figure 3.2. (a) UV/Vis absorption of *pp*-AD and *pp*-ADA, Me-*pp*-ADA and emission of these three compounds upon excitation at (b) 391 nm and (c) 504 nm.

Besides the photophysical properties of rotors in solution, their solid-state absorption and emission are important for impending applications in (opto)electronic devices.^{39,40} Accordingly, UV/Vis absorption and emission measurements of these rotors were performed in thin films. In thin films

of *pp*-ADA, three absorption peaks (centered at 335 nm, 420 nm and 542 nm) red-shifted compared to those in the solution spectra were observed (Figures 3.3). Similarly, in **Me**-*pp*-ADA, three major absorption peaks (338 nm, 400 nm and 512 nm) were observed. In thin film of *pp*-ADA, upon acceptor excitation at 542 nm, beside emission at 561 nm, an intense peak at ~ 736 nm were observed while in **Me**-*pp*-ADA, acceptor excitation at 512 nm led to emission peaks at 531 nm, 555 nm and intense peak at 640 nm was observed. Such red emission in the solid state indicates the utility of these materials in (opto)electronic device fabrication such as in excitonic solar cells.



Figure 3.3. UV/Vis and emission of *pp*-ADA and Me-*pp*-ADA in thin films.

3.2.3. Solvatochromism

Since both rotors *pp*-AD and *pp*-ADA showed TICT emission, fluorescence solvatochromism study was performed in solvents of different polarities. In non-polar solvents such as methyl cyclohexane (MCH) and toluene (Tol), *pp*-AD and *pp*-ADA showed only a peak corresponding to BODIPY emission. In TICT rotors, since the excited state shows higher dipole moment than the ground state, it is preferentially stabilized by polar solvents than the respective ground state.¹⁰ Accordingly, increasing solvent polarity leads to bathochromic shift in the emission profile of these rotors. In polar solvents such as chloroform (CHCl₃), tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2-MeTHF), *pp*-AD and *pp*-ADA showed dual emission and the longer wavelength TICT band shifted bathochromically in more polar solvents (Figure 3.4). In dichloromethane (DCM), TICT state was not observed for any of the rotors (*pp*-AD and *pp*-ADA) presumably due to rapid non-radiative deactivation. Furthermore, solvatochromic study was

performed for both the rotors in a binary mixture of polar and non-polar (THF/hexane) solvents. For *pp*-ADA, as the percentage of hexane was increased from 0 to 50% (v/v), the TICT band was hypsochromically shifted and intensity increased due to increase in hydrophobicity of the solvent mixture which renders the *pp*-ADA less twisted. Upon further increasing hexane percentage to 60% and 80% (v/v), the intensity decreased with peak while the LE emission became the prevailing peak. At 90 % hexane, only LE emission was observed and no TICT peak was observed. Thus, for *pp*-ADA, a prominent hypsochromic shift was observed from 720 nm to 522 nm and the TICT band disappeared with concomitant emergence of the LE band as a shoulder upon increasing hexane percentage from 0% to 90%. Similarly, a hypsochomic shift was observed for *pp*-AD from 724 nm to 521 nm upon increasing hexane percentage from 0% to 90% (Figure 3.4). Thus, hyposchromic shift upon decreasing solvent polarity confirmed the TICT states in *pp*-AD and *pp*-ADA.



Figure 3.4. Emission of (a) *pp*-AD and (b) *pp*-ADA excited at 504 nm in solvents of different polarities and emission of (c) *pp*-AD and (d) *pp*-ADA in different percentages of THF/hexane and (inside the box, 0%, 10% to 90% indicate the percentages of hexane in THF solutions).

3.2.4. Cyclic Voltammetry

In order to assess the redox properties and frontier molecular orbital (FMO) energy levels, cyclic voltammetry (CV) measurements were performed for *pp*-AD, *pp*-ADA, and Me-*pp*-ADA and the cyclic voltammograms are presented in Figure 3.5. The observed HOMO levels were -5.93 eV, - 5.87 eV, -5.72 eV and LUMO levels were -4.04 eV, -4.19 eV, -3.88 eV for *pp*-AD, *pp*-ADA, and Me-*pp*-ADA respectively (Table 3.1).



Figure 3.5. Cyclic voltammogram of (a) *pp*-AD, (b) *pp*-ADA and (c) **Me**-*pp*-ADA in dry DCM with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) and potentials measured vs Ag/AgCl reference electrode.

Table 3.1. Redox properties of dyad *pp*-AD and triads *pp*-ADA and Me-*pp*-ADA based on cyclic voltammetry.

Compound	E _{ox} onset (V)	*HOMO (eV)	E _{red} ^{onset} (V)	LUMO (eV)	Eg (eV)	Molar extinction coefficient (<i>ɛ</i>) (M ⁻¹ cm ⁻¹)
pp-AD	1.17	- 5.93	- 0.72	- 4.04	1.89	27370
pp-ADA	1.11	- 5.87	- 0.57	- 4.19	1.68	36280
Me-pp-ADA	0.96	- 5.72	- 0.88	- 3.88	1.84	31758

 $^{*}HOMO = -(E_{onset}^{ox} + 4.76) \text{ eV}, \text{ and } LUMO = -(E_{onset}^{red} + 4.76) \text{ eV}.$

3.2.5. DFT Calculations and Excitation Energy Transfer

Density functional theory (DFT) calculations were performed using Gaussian 09 package at the B3LYP/6-31 G (d,p) level (Figure 3.6, Table 3.2-3.5) to calculate the HOMO and LUMO energy levels as well as torsion angles in geometry optimized structures of all molecules in the ground state. Frontier molecular orbital (FMO) composition analysis were performed for all three molecules and it was found that the HOMO of *pp*-ADA was composed of 86% contribution from

BDT donor and no contribution from BODIPY acceptor, while LUMO was composed of 85% contribution from BODIPY acceptor and 2% from BDT donor.



Figure 3.6. FMO energy levels of compounds *pp*-AD, *pp*-ADA and Me-*pp*-ADA calculated by B3LYP/6-31G(d,p) method.

Table 3.2. FMO energy levels of compounds *pp*-AD, *pp*-ADA and Me-*pp*-ADA calculated by B3LYP/6-31G(d,p) method.

Compound	HOMO-1	НОМО	LUMO	LUMO+1	
	(eV)	(eV)	(eV)	(eV)	
pp-AD	-5.86	-5.23	-2.80	-1.90	
pp-ADA	-5.90	-5.28	-2.85	-2.83	
Me-pp-ADA	-5.36	-5.22	-2.36	-2.36	

This observation implies a charge transfer (CT) character corresponding to a HOMO to LUMO transition (BDT to BODIPY) for *pp*-ADA. Similar CT behaviour was indicated for a HOMO to LUMO+1 transition because LUMO+1 was composed of 88% contribution from acceptor BODIPY. Similar FMO composition was obtained for *pp*-AD where the HOMO has a 97% contribution from BDT and LUMO has 92% from BODIPY indicating CT character. The FMO composition analysis of Me-*pp*-ADA showed BDT and BODIPY contributing to 85% and 97% to HOMO and LUMO respectively, and LUMO +1 has a contribution of 98% from acceptor (Table

3.3). The FMO composition analysis indicates the possibility of CT in **Me-pp-ADA**, however, the restricted rotation of the meso phenyl substituent of the BODIPY moiety due to the presence of four methyl groups prevents the formation of a TICT state.

Compound	Orbital No.	МО	Energy (eV)	Contribution from BDT donor (%)	Contribution from BODIPY acceptor (%)	Contribution from biphenyl spacer (%)
	247	LUMO+1	-2.83	0	88	11
pp-ADA	246	LUMO	-2.85	2	85	13
	245	номо	-5.29	86	0	14
	244	HOMO-1	-5.90	0	99	1
	159	LUMO+1	-1.66	72	2	26
pp-AD	158	LUMO	-2.71	0	92	8
	157	номо	-5.3	97	0	3
	156	HOMO-1	-5.87	0	99	1
	279	LUMO+1	-2.37	0	98	2
Me-pp-	278	LUMO	-2.37	0	97	2
ADA	277	номо	-5.22	85	0	15
	276	HOMO-1	-5.36	0	100	0

Table 3.3. FMO composition analysis of pp-AD, pp-ADA and Me-pp-ADA based on DFT calculations.

The detailed FMO composition analysis with the contribution of the BDT, BODIPY and phenyl spacer towards the FMOs of dyads and triads are provided in Table 3.3. For *pp*-AD and *pp*-ADA, the ϕ_1 , ϕ_2 and ϕ_3 torsion angles were comparable for both i.e., ~ 53°, 36° and 23° respectively and the torsion angles ϕ_4 , ϕ_5 and ϕ_6 of *pp*-ADA were similar to ϕ_3 , ϕ_2 and ϕ_1 (Table 3.4). These results suggest that both *pp*-AD and *pp*-ADA are twisted in the ground state. It is well known that intramolecular rotation of meso phenyl substituent of BODIPY is the responsible rotation that imparts the TICT behaviour to BODIPY dyes.⁹ Accordingly, torsion along ϕ_1 and ϕ_6 of Me-*pp*-ADA were ~ 90° due to the presence of methyl substituents at C1, C7-positions of BODIPY. Such orthogonal arrangement in Me-*pp*-ADA is therefore energetically the most stable conformation in the ground state and the intramolecular rotation along the BODIPY-meso phenyl bond is

completely restricted due to steric reasons. As a result, **Me-pp-ADA** was TICT inactive and the D and A units being orthogonal behave as independent chromophores thereby favouring energy transfer.⁴¹ However in **Me-pp-ADA**, through-space Förster resonance energy transfer (FRET) is unlikely since the BDT (energy donor) emission and BODIPY (energy acceptor) absorption have negligible overlap as shown in Figure 3.7a.

Compounds Φ_1 (deg) $\Phi_2(\text{deg})$ Φ_3 (deg) Φ_6 (deg) Φ_4 (deg) $\Phi_5(\text{deg})$ pp-AD 53 36 23.4 -_ _ 53 pp-ADA 53.1 36 23.7 23.7 35.9 Me-pp-ADA 90.5 36.5 23.7 24.3 90.3 36.6

Table 3.4. Torsion angles in geometry optimized structures of compounds *pp*-AD, *pp*-ADA, and Me-*pp*-ADA.

Fluorescence excitation spectrum of **Me-pp-ADA** was recorded at the BODIPY emission edge (514 nm) provided peaks corresponding to the BDT, biphenyl as well as BODIPY absorption thus indicating efficient EET in this compound (Figure 3.7b).



Figure 3.7. (a) Emission of BDT and absorption of BODIPY showing a weak spectral overlap; (b) fluorescence excitation spectrum of Me-*pp*-ADA recorded at BODIPY emission at 516 nm.

3.2.6. Fluorescence Quantum Yield

Fluorescence quantum yields were determined for dyad and triads by relative method using Rhodamine B as reference dye and quantum yields of 0.034, 0.024 and 0.20 were obtained for *pp*-**AD**, *pp*-**ADA**, and **Me**-*pp*-**ADA** respectively (Table 3.5).

Compound	Absorbance			Integrated	Fluorescenc	$\begin{array}{l} Quantum \ Yield \\ \Phi = \Phi_R(I/I_R)(A_R/A) \\ (\lambda_{exR}/\lambda_{ex})(n^2/n^2_R) \end{array}$		
	1	2	3	1	2	3	Φ_{i}	Φ _{avg}
pp-AD	0.010	0.018	0.026	46789	84448	137538	0.031 0.034 0.038	0.034
pp-ADA	0.026	0.050	0.066	103785	186475	151326	0.028 0.024 0.021	0.024
Me <i>-pp-</i> ADA	0.050	0.080	0.100	61959	83432	168432	0.200 0.220 0.200	0.206
Rhodamine B (ethanol)	0.014	0.017	0.019	13388573	1374809	1667805	(0.5

Table 3.5. Relative quantum yields of triads *pp*-AD, *pp*-ADA and Me-*pp*-ADA by using relative method and Rhodamine B as a reference dye.

For obtaining the energy transfer efficiency (ETE) for **Me-pp-ADA**, the quantum yields of BDT donor and BDT acceptor in **Me-pp-ADA** were calculated using anthracene as spectroscopic reference compound (Table 3.6) in THF solution.

Table 3.6. Relative quantum yields of BDT and donor part of Me-pp-ADA using relative method and Anthracene as a reference dye.

Compound	A	bsorban	ce	Integrated	Quantum Yield $\Phi = \Phi_R(I/I_R)(A_R/A)(A_R/A)(A_R/A_R)(n^2/n^2_R)$			
	1	2	3	1	2	3	Φ	Φ _{avg}
BDT	0.039	0.060	0.080	28152562	31585520	36884900	0.223 0.16 0.13	0.17
Donor part of Me- <i>pp</i> - ADA	0.004	0.013	0.015	407004	1007515	915474	0.027 0.021 0.016	0.021
Anthracene (ethanol)	0.041	0.066	0.081	38066300	62617500	79902400	0.	27

The energy transfer efficiency (ETE) of **Me-pp-ADA** can be measured using the following equation 3.1: ⁴²

$$ETE = 1 - \Phi_{DA}/\Phi_D \qquad (3.1)$$

where Φ_{DA} is the quantum yield of BDT in triad **Me**-*pp*-**ADA** and Φ_D is the quantum yield of free BDT. Absorbance and fluorescence spectra were recorded for three different concentrations of BDT (excitation wavelength of 355 nm) and BDT donor of **Me**-*pp*-**ADA** (excitation wavelength of 391 nm) in THF solution and the quantum yields were subsequently calculated as explained above using Anthracene in ethanol as reference dye (Table 3.6). A quantum yield of 0.17 was obtained for free BDT while quantum yield of 0.021 was obtained for BDT in **Me**-*pp*-**ADA** thereby revealing excitation energy transfer with an ETE of ~ 88% from BDT to BODIPY.

3.2.7. Transient Absorption Spectroscopy^a

To further confirm the EET process, transient absorption (TA) measurements were performed for Me-pp-ADA in THF by femtosecond pump-probe technique. The TA spectrum of Me-pp-ADA excited at 500 nm (acceptor excitation) is compared with that of its (commercially available) model acceptor excited at 500 nm (Figures 3.8a, b). Upon the acceptor excitation, both the spectra exhibited a bleach of the ground state absorption immediately, and no excited state absorption (ESA) was observed in the spectral window. While upon donor excitation at 392 nm, a broad absorption band was obtained in the 600 nm to 900 nm region. Hence, the ESA appearing between 600 nm and 900 nm should be assigned to the excited donor species (Figure 3.8c). Interestingly, the ESA of donor emerges with the ground state bleach of acceptor, indicating the formation of the excited state of acceptor. Since the absorption of model acceptor at 400 nm is negligible, the excited acceptor in Figure 3.8c should arise from excitation energy transfer. The deactivation dynamics of excited molecules is further analyzed by a single wavelength fitting respectively. In both compounds, the first component (τ_1) , ~ 1 ps, can be associated with the ultrafast solvation process.^{43,44} Subsequently, the decay of the relaxed excited state to the ground state is characterized by the time constant that is comparable to the photoluminescence lifetime on ns timescale. Further details on these transient absorption studies are provided in our published work.⁴⁵

^aTransient studies were performed by Z. Wei (in the group of Prof. F. C. Grozema) at TU Delft, Netherlands.



Figure 3.8. Transient absorption spectra of (a) Me-bodipy (model acceptor) excited at 500 nm, and **Me-pp-ADA** excited at (b) 500 nm and (c) 400 nm. (d) Temporal profiles of the normalized Δ OD trace for **Me-pp-ADA** recorded at 504 nm (blue line) and for Me-bodipy recorded at 503 nm (green line) and their fittings (dashed lines).

3.2.8. Temperature Sensing Properties

The emission of molecular rotors is remarkably sensitive to multiple stimuli such as temperature and viscosity of the solvent^{2,8} thus the temperature-dependent emission of *pp*-AD and *pp*-ADA were investigated. For *pp*-AD, upon increasing the temperature from 15 °C to 55 °C in CHCl₃, a steady increase in the fluorescence intensity was observed and the TICT band shifted hypsochromically from ~ 716 nm (15 °C) to ~ 697 nm (55 °C) (Figure 3.9). This observation is attributed to thermal energy assisting the excited electron in crossing the activation barrier from TICT to LE state and the latter (LE state) gets preferentially populated resulting in a hypochromic shift accompanied with an intensity enhancement.⁴⁶ Similarly, for *pp*-ADA in the same temperature range and solvent, the TICT band shifted hypsochromically from ~ 728 nm to ~ 700 nm with nearly 2-fold intensity enhancement (Figures 3.9).



Figure 3.9. Temperature-dependent emission spectra of (a) pp-AD and (b) pp-ADA in CHCl₃.

Similar trend was observed in the temperature dependent emission spectra of *pp*-ADA in THF (Figure 3.10). However, in non-polar solvents such as in Tol, only BODIPY peak was observed and increasing the temperature from 5 °C to 95 °C led to decrease in BODIPY emission intensity that is attributed to enhanced molecular motions at higher temperatures leading to non-radiative deactivation.



Figure 3.10. Temperature-dependent emission spectra of *pp*-ADA in (a) THF and (b) Tol.

Ratiometric temperature sensing analysis was performed for *pp*-AD and *pp*-ADA by plotting the emission intensity ratios of TICT band and at another wavelength where the intensity does not change with temperature (I₁ and I₂) vs. the varying temperatures. The plot of the ratio of intensities with temperatures were fitted with linear functions^{46,47} to obtain the temperature coefficients and accordingly, positive temperature coefficients of 0.19% °C⁻¹ and 0.27% °C⁻¹ were obtained for *pp*-AD and *pp*-ADA respectively in CHCl₃ in the range 15 °C to 55 °C. In ratiometric temperature sensing plots, linearity is one of the significant features because it shows constant thermal

sensitivity in the physiological temperature range. A linear relationship of the TICT intensity ratios vs. temperature (Figure 3.11) suggested that these rotors could be used as ratiometric temperature sensors very efficiently in a wide temperature range.



Figure 3.11. Emission intensity ratio with best fit equation at different temperature for (a) *pp*-AD in CHCl₃ and for *pp*-ADA in (b) CHCl₃, (c) THF and (d) Tol.

3.2.9. Viscosity Sensing Properties

Viscosity-dependent emission measurements were performed in methanol (MeOH) and glycerol (gly) mixtures for both the rotors by increasing the percentage of gly from 0% to 90% in MeOH (0.6 cP to 454 cP).¹⁹ By increasing the viscosity, molecular rotation is restricted leading to exclusion of non-radiative deactivation pathways and enhancement in emission intensity. Accordingly, for **pp-AD** and *pp*-**ADA**, upon increasing the gly content from 0% to 90% in MeOH, the intensity of LE band and acceptor band increased by 2-fold and 3-fold respectively (Figures 3.12). From the Förster-Hoffmann analysis,^{16,17} *pp*-**AD** and *pp*-**ADA** showed viscosity sensitivities of 0.08 and 0.14 respectively similar to our earlier reported rotors *p*-**AD** (0.09) and *p*-**ADA** (0.14).³¹



Figure 3.12. Viscosity-dependent emission spectra of (a) *pp*-AD and (b) *pp*-ADA in in gly/MeOH mixture. Emission intensity ratios at different viscosities with their best fit equations for (c) *pp*-AD and (d) *pp*-ADA. Temperature-dependent emission was performed with 50% gly/MeOH solution (viscosity ~ 24 cP) to elucidate the effect of temperature on molecular rotations in a viscous medium. For *pp*-AD and **pp**-ADA, the emission intensity decreased by ~ 2-fold upon increasing the temperature from 15 °C to 55 °C (Figure 3.13) which is indicative of increased molecular motions at decreasing viscosities thereby facilitating non-radiative deactivation.



Figure 3.13. Emission spectra of (a) *pp*-AD and (b) *pp*-ADA in MeOH:Gly-50:50 (24 cP) at variable temperature.

3.2.10. Fluorescence Lifetime and Rigidochromism

In order to understand the dynamics of the TICT processes of the rotors as well as their rigidochromic behaviour (i.e., variation in fluorescence lifetimes at variable viscosity¹⁸), fluorescence lifetime measurements were performed for *pp*-AD and *pp*-ADA in CHCl₃ using time correlated single photon counting (TCSPC) technique. For *pp*-AD, the decay corresponding to 712 nm (TICT band) exhibited a longer average lifetime (τ_{avg}) of ~ 0.69 ns compared to the decay corresponding to 523 nm (acceptor channel) of 0.09 ns (Figure 3.14, Table 3.7). Similarly, the τ_{avg} of *pp*-ADA at emission wavelengths of 524 nm (acceptor channel) and 725 nm (TICT emission) were ~ 0.03 ns and ~ 0.44 ns respectively. It is well known that decay in TICT emission channels show higher lifetimes than donor or acceptor emission channels.^{31,32} Furthermore, all the decay profiles could be fitted with tri-exponential functions that indicate the presence of multiple conformers or species in solution.



Figure 3.14. Fluorescence lifetime decay collected by using TCSPC at different wavelengths in CHCl₃ samples of (a) *pp*-AD, (b) *pp*-ADA and (c) Me-*pp*-ADA.

$\begin{array}{c} Compound \\ (\lambda_{ex}=375nm) \end{array}$	λ _{em} (nm)	$ au_1(lpha_1)$ (ns)	$ au_2(a_2)$ (ns)	τ ₃ (α ₃) (ns)	$ au_{ m avg}$ (ns)	χ^2
pp-AD	523	0.38 (0.08)	0.05 (0.92)	2.52 (0.01)	0.09	1.01
	712	0.11 (0.51)	1 (0.41)	2.94 (0.08)	0.69	1.05
pp-ADA	524	0.34 (0.01)	0.03 (0.99)	2.88 (0)	0.03	1.17
	714	0.08 (0.52)	0.75 (0.46)	2.52 (0.02)	0.44	1.06
Me-pp-ADA	435	0.86 (0.99)	4.63 (0.01)	-	0.61	0.89
	516	0.93 (0.11)	2.72 (0.89)	-	0.9	1.12

Table 3.7. Fluorescence lifetime analysis of *pp*-AD, *pp*-ADA and Me-*pp*-ADA at different emission wavelength

Fluorescence lifetimes of *pp*-AD and *pp*-ADA were also measured at variable viscosities by increasing gly content from 0% to 90% (0.6 cP to 454 cP) (Figure 3.15, Table 3.8) to confirm the rigidochromic behaviour. Upon increasing the viscosity, pronounced enhancement in fluorescence lifetimes were observed due to restricted intramolecular rotations resulting in slower radiative decay and longer lifetimes. Accordingly, upon increasing the viscosity, the τ_{avg} of *pp*-AD increased from 0.08 ns to 2.02 ns while for *pp*-ADA, τ_{avg} increased from 0.2 ns to 0.87 ns. Linear correlations between fluorescence lifetimes and intensity ratios of A and D emissions (I_A/I_D) at variable viscosity (Figure 3.15) were obtained for *pp*-AD and *pp*-ADA. A linear correlation in such plot is an essential feature of rigidochromism¹⁸ and accordingly rotors *pp*-AD and *pp*-ADA are efficient ratiometric rigidochromic rotors.



Figure 3.15. Fluorescence lifetime decay at variable viscosities of (a) *pp*-AD and (b) *pp*-ADA, linear correlation between fluorescence lifetime at variable viscosity and emission intensity ratio of donor and acceptor (I_A/I_D) obtained from steady state emission of (c) *pp*-AD and (d) *pp*-ADA.

Compound $(\lambda_{ex} = 375 nm)$	Viscosity (in cP) (solvent mixture)	$ au_1(lpha_1)$ (ns)	$ \begin{aligned} \tau_2(\alpha_2) \\ (ns) \end{aligned} $	$ au_3(au_3)$ (ns)	Average lifetime τ _{avg} (ns)	χ²
	454	0.41	2.97 (0.55)	11.2 (0.02)	2.02	1.25
	434	(0.41)	2.87 (0.33)	11.5 (0.02)	2.02	1.55
	(90/10.0/V)	(0.42)				
	218	0.65	21(0.46)	10.3(0.02)	1 /19	1 18
	(80/20 y/y)	(0.52)	2.1 (0.40)	10.3 (0.02)	1.47	1.10
	(00/20 V/V glv/MeOH)	(0.52)				
nn-AD	50	1 16	8 11 (0 01)	0.25(0.82)	0.48	1 37
	(60/40 v/v)	(0.17)	0.11 (0.01)	0.23 (0.02)	0.40	1.57
	glv/MeOH)	(0.17)				
	11	0.90	7.41 (0)	0.11 (0.94)	0.18	1.28
	(40/60 v/v)	(0.06)	(0)	0111 (012-1)	0110	1.20
	glv/MeOH)	(0.00)				
	3	0.94	7.17(0)	0.07 (0.97)	0.11	1.50
	(20/80 v/v	(0.03)		(,		
	gly/MeOH)	× ,				
	0.6	0.89	6.33 (0)	0.06 (0.98)	0.08	1.26
	(0/100 v/v	(0.02)		. ,		
	gly/MeOH)	. ,				
	454	0.33	1.78 (0.3)	9.02 (0.01)	0.87	1.43
	(90/10 v/v	(0.69)				
	gly/MeOH)					
	218	1.35	0.34 (0.68)	8.69 (0.01)	0.75	1.14
	(80/20 v/v	(0.3)				
	gly/MeOH)					
pp-ADA	50	1.31	8.93 (0.01)	0.34 (0.8)	0.61	1.26
	(60/40 v/v	(0.19)				
	gly/MeOH)					
	11	1.64	0.14 (0.94)	9.51 (0.01)	0.28	1.43
	(40/60 v/v	(0.05)				
	gly/MeOH)					
	3	1.65	9.16 (0.01)	0.09 (0.96)	0.19	1.33
	(20/80 v/v	(0.03)				
	gly/MeOH)					
	0.6	1.63	8.19 (0.01)	0.08 (0.95)	0.20	1.17
	(0/100 v/v	(0.04)				
	gly/MeOH)					

Table 3.8. Fluorescence decay parameters of *pp*-AD and *pp*-ADA at variable viscosity, the decay times (τ_1 , τ_2 and τ_3) and the respective fractional contributions (α_1 , α_2 and α_3), the amplitude average decay time (τ_{avg}) and the quality of fitting (χ^2).

3.2.11. Aggregate Induced Emission

TICT rotors usually are AIE active where they are weakly emissive or non-emissive in a "good" solvent and become emissive upon addition of a "poor" solvent due to the formation of aggregates and hence restricted intramolecular rotations. AIE was investigated in dyad *pp*-AD and triads *pp*-ADA and Me-*pp*-ADA in binary mixture of THF and water. For *pp*-AD, starting from pure THF, initial increase in water content (10-50% v/v) led to a decrease in the intensity of TICT band (719 nm) due to increasing hydrophilicity of solvent that favours rapid intramolecular rotation leading to non-radiative deactivation.^{9,12} However, upon further increasing the water content to ~ 60-90%, a 6-fold enhancement in emission intensity of TICT band was observed with a concomitant bathochromic shift to 727 nm (Figure 3.16). This emission intensity enhancement was attributed to formation of (nano)aggregates which restricts the intramolecular rotations thereby reducing the non-radiative deactivation. Similarly, for *pp*-ADA, upon increasing the water content up to 50% (v/v), the intensity of TICT band (723 nm) decreased. However, upon further increase in the water content up to 50%, TICT band showed a minimal bathochromic shift to 730 nm with 5-6-fold enhancement of emission intensity. The tetramethyl substituted non-rotor Me-*pp*-ADA however did not show AIE enhancement (Figure 3.16) unlike the two rotors.



Figure 3.16. Emission of (a) *pp*-AD and (b) *pp*-ADA and (c) Me-*pp*-ADA in different percentages of THF and water.

3.3. Conclusions

In summary, D- π -A rotors dyad *pp*-AD and triad *pp*-ADA showed efficient TICT with NIR emission at 712 and 725 nm and extraordinary large Stokes shift of ~ 208 nm and ~ 221 respectively, with prominent AIE with NIR response. Viscosity-dependent enhancement of emission and pronounced increase in fluorescence lifetime were observed for rotors *pp*-AD and *pp*-ADA. A linear correlation of lifetime with intensity ratios justifies the rigidochromic behaviour

of these rotors. Compounds *pp*-AD and **pp**-ADA showed temperature as well as viscosity sensitivity, with positive temperature coefficients of 0.19% $^{\circ}C^{-1}$ and 0.27% $^{\circ}C^{-1}$ and viscosity sensitivities of 0.08 and 0.14 respectively. On the other hand, owing to the presence of tetramethyl substituents, **Me**-*pp*-ADA was TICT inactive and thus a non-rotor but showed efficient EET from BDT to BODIPY with an efficiency of ~ 88%. Furthermore, compounds *pp*-ADA and **Me**-*pp*-ADA showed red shifted emission in thin film (736 nm, 640 nm respectively) and *pp*-ADA showed solid state emission ~ 732 nm and are potentially useful for (opto)electronic applications. These multifunctional TICT rotors owing to their large Stokes shift and AIE emission in NIR region and responsiveness of their emission to multiple stimuli such as solvent polarity, temperature, viscosity are thus potentially useful for bioimaging, temperature and viscosity sensing of cellular microenvironments as well as for micromechanical imaging of (bio)materials.

3.4. Experimental section

Synthesis of 4'-bromo-[1,1'-biphenyl]-4-carbaldehyde (1):



Scheme 3.2. Synthesis of 4'-bromo-[1,1'-biphenyl]-4-carbaldehyde.³⁶

To a solution of 1-bromo-4-iodobenzene (2 g, 7.06 mmol) in Tol, catalytic amount of tetrakistriphenylphosphinepalladium Pd(PPh₃)₄ (3-5 mol%) was added followed by addition of 5 mL aqueous solution of Na₂CO₃ (2 M). A solution of 4-formyl phenyl boronic acid (1 g, 6.66 mmol) in 15 mL ethanol was added to reaction mixture and the mixture was heated to reflux for 5 hours (h). After cooling to room temperature, the reaction mixture was extracted with CHCl₃ and washed with brine solution. Subsequently, the organic layers were passed through sodium sulphate and solvent was evaporated on rotary evaporator. The crude product was purified by column chromatography using 90:10 hexane:ethylacetate to obtain white solid with 60% yield. ¹**H NMR (400 MHz, CDCl₃)** *δ* (**ppm):** 10.06 (s, 1 H), 7.95 (d, *J* = 8 Hz, 2 H), 7.72 (d, *J* = 8 Hz, 2 H), 7.61 (d, *J* = 8 Hz, 2 H), 7.50 (d, *J* = 8 Hz, 2 H).

Synthesis of Me-pp-BODIPY (2):



Scheme 3.3. Synthesis of Me-pp-BODIPY compound 2.38

Compound **1** (100 mg, 0.38 mmol) was dissolved in dry DCM and purged. Pyrrole (127 mg, 1.34 mmol) and 3-4 drops of trifluoroacetic acid was added and the reaction mixture was stirred for 5 h at room temperature. Subsequently, chloranil (102 mg, 0.41 mmol) was added and stirred for 40 minutes. The reaction intermediate compound was passed through silica column using DCM and solvent was evaporated to collect the crude intermediate. Tol was added followed by addition of triethylamine (776 mg, 7.67 mmol) and reaction mixture was stirred. After 15 minutes, boron trifluoride diethyl etherate (BF₃.Et₂O) (1.3 g, 9.1 mmol) was added and stirred at 80°C for 40 minutes and reaction was monitored by TLC. The extraction was done by ethyl acetate and the product was purified by column chromatography using DCM and hexane as eluent to obtain orange solid in 36% yield.

¹**H** NMR (400 MHz, CDCl₃) δ (ppm): 7.71 (d, J = 8 Hz, 2 H), 7.61 (d, J = 8 Hz, 2 H), 7.54 (d, J = 8 Hz, 2 H), 7.36 (d, J = 8 Hz, 2 H), 5.99 (s, 2 H), 2.56 (s, 6 H), 1.43 (s, 6 H).

Synthesis of *pp*-BODIPY (3):



Scheme 3.4. Synthesis of pp-BODIPY.³⁷

Compound **1** (200 mg, 0.77 mmol) was dissolved in dry DCM and purged nitrogen. Then pyrrole (0.16 mL, 2.31 mmol) and catalytic amount of trifluoroacetic acid and stirred for 1 h at room temperature under nitrogen atmosphere. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (174.8 mg, 0.77 mmol) was added to the reaction mixture and stirred for 0.5 h and further 6 mL of triethylamine was added followed by addition of BF₃.Et₂O (6 mL) and stirred for 3 h at room temperature. The organic phase was washed by saturated solution of Na₂CO₃, dried over sodium sulphate and filtered. The residue was purified by column chromatography using hexane and ethyl acetate as eluent to obtain red solid with 25% yield.

¹**H NMR (400 MHz, CDCl₃)** δ (**ppm):** 7.96 (s, 2 H), 7.72 (d, J = 8 Hz, 2 H), 7.65 (t, J = 8 Hz, 4 H), 7.54 (d, J = 8 Hz, 2 H), 7.01 (d, J = 4 Hz, 2 H), 6.58 (d, J = 4 Hz, 2 H).

Synthesis of Donor (4,8-di(oct-1-yn-1-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis(trimethylstannane) (D₂):



Scheme 3.5. Synthesis of D_2 (4).³¹

Synthesis of A: 2 g (15.60 mmol) of thiophene-3-carboxylic acid was added to 15 mL of DCM taken in a round-bottomed flask fitted with CaCl₂ guard tube. The solution was cooled on an ice bath and 7.92 g (62.42 mmol) of oxalyl chloride was added dropwise. The reaction mixture was stirred at room temperature for overnight. The excess oxalyl chloride was removed under vacuum. The acyl chloride intermediate was dissolved in 10 mL of dry DCM. The solution of acid chloride

was then added dropwise to the solution containing diethylamine 3.2 g (43.75 mmol) in 30 mL of dry DCM in a two necked round-bottomed flask fitted with a CaCl₂ guard tube and cooled on an ice bath. The reaction mixture was stirred for 3 hours at room temperature and washed with water. The organic fraction was dried using anhydrous sodium sulphate, solvent evaporated and purified by silica gel column chromatography using ethyl acetate/ hexane (30/70 v/v) mixture as eluent. Pure product was obtained as an oily liquid with a yield of 97%.

¹**H NMR (400 MHz, CDCl₃)** δ (**ppm):** 7.46 (d, J = 2.8 Hz, 1 H), 7.34–7.27 (m, 1 H), 7.17 (d, J = 5.0 Hz, 1 H), 3.54-3.31 (m, 4 H), 1.18 (s, 6 H).

Synthesis of B: Compound A (1.308 g, 7.1362 mmol) was dissolved in distilled THF. Then the solution was cooled to 0 °C and 6.11 mL of *n*-BuLi (1.6 M in hexane) was added dropwise while stirring under inert atmosphere. The solution was stirred at room temperature for 3 hours and later it was poured into a beaker which contained ice-water. Yellowish precipitate formed immediately and the mixture was stirred overnight. The precipitate was filtered out using Buchner apparatus and washed with water, methanol and hexane successively and dried under vacuum. 0.435 g (27%) of yellow solid was obtained as product.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.69 (d, J= 4 Hz, 2 H), 7.65 (d, J= 4 Hz, 2 H).

Synthesis of C: Isopropylmagnesium chloride (2 M in THF, 1.2 mL, 2.3971 mmol) was added dropwise to 1-octyne (0.29 g, 2.6315 mmol) at 0 °C. Then the reaction mixture was heated to 60 °C and stirred for 100 min. It was cooled to room temperature and compound **B** (100 mg, 0.4540 mmol) was added (which was already degassed with 5-6 freeze-pump-thaw cycles). The reaction mixture was heated upto 60 °C and stirred for 120 min. Then, the reaction mixture cooled to room temperature and 0.7 g of SnCl₂ in HCl solution (16 mL, 10%) was added dropwise to the reaction mixture. The reaction mixture was heated at 65 °C for 60 min, then cooled down to room temperature and poured into water and extracted with hexane twice. The organic fraction was dried over anhydrous Na₂SO₄ and concentrated under vacuum. Light yellow solid product was obtained by recrystallization of the crude from ethanol with a yield of 38%.

¹**H** NMR (400 MHz, CDCl₃) δ (ppm): 7.57 (d, J = 8 Hz, 2 H), 7.50 (d, J = 4 Hz, 2 H), 2.63 (t, J = 8 Hz, 4 H), 1.76-1.69 (m, 4 H), 1.38-1.25 (m, 12 H), 0.94-0.91 (m, 6 H).

Synthesis of $D_2(4)$: 200 mg (0.49 mmol) of C was dissolved in dry THF. The solution was cooled to -78 °C and 1.25 mL (2.5 mmol) of *n*-BuLi (2 M solution in hexane) was added drop wise while stirring under inert atmosphere and the reaction mixture was stirred at -78°C for 1 h which was followed by addition of 2.5 mL (2.5 mmol) of trimethyltin chloride (1 M solution in hexane). The reaction mixture was stirred overnight at room temperature. The reaction was quenched by adding water and extracted with diethyl ether. Compound **4** was obtained as yellow crystalline solid upon recrystallization from ethanol solution of the crude product with a yield of 80%.

Compounds D_1+D_2 was synthesized upon using different equivalents of BuLi (~ 2-2.5 equiv.) and SnMe₃Cl (~ 2-2.5 equiv.), mixture of monostannylated (D_1) and Distannylated BDT (D_2) in a 1:3.3 ratio was obtained which was used for coupling reaction without further purification.

¹H NMR (400 MHz, CDCl₃) (D₂) δ (ppm): 7.61 (s, 2 H), 2.65 (t, *J* = 6.8 Hz, 4 H), 1.72-1.53 (m, 18 H), 0.95-0.92 (m, 6 H), 0.45 (t, J = 28 Hz, 18 H).

Synthesis of *pp*-ADA (5):



Scheme 3.5. Synthesis of *pp*-ADA.³²

Compound 4 (D₂) (50 mg, 0.068 mmol) and 3 (72 mg, 0.170 mmol) were dissolved in toluene and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, Tris(dibenzylideneacetone)dipalladium (0) $Pd_2(dba)_3$, (2.1 mg, 0.0023 mmol), Tris(o-tolyl)phosphine P(o-tol)₃, (3.3 mg, 0.011 mmol) were taken and simultaneously compounds 3 and 4 were added and refluxed for 5 h. The reaction mixture was cooled and evaporated and purified by column chromatography by using CHCl₃ and hexane (80:20 of CHCl₃: hexane) to obtain a red solid with 17% yield.

¹**H** NMR (400 MHz, CDCl₃) δ (ppm): 7.97 (s, 4 H), 7.91 (d, J = 8 Hz, 3 H), 7.86 (s, 1 H), 7.81 (d, J = 8 Hz, 4 H), 7.75 (d, J = 8 Hz, 4 H), 7.68 (t, J = 8 Hz, 4 H), 7.53 (d, J = 8 Hz, 1 H), 7.42 (d,

J = 8 Hz, 1 H), 7.03 (s, 4 H), 6.58 (s, 4 H), 2.72 (t, *J* = 8 Hz, 4 H), 1.85-1.78 (m, 4 H), 1.29 (s, 12 H), 0.88 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 146.95, 144.29, 144.10, 142.85, 140.20, 139.56, 139.18, 134.86, 134.07, 133.01, 131.52, 131.27, 127.63, 126.92, 119.09, 118.63, 114.09, 100.90, 37.11, 33.86, 31.95, 31.54, 31.49, 29.73, 29.39, 29.19, 28.97, 28.85, 28.76, 22.78, 22.72, 20.11, 14.23, 14.16.

¹¹B NMR (400 MHz, CDCl₃) δ (ppm): 0.54, 0.31, 0.09.

MS (HRMS-ESI): Calculated for C₆₈H₅₆B₂F₄N₄S₂Na [M+Na]⁺: 1113.3966; found 1113.3252.



Synthesis of *pp*-AD (7):

Scheme 3.6. Synthesis of pp-AD.³²

Compounds D_1+D_2 (50 mg, 0.068 mmol) and compound **3** (72 mg, 0.170 mmol) were dissolved in toluene and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, Pd₂(dba)₃ (2.1 mg, 0.002 mmol), P(o-tol)₃ (3.3 mg, 0.011 mmol) were taken and simultaneously compound **3** and **6** were added and refluxed for 5 h. The reaction mixture was cooled and evaporated and purified by column chromatography by using different percentage of CHCl₃ and hexane. *pp*-ADA was purified by column chromatography using 90:10 CHCl₃:hexane mixture and the mixture of Bodipy and *pp*-AD was obtained at 40:60 CHCl₃:hexane mixture followed by further purification using preparative TLC using 15:85 ethyl acetate:hexane as eluting solvent mixture with ~ 8% yield. ¹**H NMR for** *pp***-AD** (**400 MHz, CDCl**₃) δ (**ppm**): 7.97 (s, 2 H), 7.93-7.81 (m, 2 H), 7.76 (d, *J* = 4 Hz, 1 H) 7.73-7.63 (m, 6 H), 7.55 (s, 2 H), 7.02 (d, *J* = 16 Hz, 2 H), 6.58 (s, 2 H), 2.89-2.54 (m, 4 H), 1.6 (s, 4 H), 1.43 (s, 8 H), 1.33 (s, 4 H), 0.96 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.51, 139.43, 135.98, 134.91, 133.89, 133.82, 131.45, 131.39, 130.67, 129.87, 129.11, 128.99, 128.93, 128.55, 128.49, 128.43, 127.57, 125.53, 124.92, 114.21, 34.43, 33.97, 32.07, 31.57, 31.55, 31.09, 30.43, 29.84, 29.66, 29.51, 29.40, 29.30, 29.09, 28.78, 22.84, 14.28.

¹¹B NMR (400 MHz, CDCl₃) δ (ppm): 0.58, 0.35, 0.12.

MS (HRMS-ESI): Calculated for C₄₇H₄₃BF₂N₂S₂Na [M+Na]⁺: 771.2826; found: 771.4825.





Scheme 3.7. Synthesis of Me-pp-ADA.³²

Compound 2 (50 mg, 0.104 mmol) and compound 4 (30 mg, 0.042 mmol) were taken in schlenk tube and degassed by freeze-pump-thaw method. In a two-neck round-bottomed flask, $Pd_2(dba)_3$ (1.28 mg, 0.0014 mmol), $P(o-tol)_3$ (2.13 mg, 0.007 mmol) were taken and simultaneously compound 2 and 4 were added and refluxed for 5 h. The reaction mixture was cooled and evaporated and purified by column chromatography by using DCM and petroleum ether (percentage) to obtain the final compound as orange solid with 30% yield.

¹**H** NMR (400 MHz, CDCl₃) δ (ppm): 7.91 (d, J = 12 Hz, 4 H), 7.86 (s, 2 H), 7.80-7.73 (m, 8 H), 7.71 (t, J = 8 Hz, 2 H), 7.39 (d, J = 8 Hz, 2 H), 6.01 (s, 4 H), 2.71 (t, J = 8 Hz, 4 H), 2.58 (t, J = 12 Hz, 12 H), 1.84-1.75 (m, 4 H), 1.47 (s, 12 H), 1.42 (m, 12 H), 0.87 (d, J = 8 Hz, 6 H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.13, 140.79, 139.32, 137.14, 135.86, 131.44, 130.95, 128.86, 128.67, 127.90, 127.45, 126.98, 124.80, 121.33, 121.29, 118.95, 114.09, 101.21, 33.87,

31.94, 31.45, 30.31, 30.19, 29.72, 29.62, 29.53, 29.46, 29.39, 29.27, 29.18, 29.09, 28.82, 25.93, 24.73, 22.71, 20.08, 14.65, 14.15.

¹¹B NMR (400 MHz, CDCl₃) δ (ppm): 1.07, 0.80, 0.55.

MS (HRMS-ESI): Calculated for C₇₆H₇₃B₂F₄N₄S₂ [M+H]⁺: 1203.5399; found: 1203.3386.

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Appendix of Chapter 3A

a. Copies of NMR spectra of chapter 3A

¹H NMR of *pp*-Biphenyl (1):



¹H NMR of Me *pp*-BODIPY (2):



¹H NMR of *pp*-BODIPY (3):















/ 1 / 0.54 / 0.03




¹H NMR of Me-pp-ADA (8):



¹³C NMR of Me-pp-ADA (8):





b. Frequencies and Coordinates of DFT Optimized Geometries

Table 3.9. Results of first three frequencies and molecular symmetries calculated from geometry optimization of dyad and triads.

Compound	Symmetry	First Three Frequencies
		9.67
pp-AD	C_1	10.81
		12.92
		3.91
pp-ADA	C_1	7.20
		7.96
		3.55
Me-pp-ADA	C_1	5.39
		6.46

Coordinates of geometry optimized structure of pp-AD

С	-9.20754	-1.34737	-2.09146	С	-6.96473	-1.37939	-2.15542
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С	1.25076	0.88426	-0.63810	Н	5.80194	5.94452	-0.00223
С	1.96452	-0.14485	0.00498	Н	5.81237	5.68455	-1.75299
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F	-10.32720	1.18660	-0.73656	Н	8.14027	-5.89408	0.01980
Н	-8.14364	-2.39763	-3.73497	Н	6.58025	-5.91917	0.85533
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Н	1.73841	-1.95227	1.16709	С	-3.07051	1.13076	0.09203
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Н	3.93079	1.93840	-0.27816	Н	-4.98394	2.10334	0.15998
С	6.77549	1.44515	-0.22097	Н	-8.02280	2.22786	3.88316
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С	8.24428	-0.53502	0.08368	Н	-10.26264	-1.46391	-2.29753
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Η	-5.85831	1.36699	2.51250	S	-2.62737	1.61078	-0.53095
Coo	ordinates of ge	ometry optir	nized	С	-1.09413	0.80020	-0.26760
stru	cture of <i>pp</i> -A	DA		С	-1.29091	-0.53072	0.18715
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С	-15.05251	2.30405	2.44636	С	-0.17480	-1.36255	0.46178
Ν	-15.74954	0.83367	0.88087	С	1.09358	-0.79675	0.26507
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				\sim	10.04001		<u>_, i i / _ U</u>

С	16.13794	-1.69235	-1.84336	С	-10.06216	1.27068	-0.15875
Ν	15.73744	-0.78456	-0.94138	С	-10.02134	-1.12035	0.10993
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Н	-1.07002	-5.26190	2.75055	Н	-17.21521	1.85554	1.99638
С	0.59599	5.22401	-1.76594	Н	12.86502	-2.05746	-1.99669
Н	1.06218	5.26461	-2.75702	Н	17.19100	-1.84953	-2.03193
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С	10.03513	0.17257	-1.15059	Co	ordinates of ge	ometry optin	nized
С	11.42555	0.19096	-1.15703	str	ucture of Me- <i>p</i>	p-ADA	
С	12.15347	-0.03335	0.02398	C	-16.13172	-0.28207	2.53659
С	11.43837	-0.28525	1.20720	С	-14.99883	-0.34489	3.37377
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Н	-1.06881	-5.72594	1.57846	Н	11.85697	2.21053	1.89354
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- Н -11.91557 -0.56852 -2.87551
- Н -11.94135 1.17567 -2.68498

BODIPY-based Regioisomers and Donor-Acceptor Rotor as Organic Photosensitizers for Maximizing Singlet Oxygen Quantum Yields and for Photooxidation of Thioanisole



Abstract

The efficient production of singlet oxygen using an organic photosensitizer (PS) is highly attractive for photocatalytic applications. Herein, we have designed and synthesized regioisomeric biphenyl-BODIPYs such as pp-BODIPY, mp-BODIPY, mm-BODIPY, T-BODIPY (thiophene at meso-position) and a triad T-ADA (based on benzodithiophene as donor and BODIPY as acceptor) as organic PSs. The singlet oxygen quantum yields reached up to 77% in **T-BODIPY** due to heavy atom (Bromine substitution in thiophene ring) and charge transfer mediated intersystem crossing and 35% in T-ADA due to charge transfer mediated ISC. The variation in connectivities of the spacers in regioisomeric BODIPYs and type of spacer in **T-BODIPY** significantly alter the photophysical properties. Among all PSs, **T-ADA** showed charge transfer band at 650 nm and showed aggregation-induced emission (AIE) with increase in water percentage in tetrahydrofuran (THF) solution. Detailed insights into the ultrafast dynamics and excited state processes were obtained using femtosecond transient absorption spectroscopy (fs-TAS). The technique allowed for a thorough investigation of these systems, indicating participation of charge-transfer (CT) states in the observed dynamics of triplet state formation. Due to the efficient generation of ${}^{1}O_{2}$ in case of all compounds, pp-BODIPY, mp-BODIPY, mm-BODIPY, T-BODIPY and T-ADA were utilized in the aerobic photooxidation of thioanisole to methyl phenyl sulfoxide with high selectivity towards sulfoxide formation.

3.1. Introduction

The field of photocatalysis where organic transformations are performed under mild conditions using light activable catalysts has attracted great attention among synthetic chemists since last few decades.^{1–4} Photocatalysis offers a powerful strategy to activate organic molecules by transferring electron or energy between excited photocatalyst and substrate that leads to formation of new chemical bonds or breakage of old bonds. There are several reports on transition metal based photocatalysts containing Ru, Ir, Pt and Pd that have demonstrated their effectiveness in variety of reactions.^{5–8} However, these photocatalysts suffer from limitations such as high cost, toxicity of the catalyst and difficulty in their disposal that has directed attention towards development of, earth-abundant, non-toxic, metal-free sustainable photocatalysts.⁹ In recent years, there are various reports on synthesis of metal-free photocatalysts and their utilization in organic transformations such as oxidation, cycloaddition, C-O bond formation, C-C bond formation, C-S bond formation and many others.^{1,2} Generally, highly efficient triplet photosensitizers (energy transfer photocatalysis), are based on fast intersystem crossing (ISC) occurring from singlet to triplet states and are more preferred for organic photocatalysis.¹⁰ Among various organic photocatalysts, 4,4-difluoro-4-bora-3a,4adiaza-s-indacene (BODIPY) based organic photocatalysts are employed in recent years because of its outstanding thermal, photochemical stabilities, strong visible light absorption, high fluorescence quantum yields and good solubility and facile accessibility of their triplet excited states.^{11–14} Moreover, few chemical modifications in the skeleton of BODIPY such as substitution by heavy atoms i.e., Bromine and Iodine, enhance spin-orbit coupling which result in the increase in population of the triplet states.¹² Furthermore, BODIPYs have been widely investigated for a variety of applications such as photodynamic therapy, chemosensing, biological labelling, organic photocatalysis, dye-sensitized solar cells and laser dyes.^{12,15} In iodo-BODIPY derivative based photocatalysts, I atom attached on the π -core of BODIPY chromophore drives efficient ISC resulting in high yields of singlet oxygen (¹O₂).¹⁶ These photocatalysts were utilized for singlet oxygen mediated aerobic oxidative coupling of amines and the photooxidation of dihydroxylnaphthalenes followed by aniline addition to the naphthoquinone intermediates. Visible light driven hydroxylation of aryl halides in water was achieved by the utilization of BODIPY photocatalyst and Ni as a co-catalyst in presence of a base.¹⁷ Iodo-BODIPY and quinine based photocatalyst, where iodo-BODIPY serve as ¹O₂ producer and quinine serve as both chiral catalyst as well as quencher of ${}^{1}O_{2}$ in absence of substrate, were synthesized and utilized for the asymmetric hydroxylation of β -dicarbonyl

compounds.¹⁸ Recently, porous organic polymers containing halogenated BODIPY were reported for the singlet oxygen mediated photo-degradation of 2-chloroethyl ethyl sulfide (chemical warfare agent) to its corresponding non-toxic sulfoxide counterpart, 2-chloroethyl ethyl sulfoxide.¹³ Conversion of 1,5-dihydroxynaphthalene to juglone was achieved using BODIPY and copper based photocatalyst.¹⁹ It was reported that substitution with I at mesoposition results into lesser singlet oxygen quantum yield (0.01) compared to 2- and 6-positions (0.83) during oxidation of sulphides.^{12,20,21} All these reports achieved photocatalyzed organic transformations by introducing heavy atoms (Br or I) directly in the BODIPY skeleton. Filatov et. al., reported heavy-atom free BODIPY and anthracene-based dyads as triplet photosensitizers in which triplet state was generated by photoinduced electron transfer.²² Anthracene-based dyad was converted into highly fluorescent species using ¹O₂ and was further utilized for imaging applications. Donor-acceptor (D-A) systems based on phenothiazine as donor and BODIPY as acceptor were synthesized and triplet excited state formation was achieved by photoinduced electron transfer and charge recombination.²³ In D-A system, upon photoexcitation, charge transfer (CT) occurs from donor to acceptor resulting in the formation of singlet excited CT state (¹CT). In the absence of heavy atoms, ¹CT states can undergo efficient ISC by CT-mediated ISC involving either radical pair ISC (RP-ISC) or by spin-orbit charge transfer ISC (SOCT-ISC).^{10,12,14}

In this work, we have synthesized biphenyl-BODIPY regioisomers *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY with Br attached at different positions of the biphenyl and thiophene BODIPY (**T-BODIPY**) where thiophene spacer functionalized with Br is attached at the mesoposition of BODIPY as shown in Figure 3.1. We have studied the effect of regioisomerism and spacer on photophysical properties as well as on photocatalysis. Compound **T-BODIPY** regioisomers due to the attachment of thiophene at meso-position compared to biphenyl-BODIPY regioisomers. Furthermore, we have also synthesized heavy atom free **T-ADA** rotor that consists of **T-BODIPY** acceptor and benzodithiophene (BDT) as the donor and the BDT was connected through thiophene spacer at meso-position of **T-BODIPY**. Rotor **T-ADA** showed pronounced charge transfer (CT) emission band at 650 nm and showed bathochromic shift upon formation of aggregates in THF and water mixture. Additionally, **T-ADA** showed efficient ¹O₂ generation efficiency most likely due to CT-mediated ISC that populated the triplet state. Due to the generation of ¹O₂ for *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, *mm*-BODIPY, **T**-

BODIPY and **T-ADA**, all compounds were utilized in aerobic photooxidation of thioanisole to methyl phenyl sulfoxide.



Figure 3.1. Chemical structures of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA synthesized and investigated in this work.

3.2. Results and Discussion

3.2.1. Synthesis

The syntheses of BODIPYs *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and triad **T-ADA** were accomplished following our earlier reported procedures.²⁴ Before synthesis of BODIPYs, the spacer biphenyl was synthesized by Suzuki coupling reaction between suitably substituted halogenated benzene and formyl phenyl boronic acid.^{25,26} Subsequently, the regioisomeric BODIPYs were synthesized by the reaction between different spacers (bromo

biphenyl carbaldehyde) and 2,4-dimethyl pyrrole by addition of catalytic amount of trifluoroacetic acid (TFA) followed by addition of chloranil, triethylamine and boron trifluoride diethyl etherate.²⁷ While for the synthesis of **T-BODIPY**, 2-methyl pyrrole was synthesized by Wolff-Kishner reduction of pyrrole-2-carboxaldehyde and then it was used for the synthesis of **T-BODIPY** using 5-bromo-2-thiophenecarboxaldehyde.²⁸ The synthesis of triad **T-ADA** was accomplished by Stille coupling reaction between **T-BODIPY** and distannylated benzodithiophene precursor (BDT).²⁴ All compounds were purified via column chromatography (TLC) and characterized using ¹H NMR, ¹³C NMR and high-resolution mass spectrometry (HRMS).

3.2.2. Absorption and Emission

UV/Vis absorption and emission spectra of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, **T**-BODIPY and **T-ADA** were recorded in CHCl₃ at a concentration of ~ 10^{-6} M. In case of *pp*-BODIPY, *mp*-BODIPY and *mm*-BODIPY, the major absorption peak was observed at 504 nm corresponding to the S₀-S₁ transition as shown in Figure 3.2-3.3. Upon excitation at 504 nm, the emission peak was observed at 513 nm. While in the case of **T-BODIPY**, apart from a minor absorption peak at 390 nm, the major absorption peak was observed at 527 nm. Upon excitation at 527 nm, the emission was observed at 548 nm as shown in Figure 3.2. Due to thiophene spacer in **T-BODIPY**, the emission was red shifted by 35 nm in comparison to regioisomeric biphenyl-BODIPYs. In case of **T-ADA**, apart from minor absorption peaks at



Figure 3.2. (a) UV/Vis absorption and (b) emission spectra of *pp*-BODIPY ($\lambda_{ex} = 504 \text{ nm}$), **T-BODIPY** ($\lambda_{ex} = 527 \text{ nm}$) and **T-ADA** ($\lambda_{ex} = 529 \text{ nm}$).

327 nm and 395 nm, the major absorption band was observed at 529 nm. The observed smaller peak at \sim 327 nm is attributed to the BDT part while the bands at 398 nm and 529 nm are attributed to BODIPY part in **T-ADA**. Upon excitation at 327 nm, apart from emission at 407 nm and 430 nm, a highly intense peak was observed at 650 nm. Upon excitation at 529 nm, the peak at \sim 650 nm was obtained while the BODIPY emission disappeared as shown in Figure

3.3. Compared to our earlier reported rotor *p*-ADA that contained a phenyl spacer (Figure 3.1),²⁹ **T-ADA** containing thiophene spacer showed significantly altered photophysics. Upon excitation at 380 nm for *p*-ADA, apart from the emission bands at 405 nm (BDT donor) and 512 nm (acceptor), a broad and intense peak ~ 698 nm (twisted intramolecular charge transfer) was observed.²⁹ However, for **T-ADA**, emission bands were observed only at 407 nm and 430 nm (BDT donor) and at 650 nm and no separate emission of BODIPY (or local excited (LE) emission) was observed. Thus, for **T-ADA**, it can be presumed that the energy barrier between LE and CT is very low such that the population immediately reaches the CT state from LE state upon photoexcitation. The molar absorption coefficients (*e*) of *pp*-BODIPY, *mp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY and **T-ADA** were 6.62×10^4 M⁻¹ cm⁻¹, 5.96×10^4 M⁻¹ cm⁻¹, 7.67×10^4 M⁻¹ cm⁻¹, 6×10^4 M⁻¹ cm⁻¹ and 1.28×10^5 M⁻¹cm⁻¹ respectively.



Figure 3.3. UV/Vis absorption and emission spectra of (a) *mp*-BODIPY ($\lambda_{ex} = 504 \text{ nm}$), (b) *mm*-BODIPY ($\lambda_{ex} = 504 \text{ nm}$) and (c) **T-ADA** ($\lambda_{ex} = 529 \text{ nm}$).

3.2.3. Fluorescence Quantum Yields

The fluorescence quantum yields were determined by relative method using Rhodamine B and 4',6-diamidino-2-phenylindole (DAPI) as reference compounds and the fluorescence quantum yields were obtained as 0.70, 0.65, 0.74, 0.14 and 0.19 for *pp*-**BODIPY**, *mp*-**BODIPY**, *mm*-**BODIPY**, **T-BODIPY** and **T-ADA** respectively (Table 3.1). In case of regioisomeric BODIPYs such as *pp*-**BODIPY**, *mp*-**BODIPY**, *mm*-**BODIPY**, the tetramethyl substitution at BODIPY, hindered the rotations which leads to the enhancement of fluorescence quantum yield. However, in case of **T-BODIPY** and **T-ADA**, due to the possibility of ISC and non-radiative deactivation the fluorescence quantum yield reduced compared to those of regioisomeric BODIPYs.

							Quantu	ım Yield
Compound	L	Absorban	ce	Integ	rated Fluor	rescence	$\Phi = \Phi_R(\mathbf{I}/\mathbf{I})$	$(\mathbf{A}_{\mathbf{R}})(\mathbf{A}_{\mathbf{R}}/\mathbf{A})$
					Intensity		$(\lambda_{exR}/\lambda_{ex})(n^2/n^2_R)$	
	1	2	3	1	2	3	Φ_{i}	Φ_{avg}
pp-BODIPY	0.021	0.033	0.045	532.13 3	766.749	1032.316	0.696 0.731 0.675	0.70
mp-BODIPY	0.024	0.044	0.052	552.47 0	960.946	1121.319	0.633 0.688 0.635	0.652
mm-BODIPY	0.023	0.032	0.042	572.99 2	778.329	1094.169	0.685 0.766 0.767	0.739
T-BODIPY	0.045	0.057	0.068	75.567	89.267	103.753	0.134 0.140 0.141	0.138
T-ADA	0.038	0.058	0.071	91.192	121.353	151.747	0.193 0.186 0.196	0.191
DAPI (DMSO)	0.044	0.0707	0.0828	629.73	867.144	1086.253		0.58
	8			2				
Rhodamine B	0.033	0.065	0.105	234.7	418.247	655.36		0.5
(ethanol)								

Table 3.1. Relative quantum yields of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA using relative method and DAPI and Rhodamine B as a reference dyes.

3.2.4. Solvatochromism of T-ADA

Among molecules *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, **T-BODIPY** and **T-ADA**, a longer wavelength emission band at 650 nm was observed for **T-ADA** that is attributed to charge transfer (CT) band. In case of CT state, due to the increase in dipole moment of the excited state, the molecule shows positive solvatochromic shifts in emission spectra.³⁰ Hence, to confirm the occurrence of CT state for **T-ADA**, solvatochromic study was performed in solvents of different polarities. In non-polar solvent such as methyl cyclohexane (MCH) and toluene (Tol), the emission of **T-ADA** was observed at 569 nm and 594 nm respectively. While in polar solvents such as dichloromethane (DCM), tetrahydrofuran (THF) and chloroform

(CHCl₃), **T-ADA** showed emission bands at 662 nm, 633 nm, and 638 nm respectively as shown in Figure 3.4. Hence, the bathochromic shift in emission from 569 nm (MCH) to 662 nm (DCM) for **T-ADA** confirmed the occurrence of CT state. Furthermore, solvatochromic study was performed for **T-ADA** in binary mixture of polar and non-polar (DCM/Tol) solvents. As the percentage of DCM was increased from 0% to 100% (v/v), the emission was bathochromically shifted from 594 nm to 660 nm with bathochromic shift of 66 nm as shown in Figure 3.4. Hence, increase in solvent polarities result in bathochromic shift in the emission that occurs because excited state having higher dipole moment is preferentially stabilized by polar solvents, thereby confirming a CT state.



Figure 3.4. Emission of **T-ADA** ($\lambda_{ex} = 529 \text{ nm}$) (a) in solvents of different polarities and (b) in different percentages of DCM/Tol (*c* ~10⁻⁶ M) respectively (inside the graph, 0%, 10% to 100% indicate the percentage of DCM in solutions).

3.2.5. Cyclic Voltammetry

In order to assess the redox properties of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA, cyclic voltammetry (CV) measurements were performed in dichloromethane (DCM) containing (0.1 M) deoxygenated tetrabutylammonium hexafluorophosphate (TBAHPF) as a supporting electrolyte (Figure 3.5, Table 3.2). The internal calibration was performed using ferrocene/ferrocenium redox couple prior to all measurements. All the regioisomeric BODIPYs showed reduction potentials of ~ - 0.99 V to -0.98 V and an oxidation potential at ~ 1.35 V to 1.43 V, indicating the ease reduction due to the boron attached to the core. Similarly, **T-BODIPY** and **T-ADA** showed reduction potential at -0.94 V and -0.96 V respectively, suggesting facile reduction facilitated by the donor attached to the chromophores. Based on the first oxidation potential onset (E_{ox}^{onset}) and first reduction potential onset (Ered^{onset}), the HOMO and LUMO levels were calculated. Accordingly, the calculated HOMO energies for *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY,





Figure 3.5. Cyclic voltammogram of (a) *pp***-BODIPY**, (b) *mp***-BODIPY**, (c) *mm***-BODIPY** (d) **T-BODIPY** and (e) **T-ADA** in dry DCM with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHPF) and potentials measured vs Ag/AgCl reference electrode.

Compound	Eox	HOMO*	Ered ^{onset}	LUMO	$\mathbf{E}_{\mathbf{g}}$
	(V)	(eV)	(V)	(eV)	(eV)
pp-BODIPY	1.17	-5.93	-0.70	-4.06	1.87
mp-BODIPY	1.19	-5.95	-0.65	-4.11	1.84
mm-BODIPY	1.12	-5.88	-0.54	-4.22	1.66
T-BODIPY	1.25	-6.01	-0.78	-3.98	2.03
T-ADA	0.98	-5.74	-0.64	-4.12	1.62
$*HOMO = -(E_{onse})$	$e_{t}^{ox} + 4.76)$	eV, and LUM	$IO = -(E_{onse})$	$e^{red} + 4.76) e^{red}$	V.

Table 3.2. Redox properties of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA based on cyclic voltammetry.

3.2.6. Spectroelectrochemistry

In order to understand the spectral profiles of radical anions or cations that can be

electrochemically generated for **T-BODIPY** and **T-ADA**, spectroelectrochemical measurements were performed in DCM containing 0.1 M TBAHPF as a supporting electrolyte as shown in Figure 3.6. Upon applying positive potential (0 to + 2V) for **T-BODIPY**, a shoulder was observed in UV/Vis spectra at ~ 600 nm due to the formation of radical cation, while no significant change was observed in **T-ADA** upon applying positive potential. Upon applying negative potential for **T-BODIPY** (0 to -2V), depletion of absorption band at ~ 390 nm and 527 nm and the emergence of a new absorption band at 680 nm was observed due to the formation of monoanion or dianion radical.

Similarly, in **T-ADA**, depletion of the absorption bands at ~ 327 nm and 529 nm and the emergence of a new band at 398 nm indicated the formation of anion radical. The corresponding changes in colour while applying the positive and negative potentials for both compounds are shown in inset of Figure 3.6. Based on spectroelectrochemical studies, both compounds are considered to be electrochromic.



Figure 3.6. Spectroelectrochemical changes of (a, b) **T-BODIPY** and (c, d) **T-ADA**, upon applying positive potential (0 to 2 V) and negative potential (0 to -2 V) in DCM upto 40 cycles. Figure insets show the change in colour of solution after applying positive or negative potentials.

3.2.7. Density Functional Theory Calculations

Density functional theory (DFT) calculations were performed for all molecules in the ground state using the Gaussian 09 package at B3LYP/6-31G(d,p) level to calculate the HOMO and LUMO energy levels as well as torsion angles in geometry optimized structures (Figure 3.7–3.8, Table 3.3). In case of regioisomeric BODIPYs *pp*-BODIPY, *mp*-BODIPY and *mm*-BODIPY, both HOMO and LUMO were completely localized on BODIPY part and LUMO +1 was localized on biphenyl part as shown in Figure 3.7. While in case of **T-BODIPY**, HOMO was localized on BODIPY part and LUMO was localized on BODIPY and a small part on BDT while LUMO +1 was completely localized on BODIPY moiety showing the possibility of charge transfer from HOMO to LUMO and HOMO to LUMO +1 as shown in Figure 3.8.



Figure 3.7. FMO energy levels of compounds *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY and T-BODIPY calculated using B3LYP/6-31G(d,p) method.



Figure 3.8. FMO energy levels of compounds **T-BODIPY** and **T-ADA** calculated using B3LYP/6-31G(d,p) method.

Table 3.3. FMO energy levels of compounds *pp***-BODIPY**, *mp***-BODIPY**, *mm***-BODIPY**, **T-BODIPY** and **T-ADA** calculated by B3LYP/6-31G(d,p) method.

Compound	HOMO-1	НОМО	LUMO	LUMO+1	ΔE (eV)	Dihedral
	(eV)	(eV)	(eV)	(eV)		angle (°)
pp-BODIPY	-6.38	-5.39	-2.40	-1.33	2.99	89.5
mp-BODIPY	-6.49	-5.39	-2.39	-1.34	3.00	90.4
mm-BODIPY	-6.46	-5.38	-2.38	-1.31	3.00	91.8
T-BODIPY	-6.47	-5.65	-2.81	-0.99	2.84	48.9
T-ADA	-5.59	-5.37	-2.90	-2.75	2.47	47.5

Frontier molecular orbital (FMO) composition analysis was conducted for *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, *T*-BODIPY and T-ADA and it was found that in case of regioisomeric BODIPYs (*pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY), the HOMO was composed of 0% contribution from biphenyl part and 100% contribution from BODIPY part. The LUMO was composed of 98% contribution from BODIPY part and 2% from biphenyl part

indicating no possibility of CT from biphenyl to BODIPY. In case of **T-BODIPY**, the HOMO was composed of 1% contribution from thiophene part and 99% contribution from BODIPY part, while LUMO was composed of 86% contribution from BODIPY part and 2% from thiophene part, suggesting a lower possibility of CT from thiophene to BODIPY part. In case of **T-ADA**, the HOMO was composed of 95% contribution from BDT part and 5% contribution from BODIPY part, while LUMO was composed of 66% contribution from BODIPY part and 34% from BDT part, indicating CT character from BDT to BODIPY part as shown in Table 3.4.

Compound	Orbital No.	МО	Energy (eV)	Contribution from donor (%)	Contribution from acceptor (%)
	124	LUMO+1	-1.33	98	2
pp-	123	LUMO	-2.40	2	98
BODIPY	122	HOMO	-5.39	0	100
	121	HOMO-1	-6.38	98	2
	159	LUMO+1	-1.34	98	2
mp-	158	LUMO	-2.39	2	98
BODIPY	157	HOMO	-5.39	0	100
	156	HOMO-1	-6.49	1	99
	279	LUMO+1	-1.31	98	2
mm-	278	LUMO	-2.38	2	98
BODIPY	277	HOMO	-5.38	0	100
	276	HOMO-1	-6.46	19	81
	279	LUMO+1	-0.99	88	12
T-BODIPY	278	LUMO	-2.81	14	86
	277	HOMO	-5.65	1	99
	276	HOMO-1	-5.37	80	20
	279	LUMO+1	-2.75	18	82
T-ADA	278	LUMO	-2.90	34	66
	277	HOMO	-5.37	95	5
	276	HOMO-1	-5.59	1	99

Table 3.4. FMO composition analysis for *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA based on DFT calculations.

The Gibbs free energy of charge separation (ΔG_{cs}^0) for **T-ADA** were calculated to assess the feasibility of charge transfer using Rehm–Weller equations ²³:

$$-\Delta G_{cs}^0 = -\mathsf{E}_{00} - \Delta G_{CR} \quad (3.1)$$

where, ΔG_{CR} is the Gibbs free energy of charge recombination and calculated by given equation no. 3.2:

$$\Delta G^{0}_{CR} = e[E_{ox}(D) - E_{red}(A)] + \Delta G_{S} \qquad (3.2)$$

where, e is the electronic charge, E_{ox} (D) is the first oxidation potential of donor and E_{red} (A) is the first reduction potential of acceptor, E_{00} is the energy of the S₀ \rightarrow S₁ transition (calculated by taking the intersection point of normalized absorption and emission spectra) and ΔG_S is the static Coulombic energy, given by the following equation no. 3.3:

$$\Delta G_S = \frac{e^2}{4\pi\varepsilon_S\,\varepsilon_0\,R_{cc}} - \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{R_D} + \frac{1}{R_A}\right) \left(\frac{1}{\varepsilon_{ref}} - \frac{1}{\varepsilon_S}\right) \quad (3.3)$$

where, ε_S is the dielectric constant of the solvent, ε_{Ref} is the dielectric constant of the solvent used for experiment, ε_0 is the permittivity of free space. R_D and R_A refer to the effective radii of donor and acceptor and were estimated from the Connolly molecular surfaces volume of the respective moieties calculated with MM2 using the Chem3D Pro software and R_{cc} is the distance between the centers of the donor and acceptor.

Standard oxidation potential of donor in DCM; $E_{D+./D}^{0} = +1.34 \text{ V}$

Standard reduction potential of acceptor in DCM; $E_{A/A-}^0 = -0.87$ V

Average radii of donor; R_A= 4.84 Å

Average radii of acceptor; R_A= 4.89 Å

Center to center distance of donor and acceptor segment, $R_{cc} = 10.48$ Å

Using the above relations, the driving force for both photoinduced charge separation and charge recombination processes between donor and acceptor were calculated and the observed values were -0.30 eV and -2.54 eV in Tol respectively. The negative values of ΔG^0_{CS} and ΔG^0_{CR} indicates that both photoinduced forward and backward electron transfer processes are exergonic and thermodynamically feasible.

Time-dependent DFT (TD-DFT) calculations of **T-BODIPY** and **T-ADA** were performed to calculate the singlet and triplet energy levels and their energies in CHCl₃ are provided in Table 3.6. Natural transition orbital (NTO) calculations were performed for the first four excited states of **T-BODIPY** and **T-ADA**. Both compounds **T-BODIPY** and **T-ADA** showed CT features in S_1 state where electrons and holes are completely separated on different parts of the molecules (i.e., on acceptor and donor respectively) as shown in Figure 3.9-3.10.



Figure 3.9. The natural transitions orbitals (NTOs) for singlet and triplet states of **T-BODIPY** calculated using TD-DFT.



Figure 3.10. The natural transitions orbitals for singlet and triplet states of T-ADA calculated using TD-DFT.

The calculated dipole moments and oscillator strengths of various singlet states are provided in Table 3.5. The larger oscillator strengths of first singlet excited states for both compounds (S_1) are indicative of larger molar absorptivities (i.e., stronger absorption) compared to other higher states. Also, the dipole moments of S_1 states of **T-BODIPY** and **T-ADA** were 9.76 D and 16.6 D respectively (Table 3.5). The large dipole moments are attributed to CT character of these states. The above results indicate that S_1 states for both molecules have CT character.

	T-BO	DIPY	T- 4	T-ADA		
Singlet states	Dipole moment	Oscillator strength	Dipole moment	Oscillator strength		
\mathbf{S}_1	9.76	0.49	16.66	1.09		
\mathbf{S}_2	7.45	0.32	16.66	0.003		
S ₃	3.22	0.06	3.50	0.059		
S_4	2.32	0.03	6.46	0.20		

Table 3.5. Calculated dipole moments and oscillator strengths of different singlet states of **T-BODIPY** and **T-ADA** in CHCl₃ by TD-DFT calculations.

Furthermore, the calculated singlet and triplet energy gaps of **T-BODIPY** (between S_1 and T_3 states) and **T-ADA** (between S_1 and T_4 states) were 0.02 eV and 0.10 eV (Table 3.6) which is well-suited for efficient ISC process. The NTO transitions of triplet states T_3 and T_4 of **T-BODIPY** and **T-ADA** respectively also showed CT character as shown in Figure 3.9-3.10. Based on these calculated energy levels, ISC could therefore occur from S_1 to T_3 in case of **T-BODIPY**, and from S_1 to T_4 in case of **T-ADA**.

Table 3.6. Singlet and triplet energies of various states of **T-BODIPY** and **T-ADA** in CHCl₃ calculated using TD-DFT calculations.

Compound	S ₁ (eV)	S ₂ (eV)	T ₁ (eV)	$T_2(eV)$	T ₃ (eV)	T ₄ (eV)	$\Delta E_{ST} (eV)$
T-BODIPY	2.73	3.04	1.47	2.44	2.75	2.98	0.02 (S ₁ and T ₃)
T-ADA	2.06	2.23	1.46	1.46	1.59	1.96	0.10 (S ₁ and T ₄)

The singlet and triplet energies were also calculated in polarization continuum model (PCM) model using CHCl₃ and heptane as solvents. In case of CHCl₃, the energy levels were slightly stabilized for **T-ADA** compared to that in heptane (Table 3.7) which indicates that the states under consideration involve CT characters and thus are preferentially stabilized in CHCl₃ compared to heptane. Hence, all results based on TD-DFT calculations are indicative of the fact that S1 state is involved in the ISC process through most-likely CT-mediated ISC mechanistic pathway and populates the triplet state which further assists in the generation of singlet oxygen (vide infra photocatalysis section).

Table 3.7. Singlet (S₁) and triplet energy (T₄) values of **T-ADA** in CHCl₃ and heptane calculated using TD-DFT using PCM.

Compound	S ₁ (eV)	T ₄ (eV)
Heptane	2.73	3.04
CHCl ₃	2.06	2.23

3.2.8. Aggregated Induced Emission

In order to investigate the aggregate induced emission (AIE) behaviour of **T-ADA**, fluorescence studies were performed in binary mixture of THF and water. As the water percentage was increased from 0% to 50% (v/v), the emission intensity was increased with a bathochromic shift of 17 nm as shown in Figure 3.11. However, upon increasing the water percentage from 50% to 80%, the emission intensity increased by 2-fold with a slight hypsochromic shift of 6 nm. Upon further increasing the water percentage from 80% to higher, the emission intensity decreased with a bathochromic shift of 27 nm. UV/Vis absorption spectra of **T-ADA** were also measured in different THF and water mixtures (Figure 3.11) where at higher percentages of water, the absorption band was bathochromically shifted with tailing in the long wavelength region indicative of the formation of nano-aggregates. Figure 3.11c shows the changes in emission intensities and wavelengths with increase in water percentages from 0% to 99% in THF solution.



Figure 3.11. (a) UV/Vis absorption; (b) emission of **T-ADA** ($\lambda_{ex} = 529$ nm in different percentages of THF and water ($c \sim 10^{-6}$ M) and (c) changes in emission intensities and emission maxima versus fraction of water (f_w) of **T-ADA**.

3.2.9. Temperature-dependent Emission of T-ADA

Emission of molecular rotors is sensitive to various stimuli such as polarity, viscosity, and temperature. Hence, to study the effect of temperature on emission of **T-ADA**, temperature-dependent fluorescence measurements were performed in polar (CHCl₃) and non-polar (Tol) solvents from -5 °C up to the boiling point of solvent as shown in Figure 3.12. In case of CHCl₃,

upon increasing the temperature, the emission intensity of **T-ADA** decreased by ~ 4-fold with a hypsochromic shift of 23 nm from the emission maximum of 650 nm. Similarly, in case of Tol, the emission intensity of **T-ADA** decreased by ~ 2-fold with a hypsochromic shift of 12 nm from 598 nm. In both cases, the emission intensities decreased with increasing temperature due to the increase in non-radiative deactivation. The ratiometric temperature analysis of **T-ADA** was performed in CHCl₃ and Tol and fitted with linear function with goodness of fit R² values of 0.96 and 0.98 and the calculated internal sensitivities were 0.46% °C⁻¹ and 0.21% °C⁻¹ respectively.



Figure 3.12. Temperature-dependent emission spectra of **T-ADA** ($\lambda_{ex} = 529 \text{ nm}$) in (a) CHCl₃ and (c) Tol in 10⁻⁶ M concentration. Emission intensity ratio in (b) CHCl₃ and (d) Tol at different temperatures with best fit equations.

3.2.10. Fluorescence Lifetimes

The fluorescence lifetimes of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, **T**-BODIPY and **T**-ADA were calculated in CHCl₃ as well as in Tol using the time correlated single photon counting (TCSPC) technique. The fluorescence lifetimes of all compounds were measured upon excitation of 510 nm laser diode (Figure 3.13, Table 3.8). All data were fitted by bi-exponential functions and the $\tau_{\alpha vg}$ values of regioisomeric BODIPYs *pp*-BODIPY, *mp*-BODIPY and *mm*-BODIPY at emission wavelength of 513 nm were 3.1 ns, 2.9 ns and 4.4 ns in CHCl₃ and 2.8 ns, 2.7 ns and 4.1 ns in Tol respectively. While the $\tau_{\alpha vg}$ values of **T-BODIPY**

at emission wavelength of 554 nm was 0.44 ns in CHCl₃ and 0.45 ns in Tol, the τ_{avg} value of **T-ADA** at emission wavelength of 650 nm was 0.45 ns in CHCl₃.



Figure 3.13. Fluorescence lifetime decays collected using TCSPC in CHCl₃ and Tol of (a) **T-BODIPY** and (b) **T-ADA**.

Table 3.8. Fluorescence lifetime analyses of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA at different emission wavelengths.

Compound	Solvent	λ _{em}	$ au_1(au_1)$	$ au_2(au_2)$	$ au_{ m avg}$	χ^2
$(\lambda_{ex} = 510 \text{ nm})$		(nm)	(ns)	(ns)	(ns)	
	CHCl ₃	513	3.1	-		1.18
pp-BODIPY	Tol	513	2.8	-	-	1.14
	CHCl ₃	513	2.9	-	-	1.12

mp-BODIPY	Tol	513	2.7	-	-	1.13
	CHCl ₃	513	4.4	-	-	1.05
mm-BDP	Tol	513	4.1	-	-	1.03
	CHCl ₃	554	0.35 (0.98)	4.74 (0.02)	0.44	1.19
T-BDP	Tol	554	0.38 (0.98)	4.39 (0.02)	0.45	0.98
T-ADA	CHCl ₃	650	0.44 (0.94)	1.17 (0.06)	0.45	1.10

3.2.11. Singlet Oxygen Quantum Yields

To confirm the ability of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA to generate ${}^{1}O_{2}$, singlet oxygen quantum yields (Φ_{Δ}) were calculated by relative method in THF and MeOH as solvent. The singlet oxygen quantum yields (Φ_{Δ}) were determined by monitoring the photooxidation of 1,3-diphenylisobenzofuran (DPBF) which is a well-known ${}^{1}O_{2}$ scavenger and rapidly gives a colourless oxidative product.^{31,32} It absorbs in visible region (~ 410 nm) and due to scavenging of ${}^{1}O_{2}$, the absorbance decreases with time. Singlet oxygen quantum yields were calculated at low concentrations (5 μ M of dyes and 50 μ M of DPBF) to minimize the possibility of quenching of ${}^{1}O_{2}$ by dyes. A solution of dyes and DPBF in THF or MeOH was irradiated with monochromatic light at specific wavelength over a time period of 0 to 10 minute and the change in absorbance of DPBF was monitored with time through recording the absorbance of the solution at different time intervals as shown in Figure 3.14-3.17. The irradiation wavelength for *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY, T-ADA and Eosin Y were 500 nm, 500 nm, 500 nm, 524 nm, 526 nm and 542 nm respectively. The quantum yields were calculated by relative method using Eosin Y³¹ (singlet oxygen quantum yield ~ 0.60) as reference dye and using the following equation no. 3.4:

$$\Phi_{\Delta}^{dye} = \Phi_{\Delta}^{ref} \left(m^{dye} \cdot F^{ref} / m^{ref} \cdot F^{dye} \right)$$
(3.4)

where $\Phi_{\Delta}^{\text{ref}}$ is the singlet oxygen quantum yield of Eosin Y, m is the slope of a plot of difference in change in absorbance of DPBF (~ 410 nm) with the irradiation time and F is the absorption correction factor given by $F = 1 - 10^{-\text{OD}}$ (optical density at irradiation wavelength). For the calculation of Φ_{Δ} , the solution of dye ($c \sim 5 \mu$ M) and DPBF ($c \sim 50 \mu$ M) in THF were taken in 20 mL round bottomed flask with a stir bar. The mixture was stirred for 2 minutes in dark and then sample were taken out for zero reading. Then the solution mixture was irradiated with



Figure 3.14. Changes in absorbance spectrum of DPBF upon irradiation in presence of (a) Eosin Y, (c) *pp*-**BODIPY**, (e) *mp*-**BODIPY**, (g) *mm*-**BODIPY** in different interval of time and plot of changes in absorption at A_0 and A with respect to irradiation time of (b) Eosin Y, (d) *pp*-**BODIPY**, (f) *mp*-**BODIPY**, (h) *mm*-**BODIPY** in THF. A₀- absorbance at time = 0 min and A- absorbance at time = t.

monochromatic light and aliquots were taken out at every interval of 1 min for all compounds. The singlet oxygen quantum yields were calculated by plotting the change in absorbance at initial time and at subsequent time intervals against irradiation time.



Figure 3.15. Changes in absorbance spectra of DPBF upon irradiation in presence of (a) **T-BODIPY**, (d) **T-ADA**, in different time intervals and plots of changes in absorption at A_0 and A with respect to irradiation time of (b), (c) **T-BODIPY**, (e) **T-ADA** in THF. A_0 - absorbance at time = 0 min and A-absorbance at time = t.

The calculated Φ_D for *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, **T-BODIPY** and **T-ADA** were 5.7%, 1.9%, 12.2%, 77% and 35.1% in THF and 0.4%, 0.3%, 0.5%, 17% and 6.4% in MeOH respectively (Table 3.9). In case of regioisomeric BODIPY's *pp*-BODIPY, *mp*-BODIPY and *mm*-BODIPY, the singlet oxygen quantum yield is significantly lower compared to **T-BODIPY** and **T-ADA**. This reduction in singlet oxygen quantum yield is attributed to the very inefficient ISC, which is a result of bromine atom being attached not directly to the BODIPY core. In case of **T-BODIPY**, Br is linked to the meso-position of BODIPY with thiophene ring as a spacer which further minimizes the distance between bromine and spin density surface of BODIPY as compared to regioisomeric biphenyl-BODIPYs. Hence, higher SOQY was observed due to the population of triplet state by higher rate of ISC and possibility of CT-mediated ISC. In **T-ADA** however, there is no heavy atom attached to the core, therefore, ISC can occur by CT-mediated intersystem crossing, involving either RP-ISC or SOCT-ISC. The dihedral angle between BODIPY and BDT was 47.5° and due to the absence of heavy atom or carbonyl groups, the spin orbit coupling effects of this compound is

expected to be small which reduces the possibility of SOCT-ISC.³³ Hence, ISC might be occurring due to RP-ISC that populates the triplet state and facilitates high singlet oxygen QY in BODIPY based photosensitizers.



Figure 3.16. Changes in absorption spectra of DPBF upon irradiation in presence of (a) Eosin Y, (c) *pp*-**BODIPY**, (e) *mp*-**BODIPY**, (g) *mm*-**BODIPY** in different time intervals and plot of changes in absorption at A_0 and A with respect to irradiation time of (b) Eosin Y, (d) *pp*-**BODIPY**, (f) *mp*-**BODIPY**, (h) *mm*-**BODIPY** in MeOH. A₀- absorbance at time = 0 min and A- absorbance at time = t.



Figure 3.17. Changes in absorbance spectra of DPBF upon irradiation in presence of (a) **T-BODIPY**, (c) **T-ADA**, in different interval of time and plot of change in absorption at A_0 and A with respect to irradiation time of (b) **T-BODIPY** and (d) **T-ADA** in MeOH. A_0 - absorbance at time = 0 min and A-absorbance at time = t.

Table 3.9. Relative singlet oxygen quantum yields of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, *T*-BODIPY and T-ADA using relative method and Eosin Y as a reference dye.

Compounds	pp-BODIPY	mp-BODIPY	mm-BODIPY	T-BODIPY	T-ADA
Singlet oxygen quantum yield (THF) (%)	5.7	1.9	12.2	77	35
Singlet oxygen quantum yield (MeOH) (%)	0.4	0.3	0.5	17	6.4

3.2.12. Transient Absorption Spectroscopy^a

To elucidate the underlying mechanism of generation of charge transfer state and singlet oxygen generation, ultrafast excited-state dynamics were systematically inspected by employing femtosecond transient absorption spectroscopy (fs-TAS) following excitation with the 400 nm pump and probing with the broadband white light probe. Details of the setup can be found elsewhere.^{34,35} For *pp*-BODIPY, after photoexcitation to higher lying S₂ state, fast

^aTransient absorption were performed by Ms. Sakshi Chawla from Dr. Arijit K. De's group at IISER Mohali.

internal conversion followed by formation of vibrationally hot ¹*pp*-**BODIPY** was observed which undergoes relaxation to local excited state (¹LE) of ¹*pp*-**BODIPY** eventually decaying radiatively to the ground state. Absence of triplet formation in *pp*-**BODIPY** is evident from absence of any T_1 - T_n absorption and high fluorescence quantum yield. In case of **T-BODIPY** and **T-ADA**, after photoexcitation, photoinduced electron transfer between the donor and acceptor (BODIPY) subunits leads to ultrafast formation of ¹CT, evident by the appearance of a new ESA band in TA spectra. This state further undergoes ISC to form ³CT state which after charge recombination (CR) populates the lowest triplet excited state. The efficient charge separation and small singlet-triplet energy gap in symmetric **T-ADA** systems encouraged the CT-mediated ISC process, which is found to the dominant mechanism for triplet formation. Two-dimensional fs-TAS contour plots in Tol are shown in Figure 3.18(a-c). To extricate the timescales of ultrafast relaxation processes, a global analysis of the fs-TAS data was carried out in which the transients at all detection wavelengths were analysed simultaneously with a single set of exponentials (i.e., the principal components) using Glotaran programming.^{37,38}.

For *pp*-BODIPY, a two-step consecutive sequential kinetic model, $A \rightarrow B \rightarrow GS$, is employed to obtain the evolution-associated difference spectra (EADS) and associated time constants related to the different excited state processes. However, for **T-BODIPY** and **T-ADA**, to reconstruct the spectra associated difference spectra (SADS) associated with the individual species, the kinetics was modelled using a target analysis of the fs-TAS matrix by assuming a branched kinetic model as shown in Figure 3.18d, e respectively (by fixing the lifetime for the emission the LE/CT state, obtained from the TCSPC measurements). Corresponding EADS and SADS are shown in Figures 3.18d, e. Additional measurements are also performed in more polar solvent THF and the corresponding time scales are summarized in Table 3.10.

A close inspection of the time scales obtained indicate that the time components for charge separation (τ_1) and ISC (τ_2) become faster in THF as compared to Tol for **T-BODIPY**. However, the time component for ISC remains unaffected with the solvent polarity in **T-ADA**, but do results in faster charge separation process in THF. Thus, the results indicate participation of ¹CT state, evident from the observed solvent polarity-dependent dynamics of triplet state formation in **T-BODIPY** and **T-ADA**.


Figure 3.18. fs-TA Contour plots for (a) *pp*-**BODIPY**, (b) **T-BODIPY** and (c) **T-ADA** in Tol after photoexcitation at 400 nm. EADS (d) and SADS (e-f). Kinetic model employed for the global analysis of TA data (g-i) for *pp*-**BODIPY**, **T-BODIPY** and **T-ADA** respectively.

Table 3.10. Time constants for photoinduced charge-separation, τ_{CS} and charge recombination, τ_{CR} for *pp*-**BODIPY**, **T-BODIPY** and **T-ADA** in solvents of varying polarity obtained from global fitting of the fs-TA data.

Compound	Solvent	Dielectric	$ au_1$	$ au_2$	$ au_3$	$ au_4^*$	$ au_5^*$	RMSE
		constant	(ps)	(ps)	(ns)	(ns)	(ns)	
pp-	Tol	2.38	46.9	-	-	-	2.9	0.0003
BODIPY	THF	7.6	25.8	-	-	-	2.8	0.0002
T-BODIPY	Tol	2.38	4.02	235.1	7.5	0.3	4.4	0.0002
	THF	7.6	3.54	218.8	5.9	0.3	4.7	0.0004
T-ADA	Tol	2.38	6.32	147.1	5.1	-	0.61	0.0005
	THF	7.6	1.73	146.1	3.2	-	0.64	0.0003

*The value was fixed during target analysis for **T-BODIPY** and **T-ADA**.

3.2.13. Photocatalysis^b

All compounds *pp*-**BODIPY**, *mp*-**BODIPY**, *mm*-**BODIPY**, **T-BODIPY** and **T-ADA** showed efficient generation of singlet oxygen which motivated us to investigate their photocatalytic abilities. Methylphenyl sulfoxides and sulfones are important compounds that are found in

^bSome of the photocatalysis reactions and control experiments were performed by Ms. Vidushi Gupta at IISER Mohali.

variety of natural products and pharmaceuticals and hence their synthesis has been widely investigated.⁴² We chose the oxidation of thioanisole to methyl phenyl sulfoxide as a model reaction to be performed in presence of O_2 and 0.5 mol% of photocatalyst in MeOH under irradiation (green light) at room temperature as shown in Scheme 3.1. The reaction was screened with *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, **T-BODIPY** and **T-ADA** as photocatalyst and the conversion percentages of sulfoxide and sulfones were calculated as shown in Table 3.11 and in ¹H-NMR in appendix page no.141-143. Thioanisole was taken in MeOH (2 mL) and 0.5 mol% of catalyst was added to the mixture and then irradiated by green light at room temperature. In case of *pp*-BODIPY photocatalyst, only 11% conversion was obtained after 6 h and 36% conversion of 95% of sulfoxide and 1% of sulfones was observed and ~ 4% thioanisole still remained unreacted even after 24 h.



Scheme 3.1. Oxidation of thioanisole using *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA as photocatalyst in MeOH in presence of oxygen.

Photocatalyst	С	onversion	(%)	Selectivity
				(Sulfoxide:Sulfone)
	6 h	12 h	24 h	_
pp-BODIPY	11	36	95	94:1
mp-BODIPY	86	99	99	99:1
mm-BODIPY	98	99	92	92:8
T-BODIPY	95	95	91	91:9
T-ADA	77	92	99	99:1

Table 3.11. The oxidation of thioanisole using *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA as photocatalyst in MeOH.

In case of *mp*-BODIPY and *mm*-BODIPY, high conversion percentages of 86% and 98% respectively were observed after 6 h and both rotors showed good selectivity of sulfoxide

formation after 24 h. Similarly, in the case of **T-BODIPY**, 95% of sulfoxide product was observed after 6 h. Compounds *mm*-BODIPY and **T-BODIPY** showed overoxidation of sulfoxide after 12 h resulting in the decrease in sulfoxide yield. Similar conversion of sulfide to sulfoxide in 6 h was observed in case of **T-ADA**, and after 24 h, 99% of sulfoxide 1% of sulfone was observed as shown in Table 3.11.

Control Experiments:

To gain further insight into the photocatalytic reaction mechanism, several control experiments conditions were performed. When the reaction was performed in absence of green light as well as without photocatalyst, no trace of the compound was obtained even after 24 h of reaction as shown in Table 3.12 and in ¹H-NMR in appendix page no. 143-144.

Photocatalysts	Conditions	Conversion (P1, %) ^a
	No light	0
mp-BODIPY	No photocatalyst	0
	DABCO	3
	Benzoquinone	8
	No light	0
T-BODIPY	No photocatalyst	0
	DABCO	38
	Benzoquinone	4
	No light	0
T-ADA	No photocatalyst	0
	DABCO	51
	Benzoquinone	11

Table 3.12. Control experiments of oxidation of thioanisole using *mp*-BODIPY, T-BODIPY and T-ADA as photocatalysts.

^aConversion was determined by ¹H NMR, all the reactions were performed at room temperature for 24 h.

Therefore, light and photocatalyst are essential for the oxidation of sulfides as revealed by the control experiments. Generally, the photocatalytic oxidation of sulfides occurs by two mechanistic pathways: either through the formation of ${}^{1}O_{2}$ due to energy transfer or through superoxide anion (O_{2} .⁻) formation by electron transfer.^{42–44} In order to confirm the mechanism of photooxidation of sulfides, additional reactions for *mp*-BODIPY, **T-BODIPY** and **T-ADA** were performed in presence of 1,4-diazabicyclo [2.2.2]-octane (DABCO) which is a singlet oxygen inhibitor and 1,4-benzoquinone which is a radical inhibitor as shown in Scheme 3.2. In

case of *mp*-BODIPY in presence of DABCO and 1,4-benzoquinone, the photocatalysis reaction was suppressed and the conversion was only 3% and 8% respectively after 12 h as shown in ¹H-NMR (appendix page no. 143) and Table 3.12. Similarly in case of **T-BODIPY**, the conversion was only 38% and 4% using DABCO and 1,4-benzoquinone respectively after 24 h. Similarly in case of **T-ADA**, the reaction was suppressed using DABCO and 1,4-benzoquinone and conversion was 51% and 11% respectively after 24 h as shown in ¹H-NMR (appendix page no. 144)



Scheme 3.2. Control experiments of oxidation of thioanisole using *mp*-BODIPY, T-BODIPY and T-ADA as photocatalyst.

Hence, the photooxidation of sulfides occurs due to the involvement of both O_2 and 1O_2 and the detailed mechanism⁴²⁻⁴⁴ is shown in Scheme 3.3. Moreover, the recyclability was further investigated, and in case of **T-ADA** (NMR spectra in appendix page no. 145), there was 71% conversion to sulfoxide product.



Scheme 3.3. Possible mechanistic pathways of photooxidation of thioanisole.

3.3. Conclusions

We have synthesized BODIPY based organic photosensitizers *pp*-BODIPY, *mp*-BODIPY, mm-BODIPY, T-BODIPY and triad rotor T-ADA in which BODIPY and BDT are connected through thiophene spacer at meso-position of BODIPY where BDT acts as donor and T-BODIPY acts as acceptor. Regioisomeric effect and type of spacer significantly alter the photophysical properties such as absorption, emission, fluorescence quantum yields and singlet oxygen quantum yields of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY and T-BODIPY. Rotor triad **T-ADA** showed emission band originating due to CT at 650 nm which was responsive to variations in solvent polarity, temperature, and solubility in solvents (water in THF solution i.e., AIE effect). Among all molecules, **T-BODIPY** and **T-ADA**, showed high singlet oxygen quantum yields of 77% and 35% in THF. Femtosecond transient absorption studies were employed to shed light on the underlying mechanisms for the triplet state formation and involvement of CT state. Furthermore, DFT calculations showing smaller singlet-triplet energy gap along with the ultrafast charge separation in T-BODIPY and T-ADA indicate a multiroute yet efficient formation of triplet states via combined effect of spin-orbit coupling and CTmediated ISC in T-BODIPY and CT-mediated ISC alone in case of T-ADA, which is most likely the cause of the high singlet oxygen quantum yields of ¹O₂ in these two systems. Regioisomers pp-BODIPY, mp-BODIPY, mm-BODIPY as well as T-BODIPY and T-ADA showed excellent selectivity in aerobic photooxidation of thioanisole to methyl phenyl sulfoxide.

3.4. Experimental Section

Synthesis of 4-bormo[1,1'-biphenyl]-4-carbaldehyde (1)



Scheme 3.4. Synthesis of 4-bormo[1,1'-biphenyl]-4-carbaldehyde (1).²⁵

Procedure: 4-formyl phenyl boronic acid (1 gm, 6.669 mmol) in 20 mL ethanol and 1-bromo-4-iodobenzene (2.018 gm, 7.135 mmol) in 20 mL Tol was taken in Schlenk tube and degassed through freeze-pump-thaw several times. In two neck round-bottomed flask, Pd(PPh₃)₄ (3-5 mol%), was taken and simultaneously 4-formyl phenyl boronic acid,1-bromo-4-iodobenzene and 2 M solution of Na₂CO₃ were added and stirred for overnight at 80-90 °C. The reaction mixture was cooled and extracted by ethyl acetate and pass-through sodium sulphate. The final compound was purified by column chromatography using ethyl acetate and hexane (10:90, v/v). The final compound was obtained as white solid with 60% yield.

¹**H NMR (400 MHz, CDCl₃):** δ 10.06 (s, 1 H), 7.95 (d, J = 8 Hz, 2 H), 7.72 (d, J = 8 Hz, 2 H), 7.61 (d, J = 8 Hz, 2 H), 7.50 (d, J = 8 Hz, 2 H).

Synthesis of 3- bromobipheny4- carbaldehyde (2)



Scheme 3.5. Synthesis of 3- bromobipheny4- carbaldehyde (2).²⁵

Procedure: 4-formyl phenyl boronic acid (100 mg, 0.66 mmol) in 5 mL ethanol and 1, 3dibromobenzene (120 mg, 0.42 mmol) in 5 mL Tol was taken in Schlenk tube and degassed through freeze-pump-thaw several times. In two neck round-bottomed flask, Pd(PPh₃)₄ (3-5 mol%), was taken and simultaneously 4-formyl phenyl boronic acid, 1, 3-dibromobenzene and 2 M solution of Na₂CO₃ were added and stirred for overnight at 80-90 °C. The reaction mixture was cooled and extracted by ethyl acetate and pass-through sodium sulphate. The final compound was purified by column chromatography using ethyl acetate and hexane (10:90, v/v). The pure oily compound was obtained with 45% yield.

¹**H-NMR (400 MHz, CDCl₃):** δ 10.05 (s, 1 H), 7.95 (d, J = 8 Hz, 2 H), 7.76 (d, J = 4 Hz, 1 H), 7.70 (d, J = 8 Hz, 2 H), 7.54 (d, J = 8 Hz, 2 H), 7.34 (t, J = 8 Hz, 1 H).

Synthesis of 3-bormo[1,1'-biphenyl]-3-carbaldehyde (3)



Scheme 3.6. Synthesis of 3-bormo[1,1'-biphenyl]-3-carbaldehyde (3).²⁶

Procedure: 3-Bromoaniline (0.32 mL, 2.906 mmol) was added in HBF₄ (1.2 mL) at room temp. An aqueous solution of sodium nitrite (200 mg NaNO₂) in 0.5 mL water was added dropwise at 0 °C over 5 min. The resulting mixture was stirred for 40 min. at 0 °C and the formed precipitate was filtered out and dried. The precipitate was re-dissolved in minimum amount of acetone and then diethyl ether was added to the solution until precipitate formed. The obtained precipitate was filtered off and washed several times with diethyl ether and dried at high vacuum. The pure brown solid was obtained with 70% yield.

Diazonium salt (325 mg, 1.2 mmol), 3-formyl phenyl boronic acid (150 mg, 1 mmol) and Pd/C (6 mg, 0.05 mmol) was dissolved in MeOH and then the reaction mixture was stirred at 50 °C until the evolution of nitrogen stopped. Then the reaction mixture was cooled and filtered through celite pad using ethyl acetate. The solvent was evaporated on rota-vapour and the compound was purified by column chromatography using ethyl acetate and hexane (10:90, v/v). The pure white solid compound was obtained with 60% yield.

¹**H-NMR (400 MHz, CDCl₃):** δ 10.08 (s, 1 H), 8.06 (s, 1 H), 7.88 (d, J = 8 Hz, 1 H), 7.82 (dt, J = 8, 1.7 Hz, 1 H), 7.76 (t, J = 4 Hz, 1 H), 7.62 (t, J = 8 Hz, 1 H), 7.53 (t, J = 8 Hz, 2 H), 7.34 (t, J = 78 Hz, 1 H).

Synthesis of pp-BODIPY



Scheme 3.7. Synthesis of *pp*-BODIPY.²⁷

Procedure: 4-Bromobiphenyl-4-carbaldehyde (1) (100 mg, 0.38 mmol) was taken in dry dichloromethane (DCM) in two neck round bottomed flask and purged with nitrogen. Then 2,4-dimethylpyrrole (127 mg, 1.34 mmol) was added in dark condition and subsequently 3 or 4 drops of TFA was added and the reaction was stirred for 5 h at room temp monitored by thin layer chromatography (TLC). Then chloranil (102 mg, 0.417 mmol) was added to the reaction mixture and stirred for 40 minutes at room temperature. Then the reaction mixture was subjected to flash column chromatography using DCM as eluent and the solvent was evaporated and dried. Subsequently, dry Tol was added to reaction mixture and triethylamine (NEt₃) (776 mg, 7.67 mmol) was added and allowed to stir for 15 min. Then boron trifluoride diethyl etherate (BF₃·Et₂O) (1.3 gm, 9.1 mmol) was added to the reaction mixture and stirred for 40 min at 80 °C. Then the reaction mixture was cooled and extracted using ethyl acetate and solvent was evaporated. The compound was purified by column chromatography using DCM and hexane (20:80, v/v). The pure red solid compound was obtained with 36% yield.

¹**H-NMR (400 MHz, CDCl₃):** δ 7.70 (d, J = 7.6 Hz, 2 H), 7.61 (d, J = 8.1 Hz, 2 H), 7.54 (d, J = 6.9 Hz, 2 H), 7.36 (d, J = 7.3 Hz, 2 H), 5.99 (s, 2 H), 2.57 (s, 6 H), 1.43 (s, 6 H).

ESI-TOF: $(M+H)^+$ of molecular formula $C_{25}H_{22}BBrF_2N_2$: Calculated 479.1105; found 479.2756.

Synthesis of mp-BODIPY



Scheme 3.8. Synthesis of mp-BODIPY.²⁷

Procedure: *mp***-BODIPY** was synthesized using the same procedure as used in the synthesis of *pp***-BODIPY**. The pure orange solid with 40% was obtained.

¹**H-NMR (400 MHz, CDCl₃):** δ 7.82 (s, 1 H), 7.71 (d, *J* = 7.5 Hz, 2 H), 7.60 (d, *J* = 7.7 Hz, 1 H), 7.52 (d, *J* = 7.3 Hz, 1 H), 7.37 (d, *J* = 7.3 Hz, 3 H), 6.00 (s, 2 H), 2.57 (s, 6 H), 1.43 (s, 7 H).

¹³C NMR (100 MHz, CDCl₃): δ 155.81, 143.08, 142.19, 141.18, 140.72, 135.83, 131.46, 130.91, 130.60, 130.10, 129.92, 127.64, 127.55, 126.65, 125.68, 123.22, 121.46, 29.83, 14.71.

ESI-TOF: $(M+H)^+$ of molecular formula C₂₅H₂₂BBrF₂N₂: Calculated 479.1105; found 479.2756.

Synthesis of mm-BODIPY



Scheme 3.9. Synthesis of *mm*-BODIPY.²⁷

Procedure: *mm***-BODIPY** was synthesized using the same procedure as used in the synthesis of *pp***-BODIPY**. The pure orange solid with 30% was obtained.

¹H-NMR (400 MHz, CDCl₃): δ 7.74 (s, 1 H), 7.69 (d, J = 8 Hz, 1 H), 7.58 (t, J = 8 Hz, 1 H), 7.55 – 7.48 (m, 3 H), 7.32 (t, J = 8 Hz, 2 H), 6.00 (s, 2 H), 2.57 (s, 6 H), 1.43 (s, 6 H).
¹³C NMR (100 MHz, CDCl₃): δ 155.77, 143.17, 142.27, 140.39, 134.77, 130.89, 130.59, 130.30, 128.81, 127.80, 125.81, 124.92, 123.23, 29.85, 14.71.

ESI-TOF: $(M+H)^+$ of molecular formula $C_{25}H_{22}BBrF_2N_2$: Calculated 479.1105; found 479.2756.

Synthesis of methyl-pyrrole



Scheme 3.10. Synthesis of methyl-pyrrole (4).⁴⁵

Procedure: Pyrrole-2-carboxyaledhyde (2 g, 21.03 mmol), NaOH (4.37 g, 109.36 mmol) and hydrazine hydrate (4.16 g, 129.97 mmol) was dissolved in ethylene glycol (40 mL) and then heated under nitrogen at 200 °C for 5 h. During the course of reaction, the organic phase was distilled using a Dean-Stark apparatus. The reaction mixture was extracted using brine solution $(4 \times 10 \text{ mL})$ and diethyl ether (3 × 10 mL) twice and then the organic layers were dried over anhydrous Na₂SO₄ and the solvent was evaporated via rotary evaporator. Pure compound was obtained in the form of yellow oily liquid with a yield of 83%.

¹**H NMR (400 MHz, CDCl₃):** *δ* 7.99 (s, 1 H), 6.73 (d, *J* = 4 Hz, 1 H), 6.26 (q, *J* = 4 Hz, 1 H), 6.04 (s, 1 H), 2.38 (s, 3 H).

Synthesis of T-BODIPY



Scheme 3.11. Synthesis of T-BODIPY.²⁸

Procedure: To a solution of 5-bromo-2-thiophenecarbaldehyde (400 mg, 2.09 mmol) and 2methylpyrrole (424 mg, 5.23 mmol) in dry dichloromethane (DCM) (40 mL) two drops of trifluoroacetic acid (TFA) was added under nitrogen, and the mixture was stirred at room temperature overnight. 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (474 mg, 2.09 mmol) was added to the reaction mixture and stirred for additional 2.5 h at room temperature. Then Et₃N (1.27 g, 12.54 mmol) was added to the reaction mixture stirred for 15 minutes and then BF₃·Et₂O (1.19 g, 8.36 mmol) were added to the reaction mixture and stirred for 2 h. The reaction mixture was poured into water (4 × 10 mL) and extracted with DCM (8 × 10 mL). The combined organic layers were extracted 5 times and was then dried over Na₂SO₄, filtered and evaporated under vacuum using rotary evaporator to give a crude product, which was purified by column chromatography on silica gel using DCM/hexane (2/1, v/v) as the eluent. The pure product was obtained as a crystalline red solid with a yield of 37%.

¹**H NMR (400 MHz, CDCl₃):** δ (ppm) 7.17 (d, J = 4 Hz, 2 H), 7.04 (d, J = 4 Hz, 2 H), 6.31 (d, J = 4 Hz, 2 H), 2.64 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.36, 136.19, 133.99, 133.37, 131.81, 130.77, 130.27, 119.88, 117.02, 29.84, 15.15.

ESI-TOF: $(M+K)^+$ of molecular formula $C_{15}H_{12}BBrF_2N_2S$: Calculated 418.9643; found 418.9643.

Synthesis of T-ADA



Scheme 3.12. Synthesis of T-ADA.²⁴

Procedure: BDT-SnMe₃ (70 mg, 0.095 mmol) and thiophene-BODIPY (91.45 mg, 0.24 mmol) were dissolved in toluene and degassed by freeze-pump-thaw method. In two neck round bottom flask, $Pd_2(dba)_3$ (2.1 mg, 0.002 mmol), $P(o-tol)_3$ (3.3 mg, 0.011 mmol) were taken and simultaneously BDT-SnMe₃ and thiophene-BODIPY was added and refluxed for 5 h. The reaction mixture was cooled and evaporate and purified by column chromatography using chloroform and hexane (80:20, v/v). The final compound was obtained as brown solid with 25% yield.

¹**H NMR (400 MHz, CDCl₃):** δ (ppm) 7.70 (s, 2 H), 7.43 (q, 4 H), 7.17 (d, *J* = 4 Hz, 4 H), 6.34 (d, *J* = 4 Hz, 4 H), 2.67 (s, 12 H), 1.78 (t, *J* = 8 Hz, 4 H), 1.43 (s, 10 H), 0.94 (t, *J* = 8 Hz, 6 H), 0.88 (t, *J* = 8 Hz, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.00, 141.86, 139.09, 137.28, 135.02, 133.99, 132.84, 130.66, 130.26, 129.11, 128.54, 126.02, 125.54, 120.30, 119.75, 112.07, 32.07, 31.53, 29.84, 29.51, 28.83, 22.84, 20.18, 15.17, 14.31.

ESI-TOF: $(M+H)^+$ of molecular formula : $C_{56}H_{52}B_2F_4N_4S_4$: Calculated 1007.3278; found 1007.3271.

Oxidation of Thioanisole



Scheme 3.13. Oxidation of thioanisole using *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA as photocatalyst in MeOH in presence of oxygen.

Oxidation of Thioanisole catalyzed by BODIPYs:

pp-BODIPY, *mp*-BODIPY, and *mm*-BODIPY as photocatalyst: To a 10 mL vial equipped with a magnetic stir bar were added BODIPYs (1.92 mg, 0.0040 mmol, 0.005 equiv) catalyst, thioanisole (94.6 μ L, 0.8050 mmol, 1.0 equiv) and methanol (2 mL). Next, a balloon was filled with oxygen and fixed on the top of the vial. The reaction mixture was stirred and irradiated by green LED at room temperature under oxygen atmosphere. Aliquots were collected at equal time intervals and ¹H NMR was recorded to calculate the conversion yields based on the integration of NMR peaks of the substrate and product.

T-BODIPY as photocatalyst: To a 10 mL vial equipped with a magnetic stir bar were added **T-BODIPY** (1.53 mg, 0.0040 mmol, 0.005 equiv) catalyst, thioanisole (94.6 μ L, 0.8050 mmol, 1.0 equiv) and methanol (2 mL). Next, a balloon was filled with oxygen and fixed on the top of the vial. The reaction mixture was stirred and irradiated by green LED at room temperature under oxygen atmosphere. Aliquots were collected at equal time intervals and ¹H NMR was recorded to calculate the conversion yields based on the integration of NMR peaks of the substrate and product.

T-ADA as photocatalyst: To a 10 mL vial equipped with a magnetic stir bar were added **T-BODIPY** (3.70 mg, 0.0040 mmol, 0.005 equiv) catalyst, thioanisole (94.6 μ L, 0.8050 mmol, 1.0 equiv) and methanol (2 mL). Next, a balloon was filled with oxygen and fixed on the top of the vial. The reaction mixture was stirred and irradiated by green LED at room temperature under oxygen atmosphere. Aliquots were collected at equal time intervals and ¹H NMR was recorded to calculate the conversion yields based on the integration of NMR peaks of the substrate and product.

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a. ¹H and ¹³C NMR spectra ¹H NMR of 1:



¹H NMR of 2:





¹H NMR of *pp*-BODIPY:



¹³C NMR of *pp*-BODIPY:



¹H NMR of *mp*-BODIPY:



¹³C NMR of *mp*-BODIPY:



¹³C NMR of *mm*-BODIPY:



¹H NMR of Compound 4:





¹³C NMR of T-BODIPY:





¹³C NMR of T-ADA:





¹H NMR of crude mixture for oxidation of thioanisole using *pp*-BODIPY

¹H NMR of crude mixture for oxidation of thioanisole using *mp*-BODIPY





¹H NMR of crude mixture for oxidation of thioanisole using *mm*-BODIPY

¹H NMR of crude mixture for oxidation of thioanisole using **T-BODIPY**







Control experiments NMR of mp-BODIPY



Control experiments NMR of T-BODIPY



Control experiments NMR of T-ADA





b. Frequencies and Coordinates of DFT Optimized Geometries

Table 3.13.	. Results of firs	t three frequend	cies and molec	ular symmetries	calculated from	geometry
optimizatio	n of pp-BODI	PY, <i>mp</i> -BODI	PY, <i>mm</i> -BOD	IPY, T-BODIP	Y and T-ADA.	

Compounds	Symmetry	First Three Frequencies		
		16.76		
pp-BODIPY	C_1	21.61		
		22.45		
		13.24		
mp-BODIPY	C_1	20.93		
		24.47		
		11.87		
mm-BODIPY	C_1	19.09		
		27.23		
		28.05		
T-BODIPY	C_1	40.38		
		54.08		
		5.47		
T-ADA	C_1	8.12		
		10.71		

Coore	dinates of	geometry	optimized	С	1.08581	-3.11802	-0.12527	
struct	ture of <i>pp</i> -B0	ODIPY		С	6.20335	-2.90034	-0.11938	
С	-1.34781	0.03846	-1.20274	Н	-1.87998	0.04122	-2.14909	
С	0.04523	0.03930	-1.20379	Н	-6.22017	-1.36674	1.65769	
С	0.76033	-0.00005	-0.00005	Н	0.58557	-0.06108	2.14551	
С	0.04525	-0.03939	1.20372	Н	-1.87993	-0.04128	2.14906	
С	-1.34778	-0.03853	1.20270	Н	-3.74976	-1.38184	1.64760	
С	-2.07290	-0.00003	-0.00001	Н	-6.22021	1.36672	-1.65759	
С	-3.55716	-0.00002	0.00001	Н	-3.74979	1.38180	-1.64758	
С	-4.28109	-0.76195	0.93211	Н	3.66431	4.45051	0.18107	
С	-5.67410	-0.76701	0.93855	Н	3.66460	-4.45049	-0.18125	
С	-6.36105	-0.00001	0.00005	Н	1.10962	4.21026	0.16100	
С	-5.67412	0.76698	-0.93847	Н	0.51955	2.76351	0.99130	
С	-4.28111	0.76191	-0.93207	Н	0.51773	2.82176	-0.76281	
Br	-8.27208	0.00000	0.00008	Н	6.31670	3.98529	0.16578	
С	2.25507	-0.00004	-0.00004	Н	6.70586	2.52050	-0.77489	
С	2.94500	-1.22260	-0.05053	Н	6.70659	2.44585	0.97828	
Ν	4.34465	-1.24347	-0.05195	Н	1.10991	-4.21044	-0.16064	
В	5.28074	0.00004	0.00011	Н	0.52055	-2.76466	-0.99308	
Ν	4.34458	1.24353	0.05216	Н	0.51710	-2.82093	0.76109	
С	2.94491	1.22256	0.05048	Н	6.70609	-2.51951	0.77484	
С	4.75858	2.52367	0.10415	Н	6.70666	-2.44626	-0.97837	
С	3.63114	3.37003	0.13754	Н	6.31701	-3.98513	-0.16466	
С	2.48665	2.58227	0.10479	Н	0.58551	0.06099	-2.14559	
С	2.48682	-2.58233	-0.10504	Coor	dinates of	geometry	optimized	
С	3.63137	-3.37001	-0.13766	struc	ture of <i>mp-</i> B	ODIPY		
С	4.75875	-2.52360	-0.10399	С	1.63747	0.29229	0.76500	
F	6.07568	0.04808	-1.14365	С	0.25947	0.13496	0.89553	
F	6.07560	-0.04793	1.14393	С	-0.57901	0.22839	-0.22256	
С	1.08560	3.11787	0.12443	С	-0.00307	0.48224	-1.47388	
С	6.20313	2.90052	0.11969	С	1.37521	0.63820	-1.60270	

С	2.22269	0.54687	-0.48625	Н	7.55969	1.14353	-0.97793
С	3.69166	0.71520	-0.62643	Н	6.01212	2.55327	-2.32573
С	4.57347	-0.07263	0.13189	Н	3.56556	2.29615	-2.08881
С	5.94749	0.09489	-0.00606	Н	-3.87958	4.27827	0.76636
С	6.48582	1.03057	-0.88637	Н	-3.02466	-4.47191	-0.66977
С	5.61052	1.81255	-1.64082	Н	-1.33024	4.32926	0.48049
С	4.23141	1.66023	-1.51442	Н	-0.70029	3.12524	-0.65322
Br	7.12624	-0.99876	1.03179	Н	-0.51502	2.87554	1.07417
С	-2.05785	0.06095	-0.08362	Н	-6.45928	3.52430	0.93621
С	-2.62296	-1.21793	-0.21766	Н	-6.60407	1.87260	1.59411
Ν	-4.00594	-1.39483	-0.09242	Н	-6.79605	2.13461	-0.13031
В	-5.05170	-0.27709	0.19448	Н	-0.51916	-3.95164	-0.85671
N	-4.24447	1.04961	0.31173	Н	0.02476	-2.61515	0.16750
С	-2.85769	1.18567	0.17844	Н	-0.16803	-2.36625	-1.55921
С	-4.77709	2.26168	0.55693	Н	-6.31912	-2.74291	-0.93505
С	-3.74298	3.21984	0.58882	Н	-6.12781	-3.01137	0.78841
С	-2.53497	2.57354	0.35515	Н	-5.69460	-4.31010	-0.35504
С	-2.03887	-2.50364	-0.47797	Н	-0.17317	-0.05322	1.87365
С	-3.09568	-3.40588	-0.49956	Coor	dinates of	geometry	optimized
С	-4.29259	-2.69969	-0.26018	struc	ture of <i>mm</i> -l	BODIPY	0.00700
F	-5.71584	-0.53982	1.39121	C	-0.82907	0.79396	0.60598
F	-5.96100	-0.19160	-0.85838	C	0.42299	1.01361	1.18950
С	-1.20035	3.25704	0.31110	C	0.51138	1.77835	2.35960
С	-6.24251	2.47036	0.75187	C	-0.64455	2.31077	2.93098
С	-0.60106	-2.87401	-0.69194	C	-1.88867	2.08617	2.34523
С	-5.68585	-3.23130	-0.18817	C	-2.00065	1.32359	1.17103
Н	2.26468	0.24183	1.64978	С	-3.32503	1.08640	0.53987
Н	-0.63941	0.54841	-2.35139	С	-3.62480	-0.15557	-0.04383
Н	1.80194	0.80760	-2.58651	С	-4.86815	-0.36408	-0.63202
Н	4.19004	-0.82927	0.80634	С	-5.84053	0.63293	-0.66005
				С	-5.54355	1.86668	-0.08016

С	-4.30311	2.09412	0.51205	Н	1.11478	4.35327	-1.31063
Br	-5.25449	-2.06892	-1.40990	Н	0.95131	3.75222	0.34615
С	1.65630	0.44584	0.56177	Н	-0.00715	3.03687	-0.93905
С	2.11467	-0.81934	0.96446	Н	5.37157	2.17970	-3.38721
Ν	3.26935	-1.36594	0.39218	Н	5.06897	0.42282	-3.32476
В	4.15599	-0.69909	-0.70088	Н	6.04572	1.17529	-2.07619
Ν	3.49328	0.67475	-1.01523	Н	0.31605	-2.58812	3.40264
С	2.33642	1.18843	-0.41738	Н	-0.52175	-1.55869	2.23294
С	3.95271	1.57007	-1.90974	Н	0.45500	-0.82637	3.49352
С	3.10071	2.69372	-1.91407	Н	4.64774	-4.36557	1.11407
С	2.08403	2.48047	-0.99092	Н	5.59425	-2.90355	0.72824
С	1.61083	-1.76433	1.92104	Н	4.61761	-3.65419	-0.52149
С	2.48432	-2.84472	1.88723	Coor	dinates of	geometry	optimized
С	3.49384	-2.57504	0.94030	struc	cture of T-BC	DIPY	
F	5.44832	-0.50641	-0.21574	Н	-0.68307	2.61760	0.55566
F	4.17963	-1.49198	-1.84666	Н	-0.14180	-3.07625	-0.03133
С	0.97788	3.45283	-0.70592	С	-1.07701	-0.34105	0.37142
С	5.17964	1.33221	-2.72639	С	-1.72334	-1.21697	1.21584
С	0.40296	-1.67614	2.80611	С	-3.14196	-1.17443	1.11976
С	4.65259	-3.43139	0.54925	С	-3.56176	-0.26756	0.18559
Н	-0.88721	0.22283	-0.31554	S	-2.24485	0.56134	-0.58328
Н	1.48135	1.95230	2.81525	Η	-1.18851	-1.85279	1.91069
Н	-0.57571	2.89641	3.84290	Н	-3.81724	-1.77849	1.71203
Н	-2.78396	2.48251	2.81384	Br	-5.33786	0.12662	-0.29502
Н	-2.90184	-0.96251	-0.01862	С	0.36856	-0.15504	0.20770
Н	-6.80250	0.44811	-1.12351	С	1.18730	-1.29222	0.06592
Н	-6.28612	2.65867	-0.10089	Ν	2.57238	-1.17589	-0.03672
Н	-4.07951	3.06858	0.93401	В	3.37627	0.16260	-0.08424
Н	3.22765	3.56946	-2.53648	Ν	2.31465	1.30366	0.02920
Н	2.41195	-3.74600	2.48126	С	0.94102	1.13141	0.19683
				С	2.59085	2.62435	0.08497

С	1.39029	3.34146	0.29336	С	0.19072	2.86749	-0.49775
С	0.36174	2.41613	0.37465	С	-0.19072	-2.86758	-0.49798
С	0.85793	-2.66941	-0.03885	С	0.29464	4.07674	-0.49257
С	2.04932	-3.36315	-0.18134	С	-0.29460	-4.07683	-0.49291
С	3.09615	-2.41202	-0.18283	С	0.42591	5.52842	-0.48504
F	4.05837	0.26227	-1.29237	С	-0.42587	-5.52852	-0.48541
F	4.25962	0.22894	0.98827	С	4.90973	-0.75687	-0.50592
С	3.97930	3.15615	-0.04554	С	-4.90973	0.75679	-0.50600
С	4.56249	-2.64481	-0.33549	С	5.53510	-1.91539	-0.92794
Н	1.31543	4.41624	0.38115	С	6.94022	-1.88459	-0.77603
Н	2.18007	-4.43071	-0.28984	С	7.41941	-0.69705	-0.25817
Н	4.43191	2.81754	-0.98233	S	6.09071	0.39620	0.07550
Н	4.61045	2.77492	0.76339	С	-5.53508	1.91528	-0.92810
Н	3.97692	4.24734	-0.01740	С	-6.94020	1.88451	-0.77620
Н	4.77824	-3.71353	-0.38885	С	-7.41941	0.69701	-0.25826
Η	5.10859	-2.20558	0.50489	S	-6.09073	-0.39622	0.07549
Н	4.93377	-2.15492	-1.24104	С	8.81162	-0.34504	0.02711
Coo	rdinates of	geometry	optimized	С	-8.81163	0.34505	0.02704
stru	cture of T-AD	A		С	9.62500	-1.28209	0.69674
С	-1.16710	0.78953	-0.50634	Ν	10.97332	-1.02608	0.93816
С	-1.22735	-0.63033	-0.50369	В	11.72892	0.29549	0.59159
С	-0.08977	-1.44960	-0.50247	Ν	10.67232	1.22922	-0.08051
С	1.16709	-0.78961	-0.50638	С	9.34685	0.89948	-0.36190
С	1.22735	0.63024	-0.50363	С	-9.62499	1.28220	0.69656
С	0.08977	1.44952	-0.50235	Ν	-10.97331	1.02624	0.93799
С	2.46657	-1.38340	-0.49766	В	-11.72895	-0.29535	0.59157
С	3.48985	-0.47164	-0.49968	Ν	-10.67235	-1.22920	-0.08037
S	2.88866	1.19495	-0.51321	С	-9.34687	-0.89952	-0.36178
С	-2.46657	1.38332	-0.49762	С	9.31418	-2.54423	1.26705
С	-3.48985	0.47155	-0.49972	С	10.48389	-3.03961	1.82285
S	-2.88866	-1.19504	-0.51334				

С	11.49550	-2.07542	1.60981	Н	0.00603	-5.97100	-1.39020
С	10.92603	2.45556	-0.58671	Н	4.99446	-2.74760	-1.36249
С	9.75946	2.94920	-1.21346	Н	7.59788	-2.68924	-1.08076
С	8.77688	1.97959	-1.08665	Н	-4.99443	2.74746	-1.36271
С	-9.31415	2.54438	1.26676	Н	-7.59786	2.68914	-1.08101
С	-10.48384	3.03983	1.82251	Н	8.33713	-3.00267	1.27848
С	-11.49547	2.07564	1.60956	Н	10.61928	-3.97755	2.34302
С	-10.92606	-2.45562	-0.58637	Н	9.67644	3.90787	-1.70599
С	-9.75949	-2.94937	-1.21303	Н	7.77014	2.01810	-1.47350
С	-8.77689	-1.97975	-1.08636	Н	-8.33709	3.00281	1.27812
С	12.92472	-2.11760	2.03826	Н	-10.61921	3.97783	2.34258
С	12.26473	3.10573	-0.47201	Н	-9.67647	-3.90811	-1.70541
F	12.76620	0.03541	-0.29868	Н	-7.77016	-2.01833	-1.47320
F	12.21472	0.88256	1.75577	Н	13.15326	-3.07007	2.52018
С	-12.92465	2.11781	2.03817	Н	13.13874	-1.29977	2.73335
С	-12.26474	-3.10579	-0.47154	Н	13.58612	-1.97856	1.17763
F	-12.76617	-0.03536	-0.29881	Н	12.24368	4.10701	-0.90633
F	-12.21484	-0.88222	1.75580	Н	13.02439	2.50589	-0.98305
Η	2.62116	-2.45465	-0.46337	Н	12.57000	3.17064	0.57664
Η	-2.62117	2.45456	-0.46330	Н	-13.15360	3.07099	2.51849
Η	0.01953	5.96872	-1.40266	Н	-13.13812	1.30110	2.73476
Η	1.47718	5.82552	-0.40874	Н	-13.58610	1.97689	1.17790
Η	-0.10912	5.97042	0.36300	Н	-12.24382	-4.10696	-0.90610
Η	-1.47883	-5.82560	-0.43772	Н	-13.02450	-2.50579	-0.98226
Н	0.08531	-5.96833	0.37835	Н	-12.56980	-3.17095	0.57717

Aminoindole and Naphthalimide based Charge Transfer Fluorescent Probes for pH Sensing and Live Cell Imaging



Abstract: Fluorescent probes are essential for imaging of Cancer cells and to track organelles inside the cells. We have synthesized three molecular rotors AIN, AINP and F-AINP based on 1-aminoindole (AI) as electron donor and naphthalimide as electron acceptor. All compounds showed charge transfer (CT) character, aggregate induced emission (AIE) and emission responsiveness towards temperature variation and solvent viscosity. AINP was most sensitive towards viscosity among all molecules with viscosity sensitivity of ~ 0.37. AIN, AINP and F-AINP showed negative temperature coefficients in chloroform with internal sensitivities of - 0.04% °C⁻¹, - 0.08% °C⁻¹ and - 0.1% °C⁻¹ respectively. Furthermore, all the rotors were sensitive towards the pH of solvent as revealed by acid titration and base back-titration and serve as colorimetric pH sensors with intriguing photophysical characteristics. Additionally, AINP and F-AINP were utilized to image live Cancer cell line A549 and fibroblast cell line L929 and the imaging studies revealed the incorporation of dyes in the cytoplasmic space of the cells except the nuclei.

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4.1. Introduction

Dual or multiple emissive donor-acceptor (D-A) rotor molecules are extremely important for their utilization in optical switching, bioimaging and biosensing, temperature and viscosity sensing, biomedical and theranostic applications.^{1–5} The most desirable features in such molecules are their high fluorescence quantum yields, large Stokes shifts and multi-stimuli responsive emission behavior for multi-analyte/parameter sensing. Due to distinct emission behavior tunable by various stimuli such as viscosity, temperature, pH etc., these rotor molecules have been extensively utilized for ratiometric temperature sensing,^{2,6,7} viscosity sensing,^{4,8} biosensing and bioimaging.^{1,9} Among the various stimuli-responsive rotors, pH dependent rotor molecules were extensively used to visualize changes in intracellular pH.^{10,11} The value of intracellular pH is a crucial factor that regulates the organelle's functions, various enzyme activity, protein degradation and several other cellular behavior.¹² Generally, abnormal intracellular pH indicates diseases such as Alzheimer's, Stroke and Cancer.^{13,14} Cancerous cells are known to show abnormal intracellular pH value^{15,16} hence, it is important to develop rotor molecules that can image or identify Cancerous cells. Synthetic organic rotor luminophores are well-suited to stain biological samples for imaging applications.^{17,18} Due to their outstanding sensitivity and ease of use, organic fluorescent rotors are widely useful as imaging probes for observing areas of cells, model organisms, and biological processes with appreciable spatiotemporal resolutions.¹⁹⁻²² The fluorescence of hydrophobic organic rotor molecules is quenched in the hydrophilic bio-environment due to aggregation which is known as aggregation caused quenching (ACQ). Hence, ACQ limits the use of rotor molecules in fluorescence imaging. However, the concept of aggregation induced emission (AIE) introduced in 2001 revealed that enhancement of emission intensity can be achieved by restricted intramolecular motions and inhibition of non-radiative decay.^{23,24} Generally, AIE active molecules are non-emissive or weakly emissive in solution, while they become highly emissive in binary mixture of good and bad solvent due to the formation of aggregates. Hence, contrary to ACQ effect, AIE is a widely applicable phenomenon suitable for multitude of applications.^{25–28} Due to hydrophilic cellular environment, the AIE luminogens (AIEgens) show the enhancement of emission intensity inside a cell and hence AIEgens are one of the best rotor candidates for bioimaging.²⁹⁻³² Among various AIEgens, naphthalimide and its derivatives are considered as versatile chromophore due to their unique photophysical properties and wide applications as stimuli sensors, cell imaging probes, drug delivery agents and optoelectronic materials.³² Naphthalimides exhibit tunable optical properties, facile



Figure 4.1. Chemical structures of **AIN**, **AINP** and **F-AINP** synthesized and investigated in this work. synthetic modifications and very good thermal stability and high fluorescent quantum yields. The fluorescence of naphthalimide core can be tuned by functionalization of electron donor moieties at aromatic core. Xia et. al., synthesized napthalimide based thermoresponsive fluorescent rotor utilized as viscometer and viscosity related thermometer.³³ Recently, Wang et. al., reported napthalimide based thermometer that showed turn-on fluorescence upon varying temperature.³⁴ Song and co-workers synthesized napthalimide and indole based fused fluorophores and utilized them for detection of thiophenol³⁵ and biothiol³⁶ in living cells using 2,4-dinitrobenzene and 2,4-dinitrobenzene sulfonyl group as recognition site respectively.

Indole unit is a widely studied heterocycle among which 1-aminoindole is the most important sub-family that exhibits promising biological activities, cell imaging, pH sensitivity and metal ion sensitivity.^{37,38} Recently, Wang et al., reported indole based fluorescent probe used for detection of fluoride ion and cell imaging.³⁹ Benitez-Martin et. al., developed two pH-sensitive indolenine based probes and used as cytoplasmic pH sensor and for lysosome targeting.⁴⁰ Li et. al., synthesized indole-based turn-on fluorescent sensor used for fluoride ion sensing.⁴¹

In this work, we have developed aminoindole and naphthalic anhydride/naphthalimide functionalized D- π -A systems **AIN** (with nahpthalic anhydride), **AINP** (with 2,6-diisopropyl amine substitution in napthalic anhydride) and **F-AINP** (fluoro substitution in 7-position of indole to study the influence of H-bonding between NH- and F on photophysical properties) where aminoindole moiety acts as an electron donor, naphthalene as the π bridge and imide part as an electron acceptor (Figure 4.1). These systems exhibit intramolecular charge transfer (ICT) and are sensitive towards viscosity changes, pH changes and temperature variations. Furthermore, these molecules showed efficient aggregation induced emission with emission enhancement upto ~ 5 fold in **AINP**. Additionally, lung cancer cell line A549 and fibroblast cell line L929 were treated with **AINP** and **F-AINP**, and the imaging of live cells were performed. By contrasting the cell imaging of **AINP** and **F-AINP** with the cell imaging of other trackers, such as lysosome tracker, nucleus tracker and membrane tracker, it was possible to detect the presence of dyes in the cytoplasmic space of the A549 cell line.
4.2. Results and Discussion

4.2.1. Synthesis

The synthesis of **AIN**, **AINP** and **F-AINP** were accomplished as outlined in Scheme 4.1. For the synthesis of final compounds, 1-aminoindole (AI) and 7-fluoro,1-amoinoindole (F-AI) were synthesized by treating indole and 7-fluoroindole with hydroxylamine o-sulfonic acid (aminating agent).⁴² Further AI and F-AI were subjected to Buchwald-Hartwig coupling reaction with different naphthalimide derivatives to obtain final compounds **AIN**, **AINP** and **F-AINP**.³⁷ The compound 6-bromo-2-(2,6-diisopropylphenyl)naphthalimide (**NP**) was synthesized by refluxing 6-bromo-1,8-naphthalic anhydride with 2,6-diisopropylaniline in acetic acid⁴³ as shown in Scheme 4.1. All compounds were purified via column chromatography and characterized using ¹H NMR, ¹³C NMR and high-resolution mass spectrometry (HRMS).



Scheme 4.1. Synthesis of AIN, AINP and F-AINP.

4.2.2. Photophysical Characterization

UV/Vis absorption and emission spectra of **AIN**, **AINP** and **F-AINP** were measured in chloroform (CHCl₃) at $c \sim 10^{-6}$ M. In case of **AIN**, the major absorption peak was observed at 394 nm corresponding to S₀-S₁ transition (Figure 4.2). Upon excitation at 394 nm, two emission peaks were observed at ~ 408 nm and ~ 433 nm. Furthermore, absorption and emission spectra

were also recorded at different concentrations of **AIN**. In absorption spectra, upon increasing the concentration of **AIN**, only the absorbance increased as shown in Figure 4.2. While in case of emission spectra upon increasing the concentration of solution to $c \sim 10^{-5}$ M, a new emission band at 530 nm was observed apart from emission bands at 408 nm and 433 nm. Upon further increasing the concentration (up to 10^{-4} M) of **AIN**, the intensity of both peaks in blue region decreased while the peak at 530 nm intensified. Likewise, in **AINP** and **F-AINP**, the major absorption peaks were observed at 393 nm and 388 nm respectively. In **AINP**, upon excitation at 393 nm, two emission peaks at 407 nm and 432 nm and a shoulder peak at 510 nm were observed.



Figure 4.2. Concentration dependent UV/Vis absorption of: (a) **AIN**, (c) **AINP** and (e) **F-AINP** and emission of: (b) **AIN** ($\lambda_{ex} = 394 \text{ nm}$), (d) **AINP** ($\lambda_{ex} = 393 \text{ nm}$) and (f) **F-AINP** ($\lambda_{ex} = 388 \text{ nm}$). With the increasing concentration of **AINP** in CHCl₃, no change in absorption spectra was observed while in emission, a major peak at 510 nm was observed as shown in Figure 4.2. Similarly, in **F-AINP**, upon excitation at 388 nm, two emission peaks were obtained at 408 nm

and 432 nm and a shoulder peak at 494 nm was observed. At higher concentration of **F-AINP** (10^{-5} M), apart from emission bands at 408 nm and 432 nm, a bathochromically shifted band at ~ 500 nm was also observed. Further, with increasing the concentration of **F-AINP** (up to 10^{-4} M), the intensity of both peaks in blue region decreased while that of the peak at 500 nm increased. Furthermore, with increasing concentration ($c \sim 10^{-3}$ M), the fluorescence intensity was quenched as shown in Figure 4.2. The molar absorption coefficients (ε) of **AIN**, **AINP** and **F-AINP** were 22197 M⁻¹ cm⁻¹, 23175 M⁻¹ cm⁻¹ and 19119 M⁻¹ cm⁻¹ respectively. To understand the effect of concentration on structural variation and photophysical properties, ¹H-NMR was recorded for **AINP** at various concentrations. However, upon increasing concentration, no change in ¹H-NMR was observed (Figure 4.3). Hence, UV/Vis absorption and ¹H-NMR experiments indicate that the emission peak observed at higher concentration can possibly be attributed to the formation of excited state species.



Figure 4.3. Concentration dependent ¹H-NMR of AINP in DMSO.

The fluorescence quantum yields were determined by relative method (as described in Chapter 2, experimental section) using 4',6-diamidino-2-phenylindole (DAPI) as a reference dye and the quantum yields of 0.032, 0.056 and 0.346 were obtained for **AIN**, **AINP** and **F-AINP** respectively (Table 4.1).

							Quar	ntum
							Yie	eld
Compound	А	bsorban	ce	Integrated	Fluorescend	ce Intensity	$\Phi = \Phi_R($	I/I_R)(A _R
							/A)(λ _{exR}	λ_{ex})(n ² /
							n ²	R)
	1	2	3	1	2	3	Φ_{i}	$\Phi_{\rm avg}$
AIN	0.0712	0.089	0.0104	79.56	71.45	61.03	0.040	
							0.033	0.032
							0.023	
AINP	0.0821	0.0906	0.0985	130.31	138.13	140.51	0.055	
							0.061	0.056
							0.053	
F-AINP	0.0557	0.0721	0.086	532.14	661.87	785.07	0.331	
							0.367	0.346
							0.341	
DAPI	0.0448	0.0707	0.0828	629.732	867.144	1086.253	0.:	58
(DMSO)								

Table 4.1. Relative quantum yields of AIN, AINP and F-AINP using relative method and DAPI as a reference dye.

In case of **F-AINP**, the internuclear distance between NH- and F is ~ 3 Å (calculated by DFT optimized structure), which is effective for forming H-bonding. To confirm the H-bonding in **F-AINP**, temperature dependent ¹H-NMR was recorded in CHCl₃ over the temperature range of 233-313 K as shown in Figure 4.4. Due to strengthening of H-bonding at lower temperature, NH-peak was observed to be deshielded with lowering of temperature. Hence, due to possible hydrogen bonding between the NH- and F at the 7-position of the indole, a modest restriction

of rotation led to a decrease in non-radiative deactivation and an increase in quantum yield for **F-AINP**.



Figure 4.4. (a) Effect of temperature on ¹H-NMR and (b) plot of change of chemical shift of NH-peak vs temperature of **F-AINP**.

4.2.3. Solvatochromism

The longer wavelength peak at ~ 500 nm for **AIN**, **AINP** and **F-AINP** at higher concentrations can be attributed either to charge transfer (twisted intramolecular charge transfer (TICT), planarized intramolecular charge transfer (PLICT) etc.) or excimer formation. In case of charge transfer, the dipole moment of excited state of the molecule changes, hence the molecule should show solvatochromic shifts in emission spectra.⁴⁴ On the other hand, emission from excimer species will not show significant changes in solvatochromic behaviour because their dipole moment is small and it is solvent-polarity independent.⁴⁴ Since all compounds showed longer wavelength emission at higher concentrations, solvatochromic study was performed at $c \sim 10^{-5}$ M. In case of **AIN**, in non-polar solvent such as methyl cyclohexane (MCH), the emission

was observed at ~ 455 nm while in toluene (Tol), the emission was observed at 485 nm. In case of polar solvents such as acetonitrile (ACN), dichloromethane (DCM), chloroform (CHCl₃) and dimethyl sulfoxide (DMSO), the emission was observed at 530 nm with bathochromic shift of 75 nm. While in methanol (MeOH), the intensity of longer wavelength peak decreased due to non-radiative deactivation in polar protic solvent. Furthermore, solvatochromic study was also performed in binary mixture of polar and non-polar (CHCl₃/MCH) solvents.



Figure 4.5. Emission of **AIN** ($\lambda_{ex} = 394 \text{ nm}$), **AINP** ($\lambda_{ex} = 393 \text{ nm}$) and **F-AINP** ($\lambda_{ex} = 388 \text{ nm}$) (a), (c) and (e) in solvent of different polarity and (b), (d) and (f) in different percentage of CHCl₃/MCH ($c \sim 10^{-5}$ M) respectively (inside the graph, 0%, 10% to 100% indicate the percentage of CHCl₃ in solutions).

As the percentage of CHCl₃ was increased from 0% to 100% (v/v), the emission was bathochromically shifted from 455 nm to 530 nm as shown in Figure 4.5. Similarly, the solvatochromic study was also performed for **AINP** and **F-AINP**. In case of **AINP** in non-

polar solvent such as MCH, the emission was observed at ~ 455 nm while in Tol, the emission was observed at 470 nm. In case of polar solvents such as THF, DCM, CHCl₃ and DMSO, the emission was observed at ~ 510 nm with bathochromic shift of 55 nm. Solvatochromism study was also performed in binary mixture of polar and non-polar (CHCl₃/MCH) solvents. As the percentage of CHCl₃ was increased from 0% to 100% (v/v), the emission was red shifted from 455 nm to 510 nm as shown in Figure 4.5. In case of **F-AINP** in non-polar solvent such as MCH, the emission was observed at ~ 446 nm and in Tol the emission was observed 465 nm. In case of polar solvents such as THF, DCM, CHCl₃ and DMSO, the emission was observed at ~ 500 nm with a bathochromic shift of 54 nm. As the percentage of CHCl₃ in a mixture of CHCl₃/MCH was increased from 0% to 100% (v/v), the emission was red shifted from 446 nm to 500 nm. Thus, the bathochromic shift in emission with increasing solvent polarity indicates higher dipole moments in excited state than ground state and a possible charge transfer state.

4.2.4. Cyclic Voltammetry

In order to study the redox properties and frontier molecular orbital (FMO) energy levels, cyclic voltammetry (CV) measurements were performed for **AIN**, **AINP** and **F-AINP** in deoxygenated dichloromethane (DCM) containing (0.1 M) tetrabutylammonium hexafluorophosphate (TBAHFP) as a supporting electrolyte (Figure 4.6). The calculated HOMO levels were -5.85 eV, -5.89 eV and -5.93 eV and the corresponding LUMO levels were -3.93 eV, -3.86 eV and -3.90 eV for **AIN**, **AINP** and **F-AINP** respectively as shown in Table 4.2.



Figure 4.6. Cyclic voltammogram of (a) **AIN**, (b) **AINP**, (c) **F-AINP** in dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) and potentials measured vs Ag/AgCl reference electrode.

Compounds	Е	Eonsetox	*HOMO	Eonset ^{red}	LUMO	Egcv	
	$(M^{-1} cm^{-1})$	(V)	(eV)	(V)	(eV)	(eV)	
AIN	22197	1.09	-5.85	-0.82	-3.93	1.91	
AINP	23175	1.13	-5.89	-0.89	-3.86	2.03	
F-AINP	19119	1.17	-5.93	-0.86	-3.90	2.03	
*HOMO = $-(E_{onset}^{ox} + 4.76) \text{ eV}$, and LUMO = $-(E_{onset}^{red} + 4.76) \text{ eV}$.							

Table 4.2. Redox properties based on cyclic voltammetry and molar absorption coefficients (ε) of **AIN**, **AINP** and **F-AINP**.

4.2.5. Density functional theory (DFT) calculations

Density functional theory (DFT) calculations were performed for all molecules in the ground state using the Gaussian 09 package at B3LYP/6-31G(d,p) level to calculate the HOMO and LUMO energy levels as well as torsion angles in geometry optimized structures (Figure 4.7–4.10, Table 4.3). In all rotors, HOMO was completely localized on aminoindole part while the LUMO and LUMO +1 were localized on naphthalimide part as shown in Figure 4.7. Hence, charge transfer can be understood to be occurring from HOMO to LUMO transitions as well as from HOMO to LUMO+1 transitions.



Figure 4.7. FMO energy levels of compounds **AIN**, **AINP** and **F-AINP** calculated using B3LYP/6-31G(d,p).

DFT calculations of protonated compounds (**AIN**⁺, **AINP**⁺ and **F-AINP**⁺) and deprotonated compounds (**AIN**⁻, **AINP**⁻ and **F-AINP**⁻) were performed to see the effect on delocalization of

electron density. In **AINP** and **F-AINP**, the HOMO was not localized on aminoindole moiety in the protonated compounds which was an indication of weak ICT from aminoindole donor to imide acceptor upon protonation (Figure 4.8-4.10). While in case of deprotonation of all compounds, the bond length **N₃-C₄**, reduced indicates of double bond character which further enhanced electron transfer from aminoindole part to imide part as shown in Table 4.3.



Figure 4.8. DFT calculated (B3LYP/6-31G(d,p)) geometry optimized structures of AIN, AIN⁻ and AIN⁺ with energy levels.



Figure 4.9. DFT calculated (B3LYP/6-31G(d,p)) geometry optimized structures of **AINP**, **AINP**⁻ and **AINP**⁺ with energy levels.



Figure 4.10. DFT calculated (B3LYP/6-31G(d,p)) geometry optimized structures of **F-AINP**, **F-AINP**⁻ and **F-AINP**⁺ with energy levels.

Table 4.3. Dihedral angles (in degrees), HOMO and LUMO (eV) energy levels and bond length calculated by B3LYP/6-31G (d,p) method for dyads and triads.

				Dihedral angle	Bond length (Å)		(Å)
Compounds	НОМО	LUMO	ΔE	(°)			
	(eV)	(eV)	(eV)	(C ₁ -N ₂ -N ₃ -C ₄)	C ₁ -N ₂	N ₂ -N ₃	N ₃ -C ₄
AIN	- 6.00	- 2.59	3.41	106.2	1.39	1.38	1.39
AIN ⁻	- 1.69	1.27	2.96	71.7	1.38	1.40	1.32
AIN^+	- 9.78	- 6.33	3.45	60.2	1.42	1.46	1.48
AINP	- 5.87	- 2.30	3.57	126.9	1.39	1.38	1.41
AINP ⁻	- 1.62	1.32	2.94	- 71.7	1.38	1.40	1.33
AINP ⁺	- 8.30	- 5.87	2.43	58.4	1.42	1.46	1.48
F-AINP	- 5.93	- 2.25	3.68	122.5	1.39	1.39	1.41
F-AINP-	- 1.71	1.35	3.06	- 98.7	1.37	1.41	1.33
F-AINP ⁺	- 8.28	- 5.82	2.46	67.3	1.42	1.46	1.47

4.2.6. Temperature-dependent Emission

The emission of rotor molecules is sensitive towards multiple stimuli such as polarity, temperature and viscosity.^{5,17} In polar solvents, ICT or TICT rotors show hypsochromic shift with enhancement of emission intensity upon increasing the temperature of the solvent. A hypsochromic shift is observed because the excited electron crosses the activation barrier from ICT or TICT to LE (local excited) state.⁴⁵ Hence, LE state gets more populated and emission takes place from LE with enhancement of intensity. In case of non-polar solvents, TICT rotors emit from LE state and hence upon increasing the temperature, the emission intensity decreased due to non-radiative deactivation. To study these effects in our designed rotors, temperaturedependent emission of AIN, AINP and F-AINP were recorded in polar (CHCl₃) and non-polar (Tol) solvent from -5 °C up to the boiling point of solvent. In case of AINP in CHCl₃, upon increasing the temperature, the enhancement of fluorescence intensity as well as smaller hypsochromic shift from 510 nm to 501 nm was observed as shown in Figure 4.11. Interestingly, in case of Tol, two types of trends were observed upon increasing temperature. At lower temperature range (from -5 °C to 40 °C), the emission intensity decreased. Upon further increasing the temperature from 40 °C to 90 °C, the emission intensity increased with hypsochromic shift from 470 nm to 466 nm as shown in Figure 4.12. The ratiometric temperature analysis of AINP was performed in CHCl₃ and fitted with linear function with goodness of fit R² value of 0.87 and the calculated internal sensitivity of - 0.08% °C⁻¹ (Table 4.4). Likewise, in case of **F-AINP** in CHCl₃, upon increasing the temperature, the enhancement of intensity as well as smaller hypsochromic shift from 503 nm to 489 nm was observed as shown in Figure 4.11. In case of Tol, however, at lower temperature range (from -10 °C to 25 °C), the emission intensity decreased. Upon further increasing the temperature from 25 °C to 90 °C, the emission intensity increased with hypsochromic shift from 463 nm to 458 nm as shown in Figure 4.12. The ratiometric temperature analysis of F-AINP was performed in CHCl₃ and fitted with linear function with goodness of fit R² value of 0.87 and the calculated internal sensitivity was - 0.1% °C⁻¹. Similarly, in case of **AIN** in CHCl₃, upon increasing the temperature, the enhancement of intensity as well as smaller hypsochromic shift from 530 nm to 522 nm was observed as shown in Figure 4.11. Like in above cases in Tol, two different trends were observed upon increasing temperature. At lower temperature range (from -5 °C to 25 °C), the emission intensity remained constant. Upon further increasing of temperature range from 25 °C to 90 °C, hypsochromic shift of the 488 nm band to 476 nm was observed as shown in Figure 4.12. The ratiometric temperature analysis of **AIN** was performed in CHCl₃ and fitted with linear function with goodness of fit R^2 value of 0.98 and the calculated internal sensitivity was - 0.04% °C⁻¹. Hence, **AIN**, **AINP** and **F-AINP** showed negative temperature coefficients in CHCl₃ with internal sensitivities of -0.04% °C⁻¹, -0.08% °C⁻¹ and -0.1% °C⁻¹ (Table 4.4) respectively.



Figure 4.11. Temperature-dependent emission spectra of (a) **AIN** ($\lambda_{ex} = 394 \text{ nm}$), (c) **AINP** ($\lambda_{ex} = 393 \text{ nm}$) and (c) **F-AINP** ($\lambda_{ex} = 388 \text{ nm}$) in CHCl₃ in 10⁻⁵ M concentration. Emission intensity ratio in CHCl₃ at different temperatures with best fit equations for (b) **AIN**, (d) **AINP** and (f) **F-AINP** are shown.

Table 4.4. Fitted parameters for temperature-dependent fluorescence intensities and sensitivities for **AIN**, **AINP** and **F-AINP** in CHCl₃.

Compounds	R ²	Equation	Sensitivity
		$Y = I_1/(I_1+I_2), x = T(^{\circ}C)$	% °C⁻¹
AIN	0.98	$Y = -4.31 e^{-4} + 0.23$	- 0.04
AINP	0.87	$Y = -8.71 e^{-4} + 0.17$	- 0.08
F-AINP	0.86	$Y = -1.02 e^{-3} + 0.20$	- 0.1



Figure 4.12. Temperature-dependent emission spectra of (a) **AIN** ($\lambda_{ex} = 394 \text{ nm}$), (b) **AINP** ($\lambda_{ex} = 393 \text{ nm}$) and (c), (d) **F-AINP** ($\lambda_{ex} = 388 \text{ nm}$) in toluene in 10⁻⁵ M concentration.

4.2.7. Viscosity-dependent Emission

Viscosity-dependent emission study was performed in a mixture of MeOH and glycerol (gly). By increasing the viscosity, the molecular rotations were restricted which further increased the emission intensity due to inhibited non-radiative deactivation pathways. In **AIN**, upon increasing the percentage of gly from 0% to 90% in MeOH, the intensity of longer wavelength peak was increased by ~ 4-fold as shown in Figure 4.13. The change of colour could also be observed under UV light (365 nm) at 30% gly and 90% gly. Similarly, the emission intensity was increased by ~ 13-fold in **AINP** and ~ 2.5-fold in **F-AINP** upon increasing the percentage of gly from 0% to 90% in MeOH as shown in Figure 4.13. In case of **F-AINP**, due to hydrogen bonding between the NH- and F at 7-position of indole, the structure is more resistant to intramolecular rotations and thus, the change in emission upon changing viscosity was less compared to **AINP**. Quantitatively, the viscosity sensitivity was calculated using Förster-Hoffmann theory: ^{4,8}

$$\log (I/I_0) = C + x \log \eta \tag{4.1}$$

where, I_0 and I are the emission intensities at the initial viscosity i.e., in 100 % MeOH and intensity at different viscosities respectively. The viscosity of the medium is given by η , C is the experimental temperature and concentration dependent constant and x is the viscosity sensitivity of the molecular rotors. The calculated viscosity sensitivities of **AIN**, **AINP** and **F**-



Figure 4.13. Viscosity-dependent emission spectra in gly/MeOH mixtures and emission intensity ratio of (a), (b) **AIN** ($\lambda_{ex} = 394$ nm), (c), (d) **AINP** ($\lambda_{ex} = 393$ nm) and (c), (d) **F-AINP** ($\lambda_{ex} = 388$ nm) respectively at different viscosity of solution with best fit equations.

AINP were 0.16, 0.37 and 0.23 respectively which is higher than our earlier reported rotors p-**ADA** (0.14)⁴⁶ and pp-**ADA** (0.14).⁴⁷ Among all the rotors in this work, **AINP** was most sensitive to viscosity and showed the best viscosity sensing characteristics. Therefore, these rotors can act as viscosity probes. Furthermore, the effect of temperature at a particular viscosity was also investigated for all compounds. In all cases, with increasing temperature, the emission intensity decreased as shown in Figure 4.14. This effect can be attributed to decreased solvent viscosity at higher temperature and thus faster intramolecular rotations and non-radiative deactivation.^{46,47}



Figure 4.14. Temperature-dependent emission spectra of (a) **AIN**, (b) **AINP** and (c) **F-AINP** in glycerol/methanol 70/30 v/v (104 cP) solution.

4.2.8. Fluorescence Lifetime

The fluorescence lifetimes of **AIN**, **AINP** and **F-AINP** were calculated in CHCl₃ as well as in Tol using time correlated single photon counting (TCSPC) technique. The fluorescence lifetimes of **AIN**, **AINP** and **F-AINP** were measured upon excitation of 375 nm laser diode (Figure 4.15, Table 4.5-4.6). All the data were fitted by tri-exponential functions. The τ_{avg} values of **AIN** at emission wavelengths of 530 nm were ~ 0.20 ns and ~ 0.41 ns, in CHCl₃ and Tol respectively. In polar solvent such as CHCl₃, the ICT or TICT rotors showed larger lifetimes as compared to the lifetimes in non-polar Tol. But in present case, the lifetime in Tol was greater than the lifetime in CHCl₃. The τ_{avg} values of **AINP** at emission wavelengths of 510 nm was ~ 0.04 ns in Tol and the τ_{avg} value of **F-AINP** at emission wavelengths of 500 nm was ~ 0.11 ns in CHCl₃. The fluorescence lifetimes of **AIN**, **AINP** and **F-AINP** were also measured at different viscosities by changing glycerol amount from 0% to 90% in MeOH solution. In case of **AIN**, upon increasing viscosity, the lifetime showed a minor change from 0.49 ns to 0.37 ns while in case of **AINP** and **F-AINP**, the lifetime increased from 0.002 ns to 0.15 ns and from 0.006 ns to 0.6 ns respectively.



Figure 4.15. Fluorescence lifetime decays collected using a single photon counting technique in CHCl₃ and Tol of (a) **AIN**, (b) **AINP** and (c) **F-AINP** and in solvent of different viscosities for (d) **AIN**, (e) **AINP** and (f) **F-AINP**.

Table 4.5.	Fluorescence	lifetime analy	vses of AIN	I. AINP ar	nd F-AINP a	at different	emission	wavelength.

Compound ($\lambda_{ex} = 375$ nm)	Solvent	λ _{em} (nm)	$\tau_1(\alpha_1)$ (ns)	$\tau_2(\alpha_2)$ (ns)	$\tau_3(\alpha_3)$ (ns)	τ _{avg} (ns)	χ^2
,	CHCl ₃	530	1.47 (0.03)	6.73 (0.02)	0.038 (0.96)	0.20	1.09
AIN	Tol	485	2.37 (0.03)	7.39 (0.04)	0.053 (0.93)	0.41	1.03
	*CHCl ₃	510	-	-	-	-	-
AINP	Tol	470	1.16 (0)	6.46 (0)	0.02 (1.0)	0.04	0.86

	CHCl ₃	500	1.27 (0.01)	6.73 (0.01)	0.035 (0.98)	0.11	1.01
F-AINP	*Tol	464	-	-	-	-	-

*Lifetime not detected.

Table 4.6. Fluorescence decay parameters of **AIN**, **AINP** and **F-AINP** at variable viscosities⁴⁸, the decay times (τ_1 , τ_2 and τ_3) and the respective fractional contributions (α_1 , α_2 and α_3), the amplitude average decay time (τ_{avg}) and the quality of fitting (χ^2).

Compound $(\lambda_{ex} = 375nm)$	Viscosity (in cP) (solvent mixture)	$ au_1(lpha_1)$ (ns)	τ ₂ (α ₂) (ns)	τ ₃ (α ₃) (ns)	Average lifetime $ au_{avg}$ (ns)	χ^2
	454	0.98 (0.17)	0.15 (0.82)	8.45 (0.01)	0.37	1.17
	(90/10 v/v					
	gly/MeOH)	0.09 (0.12)	9 42 (0 01)	0.00(0.97)	0.26	1 00
A IN	218 (80/20 y/y	0.98 (0.12)	8.42 (0.01)	0.09 (0.87)	0.26	1.28
AIN	(80/20 V/V)					
	50	1.02 (0.11)	8 77 (0 01)	0.08 (0.88)	0.25	1 28
	(60/40 v/v	1.02 (0.11)	0.77 (0.01)	0.00 (0.00)	0.25	1.20
	gly/MeOH)					
	11	0.06 (0.19)	8.76 (0.01)	0.01 (0.80)	0.39	1.31
	(40/60 v/v					
	gly/MeOH)					
	3	1.01 (0.23)	7.18 (0.01)	0.01 (0.76)	0.4	1.30
	(20/80 v/v					
	gly/MeOH)					
	0.6	0.14 (0.58)	0.9 (0.41)	5.11 (0.01)	0.49	1.29
	(0/100 V/V)					
	gly/MeOH)	1 22 (0.02)	7.76(0)	0.08(0.06)	0.15	1 22
	434	1.55 (0.05)	7.70(0)	0.08 (0.90)	0.15	1.22
	(90/10 V/V glv/MeOH)					
	218	1 12 (0 01)	7 82 (0)	0.02 (0.99)	0.04	115
AINP	(80/20 v/v)	1.12 (0.01)	,	0.02 (0.99)	0.01	1.10
	gly/MeOH)					
	50	1.35 (0)	8.71 (0)	0.002(1)	0.002	1.29
	(60/40 v/v	. ,				
	gly/MeOH)					
	11	1.4 (0)	0.003 (1)	8.97 (0)	0.003	1.24
	(40/60 v/v					
	gly/MeOH)					
	3	0.003 (1)	1.26 (0)	7.66 (0)	0.003	1.23
	(20/80 v/v)					
	giy/MeOH)	0.002(1)	1.16(0)	5.1 (0)	0.002	1 01
	(0/100 y/y)	0.002(1)	1.10(0)	5.1 (0)	0.002	1.21
	(0/100 V/V) $\sigma V/MeOH$					
	(40/60 v/v gly/MeOH) 3 (20/80 v/v gly/MeOH) 0.6 (0/100 v/v gly/MeOH)	0.003 (1) 0.002 (1)	1.26 (0) 1.16 (0)	7.66 (0) 5.1 (0)	0.003	1.24 1.23 1.21

	454	0.78 (0.09)	6.63 (0.01)	0.16 (0.89)	0.3	1.22
	(90/10 v/v					
	gly/MeOH)					
	218	0.92 (0.02)	6.9 (0.01)	0.05 (0.97)	0.12	1.21
	(80/20 v/v					
F-AINP	gly/MeOH)					
	50	1.16 (0.01)	7.14 (0)	0.03 (0.99)	0.06	1.18
	(60/40 v/v					
	gly/MeOH)					
	11	1.44 (0)	7.38 (0)	0.003 (1)	0.003	1.20
	(40/60 v/v					
	gly/MeOH)					
	3	1.38 (0)	7.48 (0)	0.003 (1)	0.003	1.15
	(20/80 v/v					
	gly/MeOH)					
	0.6	1.28 (0)	7.51 (0)	0.006 (1)	0.006	1.22
	(0/100 v/v					
	gly/MeOH)					

4.2.9. Aggregate Induced Emission (AIE)

Aggregate induced emission study was performed for all three rotors in binary mixture of THF and water. In AIN, starting from pure THF, the peak at 530 nm completely disappeared while the intensity of higher energy peaks (408 nm and 433 nm) increased with the increasing percentage of water from 10% to 70% (v/v). However, upon further increasing water percentage from 70% onwards, the intensity of 530 nm peak increased with a hypsochromic shift of ~ 30 nm as shown in Figure 4.16. The enhancement of intensity can be attributed to the formation of aggregates at higher percentage of water, which restricts the intramolecular rotations and hence reduce the possibility of non-radiative deactivation. The change in colour could also be observed from blue (lower percent of water; 10% to 40%) to yellow (higher percent of water; 80% and 90%) under UV light (365 nm). Similarly, AIE study was performed for AINP and F-AINP in binary mixture of water and THF. In both cases, the intensity of peak at ~ 510 nm was decreased with the increasing water percentage in THF from 10% to 70% (v/v). However, upon further increasing water percentage from 70% onwards, the intensity of ~ 510 nm peak increased. Figure 4.16d shows change in the fluorescence intensity ratio with the increasing of water percentage from 0% to 90% (v/v) for all three molecules and compound AINP showed the most prominent AIE effect. In case of F-AINP, owing to the possibility of hydrogen bonding, the rotational freedom was somewhat restricted at all water/THF mixtures and thus the AIE effect was much less prominent.



Figure 4.16. Emission of (a) **AIN** ($\lambda_{ex} = 394 \text{ nm}$), (b) **AINP** ($\lambda_{ex} = 393 \text{ nm}$) and (c) **F-AINP** ($\lambda_{ex} = 388 \text{ nm}$) in different percentage of THF and water ($c \sim 10^{-5} \text{ M}$) and (d) the plot of I/I_0 versus f_w of **AIN**, **AINP** and **F-AINP**. $I_0 =$ Intensity at $f_w = 0$.

UV/Vis absorption spectra of **AIN**, **AINP** and **F-AINP** were also measured in THF and water (Figure 4.17). In both cases, at higher percentage of water, the absorption band was bathochromically shifted with slight tailing in the long wavelength region indicating the formation of nano-aggregates.



Figure 4.17. UV/Vis absorption of (a) AIN, (b) AINP and (c) F-AINP in different percentages of THF and water.

4.2.10. pH Sensing

Addition of TFA in the Solution of Rotors

The effect of pH variation on absorption and emission properties of **AIN** was investigated with the addition of trifluoroacetic acid (TFA) (equivalents were calculated with respect to **AIN**) in the CHCl₃ solution of **AIN**. In the absorption spectra, the absorbance of the peak at ~ 394 nm first increased and then decreased with bathochromic shift with further addition of TFA from 3275 to 98250 equivalents. At higher equivalents of TFA, a new peak at ~ 505 nm was formed as shown in Figure 4.18. In emission spectra, when the TFA equivalents were increased from



Figure 4.18. Absorption and emission of (a, b) **AIN**, (c, d) **AINP** and (e, f) **F-AINP** in CHCl₃ ($c \sim 10^{-5}$ M) upon addition of TFA respectively.

0 to 1965, the intensity of longer wavelength (~ 530 nm) emission decreased with a hypsochromic shift of 47 nm. Upon further addition of TFA from 1965 to 98250 equivalents, the intensity of the peak increased with further hypsochromic shift of 22 nm. Similarly, in the absorption spectra of **AINP**, upon addition of TFA amount, firstly the absorbance increased followed by decrease and concomitant bathochromic shift of 27 nm. In emission spectra, upon addition of TFA equivalent from 0 to 12107 equivalents, the emission intensity decreased with hypsochromic shift of 43 nm. Upon further addition of TFA amount from 12107 to 95312 equivalents, the emission intensity increased with hypsochromic shift of 17 nm as shown in Figure 4.18c, d.

Likewise, in **F-AINP** upon increasing the amount of TFA, the absorbance firstly increased and then decreased with bathochromic shift of 27 nm. In emission spectra, upon addition of TFA amount the emission intensity decreased with hypsochromic shift of 61 nm and then increased as shown in Figure 4.18e, f. In all three compounds, the emission intensity decreased with hypsochromic shift because addition of TFA resulted in the protonation at donor (Nitrogen atom) which disrupted the intramolecular charge transfer process and as the amount of TFA was further increased, the emission observed originated from local excited state.¹⁸ To substantiate this observation, DFT calculations of protonated compounds (**AIN**⁺, **AINP**⁺ and **F-AINP**⁺) showed the HOMO was not localized on aminoindole moiety in the protonated compounds which was also an indication that ICT was not feasible from aminoindole donor to imide acceptor (Figure 4.8-4.10) upon protonation.

Addition of tetrabutylammonium fluoride (TBAF) in Sample containing TFA

To check the reversibility of emission with pH reversal, TBAF was added in the solution of **AIN** containing TFA. With the addition of TBAF, the absorption peak at ~ 394 nm regained its original absorbance but the absorbance of the peak ~ 505 nm increased further as shown in Figure 4.19. While in case of emission spectra, the intensity of longer wavelength peak (530 nm) decreased with bathochromic shift of 55 nm. The same peak at 530 nm regained its original intensity with 40 equivalents of TBAF. Similarly, the reversible behaviour of **AINP** and **F**-**AINP** were investigated. Upon addition of TBAF in **AINP** and **F**-**AINP** solution containing TFA, the absorption spectra showed increase in absorbance with hypsochromic shift. While in the emission spectra of **AINP**, the intensity first decreased with bathochromic shift of 10 nm upto 8 equivalents of TBAF and then increased with bathochromic shift of 49 nm upto 83 equivalents of TBAF. Similarly, the emission spectra of **F**-**AINP**, first showed decreased



Figure 4.19. Absorption and emission of (a, b) **AIN**, (c, d) **AINP** and (e, f and g) **F-AINP** in CHCl₃ and TFA upon addition of TBAF respectively.

intensity with bathochromic shift of 5 nm upto 3.4 equivalents and then further increased with bathochromic shift of 24 nm upto 68 equivalents of TBAF. Upon further addition of TBAF up

to 179 equivalents, the emission intensity decreased with bathochromic shift of 40 nm and original peak of the compound was retained (Figure 4.19). Hence change in acidity and basicity of the medium in which these molecules are dissolved led to distinct differences in absorption and emission properties. The photophysical properties of all the compounds were found to be reversible in acid-base titration experiments.

Effect of addition of TBAF in the Solutions of Rotors

To check the effect of TBAF on the photophysical properties of **AIN**, TBAF was added in **AIN** solution of CHCl₃. Upon addition of TBAF, the colour of the solution immediately changed from yellow to pink (inset Figure 4.20a). In UV/Vis absorption spectra, the peak at ~ 394 nm completely disappeared and new peak was formed at ~ 345 nm and ~ 516 nm. In emission spectra, upon addition of TBAF, the longer wavelength peak (~ 530 nm) disappeared and



Figure 4.20. Absorption and emission of (a, b) **AIN** ($\lambda_{ex} = 394 \text{ nm}$), (c, d) **AINP** ($\lambda_{ex} = 393 \text{ nm}$) and (e, f) **F-AINP** ($\lambda_{ex} = 388 \text{ nm}$) in CHCl₃ upon addition of TBAF respectively.

emission peak appeared only at lower wavelength (~ 465 nm) region. The quenching of fluorescence further indicates that intramolecular charge transfer (ICT) might be operative here. Similarly, in absorption spectra of **AINP** and **F-AINP**, upon addition of TBAF the peaks at ~ 394 nm and ~ 388 nm completely disappeared and new peaks formed at ~ 334 nm, ~ 524 nm and ~ 334 nm, ~ 516 nm respectively as shown in Figure 4.20. While in emission spectra, upon addition of TBAF, the longer wavelength peak disappeared and emission peak appeared only at lower wavelength region.

Addition of TFA in Sample containing TBAF

To check the reversible behaviour, TFA was added in the solution of **AIN** containing TBAF. Upon addition of TFA, the longer wavelength absorption peak at 516 nm disappeared and original peak at 396 nm was retained as shown in Figure 4.21. In emission spectra, upon



Figure 4.21. Absorption and emission of (a, b) **AIN**, (c, d) **AINP** and (e, f) **F-AINP** in CHCl₃ and TBAF upon addition of TFA respectively.

increasing TFA equivalent from 0 to 2, the emission intensity first increased with bathochromic shift and then decreased with hypsochromic shift of 15 nm on adding 2 to 49 equivalents of TFA. Similar reversible behaviour was obtained for **AINP** and **F-AINP** (Figure 4.21). DFT calculations were performed to obtain insights about these photophysical behaviour. All the deprotonated compounds (**AIN**⁻, **AINP**⁻ and **F-AINP**⁻) showed that the torsion angle between $C_{1}-N_{2}-N_{3}-C_{4}$ and the $N_{3}-C_{4}$ bond length decreased indicating a double bond character and a possibility of photoinduced electron transfer (Figure 4.8-4.10, Table 4.3) in all compounds giving rise to the pronounced colorimetric variations upon TBAF additions.

Sensing of pH in THF/Water Mixture

Since **AIN**, **AINP** and **F-AINP** are insoluble in water, pH sensing was carried out in a THF/water mixture (10/90, v/v). As evident from AIE study, all rotor molecules formed aggregates at higher ratio of water in THF solution. Hence the pH-sensing showed different behaviour in THF/water mixture as compared to CHCl₃. Upon addition of HCl in aqueous buffer solutions of **AIN**, **AINP** and **F-AINP**, the absorbance decreased with a bathochromic shift of 29 nm, 47 nm and 30 nm respectively as shown in Figure 4.22-4.24. While in case of emission spectra of **AIN**, **AINP** and **F-AINP**, the intensity first increased and then decreased with the addition of HCl. Thus, these rotor molecules **AIN**, **AINP** and **F-AINP** act as colorimetric pH sensors in organic as well as semi-aqueous solutions as evident from these studies.



Figure 4.22. (a) Absorption, (b) plot of change in absorbance with the change in pH and (c) emission of **AIN** in THF/water mixture upon addition of HCl respectively.



Figure 4.23. (a) Absorption, (b) plot of change in absorbance with the change in pH and (c) emission of **AINP** in THF/water mixture upon addition of HCl respectively.



Figure 4.24. (a) Absorption, (b) plot of change in absorbance with the change in pH and (c) emission of **F-AINP** in THF/water mixture upon addition of HCl respectively.

4.2.11. Live Cell Imaging^a

In order to demonstrate the potential application of rotors **AINP** and **F-AINP** in imaging of biological systems, live-cell fluorescence imaging experiments were performed with A549 (lung cancer) and L929 (fibroblast) cell lines using fluorescence microscopy and A549 cells are more acidic than L929.¹⁰ Before performing live cell imaging, the cytotoxic effects of both rotors were monitored in A549 cell using methyl thiazolyl tetrazolium (MTT) assay. It was observed that the cells were viable till the limit of 0.005 mg/mL of the dyes. As shown in Figure 4.25, both cells showed a bright fluorescence after 10 minutes of dye incubation, but the cells without dye incubation showed no fluorescence. As evident from pH titration in THF/water mixture that the intensity increased with decrease in pH to some extent as shown in Figure 4.22-4.24. Also, a brighter fluorescence emission was observed with A549 cells (slightly more acidic) as compared to L929 cells for **AINP** and **F-AINP** when all parameters, including dye concentrations (for both **AINP** and **F-AINP**), media composition and cell-incubation conditions were uniformly maintained. We anticipated that the difference in brightness was due to the differences in intracellular pH (Figure 4.25). Since **AINP** and **F-AINP** showed AIE

^aImaging studies were performed by Dr. Sai Srinivas from Dr. Sabyasachi Rakshit's group at IISER Mohali



Figure 4.25. MTT assays were performed with A549 cells treated with **AINP** (a) and **F-AINP** (b), and the percentage of viable cells was plotted against dye concentration. Error bars represent the standard deviation measured for three independent experiments. (c) The representative bright field and fluorescence images of A549 and L929 cells treated and untreated (control) with **AINP** and **F-AINP**. Scale bar: 50 μ m.

in THF/water mixture, fluorescence recovery after photobleaching (FRAP) experiment was carried out using A549 cells to confirm that the emission in the cellular environment was due to the formation of aggregates as shown in Figure 4.26. There was no complete recovery observed in the fluorescence from the photobleached region. Furthermore, these condensates were not fusing with each other over time. The average aggregate size did not change with time, which indicates that these were aggregates and do not have liquid-like characteristics. No change in the fluorescence in the vicinity along the red line in Figure 4.26 indicates the nearby fluorescence spots are not mobile, rather they are aggregates. Collectively, these observations indicate that the intracellular fluorescence signals in cells are from the aggregates.



Figure 4.26. The rotors (AINP and F-AINP) induce aggregation in the cellular microenvironment. (a) The representative bright field and fluorescence images of A549 cells treated with F-AINP dye. The FRAP experiment is performed on the cell marked with a rectangle (red) in the fluorescence image. Scale bar: 10 μ m. (b) The average aggregate size (μ m) is plotted against time (min) for the A549 cell (marked in the rectangle (red)) treated with F-AINP. The error bars represent the standard deviation for n=15 aggregates. The average aggregate size did not change with time, which indicates that they are aggregates and do not have liquid-like characteristics. (c) The circle (red) indicates the confocal volume for the FRAP experiment. The cross-sections of fluorescence images indicate the regions of pre-bleach, bleach, and post-bleach recovery at the selected time points. The fluorescence in the vicinity along the line indicates the nearby fluorescence spots are not mobile rather, they are aggregates. (d) The fluorescence intensity profile along the red line is plotted with the recovery time points.

To map the localization of dyes within the cells, A549 cell lines were stained with membrane, lysosome, and nucleus tracker. The live cell microscopy indicated the localization of **AINP** and **F-AINP** in the cytoplasmic space of A549 cells except the nuclei (Figure 4.27).



Figure 4.27. AINP and **F-AINP** localized at the cytoplasmic region of the cells. The representative fluorescence images of A549 cells stained with membrane and lysozymes (1st column), Nucleus (2nd column), dye (3rd column), and merged (4th column). **AINP** treated cells (top panel) and **F-AINP** treated cells (bottom panel). Scale bar: 10 μ m.

4.3. Conclusions

Three rotors AIN, AINP and F-AINP based on 1-aminoindole (AI) and naphthalimide were successfully synthesized and characterized where AI act as electron donor and naphthalimide core as electron acceptor. Solvatochromic investigation revealed that the emission changes occur due to CT interactions at higher concentration. All the rotors showed AIE in binary mixture of water and THF and were sensitive towards viscosity and temperature. AINP was most sensitive towards viscosity among all rotors with viscosity sensitivity of ~ 0.37 . AIN, AINP and F-AINP showed negative temperature coefficients in chloroform with internal sensitivities of - 0.04% °C⁻¹, - 0.08% °C⁻¹ and - 0.1% °C⁻¹ respectively. All the rotors showed responsiveness towards pH change of the medium. Upon protonation (lowering of pH), the intensity of CT band decrease which indicate that CT weakened due to protonation on donor part and could be reverted upon addition of base (TBAF). Upon deprotonation (adding base), photoinduced electron transfer (PET) occurred and hence in emission the long wavelength peak quenched that could be reverted after addition acid in the same solution. Thus, these rotors act as colorimetric pH sensors as evident from these studies. Additionally, the rotors AINP and F-AINP were utilized for live cell imaging on A549 and L929 cell lines. The live cell microscopy revealed the localization of AINP and F-AINP dyes in the cytoplasmic space of A549 cell.

4.4. Experimental Section

4.4.1. Synthesis Procedures

Synthesis of 1-Aminoindole (AI)



Scheme 4.2. Synthesis of 1-Aminoindole (AI).⁴²

Procedure: Crushed potassium hydroxide (KOH) (4.99 g, 88.94 mmol) was added in the solution of indole (500 mg, 4.27 mmol) in anhydrous DMF. Hydroxylamine O-Sulfonic acid (HOSA) (1.78 g, 15.75 mmol) was added portion wise (HOSA and DMF mixture) to this suspension solution and stirred for 4 h at room temperature. The reaction mixture was poured in cold water and extraction was performed by ethyl acetate. The organic layer was dried over Na₂SO₄ and evaporated under vacuum using rotary evaporator to give a crude product, which was purified by column chromatography on silica gel using ethyl acetate/hexane (1/9 v/v) as the eluent. The pure product was obtained as a brownish liquid with a yield of 37%.

¹**H NMR (400MHz, CDCl₃):** δ (ppm) 7.60 (d, J = 8 Hz, 1 H), 7.37 (d, J = 8 Hz, 1 H), 7.23 (t, J = 8 Hz, 1 H), 7.11 (t, J = 8 Hz, 2 H), 6.37 (s, 1 H), 4.68 (s, 2 H).

Synthesis of 7-fluoroAminoindole (F-AI):



Scheme 4.3. Synthesis of 7-fluoroAminoindole (F-AI).⁴²

Procedure: Crushed potassium hydroxide (KOH) (4.32 g, 77.11 mmol) was added in the solution of indole (500 mg, 3.7 mmol) in anhydrous DMF. A solution of HOSA (1.54 g, 13.65 mmol) was added drop wise to this suspension and stirred for 4 h at room temperature. The reaction mixture was poured in cold water and extraction was performed by ethyl acetate. The

organic layer was dried over Na₂SO₄ and evaporated under vacuum using rotary evaporator to give a crude product. The crude compound was further used without purification at this step.

Synthesis of 6-Bromo-2-(2,6-diisopropylphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NP, 3):



Scheme 4.4. Synthesis of 6-Bromo-2-(2,6-diisopropylphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NP, 3)⁴³

Procedure: To a solution of 6-bromo-1,8-napthalic anhydride (1) (500 mg, 1.8 mmol) in acetic acid (10 mL) in two neck round-bottomed flask, 2,6-diisopropylaniline (1.36 mL, 7.22 mmol) was added dropwise in nitrogen atmosphere and reflux for 5 h. The reaction mixture was cooled down and added in ice cold water and then formed precipitate was filtered, washed with water and dried. Compound **3** was purified by column chromatography using hexane/ethyl acetate (80/20, v/v) as the eluent. The pure product was obtained as a white solid with a yield of 92%.

¹**H NMR (400MHz, CDCl₃):** δ (ppm) 8.73 (dd, J = 8 Hz, 1 H), 8.67 (dd, J = 8 Hz, 1 H), 8.49 (d, J = 8 Hz, 1 H), 8.10 (d, J = 8 Hz, 1 H), 7.91 (dd, J = 8 Hz, 1 H), 7.51 – 7.46 (t, J = 8 Hz, 1 H), 7.34 (s, 1 H), 7.32 (s, 1 H), 2.76 – 2.66 (m, 2 H), 1.15 (d, J = 8 Hz, 12 H).

Synthesis of 6-(1H-indole-1-y1)amino)-1H,3H-benzo[de]isochromene-1,3-dione (AIN):



Scheme 4.5. Synthesis of 6-(1H-indole-1-y1)amino)-1H,3H-benzo[de]isochromene-1,3-dione (AIN).³⁷

Procedure: 1-Aminoindole (50 mg, 0.378 mmol) and 6-bromo-1,8-napthalic anhydride (105 mg, 0.378 mmol) were dissolved in toluene and degassed by freeze pump thaw method. In a two neck round-bottomed flask, $Pd_2(dba)_3$ (2.5 mol%), XPhos (5 mol%), LiCl (32.04 mg, 0.756 mmol) and *t*-BuOK (63.62 mg, 0.567 mmol) were taken and simultaneously 1-Aminoindole and 6-bromo-1,8-napthalic anhydride were added and stirred for 4-5 h at 130 °C. The reaction

mixture was cooled and filtered through celite pad using ethyl acetate and the final compound was purified by column chromatography using ethyl acetate and hexane (20:90 of ethyl acetate/hexane). The final compound was obtained as yellow solid with 45% yield.

¹**H NMR (400 MHz, DMSO-***d*₆): δ (ppm) 11.24 (s, 1 H), 8.90 (d, J = 8 Hz, 1 H), 8.57 (d, J = 8 Hz, 1 H), 8.24 (d, J = 8 Hz, 1 H), 7.94 (m, 1 H), 7.71 (d, J = 4 Hz, 1 H), 7.63 (d, J = 8 Hz, 1 H), 7.23 (s, 1 H), 7.17 (s, 2 H), 6.72 (s, 1 H), 5.99 (d, J = 8.4 Hz, 1 H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 161.90, 160.66, 151.39, 136.17, 135.18, 133.50, 131.97, 129.98, 129.35, 126.82, 126.62, 123.08, 121.67, 121.03, 119.46, 119.30, 109.51, 108.42, 105.97, 102.01.

ESI-TOF: $(M+H)^+$ of molecular formula $C_{20}H_{12}N_2O_3$: Calculated 329.0926; found 329.0941. **Synthesis of 6-((1H-indol-1-yl)amino)-2-(2,6-diisopropylphenyl)-1Hbenzo[de]isoquinoline-1,3(2H)-dione (AINP):**



Scheme 4.6. Synthesis of 6-((1H-indol-1-yl)amino)-2-(2,6-diisopropylphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**AINP**).³⁷

Procedure: 1-Aminoindole (37 mg, 0.276 mmol) and the compound **3** (100 mg, 0.23 mmol) were dissolved in toluene and degassed by freeze pump thaw method. In a two-neck round-bottomed flask, $Pd_2(dba)_3$ (2.5 mol%), XPhos (5 mol%), LiCl (20 mg, 0.46 mmol) and *t*-BuOK (39 mg, 0.345 mmol) were taken and simultaneously 1-Aminoindole and compound **3** were added and stirred for 4-5 h at 130 °C. The reaction mixture was cooled and filtered through celite pad using ethyl acetate and the final compound was purified by column chromatography using ethyl acetate and hexane (10:90, v/v) as eluent. The final compound was obtained as yellow solid with 40% yield.

¹**H NMR (400 MHz, DMSO):** δ (ppm) 11.14 (s, 1 H), 8.92 (d, J = 8 Hz, 1 H), 8.62 (d, J = 6.4 Hz, 1 H), 8.27 (d, J = 8 Hz, 1 H), 7.94 (dd, J = 8 Hz, 8 Hz, 1 H), 7.70 (dd, J = 8 Hz, 1 H), 7.61 (d, J = 4 Hz, 1 H), 7.44 – 7.40 (m, 1 H), 7.31 – 7.26 (m, 3 H), 7.20 – 7.13 (m, 2 H), 6.71 (dd, J = 4 Hz, 1 H), 6.02 (d, J = 12 Hz, 1 H), 2.62 (m, 2 H), 1.04 (dd, J = 8 Hz, 4 Hz, 12 H).

¹³C NMR (101 MHz, DMSO): δ (ppm) 163.94, 163.15, 150.48, 145.41, 134.83, 134.23, 131.82, 131.42, 129.54, 128.99, 128.92, 126.36, 126.03, 123.60, 122.55, 121.99, 121.18, 120.50, 119.14, 111.95, 109.16, 105.45, 101.41, 28.55, 23.61.

ESI-TOF: $(M+H)^+$ of molecular formula $C_{32}H_{29}N_3O_2$: Calculated 488.2338; found 488.2355. In order to confirm the presence of N-H peak proton NMR spectra was recorded in DMSO-D₂O solvent mixtures.

¹**H NMR (400 MHz, DMSO + D₂O)** δ (ppm) 8.88 (d, *J* = 8 Hz, 1 H), 8.60 (d, *J* = 8 Hz, 1 H), 8.21 (d, *J* = 8 Hz, 1 H), 7.92 (t, *J* = 8 Hz, 1 H), 7.71 – 7.67 (m, 1 H), 7.53 (d, *J* = 4 Hz, 1 H), 7.41 (t, *J* = 8 Hz, 1 H), 7.29 – 7.20 (m, 3 H), 7.14 (m, 2 H), 6.69 (d, *J* = 4 Hz, 1 H), 5.97 (d, *J* = 8 Hz, 1 H), 2.58 (m, 2 H), 1.00 (dd, *J* = 8, 4 Hz, 12 H).

Synthesis of 2-(2,6-diisopropylphenyl)-6-((7-fluoro-1H-indol-1-yl)amino)-1Hbenzo[de]isoquinoline-1,3(2H)-dione (F-AINP):



Scheme 4.7. Synthesis of 2-(2,6-diisopropylphenyl)-6-((7-fluoro-1H-indol-1-yl)amino)-1H-benzo[de]isoquinoline-1,3(2H)-dione (F-AINP).³⁷

Procedure: The mixture of compound **F-AI** (100 mg, 0.666 mmol) and **2** (242 mg, 0.555 mmol) were dissolved in toluene and degassed by freeze pump thaw method. In a two-neck round-bottomed flask, $Pd_2(dba)_3$ (2.5 mol%), XPhos (5 mol%), LiCl (47 mg, 1.11 mmol) and *t*-BuOK (93 mg, 0.832 mmol) were taken and simultaneously F-AI and 2 were added and stirred for 4-5 h at 110 °C. The reaction mixture was cooled and filtered through celite pad using ethyl acetate and the final compound was purified by column chromatography using ethyl acetate and hexane (10:90, v/v) as eluent.

¹**H NMR (400 MHz, DMSO):** δ (ppm) 11.26 (s, 1 H), 8.85 (d, J = 8.6 Hz, 1 H), 8.62 (d, J = 7.3 Hz, 1 H), 8.29 (s, 1 H), 7.97 – 7.92 (m, 1 H), 7.66 (d, J = 3.3 Hz, 1 H), 7.52 (d, J = 7.7 Hz, 1 H), 7.43 (t, J = 7.8 Hz, 1 H), 7.31 (d, J = 7.7 Hz, 2 H), 7.10 (m, J = 7.9, 4.5 Hz, 1 H), 6.97 (dd, J = 12.5, 7.6 Hz, 1 H), 6.78 (t, J = 2.8 Hz, 1 H), 6.09 (d, J = 8.4 Hz, 1 H), 2.69 – 2.61 (m, 2 H), 1.04 (t, J = 7.6 Hz, 12 H).

¹³C NMR (400 MHz, DMSO) δ (ppm) 163.95, 163.19, 150.82, 147.58, 134.29, 131.88, 131.41, 131.14, 130.86, 130.82, 129.49, 128.96, 128.73, 126.23, 123.64, 122.04, 121.04, 119.02, 117.44, 112.12, 105.35, 102.18, 28.57, 23.65.

ESI-TOF: $(M+H)^+$ of molecular formula $C_{32}H_{28}N_3O_2F$: Calculated 506.2244; found 506.2268.

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Appendix of Chapter 4 A4.1. Copies of NMR spectra of chapter 4 ¹H NMR of AI



¹H NMR of NP


¹H NMR of AIN



¹³C NMR of AIN in DMSO



¹H NMR of AINP in DMSO



¹³C NMR of AINP in DMSO



¹H NMR of AINP in DMSO & D₂O



¹H NMR (400 MHz, DMSO) of F-AINP:



¹³C NMR (400 MHz, DMSO) of F-AINP:



Frequencies and Coordinates of DFT Optimized Geometries

Table 4.7. Results of first three frequencies and molecular symmetries calculated from geometry optimization of AIN, AINP and F-AINP.

		Compounds	Symmetry	First	Three Freque	ncies	
					23.76		
		AIN	C_1		26.11		
					33.92		
					12.84		
		AINP	C_1		15.47		
					21.10		
					13.66		
		F-AINP	C_1		16.13		
					20.84		
Coordinates of geometry optim		ometry optim	ized	С	3.61432	0.19448	1.48813
stru	cture of AIN			С	3.35346	-0.26003	0.19373
С	5.70056	1.12330	0.62647	С	4.24718	-0.05391	-0.88883
С	4.80329	0.88924	1.68736	С	5.43420	0.66020	-0.65636

Ν	2.25302	-0.94694	-0.31012	Н	1.23121	1.13002	0.25748
С	2.48403	-1.24625	-1.65558				
С	3.66770	-0.69116	-2.04443	Cool	rdinates of ge	cometry opti	mized
Ν	1.32194	-1.58227	0.50052	struc	cture of AIN ⁺	-	
С	-0.05362	-1.33671	0.35996	С	-6.45273	-0.10509	0.15388
С	-0.90406	-2.43367	0.47663	С	-5.82324	0.70160	1.11488
С	-2.29393	-2.29613	0.40519	С	-4.44864	0.94327	1.06658
С	-2.86415	-1.05302	0.19266	С	-3.73924	0.32939	0.03927
С	-2.03306	0.09088	0.08314	С	-4.34509	-0.50449	-0.92146
С	-0.60825	-0.02089	0.18637	С	-5.72870	-0.70669	-0.87357
С	-2.62320	1.36779	-0.10595	Ν	-2.36022	0.44145	-0.30680
С	-1.84056	2.50685	-0.16825	С	-2.11245	-0.47370	-1.37301
С	-0.44566	2.40507	-0.03000	С	-3.29066	-0.98519	-1.79755
С	0.15771	1.17452	0.14262	Ν	-1.44194	0.37169	0.83315
С	-4.32683	-0.93421	0.08764	С	-0.02044	0.63420	0.50572
0	-4.84322	0.33851	-0.12777	С	0.33164	1.94032	0.24467
С	-4.09176	1.49776	-0.22913	С	1.67358	2.24876	-0.04259
0	-4.67695	2.53672	-0.40973	С	2.61968	1.24143	-0.05374
0	-5.10754	-1.85029	0.17078	С	2.25957	-0.10380	0.20567
Н	6.61697	1.67284	0.81884	С	0.89729	-0.45056	0.48475
Н	5.04395	1.25724	2.68007	С	3.24975	-1.11879	0.18522
Н	2.91863	0.00435	2.29845	С	2.91100	-2.43509	0.42712
Н	6.13412	0.84088	-1.46700	С	1.56773	-2.78085	0.68855
Н	1.74536	-1.80250	-2.21457	С	0.58151	-1.81737	0.71572
Н	4.08151	-0.71911	-3.04253	С	4.04045	1.59202	-0.34664
Н	1.53874	-2.56549	0.63135	0	4.95629	0.56277	-0.34577
Н	-0.47447	-3.42342	0.60788	С	4.66790	-0.77274	-0.10032
Н	-2.94172	-3.16180	0.48960	0	5.56364	-1.56929	-0.13102
Н	-2.32650	3.46575	-0.31187	0	4.41231	2.70986	-0.57805
Н	0.16499	3.30163	-0.05505	Н	-7.52505	-0.25797	0.21301
••	0.10177	2.20102	0.00000	Н	-6.41440	1.15877	1.90095

Η	-3.98618	1.60233	1.79788
Н	-6.22520	-1.32159	-1.61692
Н	-1.11888	-0.55869	-1.78622
Н	-3.42268	-1.61082	-2.66981
Н	-0.41655	2.72761	0.25329
Н	1.98032	3.26774	-0.24892
Н	3.68890	-3.19046	0.40653
Н	1.30874	-3.81923	0.86510
Н	-0.44229	-2.13837	0.89215
Н	-1.76468	1.09351	1.48635
Н	-1.53810	-0.53142	1.32202
Coo stru	rdinates of ge cture of AIN ⁻	eometry opti	mized
С	-6.07476	0.27980	-1.31249
С	-5.00364	1.05517	-1.81091
С	-3.75556	1.03392	-1.20178
С	-3.59960	0.21905	-0.07430
С	-4.66923	-0.56457	0.45830
С	-5.91688	-0.52476	-0.19102
N	-2.48724	0.00439	0.70641
С	-2.83070	-0.85314	1.73189
С	-4.14788	-1.23683	1.60989
N	-1.31376	0.77243	0.60905
С	-0.21203	0.07476	0.35422
С	-0.10893	-1.33442	0.10167
С	1.10237	-1.93511	-0.16003
С	2.31781	-1.22067	-0.18683
С	2.28153	0.17940	0.05160
С	1.04637	0.84247	0.32041
С	3.47829	0.94251	0.02471

С	3.45574	2.31550	0.25611
С	2.24482	2.95974	0.52266
С	1.06117	2.22624	0.55539
С	3.55933	-1.89265	-0.45634
0	4.72545	-1.08203	-0.47155
С	4.75994	0.27392	-0.25095
0	5.84066	0.83188	-0.29653
0	3.73931	-3.07627	-0.67466
Н	-7.03724	0.31620	-1.81702
Η	-5.15989	1.67738	-2.68851
Η	-2.92075	1.62121	-1.56841
Н	-6.74909	-1.11630	0.18446
Н	-2.08889	-1.11640	2.47161
Н	-4.67503	-1.91578	2.26611
Н	-1.01464	-1.92862	0.09482
Н	1.14637	-3.00184	-0.36229
Н	4.39562	2.85735	0.22524
Н	2.22582	4.03015	0.70796
Н	0.11251	2.70822	0.76656

Coordinates of geometry optimized structure of AINP

С	-0.16453	-1.60072	2.07236
С	1.19722	-1.93675	1.98111
С	1.92217	-1.63860	0.84452
С	1.31676	-0.98640	-0.26289
С	-0.07924	-0.66851	-0.17472
С	-0.79618	-0.98009	1.01027
С	2.00360	-0.64369	-1.47840
С	1.29857	-0.06079	-2.52702
С	-0.06933	0.21717	-2.42724

С	-0.76018	-0.06650	-1.26319	Н	5.07459	-2.73767	-0.68640
Ν	3.35788	-0.95445	-1.72009	Н	6.93093	-1.71386	1.01154
С	-2.19892	0.26781	-1.18307	Н	7.28687	1.12714	1.95638
Ν	-2.85447	-0.04718	0.02474	Н	6.33259	3.40254	1.70610
С	-2.24212	-0.65797	1.13429	Н	4.37339	3.80374	0.25251
0	-2.88474	-0.90908	2.14302	Н	3.29676	1.93614	-0.98284
0	-2.80801	0.79462	-2.10312	Н	-8.01364	1.14102	0.40742
Ν	4.32846	-0.73703	-0.75128	Н	-7.31421	-1.14524	-0.24900
С	5.20847	-1.72734	-0.32915	С	-4.78772	-2.11423	-0.53865
С	6.13121	-1.18111	0.51727	Н	-2.89700	2.31501	1.56524
С	5.83911	0.22485	0.62069	Н	-3.00920	2.86060	-0.11324
С	4.70896	0.48267	-0.20115	Н	-4.06876	3.56179	1.11774
С	6.42434	1.29535	1.31789	Н	-5.65897	-2.73017	-0.77473
С	5.88708	2.56778	1.17360	Н	-4.13526	-2.10386	-1.41822
С	4.77007	2.79738	0.34559	Н	-4.24115	-2.60240	0.27546
С	4.16206	1.75999	-0.35298				
Η	-0.74575	-1.82366	2.96043	Coor	rdinates of ge	eometry opti	mized
Η	1.68512	-2.43664	2.81171	struc	cture of AIN	P +	
Η	2.96710	-1.91160	0.80380	С	-0.61421	2.61572	0.85120
Η	1.82718	0.19539	-3.44187	С	0.78012	2.81881	0.77604
Н	-0.60513	0.67751	-3.25011	С	1.60872	1.86043	0.22926
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Ν	4.06286	-0.28840	0.14546
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С	5.44714	-0.00146	-0.02878
С	7.55670	-0.79533	0.85728
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С	7.45283	1.08237	-0.69456
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Coordinates of geometry optimized structure of AINP⁻

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Diindolocarbazole-based Twisted Organic TADF Conjugates for Efficient Photoisomerization of Stilbene and Photo-arylation of Heteroarenes



Abstract: The design and synthesis of two organic thermally activated delayed fluorescence (TADF) conjugates **DI-PF** and **DI-PI** based on diindolocarbazole (DI) as donor and phenanthrene derivatives as an acceptor is reported in this chapter. Conjugates **DI-PF** and **DI-**PI showed strong charge transfer bands at 590 nm with 196 nm Stokes shift and 519 nm with 126 nm Stokes shift respectively. Among both molecules, **DI-PF** showed aggregate induced emission (AIE) with increase in water percentage in THF solution of compound. For effective TADF properties, theoretical and experimental studies revealed small to relatively modest ΔE_{ST} values of 0.01 eV and 0.37 eV for **DI-PF** and **DI-PI** respectively. Transient photoluminescence decay profiles of **DI-PF** and **DI-PI** indicated shorter prompt components of 40 ns and 13.38 ns respectively and longer delayed components of 6.15 µs and 2.05 µs respectively confirming the TADF nature for both compounds. The sufficiently long-lived lifetime components render them suitable to participate in organic photocatalysis. Furthermore, both compounds showed tunable and suitable excited state redox potentials for electron transfer photocatalysis. Accordingly, **DI-PF** and **DI-PI** have been employed in E to Z photoisomerization of stilbene based on their suitable triplet energy levels and in arylation of various heteroarenes with excellent yields of ~ 66% for isomerization and 86% for heteroarene photo-arylation.

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5.1. Introduction

Utilization of thermally activated delayed fluorescence (TADF) molecules as photocatalysts for catalyzing a broad variety of organic transformations has expanded rapidly in the last five years.¹⁻⁴ Upon visible light excitation, a photocatalyst (PC) consisting of transition metals or organic dyes, gets photoexcited (PC*) and enables either photoinduced energy transfer (PEnT) or single electron transfer (SET) to/from the substrates. Development of metal-free PCs have attracted tremendous attention in the field of photocatalytic reactions due to their sustainability and cost-effectiveness compared to conventional transition metal-based PCs. Therefore, organic photocatalysts have been utilized in various organic transformations based on tuning of excited state energies and redox properties of PCs.^{5,6} A well-populated triplet state with longer lifetimes is one of the major pre-requisites of an efficient photocatalyst.⁷ TADF emitters have been extensively studied as organic light emitting diodes (OLEDs) because of their smaller singlet-triplet energy gap (ΔE_{ST}) and ability to harvest both singlet and triplet excitons through reverse inter system crossing (RISC).^{8–13} Generally, TADF emitters are designed based on twisted donor-acceptor (D-A) systems with large dihedral angles which increase the spatial separation of HOMO and LUMO and reduce ΔE_{ST} of emitters. Recently, TADF emitters have been utilized in various photocatalytic reactions because of their longer lifetime component, strong visible light absorbing ability and tunable redox properties.^{14–16} In 2016, Luo and Zhang first reported the utilization of well-known TADF emitter 1,2,3,5-tetrakis(carbazol-9-yl)-4,6dicyanobenzene (4CzIPN) known from the pivotal work of Adachi and co-workers,¹⁷ as a photocatalyst for dual catalyzed cross-coupling reactions involving Nickel (II).¹⁸ The emitter 4CzIPN showed absorption in visible region ($\lambda_{max} = 435$ nm) with large excited state lifetime (1390 ns in acetonitrile) and suitable redox potentials.¹⁹ The excited state oxidation potential and reduction potential of 4CzIPN are 1.35 V and - 1.21 V which is sufficiently enough to oxidize the decarboxylated butoxycarbonyl-proline with oxidation potential of 0.95 V and enough to reduce the Nickel (I) to Nickel (0) with reduction potential of -1.10 V.¹⁸ After the initial report, a variety of TADF molecules were utilized in various organic photocatalytic reactions.^{1,2} The E to Z isomerization of stilbene (triplet state energy (E_T) of E-stilbene = 2.2 eV and E_T of Z-stilbene= 2.5 eV) was utilized as the most fundamental example of PEnT reaction to evaluate the effectiveness of TADF materials as photocatalyst.^{1,16,20–22} To maximize the E/Z isomerization of stilbene, the triplet energy (E_T) of PC should be higher than E_T of Estilbene but lower than E_T of Z-stilbene.²⁰ Bergens and co-workers reported functionalized 4CzIPN, immobilized on carbon indium-doped tin oxide electrodes for E to Z isomerization of stilbene with ~ 84% of conversion after 48 h.²¹ Zhang and co-workers reported E to Z isomerization of stilbene with 90% conversion using 4CzIPN as PCs.²⁰ Colman and co-workers reported multi-resonant TADF molecule and utilized for E to Z isomerization of stilbene and others photocatalytic reactions.²²

TADF materials have been also utilized as PC in variety of photoredox catalysis reactions where the PC can show either reductive quenching or oxidative quenching based on the excited state redox potentials of PC and substrate.^{1,16} Recently, Colman and co-workers reported TADF material 9,9'-(sulfonylbis(pyrimidine-5,2-diyl))bis(3,6-di-tert-butyl-9H-carbazole) (pDTCz-DPmS) as PC and utilized in various reactions such as reductive quenching, oxidative quenching, energy transfer and dual catalysis using Ni (II) as co-catalyst.¹⁶ Synthesis of arylated heteroarenes by photocatalytic method is most well-studied among other reactions such as C-H activation and transition metal catalyzed cross-coupling reaction.²³ This transformation has been efficiently performed by photocatalysis using Ru, Ir complexes or organic dyes such as Eosin Y. Heinrich and co-workers reported the formation of aryl radical using TiCl₃ as a photocatalyst for arylation of various unsaturated compounds.²⁴ Recently, Wang et. al. reported the arylation of indole using Pd and Ir as photocatalysts through oxidative quenching.²⁵ König and co-workers reported the arylation of heteroarenes by photocatalyzed single electron transfer process using aryl diazonium salts as aryl source and Eosin Y as the photocatalyst²⁶ and observed 80% yield in dimethyl sulfoxide (DMSO) and ~ 12% yield in acetonitrile (ACN). The reduction potential of aryl diazonium salts is -0.10 V to - 0.2 $V^{27,28}$ therefore, any diazonium salts are well-known for radical formation and are utilized as oxidative quenchers in photocatalysis. Recently, TADF compounds have been utilized in various photoredox reactions.^{1,22} However, to our best knowledge, except Eosin Y, utilization of organic twisted D-A TADF compounds as photoredox catalysts for arylation of heteroarenes are not reported in the literature.

In this work, we have designed and synthesized two twisted D-A conjugates composed of diindolocarbazole (DI) as donor and phenanthrene derivatives difluorodibenzophenazine (PF) and phenanthroimidazole (PI) as acceptors, namely, diindolocarbazole difluorodibenzophenazine (**DI-PF**) and diindolocarbazole phenanthroimidazole (**DI-PI**) respectively as shown in Figure 5.1. Diindolocarbazole (DI) is an efficient electron donor that possesses rigid, planar, conjugated structure with three indole rings fused with a central benzene ring.^{29–31} A high oscillator strength can be obtained because it provides large spatial HOMO volume to the emitter, which leads to high photoluminescence quantum yield (PLQY).

Due to the steric hindrance of adjacent hydrogens of donor and acceptor, large dihedral angles can be obtained which decrease the overlap between HOMO and LUMO that further reduces ΔE_{ST} . Accordingly, record external quantum efficiencies (~ 38%) of OLED devices have been achieved using DI as a donor.³⁰ Phenanthrene is a rigid π -conjugated acceptor with deep LUMO level and shows excellent photo- and thermal-stabilities. Recently, Wang and coworkers reported phenanthrene based orange TADF emitters with acridine and triphenylamine as donor with 17% external quantum efficiency.³² Hence, combination of DI donor and phenanthrene derivatives as acceptors are expected to exhibit molecular and electronic properties conducive to TADF such as low ΔE_{ST} and large dihedral angles between donor and acceptor. **DI-PF** and **DI-PI** showed orange and green emission with efficient PLQY. Among both conjugates, **DI-PF** showed prominent aggregate induced emission (AIE) in water/THF mixture. To our best knowledge, DI based TADF emitters have never been utilized for photocatalytic transformations. Due to their inherent favourable excited state redox potentials and properties, emitters **DI-PF** and **DI-PI** serve as efficient energy transfer mediated photocatalysts for E to Z isomerization of stilbene and electron transfer to diazonium salts resulting in arylation of a wide variety of heteroarenes.



Figure 5.1. Chemical structures of DI-PF and DI-PI synthesized and studied in this work.

5.2. Results and Discussion

5.2.1. Synthesis

The synthesis of **DI-PF** and **DI-PI** were accomplished as shown in Scheme 5.1. The donor DI was synthesized by refluxing 2-oxoindole in phosphorus oxychloride followed by protection

of two -NH groups by tert-butyl phenyl group by Buchwald-Hartwig coupling reaction^{33,34}. Two tertiary butyl chains were incorporated in the phenyl group to minimize the possibility of self-aggregation of these molecules in the solid state. Subsequently, acceptor PF was synthesized by condensation reaction between dibromophenanthrene-9,10-dione (6) and 1,2-Diamino-4,5-difluorobenzene in acetic acid and acceptor PI was synthesized by a condensation (6), reaction between dibromophenanthrene-9,10-dione benzaldehyde, 5-amino-2fluorobenzonitrile (9) and ammonium acetate in glacial acetic acid.^{35–37} Finally, the synthesis of conjugates **DI-PF** and **DI-PI** was accomplished by Buchwald-Hartwig coupling reaction between donor DI and acceptors PF and PI using tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) as catalyst, tri-tert-butylphosphine tetrafluoroborate as co-catalyst and sodium tert-butoxide as a base as shown in Scheme 5.1.29 All compounds were purified by column chromatography and characterized using ¹H NMR, ¹³C NMR and high-resolution mass spectrometry (HRMS).



Scheme 5.1. Synthesis scheme of TADF conjugates DI-PF and DI-PI.

5.2.2. UV/Vis Absorption and Emission

The UV/Vis absorption and fluorescence studies of **DI-PF** and **DI-PI** were performed in toluene (Tol) at a concentration (*c*) of ~ 10⁻⁶ M. In UV/Vis absorption of **DI-PF**, the main absorption band was observed at 279 nm ascribed to π – π ^{*} transition and a longer wavelength band at 394 nm. Similarly, in UV/Vis absorption spectra of **DI-PI**, the main absorption band was obtained at 328 nm ascribed to π – π ^{*} transition and a longer wavelength band at 393 nm. The molar extinction coefficients (ε) of **DI-PF** and **DI-PI** were 4.83 × 10⁴ M⁻¹cm⁻¹

and $8.08 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ respectively. In emission spectra of **DI-PF** in Tol, upon excitation at 394 nm, a major band was observed at 590 nm that might correspond to a charge transfer (CT) state (as elucidated further by solvatochromic study), with a high Stokes shift of 196 nm. Since there was no observed longer wavelength emission band in Tol, the emission spectra of **DI-PI** was recorded in chloroform (CHCl₃). Upon excitation at 393 nm, a minor locally excited (LE) band was observed at 438 nm and a major emission band was observed at 519 nm that might correspond to CT state with a reasonable Stokes shift of 126 nm as shown in Figure 5.2 and Table 5.1. A larger Stokes shift reduces the possibility of self-reabsorption or self-quenching of the emitters which enhance the emission properties of these molecules for their utilization in OLEDs. The CT state is more stabilized as compared to locally excited (LE) state. Consequently, the energy gap between singlet CT state and triplet state is reduced, enhancing the possibility of reverse intersystem crossing in TADF materials.



Figure 5.2. UV/Vis absorption and emission spectra of **DI-PF** in Tol and **DI-PI** in CHCl₃ ($c \sim 10^{-6}$ M) upon excitation at ~ 394 nm.

Table 5.1. Absorption wavelength (λ_{abs}), emission wavelength (λ_{em}), Stokes shift and molar extinction coefficient (ε) of **DI-PF** and **DI-PI**.

Compounds	λ_{abs}	λ_{em}	Stokes	$\varepsilon (M^{-1} \text{ cm}^{-1})$	
	(nm)	(nm)	(nm)		
DI-PF	279, 373,	448,	196	$4.83 imes 10^4$	
	394	590			
DI-PI	328, 363,	440,	126	$8.08 imes10^4$	
	393	519			

Furthermore, the fluorescence spectra of **DI-PF** and **DI-PI** were also recorded after degassing the solution by N_2 gas and a significant enhancement of fluorescence intensity was observed as shown in Figure 5.3. The oxygen of solution was replaced by N_2 purging, which reduce the possibility of quenching of the triplet states. Hence, the sensitivity of emission intensity

towards nitrogen purging can be attributed to the likely involvement of TADF process in these conjugates.



Figure 5.3. Emission spectra of (a) **DI-PF** and (d) **DI-PI** in aerated solution and nitrogen degassed solution of Tol and CHCl₃ upon excitation at ~ 394 nm respectively.

5.2.3. Density Functional Theory (DFT) Calculations

To understand the electronic properties of **DI-PF** and **DI-PI**, DFT calculations were performed for optimized structures and time dependent DFT (TD-DFT) for energy calculations using the Gaussian 09 package at the B3LYP/6-31G(d,p) level. Due to large steric interactions between donor and acceptor, **DI-PF** and **DI-PI** showed large twist angles of 65.7° and 66.3° respectively (Table 5.2). Therefore, in case of **DI-PF**, HOMO was completely localized on the donor part and LUMO was completely localized on the acceptor as shown in Figure 5.4. In case of **DI-PI**,



Figure 5.4. Geometry optimization and FMO energy levels of DI-PF and DI-PI calculated using B3LYP/6-31G(d, p).

HOMO was completely localized on donor and LUMO was localized on phenyl ring of acceptor and LUMO+1 completely localized on the acceptor. Such spatial separation of HOMO and LUMO levels are indicative of a small ΔE_{ST} and good CT character resulting in efficient TADF properties. TD-DFT calculations were performed for **DI-PF** and **DI-PI** in CHCl₃ solvent to calculate the singlet-triplet energy levels and their energy values are provided in Table 5.2.

Table 5.2. FMO energy levels dihedral angle and singlet energy (S_1) and triplet energy (T_1) singlet- of compounds **DI-PF** and **DI-PI** calculated by B3LYP/6-31G(d,p).

Compound	HOMO-1 (eV)	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)	Dihedral angel (°)	S 1 (eV)	T ₁ (eV)
DI-PF	- 4.81	- 4.80	- 2.48	- 1.43	65.7	2.07	2.02
DI-PI	- 4.75	- 4.74	- 2.02	- 1.40	66.3	2.60	2.59

To obtain the singlet and triplet energies of **DI-PF** and **DI-PI** experimentally, fluorescence and phosphorescence measurements were performed at 77 K in deaerated Tol and CHCl₃ respectively as shown in Figure 5.5. The singlet and triplet energies were calculated by the onset of their fluorescence and phosphorescence spectra and their differences were calculated to obtain ΔE_{ST} . The calculated singlet energies were 2.39 eV and 3.14 eV and the calculated triplet energies were 2.38 eV and 2.77 eV for **DI-PF** and **DI-PI** respectively. Hence, the observed ΔE_{ST} values were 0.01 eV and 0.37 eV for **DI-PF** and **DI-PI** respectively which is sufficient to exhibit RISC and TADF features.



Figure 5.5. Low temperature (77 K) fluorescence and phosphorescence of (a) **DI-PF** in Tol and (b) **DI-PI** in CHCl₃ ($c \sim 10^{-6}$ M) upon excitation at ~ 394 nm at 77 K.

5.2.4. Solvatochromism

Solvatochromic study was performed for **DI-PF** and **DI-PI** in solvents of different polarities and in binary mixture of methylcyclohexane (MCH) and CHCl₃ as shown in Figure 5.6. In case of **DI-PF**, in polar solvents such as CHCl₃, dichloromethane (DCM) and tetrahydrofuran (THF), the long wavelength peak was not observed due to rapid non-radiative deactivation. While in non-polar solvents such as Tol and MCH, the emission was observed at 593 nm and 528 nm respectively. In case of **DI-PI**, in non-polar solvents (Tol and MCH), only an emission peak was observed at 440 nm, the long wavelength peak was not observed while in polar solvents DCM and THF, along with peak around 440 nm, a shoulder was observed around 510 nm. In CHCl₃, the emission peak was obtained at 519 nm. In case of both conjugates **DI-PF** and **DI-PI** in binary mixture of MCH and CHCl₃, hypsochromic shift of 110 nm and 58 nm was obtained with the increasing percentage of MCH from 0% to 90% respectively. Hence, positive solvatochromism was observed for both compounds which indicates the long wavelength peak is ascribed to CT transition.



Figure 5.6. Normalized fluorescence emission spectra of **DI-PF** (a) in solvents of different polarities and (b) in different MCH/CHCl₃ (v/v) solvent mixtures; and of **DI-PI** (c) in solvents of different polarity and (d) in different MCH/CHCl₃ (v/v) solvent mixtures upon excitation at ~ 394 nm.

5.2.5. Aggregate Induced Emission (AIE)

Aggregate induced emission (AIE) study of **DI-PF** and **DI-PI** was performed in binary mixture of THF and water. In UV/Vis absorption spectra of **DI-PF**, no change was observed upto 50% of water (v/v) in THF solution. On increasing water percentage from 60% to higher, bathochromic shift was observed in absorption that indicate aggregate formation in high percentage of water as shown in Figure 5.7. In emission spectra, the long wavelength peak was not observed up to 40% of water. However, upon further increasing of water percentage from 50% to 60%, the emission intensity increased by 12 folds. The enhancement of the emission intensity can be attributed to the formation of aggregates at a higher percentage of water, which restricts the intramolecular rotations and hence reduces the possibility of non-radiative deactivation. With further increase of water percent from 60% to higher, the emission intensity decreased. Figure 5.7c shows the changes in the fluorescence intensity ratios with the increasing water percentage from 0% to 90% (v/v). Hence enhancement in emission intensity of **DI-PF** with increasing percentage of water showed AIE property. Conjugate **DI-PI** did not show any enhancement in intensity with the increase in water percentage. This observation might be attributed to the restriction of intramolecular rotations of donor part due to cyano and fluoro- substituted phenyl ring (i.e., steric hindrance or possibility of intramolecular H-bonding between H atom of DI and F or CN of phenyl ring). Therefore, the rotational freedom of donor part is somewhat restricted in THF/water mixture and hence, AIE effect was not observed in DI-PI.



Figure 5.7. (a) UV/Vis absorption and (b) emission of **DI-PF** in different percentages of THF and water, (c) changes in emission intensities of **DI-PF** in different fraction of water (f_w); inset in (c) Image of **DI-PF** in 0% and 60% of water under UV lamp.

5.2.6. Validation of TADF Behavior of DI-PF and DI-PI by Transient Photoluminescence Decay and Fluorescence Quantum Yields

To confirm the TADF behaviour of both conjugates **DI-PF** and **DI-PI**, time-resolved photoluminescence (TRPL) measurements were performed in 0.5 wt% doped thin film of emitters with ZEONEX at room temperature as shown in Figure 5.8. In case of **DI-PF**, two components were observed, shorter prompt component with a lifetime of 40 ns and a longer delayed component with a lifetime of 6.15 μ s. Likewise, in case of **DI-PI**, the lifetime of two components were 13.5 ns and 2.05 μ s. The long-delayed component of **DI-PF** and **DI-PI** with 6.15 μ s and 2.05 μ s respectively, indicates TADF behaviour which could be utilized in photocatalysis.



Figure 5.8. Fluorescence lifetime decays of **DI-PF** and **DI-PI** in 0.5 wt% of ZEONEX:TADF conjugate films.

Additionally, the fluorescence quantum yields for **DI-PF** and **DI-PI** were determined by relative method using Rhodamine B as reference dye in aerated solution and N₂ degassed solution and the values are provided in Table 5.3-5.4. The fluorescence quantum yields of **DI-PF** and **DI-PI** in aerated solutions were 2.5% and 4% and in N₂ degassed solution were 5.2% and 6% respectively. The increase in fluorescence quantum yields in N₂ degassed solution further indicates the occurrence of TADF processes in both compounds.³⁸

Compound	Absorbance		Integrated	$\begin{array}{c} Quantum \\ Yield \\ \Phi = \Phi_R(I/I_R)(A_R \\ /A)(\lambda_{exR}/\lambda_{ex})(n^2 / n^2_R) \end{array}$				
	1	2	3	1	2	3	Φ_{i}	Φ_{avg}
DI-PF	0.066	0.074	0.097	12.74	13.26	15.63	2.5	
							2.6	2.5
							2.4	
DI-PI	0.071	0.092	0.112	22.93	25.18	28.67	4.2	
							4.0	4.0
							3.8	
Rhodamine B (EtOH)	0.033	0.065	0.105	234.7	418.24	655.36	5	60

Table 5.3. Relative quantum yields of **DI-PF** and **DI-PI** using relative method and Rhodamine B as a reference dye in aerated solution.

Table 5.4. Relative quantum yields of **DI-PF** and **DI-PI** using relative method and Rhodamine B as a reference dye in N_2 degassed solution.

Compound	Absorbance		Integrated	$\begin{array}{c} Quantum \\ Yield \\ \Phi=\!\Phi_R(I/I_R)(A_R \\ /A)(\lambda_{exR}/\lambda_{ex})(n^2 / \\ n^2_R) \ (\%) \end{array}$				
	1	2	3	1	2	3	Φ_{i}	Φ_{avg}
DI-PF	0.066	0.074	0.097	18.814	32.817	35.985	3.7	
							6.4	5.2
							5.6	
DI-PI	0.071	0.092	0.112	30.537	37.99	46.408	5.6	
							6.0	6.0
							6.3	
Rhodamine B (EtOH)	0.033	0.065	0.105	234.7	418.24	655.36	5	50

5.2.7. Cyclic Voltammetry

The redox properties and HOMO and LUMO energy levels of **DI-PF** and **DI-PI** were measured using cyclic voltammetry (CV) in dry dichloromethane (DCM) with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte and Ag/AgCl as reference electrode as shown in Figure 5.9. Based on the first oxidation potential onset (E_{onset}^{ox}) and first reduction potential onset (E_{onset}^{red}), the HOMO and LUMO levels were calculated as shown in Table 5.5. Accordingly, the calculated HOMO energies for **DI-PF** and **DI-PI** were -5.49 eV and -5.48 eV respectively and LUMO energies were -3.98 eV and -4.03 eV respectively. Furthermore, to check their potential applications in photocatalysis, the excited state oxidation potential (E_{ox}^*) and reduction potential (E_{red}^*) were calculated using the following equations 5.1 and 5.2:¹

$$E_{ox}^{*} = E_{ox} - E_{0,0}, \qquad (5.1)$$
$$E_{red}^{*} = E_{red} + E_{0,0} \qquad (5.2)$$

where, E_{ox} and E_{red} is the half oxidation potential and half reduction potential respectively and $E_{0,0}$ is the energy of the S₀ to S₁ excited state and calculated by taking the interaction point of normalized absorption and normalized emission spectra. Accordingly, the calculated excited state potentials are provided in Table 5.5.



Figure 5.9. Cyclic voltammogram of (a) **DI-PF** and (b) **DI-PI** in dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHPF) and potentials measured vs Ag/AgCl reference electrode.

Compound	<i>Е^{ох}</i> (V)	E ^{red} (V)	*HOMO (eV)	*LUMO (eV)	<i>E</i> _{0,0} (eV)	<i>E</i> [*] _{ox} (eV)	E [*] _{red} (eV)
DI-PF	0.93	-1.11	- 5.49	- 3.98	2.37	-1.44	1.26
DI-PI	0.89	-0.99	- 5.48	- 4.03	3.03	-1.48	1.47

Table 5.5. Ground and excited state redox properties and energy levels of **DI-PF** and **DI-PI** based on cyclic voltammetry.

*HOMO = $-(E_{onset}^{ox} + 4.76) \text{ eV}$, and LUMO = $-(E_{onset}^{red} + 4.76) \text{ eV}$.

5.2.8. Photocatalysis

Due to the longer lifetime of triplet states and wider excited state redox potentials of TADF materials, they have been well studied as photocatalysts in various photochemical reactions in recent years.¹ Among many TADF materials, 4CzIPN was extensively utilized in photocatalytic reactions based on photoinduced energy transfer (PEnT) and photoinduced electron transfer (PET) because of microsecond emission lifetimes and redox properties similar or better than conventional transition metal-based photocatalysts.^{1,2} Based on the suitable triplet energies and redox potentials of **DI-PF** and **DI-PI**, these emitters have been utilized as photocatalysts both in PEnT and PET mechanisms.

a) Energy transfer photocatalysis: E to Z isomerization of stilbene

To maximize the E/Z isomerization of stilbene and to prevent the reverse isomerization of Zsyilbne to E-stilbene, the triplet energies of PCs should be intermittent to those of the two configurational isomers E-stilbene and Z-stilbene.²⁰ Based on the E_T of **DI-PF** (2.38 eV) and **DI-PI** (2.77 eV) (Table 5.5), photocatalysis reactions were performed in acetonitrile (ACN) at room temperature under blue LED light irradiation (Scheme 5.2). In case of **DI-PF** as PC, only 21% of E-stilbene was converted into Z-stilbene after 3 h and after 24 h, 66% of E-stilbene was converted into Z-stilbene as shown in Figure 5.10 a and Table 5.6. In case of **DI-PI**, only 16% conversion of E-stilbene to Z-stilbene was achieved even after 24 h and this low conversion is attributed to the much higher E_T of **DI-PI** compared to E-stilbene (2.5 eV).



Scheme 5.2. Synthesis scheme of isomerization of stilbene using DI-PF and DI-PI as photocatalysts.

Photocatalyst		Convers	, , , , , , , , , , , , , , , , , , ,	
-	3 h	6 h	12 h	24 h
DI-PF	21	36	44	66
DI-PI	1.2	3	6	16

Conversion (%)^a

Table 5.6. Conversion of E-stilbene to Z-stilbene using DI-PF and DI-PI as photocatalysts.

^aConversion % was calculated by ¹H-NMR.

Furthermore, control experiments without PC and light showed no conversion, indicating that both PC and light were essential for the conversion. On the basis of control experiments and well documented literature reports on mechanism,^{1,39} the plausible mechanism is shown in Figure 5.10 b. Upon photoexcitation, PC is photoexcited and the triplet state is populated through inter-system crossing (ISC) followed by energy transfer to the substrate (E-stilbene) through Dexter mechanism. The formation of a triplet biradical intermediate led to the subsequent generation of Z-stilbene via ISC.^{1,39}



Figure 5.10. (a) Conversion of E-stilbene to Z-stilbene using **DI-PF** and **DI-PI** as photocatalysts at room temperature in ACN under blue light irradiation and (b) Plausible mechanistic pathway of photocatalytic isomerization of stilbene.

b) Photoredox catalysis: Synthesis of Arylated heteroarenes

We have utilized TADF conjugates **DI-PF** and **DI-PI** as photocatalysts for C-H arylation of heteroarenes with aryl diazonium salts. Since the E_{ox}^* of **DI-PF** and **DI-PI** are more negative (Table 5.5) than E_{red} of diazonium salts, both compounds are well suited for facilitating PET to diazonium salts. First, the reaction conditions were optimized with bromo-substituted diazonium salt (1a) and thiophene in presence of **DI-PF** (1 mol%) as photoredox catalyst in acetonitrile (ACN) at room temperature with blue LED light irradiation as shown in Scheme

5.3. A maximum of 52% isolated product yield was obtained after 2 h of irradiation in argon atmosphere as shown in Table 5.7. After optimizing the photocatalyst, we have also screened two other diazonium salts 1b and 1c, in dry ACN and 1 mol % of DI-PF as photocatalyst for 2 h at room temperature (Table 3, entries 2, 3). Among both diazonium salts, 1c was found to be most efficient for product formation and delivered highest yield of 86%. Additionally, the C-H arylation of thiophene using **DI-PI** as PC and **1b** diazonium salt in ACN, produced moderate yield of 42% as shown in Table 3 (entry 4). Additionally, the photo-arylation was carried out for various heteroarenes such as furan, thienothiophene and 1-methylindole (Table 3, entries 5-8). The C-H arylation of furan using diazonium salt 1a in ACN and DI-PF as photocatalyst produced moderate yield 48% (entry 5). The C-H arylation of thienothiophene using 1a delivered mono-substituted arylation of thienothiophene with 56% yield (entry 6) which is difficult to synthesis and could be utilized in organic photovoltaics. The similar reaction was also performed with 1b diazonium salt and produced 60% yield (entry 7). In case of arylation of 1-methyl indole (entry 8), a mixture of regioisomers 2- and 3-substituted arylated indole was observed with 63% overall yield. Moreover, the PC DI-PF was recycled efficiently up to four times as shown in Figure 5.11.



Scheme 5.3. Synthesis scheme of photo-arylation of various heteroarenes under blue LED using **DI**-**PF** and **DI-PI** as photocatalyst in ACN.

Entry	Conditions (PC, 1 mol %)	Diazonium Salt	Heteroarenes	Product	Yield* (%)
1	DI-PF	1 a	S I	Br	52
2	DI-PF	1b	S	F ₃ C F ₃ C	72
3	DI-PF	1c	S	F F	86
4	DI-PI	1b	S	F ₃ C F ₃ C	42
5	DI-PF	1a	\langle	Br - C	48
6	DI-PF	1a	S↓ S	Br	56
7	DI-PF	1b	S S	F ₃ C F ₃ C	60
8	DI-PF	1a			63
9	DI-PF (without light, 24 h),	1a	S	No product	
10	Blue light (without PC, 24 h)	1 a	S	Br	(10)
11	DI-PF (TEMPO),	1 a	s l		

Table 5.7. Optimization of reaction conditions using various photocatalysts (PC) and diazonium salts.

*Isolated yields after purification by column chromatography using *n*-hexane.



Figure 5.11. Isolated yields obtained during recycling of **DI-PF** in four successive photocatalytic cycles.

Control experiments such as without light, without PC or with radical scavenger such as 2,2,6,6-tetramethylpiperidinoxyl (TEMPO) were performed for the confirmation of mechanistic pathway of the reaction. Control experiment results demonstrated that PC and light are both essential for efficient conversion (Table 5.7, entries 9, 10). To confirm the arylation of heteroarenes through radical mechanism, the reaction of diazonium salt 1a was conducted in presence of TEMPO (Table 5.7). Accordingly, TEMPO adducts (D and E) were detected (Scheme 5.4) after 2 h of irradiation of the reaction mixture with blue light that was confirmed by mass spectrometry. On the basis of control experiments and literature reports, ^{28,40} a plausible mechanism was proposed as shown in Scheme 5.4. After photoexcitation of the PC, the photocatalysis cycle is initiated by single electron transfer (SET) from excited PC to aryl diazonium salt to give aryl radical (A). The aryl radical further reacts with double bond of heteroarene and can form intermediate B which can further oxidize to form carbocation intermediate C by two possible pathways: (a) either by transferring an electron to oxidize photocatalyst with closing the catalytic cycle, or (b) by transferring an electron to other diazonium salt molecule to initiate radical chain transfer mechanism. Finally, the carbocation intermediate is deprotonated and produces the desired aryl substituted heteroarene. Compared to literature reports, synthesized TADF conjugates DI-PF and DI-PI could catalyze C-H arylation of heteroarenes with up to 86% yield of arylated products in ACN, a solvent with lower boiling point that is easier to handle compared to literature method of Eosin Y based on DMSO. Hence both TADF conjugates **DI-PF** and **DI-PI** serve as efficient photocatalysts suitable for energy transfer and electron transfer mediated photocatalytic reactions.



Scheme 5.4. Mechanistic pathway of photocatalytic C-H arylation of heteroarenes.

5.3. Conclusions

In conclusion, we have successfully designed and synthesized two twisted D-A TADF conjugates **DI-PF** and **DI-PI** where DI serves as donor and PF and PI as acceptors. In emission spectra of **DI-PF**, a CT band was observed at 590 nm with Stokes shift of 196 nm while in case of **DI-PI**, the CT band was observed at 519 nm with Stokes shift of 126 nm. Compounds **DI-PF** and **DI-PI** showed experimental ΔE_{ST} values of 0.01 eV and 0.37 eV. Time-resolved photoluminescence measurements in thin films of these conjugates showed delayed components with longer lifetimes of 6.15 µs and 2.05 µs indicate TADF properties which were utilized for effective energy transfer and electron transfer mediated organic transformations such as isomerization of E to Z stilbene with maximum of 66% conversion and photo-arylation of various heteroarenes with isolated yield of up to 86%. Further applications of these compounds in other types of photocatalytic reactions to expand their scope in photocatalysis and for OLED device fabrication will be pursued in future.

5.4. Experimental Section

Synthesis of 10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (2):



Scheme 5.5. Synthesis of 2.³³

Procedure: A solution of 2-indolinone (2 g, 15 mmol) in POCl₃ (10 mL) was heated at 100 °C for overnight. Then, the reaction mixture was poured into ice and neutralized carefully with KOH. After neutralization, the precipitate was filtered and dried. The compound was separated by column chromatography using ethyl acetate and hexane (20/80, v/v) as eluent. Further, the compound was purified by recrystallization in acetone and hexane mixture to obtain pale-yellow solid with 60% yield.

¹**H NMR (400 MHz, DMSO):** δ (ppm) 11.88 (s, 3 H), 8.67 (d, *J* = 8 Hz, 3 H), 7.72 (d, *J* = 8 Hz, 3 H), 7.41-7.31 (m, 6 H).

5,10-Bis(4-(tert-butyl)phenyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (4):



Scheme 5.6. Synthesis of DI (4).³⁴

Procedure: Diindolocarbazole (2) (200 mg, 0.579 mmol) and 4-tert-butyliodobenzene (316 mg, 1.216 mmol) were dissolved in 1,4-dioxane and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, $Pd(OAc)_2$ (5.2 mg, 0.023 mmol), tri-tert-butylphosphine tetrafluoroborate (25 mg, 0.087 mmol) and sodium tert-butoxide (260 mg, 2.316 mmol) were taken and simultaneously **2** and compound **3** were added and heated at 100 °C for 18 h. The

reaction was cooled and diluted with DCM and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using ethyl acetate and hexane (5/95, v/v) as eluent to obtain an off-white solid with 20% yield.

¹H NMR (400 MHz, DMSO): δ 11.95 (s, 1 H), 8.83 (d, J = 8.0 Hz, 1 H), 7.74 (dd, J = 4 Hz, 4 Hz, 4 H), 7.65 (t, J = 8 Hz, 3 H), 7.58 (d, J = 8 Hz, 2 H), 7.49 – 7.37 (m, 3 H), 7.22 – 7.11 (m, 3 H), 6.66 – 6.56 (m, 2 H), 5.76 (d, J = 8 Hz, 1 H), 5.54 (d, J = 8 Hz, 1 H), 1.48 (s, 18 H). Synthesis of 2,7-dibromophenanthrene-9,10-dione (6):



Scheme 5.7. Synthesis of 6.35

Procedure: To a solution of phenanthrene-9,10-dione (500 mg, 2.4 mmol) in H_2SO_4 (10 mL), N-bromosuccinimide (NBS) (1 g, 6 mmol) was added while stirring. The reaction mixture was stirred for 3 h at room temperature and then the reaction mixture was poured onto ice. The orange precipitate was filtered out and recrystallized in dimethyl sulfoxide (DMSO) to obtain pure compound as an orange solid with 70% yield.

¹**H** NMR (400 MHz, DMSO): δ (ppm) 8.25 (d, J = 8 Hz, 2 H), 8.08 (d, J = 4 Hz, 2 H), 7.96 (dd, J = 8.4 Hz, 2 H).

2,7-dibromo-11,12-difluorodibenzo[a,c]phenazine (PF):



Scheme 5.8. Synthesis of PF (7).³⁶

Procedure: To a solution of dibromophenanthrene-9,10-dione (**6**), (100 mg, 0.273 mmol) in acetic acid, 1,2-Diamino-4,5-difluorobenzene (47mg, 0.327 mmol) was added while stirring and the mixture was refluxed for 8 h. The reaction mixture was cooled and then poured in ice and then filtered followed by washing with water and methanol that afforded greenish solid with 75% yield.

¹**H NMR (400 MHz, CDCl₃)** δ 9.47 (d, J = 2.3 Hz, 2 H), 8.38 (d, J = 8 Hz, 2 H), 8.07 (t, J = 8 Hz, 2 H), 7.91 (dd, J = 4 Hz, 2 H).

Synthesis of PI:



Scheme 5.9. Synthesis of PI (10).³⁷

Procedure: Compound **8** (100 mg, 0.53 mmol) was dissolved in 10 mL NMP and then copper (I) cyanide (71 mg, 0.8 mmol) was added and heated at 150 °C for 3 h. The reaction mixture cooled to room temperature and then water, ammonium hydroxide was added to reaction mixture and stirred for 30 minutes. Then the mixture was extracted three times by ethyl acetate and dried in rotary evaporator. The pure compound was obtained by column chromatography using ethyl acetate and hexane (2/98, v/v) as eluent.

A mixture of compound **6** (100 mg, 0.27 mmol), compound **9** (44 mg, 0.32 mmol), benzaldehyde (29 mg, 0.27 mmol) and ammonium acetate (104 mg, 1.35 mmol) in 8 mL glacial acetic acid was refluxed for 14 h. After completion of reaction, the reaction mixture was cooled to room temperature and then added to ice water. The pale-yellow precipitate was formed and

collected by filtration followed by washing with water and methanol to obtain off-white solid with 60% yield.

¹**H NMR (400 MHz, DMSO)** δ (ppm) 8.86 (d, J = 8.0 Hz, 1 H), 8.80 (d, J = 8 Hz, 1 H), 8.74 (d, J = 4 Hz, 1 H), 8.60 (dd, J = 4 Hz, 4 Hz, 1 H), 8.32 – 8.26 (m, 1 H), 7.95 (t, J = 8 Hz, 1 H), 7.82 (dd, J = 8 Hz, 1 H), 7.74 (dd, J = 8 Hz, 1 H), 7.60 – 7.55 (m, 2 H), 7.43 (d, J = 8 Hz, 3 H), 7.02 (d, J = 4 Hz, 1 H).

Synthesis of DI-PF:



Scheme 5.10. Synthesis of DI-PF.²⁹

Procedure: Compounds **4** (50 mg, 0.105 mmol) and **7** (160 mg, 0.262 mmol) were dissolved in Tol and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, $Pd_2(dba)_3$ (5 mg, 0.0053 mmol), tri-tert-butylphosphine tetrafluoroborate (5 mg, 0.016 mmol) and sodium tert-butoxide (50 mg, 0.525 mmol) were taken and simultaneously compound **4** and compound **7** were added and heated at 110 °C for 12 h. The reaction was cooled and diluted with DCM and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using chloroform and hexane (10/90, v/v) as eluent to obtain an orange solid with 55% yield.

¹**H** NMR (400 MHz, CDCl₃) δ (ppm) 9.79 (d, J = 2.3 Hz, 2 H), 9.44 (dd, J = 7.9 Hz, 2 H), 8.75 (d, J = 8.8 Hz, 2 H), 8.63 (d, J = 7.3 Hz, 2 H), 8.07 (dd, J = 10.5 Hz, 2 H), 7.94 (ddd, J = 8.3 Hz, 4 H), 7.91 – 7.82 (m, 4 H), 7.67 (s, 6 H), 7.52 (d, J = 7.9 Hz, 2 H), 7.39 (d, J = 7.8 Hz, 2 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.19 (q, J = 7.7 Hz, 4 H), 7.01 (t, J = 7.6 Hz, 2 H), 6.78 – 6.71 (m, 4 H), 6.49 (t, J = 7.0 Hz, 2 H), 6.32 (d, J = 8.1 Hz, 2 H), 5.94 (dd, J = 11.4 Hz, 4 H), 1.51 (s, 18 H), 1.50 (s, 18 H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 151.97, 138.24, 138.18, 138.12, 134.79, 131.85, 128.93, 127.04, 127.02, 126.99, 126.96, 126.93, 123.13, 123.09, 122.98, 122.95, 122.89, 122.85,
122.23, 120.14, 120.06, 119.78, 119.64, 110.98, 110.11, 110.00, 109.90, 42.01, 35.14, 31.73, 31.66, 28.59, 26.90, 22.73, 14.22.

ESI-TOF: $(M+H)^+$ of molecular formula $C_{108}H_{84}F_2N_8$: Calculated 1531.6878; found 1531.6588.

Synthesis of DI-PI:



Scheme 5.11. Synthesis of DI-PI.²⁹

Procedure: Compounds **4** (122 mg, 0.2 mmol) and **10** (50 mg, 0.087 mmol) were dissolved in Tol and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, $Pd_2(dba)_3$ (4 mg, 0.004 mmol), tri-tert-butylphosphine tetrafluoroborate (4 mg, 0.013 mmol) and sodium tert-butoxide (42 mg, 0.435 mmol) were taken and simultaneously compound **4** and compound **10** were added and heated at 110 °C for 12 h. The reaction was cooled and diluted with DCM and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using chloroform and hexane (10/90, v/v) as eluent to obtain off-white solid with 70% yield.

¹**H NMR (400 MHz, DMSO)** δ (ppm) 11.94 (s, 2 H), 8.83 (d, J = 4 Hz, 2 H), 7.74 (dd, J = 4 Hz, 11 H), 7.71 – 7.60 (m, 9 H), 7.58 (d, J = 8 Hz, 5 H), 7.49 – 7.37 (m, 8 H), 7.22 – 7.11 (m, 8 H), 6.66 – 6.56 (m, 5 H), 5.76 (d, J = 8.1 Hz, 2 H), 5.55 (d, J = 8.1 Hz, 2 H), 1.47 (s, 36 H).

¹³C NMR (101 MHz, DMSO) δ (ppm) 151.69, 151.55, 140.80, 139.30, 137.53, 137.27, 136.05, 134.68, 128.71, 128.32, 126.95, 123.62, 122.90, 122.34, 121.62, 121.34, 120.61, 120.16, 119.41, 110.81, 110.15, 109.50, 102.69, 102.04, 34.76, 31.30.

ESI-TOF: $(M-C_{13}H_8FN-2H)^-$ of molecular formula $C_{103}H_{82}N_8$: Calculated 1428.6486; found 1428.6592.

Synthesis aryl diazonium tetrafluoroborates

General procedure for the preparation of aryl diazonium tetrafluoroborates²⁶

To the solution of appropriate aniline (5 mmol) in 2 mL distilled water 50% hydrofluoroboric acid (1.5 mL) was added and then after cooling the reaction mixture at 0° C, sodium nitrite (0.35 g in 1 mL water) solution was added dropwise in 5 min. interval of time. The reaction mixture was stirred for 30-40 minutes at same temperature and then the formed precipitate was collected by filtration. The precipitate was re-dissolved in minimum amount of acetone and then diethyl ether was added to the solution until the formation of precipitation of diazonium salt. The formed precipitate was washed several times by diethyl ether and dried under vacuum.

Synthesis scheme of 1a:

Synthesis scheme of 1b:



¹**H NMR (400 MHz, CDCl₃):** δ (ppm) 8.58 (d, J = 9.0 Hz, 2 H), 8.26 (d, J = 9.0 Hz, 2 H).



¹**H NMR (400 MHz, DMSO-***d*₆) δ (ppm) 9.51 (s, 2 H), 9.18 (s, 1 H).

Synthesis scheme of 1c:



¹**H NMR (400 MHz, DMSO-***d*₆) δ (ppm) 8.64 (dd, *J* = 5.7, 2.4 Hz, 2 H), 8.44 (tt, *J* = 8 Hz, 2.4 Hz, 1 H).

Synthesis scheme of 1-methyl indole (1d):



Procedure: Sodium hydride (60% in mineral oil, 15 mmol, 1.5 equiv) was added to a solution of indole (10 mmol, 1.0 equiv) in THF at 0 °C and then the reaction mixture was allowed to room temperature and stirred for 30 minutes. Subsequently, the reaction mixture was again cooled to 0 °C and methyl iodide (12 mmol, 1.2 equiv) was added dropwise and then reaction mixture was stirred at room temperature until the reaction was completed. After monitoring by TLC, the reaction mixture was cooled to 0 °C and quenched with saturated ammonium chloride solution and extracted by diethyl ether. The compound was purified by column chromatography using ethyl acetate and hexane (10/90, v/v) as eluent to obtain an oily compound with 90% yield.

¹**H NMR (400 MHz, CDCl₃)** δ (ppm) 7.73 (d, J = 7.9 Hz, 1 H), 7.43 – 7.38 (m, 1 H), 7.35 – 7.29 (m, 1 H), 7.20 (td, J = 7.5 Hz, 7.1 Hz, 1.0 Hz, 1 H), 7.11 (d, J = 3.1 Hz, 1 H), 6.59 – 6.56 (m, 1 H), 3.83 (s, 3 H).

General procedure for the reaction of aryl diazonium tetrafluoroborates with heteroarenes

The compounds aryl diazonium tetrafluoroborate (1 equiv.), photocatalyst (0.01 equiv.) and thiophene or furan (5 equiv.) were dissolved in dry ACN in a Schlenk tube and the resulting mixture was degassed by freeze-pump-thaw method. The reaction mixture was irradiated by blue LED light and stirred at room temperature for 2 h in N₂ atmosphere. Then the reaction mixture was diluted with ethyl acetate and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using *n*-hexane as eluent.

2-(4-bromophenyl)thiophene (1P):



¹**H NMR (400 MHz, CDCl**₃) δ (ppm) 7.51 (d, J = 4 Hz, 4 H), 7.32 (d, J = 4 Hz, 2 H), 7.11 (t,

J = 4 Hz, 1 H).

2-(3,5-bis(trifluoromethyl)phenyl)thiophene (2P):



¹**H NMR (400 MHz, CDCl**₃) δ (ppm) 8.00 (s, 2 H), 7.77 (s, 1 H), 7.43 (dd, *J* = 8, 4 Hz, 2 H), 7.15 (t, *J* = 4 Hz, 1 H).

2-(3,5-difluorophenyl)thiophene (3P):



¹**H NMR (400 MHz, CDCl₃)** δ (ppm) 7.34 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, J = 4 Hz, 6 Hz, 7 Hz

= 8 Hz, 1 H).

2-(4-bromophenyl)furan (4P):



¹**H NMR (400 MHz, CDCl**₃) δ (ppm) 7.52 (q, *J* = 8 Hz, 4 H), 7.47 (m, *J* = 4 Hz, 1 H), 6.65 (d, *J* = 4 Hz, 1 H), 6.48 (dd, *J* = 4 Hz, 1 H).

2-(4-bromophenyl)thieno[3,2-b]thiophene (5P):



¹**H NMR (400 MHz, CD₂Cl₂)** *δ* (ppm)7.53 (s, 5 H), 7.42 (d, *J* = 5.0 Hz, 1 H), 7.28 (d, *J* = 4.8 Hz, 1 H).

2-(3,5-bis(trifluoromethyl)phenyl)thieno[3,2-b]thiophene (6P):



¹**H NMR (400 MHz, CD₂Cl₂)** δ (ppm) 8.01 (s, 2 H), 7.78 (s, 1 H), 7.64 (s, 1 H), 7.49 – 7.43 (m, 1 H), 7.29 (d, J = 4.7 Hz, 1 H).

3-(4-bromophenyl)-1-methyl-1H-indole (7P):



¹**H NMR** (**400 MHz, CD₂Cl₂**) δ (ppm) 8.63 (d, J = 8 Hz, 1 H), 7.63 (dd, J = 12, 8 Hz, 3 H), 7.50 (dd, J = 12, 8 Hz, 6 H), 7.37 (dt, J = 12, 8 Hz, 4 H), 7.25 – 7.17 (m, 3 H), 6.57 (d, J = 8 Hz, 1 H), 3.96 (s, 3 H), 3.85 (s, 3 H).

TEMPO Adducts (8P and 9P):



HRMS (ESI): Calculated for **8P**: 312.0962; found: 312.1136 and calculated for **9P**: 396.0996; found: 396.2120.

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Appendix of Chapter 5

a. ¹H and ¹³C NMR spectra ¹H NMR spectra of 2



¹H NMR spectra of DI



¹H NMR spectra of 6



¹H NMR spectra of PF





¹H NMR spectra of DI-PF



¹³C NMR spectra of DI-PF



¹H NMR spectra of DI-PI



¹³C NMR spectra of DI-PI



¹H-NMR spectra of isomerization of stilbene using DI-PF as PC



^{7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60 6.5} f1 (ppm)

¹H-NMR spectra of isomerization of stilbene using DI-PI as PC



.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60 6.55 6.50 6.45 6.40 6. f1 (ppm)

¹H-NMR spectra of arylation of heteroarenes (electron transfer reactions) ¹H NMR spectra of 1a



¹H NMR spectra of 1b







¹H NMR spectra of 1d







¹H NMR spectra of 2P







¹H NMR spectra of 4P







¹H NMR spectra of 6P



¹H NMR spectra of 7P



				a .		X		
		Compor	unds S	Symmetry		First Three	•	
						Frequencies	5	
						4.35		
		DI-P	F	C_1		4.77		
						8.34		
						5.19		
		DI-P	Ί	C_1		5.61		
						8.36		
Coo	rdinates of ge	eometry optin	mized		С	5.83808	4.64907	0.55253
stru	clure of DI-P	F 2 (1200	0.750		С	4.53554	4.83592	1.00478
c	5.20858	-2.41309	0.7599	96	С	3.68963	3.73842	1.21940
С	6.59931	-2.57830	0.5406	50	С	4.12376	2.43894	0.97601
С	7.11838	-1.27338	0.1515	57	С	11.73070	-0.79446	-1.65826
С	6.04162	-0.35563	0.2599	95	С	12.47642	0.28354	-2.12412
Ν	4.87075	-1.06070	0.5780	01	С	11.95740	1.58563	-2.07394
С	8.36284	-0.76390	-0.299′	75	С	10.69490	1.83664	-1.54581
С	8.58729	0.62870	-0.4886	53	С	3.54540	-0.65759	0.25794
С	7.53383	1.51449	-0.1493	14	С	8.66990	3.76764	0.04122
С	6.23516	1.04615	0.1893	39	С	9.64250	-2.84104	-0.98995
С	4.37292	-3.47903	1.0965	55	С	8.83372	4.85280	-0.82394
С	4.95373	-4.72994	1.2866	65	С	9.91858	5.71529	-0.66281
С	6.33767	-4.90368	1.1501	13	С	10.86212	5.51294	0.35190
С	7.15985	-3.84411	0.7787	76	С	10.68226	4.41748	1.20877
N	7.53541	2.91256	-0.0978	88	C	9 59580	3 55868	1 06851
С	6.26286	3.34310	0.3011	10	C	8 85597	-3 40120	-2 00141
С	5.42498	2.21678	0.4936	59	C	0.00007	<i>A</i> 7 <i>A</i> /10	2.00141
N	9.52363	-1.45709	-0.658	53	C	0.05111	5 55210	1 60054
С	10.46742	-0.53307	-1.123	69	C C	10 7/250	-5.55510 1 07070	0 62001
С	9.92617	0.77335	-1.0414	44	C C	10.74330	-4.91210	0 2271 /
•	<i>,,,</i> <u></u> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	01110000	110.11		С	10.59196	-3.63121	-0.33714

b. Frequencies and Coordinates of DFT Optimized Geometries

optimization of **DI-PF** and **DI-PI**.

Table 5.13. Results of first three frequencies and molecular symmetries calculated from geometry

255

С	3.25743	-0.10337	-1.00233	С	-6.04544	5.36030	-2.11263
С	1.96207	0.26133	-1.32250	C	-6.85028	4.27194	-1.78906
С	0.89175	0.07514	-0.42241	Ν	-7.09496	-2.51630	-1.14401
С	1.19195	-0.49477	0.84050	C	-5.80766	-2.90879	-1.53367
С	2.51373	-0.84273	1.16881	С	-4.98911	-1.76070	-1.67486
С	-0.48985	0.44949	-0.75321	Ν	-9.17920	1.79076	-0.46409
С	-1.52985	0.24209	0.18869	C	-10.11062	0.83253	-0.04485
С	-1.22599	-0.34168	1.49658	С	-9.54237	-0.45944	-0.16534
С	0.12446	-0.71095	1.81872	С	-5.35330	-4.19788	-1.81803
С	-0.84129	1.01659	-1.99594	C	-4.03911	-4.34639	-2.25003
С	-2.14970	1.35589	-2.29795	C	-3.21067	-3.22699	-2.41222
С	-3.17035	1.15024	-1.35281	C	-3.67451	-1.94421	-2.13681
С	-2.85207	0.60251	-0.11769	C	-11.38576	1.05032	0.48093
N	-2.21576	-0.51975	2.36499	C	-12.11627	-0.05765	0.89809
С	-1.91543	-1.06525	3.56129	C	-11.57096	-1.34679	0.80929
С	-0.56670	-1.43904	3.88151	C	-10.29674	-1.55445	0.29049
N	0.43140	-1.25073	2.99385	C	-8.20934	-3.38894	-1.32777
С	-2.94900	-1.27353	4.51657	C	-9.32625	3.15828	-0.08006
С	-2.63416	-1.82839	5.72494	C	-9.12422	-3.16543	-2.36185
С	-1.29730	-2.19905	6.04226	C	-10.19089	-4.04063	-2.54601
С	-0.27856	-2.01415	5.15047	C	-10.36091	-5.16648	-1.72741
С	-4.87062	2.88150	-1.79350	C	-9.42828	-5.38272	-0.70549
С	-6.26694	3.01016	-1.58669	C	-8.36364	-4.50454	-0.50034
С	-6.76129	1.68214	-1.24801	C	-10.28541	3.95598	-0.70919
С	-5.66365	0.79093	-1.37266	C	-10.46453	5.27966	-0.30562
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Н	-2.30949	1.31426	-1.37590	Н	-5.62108	-3.48298	2.47535	
Н	-11.81005	-0.87575	-1.31904	Н	-2.46033	-3.07549	4.91164	
Н	-12.92083	0.52300	0.40481	Н	-2.74468	-3.27657	7.34236	
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Н	-9.15032	2.21710	1.56138	Н	0.78510	-0.90200	7.96636	
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Н	-8.27646	5.28856	3.43728	Н	-2.77285	0.45679	3.52479	
Н	-9.40275	5.59303	-0.69563					

Rigid Donor-Acceptor TADF Conjugates based on Diindolocarbazole and Phenyl Carbazole Donors for Energy and Electron Transfer Photocatalysis and Green Organic Light-emitting Diodes



Abstract: The design and synthesis of four twisted donor-acceptor (D-A) thermally activated delayed fluorescence (TADF) molecules CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ is presented based on diindolocarbazole (DI) and phenyl carbazole as donor and indoloquinoxalines as acceptor. These compounds serve as photocatalysts for organic transformations and green emitters for organic light-emitting diodes (OLEDs). Theoretical calculations and fluorescence and phosphorescence studies showed reasonable singlet and triplet energy gaps of 0.17-0.26 eV for all compounds. All molecules showed increase in fluorescence quantum yields after degassing the solution and the transient photoluminescence decay showed two components: shorter prompt components (11.4 ns to 31 ns) and longer delayed components (36.4 ns to 1.5 µs) which further indicate the occurrence of TADF process. Cyclic voltammetry studies indicated well-suited excited state redox potentials of all compounds to catalyze organic transformations such as heteroarene arylation. Accordingly, photocatalytic C-H arylation of heteroarenes were performed using these compounds with excellent isolated yields of upto 80%. Due to their suitable efficient triplet energy levels, all the emitters were also employed as energy transfer photocatalysts in E to Z isomerization of stilbene with the excellent conversion of ~ 90% and solution-processed green OLEDs were fabricated using TADF emitters CBZ-IQ, DI-IQ and DI-2FIQ.

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6.1. Introduction

Thermally activated delayed fluorescence (TADF) materials have attracted tremendous attention in the field of organic light-emitting diodes (OLEDs) because of their high electroluminescence efficiency and low cost.¹⁻⁹ Due to the up conversion of 75% triplet excitons into singlet excitons through reverse intersystem crossing (RISC), TADF materials theoretically can achieve 100% internal quantum efficiency (IQE) and consequently higher external quantum efficiency (EQE) are achieved than fluorescent OLEDs.^{5,10,11} Adachi and co-workers in their seminal work reported 2biphenyl-4,6-bis(12-phenylindolo[2,3-a]carbazole-11-yl)-1,3,5-triazine (PIC-TRZ) which showed emission at 506 nm with small singlet-triplet energy (ΔE_{ST}) gap of 0.11 eV and the EQE of 5.3% in OLED.³ Followed by the first report on TADF, rapid and exponential progress have been made towards developing highly efficient OLEDs with the current state-of-the-art TADF OLEDs reaching up to 42% EQE presently.¹² The maximum EQE can be achieved by either decreasing the ΔE_{ST} or by increasing the photoluminescence quantum yield (PLQY).^{8,9} In twisted donoracceptor (D-A) molecules (with large dihedral angle), lower ΔE_{ST} can be achieved by reducing the overlap integral of HOMO and LUMO. However, small overlap integrals lead to a decrease in transition dipole moments between a ground state and excited state and therefore lower oscillator strength that significantly decrease PLQY and limit performance of OLED devices.¹³ Therefore, it is necessary to balance ΔE_{ST} and PLQY of D-A charge transfer (CT) molecules. Insertion of a phenyl ring between twisted D-A TADF molecule leads to high PLQY and smaller ΔE_{ST} , which results in high EQE.¹⁴ In 2015, Adachi and co-workers showed that an increase in the number of carbazoles on the donor led to high oscillator strength and smaller ΔE_{ST} with EQE of upto 20%.⁴ Bulky and rigid structure of D-A leads to smaller ΔE_{ST} due to high steric hindrance and hence the spatial separation of frontier molecular orbitals, high PLQY due to reduced vibronic coupling leading to higher EQE. Recently, Kwon and co-workers reported highly efficient green TADF emitters using a new rigid donor called diindolocarbazole (DI) and reported high efficiency without any out-coupling and a very low-efficiency roll-off characteristics.¹⁵ Diindolocarbazole (DI) has two fused indole rings with one carbazole unit that possess high thermal stability and electron donor properties which further provides a large and rigid HOMO volume to the emitter.¹⁵ Few other groups have also reported DI-based blue emitters with record efficiencies in OLEDs.^{16–} ¹⁸ Photocatalysis is another domain where TADF compounds have received tremendous attention as earth-abundant, non-toxic, sustainable photocatalysts (PC) because of their metal-free nature

and longer triplet state lifetimes.¹⁹⁻²² TADF compounds have emerged as promising candidates compared to conventional PC due to their high exciton utilization, longer exciton lifetime, efficient harvesting of triplet excitons and the ability to tune their ground state and excited state redox potentials by varying the donor and acceptor groups.^{19,22} Typically, because of their longer exciton lifetime and involvement of triplet state, TADF compounds actively participate in photocatalytic reactions instead of primarily undergoing luminescence that make them attractive choices for driving photocatalysis reactions with high efficiency and minimizing the loss of energy by luminescence. Upon visible light photoexcitation, PC is photoexcited and can interact with organic substrates either through photoinduced energy transfer (PEnT) or electron transfer (PET) processes. TADF compounds have been studied as energy transfer photocatalysts as well as electron transfer (photo redox) catalysts in recent years based on their triplet state energy levels and excited state redox potentials of PC and substrates.^{19,23-27} The most popular D-A TADF material based on carbazole donor and dicyanobenzene acceptor 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN), has been extensively studied in photocatalysis due to its long-lived triplet state (1.3 µs), suitable redox potentials and the similar properties as Iridium (Ir) based photocatalysts.^{19,20,27} In 2016, Luo and Zhang reported 4CzIPN as photocatalyst for dual catalyzed cross-coupling reaction for the first time.²⁸ Thereafter, several examples of TADF materials in various photocatalysis reactions have been reported.^{19,20} In 2018, Zhang and co-workers reported the effectiveness of TADF materials in PEnT with the utilization of E to Z isomerization of stilbene and found a conversion of upto ~ 90% after 24 h. They further utilized the materials in PEnTmediated cross-coupling of various carboxylic acids and aryl halides with excellent yields.²⁴ To enhance the E/Z isomerization of stilbene, the triplet energy (E_T) of PC should be higher than the E_T of E-stilbene but lower than that of Z stilbene (E_T of E-stilbene = 2.2 eV and E_T of Z-stilbene = 2.5 eV). Bergens and co-workers reported the synthesis of functionalized 4CzIPN and further immobilized it on carbon and indium-doped tin oxide electrodes and utilized for E to Z isomerization of stilbene with ~ 84% conversion after 48 h.²⁹ Recently, Zysman-Colman and coworkers utilized the E to Z isomerization of stilbene to evaluate the effectiveness of PEnT of various TADF materials.^{19,22,23}

Arylation of heteroarenes is another reaction that proceeds via photocatalytic method (using transition metal complex or Eosin Y as PC) in a facile way. In 2012, Hari and co-workers reported the arylation of various heteroarenes by a photocatalytic method using aryl diazonium salts as an

aryl source and Eosin Y as the PC and obtained upto 80% in dimethyl sulfoxide (DMSO) and upto $\sim 12\%$ yield in acetonitrile (ACN).³⁰ The reduction potential of aryl diazonium salts is ~ -0.10 V - 0.20 V V³¹ and therefore, they are well known for radical formation upon oxidative quenching of PC. Recently, Wang and co-workers reported the synthesis of 2-arylated indole by a two-step cross-coupling reaction using Pd and Ir as PC.³² However, to our best knowledge, arylation of heteroarenes using twisted organic D-A TADF compounds as photoredox catalysts except for Eosin Y as PC is not reported in the literature to date.



Figure 6.1. Chemical structures of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ synthesized and investigated in this work.

In this work, we have designed and synthesized four twisted D-A TADF molecules phenyl carbazole indoloquinoxaline (**CBZ-IQ**), phenyl carbazole difluoroindoloquinoxaline (**CBZ-2FIQ**), diindolocarbazole indoloquinoxaline (**DI-IQ**) and diindolocarbazole difluoroindoloquinoxaline (**DI-2FIQ**), where diindolocarbazole (DI) and phenyl carbazole (CBZ) act as donor and indoloquinoxaline (IQ) and difluoro-substituted indoloquinoxaline (2FIQ) act as an acceptor (Figure 6.1). Indoloquinoxaline (IQ) and 2F-IQ are fused systems of alkylated indole and quinoxaline or difluoro-substituted quinoxaline having a planar structure with strong electron-

withdrawing characteristics. Indoloquinoxaline derivatives have been utilized extensively in biochemistry and medicinal chemistry^{33,34} and have significant applications as host materials of OLEDs.^{35,36} Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations showed well-separated HOMO and LUMO of all molecules and small ΔE_{ST} values for efficient RISC, therefore all molecules are expected to exhibit TADF behaviour. All compounds showed green emission with high PLQY and showed prominent aggregate-induced emission (AIE) in the water/THF mixture. Due to the long-delayed component (1.5 µs), efficient triplet energy levels and suitably excited state redox potentials, all compounds **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** have been employed as photocatalysts in E to Z isomerization of stilbene with a maximum of 90% conversion and C-H arylation of heteroarenes with upto ~ 80% yield. Additionally, solution-processable green OLEDs were fabricated using **CBZ-IQ**, **DI-IQ** and **DI-2FIQ** as emitters and the maximum EQE reached upto ~ 1%.

6.2. Results and discussion

6.2.1. Synthesis

The synthesis of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ was accomplished as shown in Scheme 6.1. Acceptor parts IQ and 2FIQ were synthesized by condensation reaction between 5bromoisatin and phenylenediamine or difluoro substituted phenylenediamine followed by alkylation of 5-bromoisatin with hexyl bromide and potassium carbonate.³⁷ The donor DI was synthesized by refluxing 2-oxoindole in phosphorus oxychloride followed by protection of two -NH groups by tert-butyl benzene groups.^{38,39} Two tertiary butyl groups were incorporated in the phenyl group to minimize the possibility of self-aggregation of these molecules in the solid state. Donor Ph-CBZ was synthesized by bromination of carbazole followed by Suzuki coupling reaction with phenylboronic acid.⁴⁰ Finally, the TADF molecules were synthesized by Buchwald-Hartwig coupling reaction between donors DI, Ph-CBZ and acceptors IQ, 2FIQ using tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) as catalyst, tri-tert-butylphosphine tetrafluoroborate as co-catalyst and sodium tert-butoxide as base as shown in Scheme 6.1.¹⁶ All compounds were purified via column chromatography and characterized using ¹H NMR, ¹³C NMR and high-resolution mass spectrometry (HRMS).



Scheme 6.1. Synthesis scheme of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ.6.2.2. UV/Vis Absorption and Emission

UV/Vis absorption and emission spectra of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ were recorded in toluene (Tol) at $c \sim 10^{-6}$ M. In UV/Vis absorption spectra of CBZ-IQ and CBZ-2FIQ, the main absorption peak was obtained at 298 nm due to π - π^* transition and a charge transfer (CT) band was observed at 398 nm. Similarly, in UV/Vis absorption spectra of DI-IQ and DI-2FIQ, the main absorption peak was obtained at 316 nm due to π - π^* transition and a CT band was observed at 373 nm as shown in Figure 6.2 and Table 6.1. In the emission spectra of CBZ-IQ and CBZ-2FIQ, upon excitation at ~ 398 nm, the major peak was observed at 512 nm and 527 nm respectively, corresponding to the CT state. Due to the presence of Fluorine (F) atoms in the acceptor part (IQ), the emission was slightly red-shifted in the case of CBZ-2FIQ, because of strong interactions of donor and acceptor. While in emission spectra of DI-IQ and DI-2FIQ, upon excitation at ~ 373 nm, a major peak was observed at 523 nm and 546 nm respectively corresponding to CT states as shown in Figure 6.2. Similarly in DI-2FIQ, the emission was red-shifted due to the presence of F atoms. The molar absorption coefficients (ε) of CBZ-1Q, CBZ-2FIQ, DI-IQ and DI-2FIQ were 5.7 × 10⁴ M⁻¹cm⁻¹, 6.9 × 10⁴ M⁻¹cm⁻¹, 6.8 × 10⁴ M⁻¹cm⁻¹ and 7.2 × 10⁴ M⁻¹cm⁻¹¹ respectively.



Figure 6.2. UV/Vis absorption and emission spectra of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** in Tol $(c \sim 10^{-6} \text{ M})$ upon excitation at 398 nm, 398 nm, 373 nm and 373 nm respectively.

Table 6.1. Excitation wavelength (λ_{ex}), emission wavelength (λ_{em}) and molar absorption coefficient (ε), singlet energy (S₁), triplet energy (T₁) and singlet-triplet energy gap (ΔE_{ST}) of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ**.

Compounds	$\lambda_{ex} (nm)$	λ_{em}	8	S ₁	T_1	ΔE_{ST}
		(nm)	$(M^{-1}cm^{-1})$	(eV)	(eV)	(eV)
CBZ-IQ	298, 351,	512	$5.7 imes 10^4$	2.54	2.37	0.17
	398					
CBZ-2FIQ	298, 351,	527	$6.9 imes 10^4$	2.63	2.37	0.26
	398					
DI-IQ	316, 333,	523	$6.8 imes 10^4$	2.51	2.34	0.17
	351, 373					
DI-2FIQ	316, 333,	546	$7.2 imes 10^4$	2.57	2.37	0.20
	351, 373					

Furthermore, emission spectra were also recorded after degassing the solution by N_2 gas and the significant enhancement of intensity was observed as shown in Figure 6.3. The sensitivity of emission intensities towards nitrogen purging can be attributed to the involvement of TADF process in these molecules.



Figure 6.3. Emission spectra of (a) **CBZ-IQ**, (b) **CBZ-2FIQ**, (c) **DI-IQ** and (d) **DI-2FIQ** in aerated solution and nitrogen degassed solution of Tol upon excitation at ~ 398 nm, 398 nm, 373 nm and 373 nm respectively.

The emission was also recorded in the solid state for all compounds and shown in Figure 6.4. The major emission was observed at 508 nm, 514 nm, 536 nm and 528 nm for **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** respectively.



Figure 6.4. (a) Normalized absorption and (b) emission spectra of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ in solid-state.

6.2.3. Density Functional Theory (DFT) Calculations

To determine the electronic properties of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ**, DFT calculations were performed for optimized structures and TD-DFT for energy calculations using the Gaussian 09 package at the B3LYP/6- 31G(d,p) level. The large steric hindrance between donor and acceptor parts of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ**, results in moderate to large twist angles of 59.5°, 58.9°, 69.3° and 69.1° respectively as shown in Figure 6.5 and Table 6.2. Therefore, in the case of **CBZ-IQ** and **CBZ-2FIQ**, the HOMO was localized on the donor as well as some components on the acceptor part (IQ and 2FIQ) and the LUMO was completely localized on acceptor part as shown in Figure S3. In the case of **DI-IQ** and **DI-2FIQ**, HOMO was completely localized on the donor (DI) part and LUMO was completely localized on the acceptor part. Such separations of HOMO and LUMO level leads to a small ΔE_{ST} for better TADF properties.



Figure 6.5. Frontier molecular orbital (FMO) energy levels of compounds **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** calculated using B3LYP/6-31G(d,p).

Compound	HOMO-1	HOMO	LUMO	LUMO+1	Dihedral	ΔE (eV)
	(eV)	(eV)	(eV)	(eV)	angel (°)	
CBZ-IQ	- 5.66	- 5.15	- 2.13	- 0.78	59.5	3.02
CBZ-2FIQ	- 5.71	- 5.21	- 2.33	- 0.92	58.9	2.88
DI-IQ	- 4.77	- 4.76	- 2.03	- 0.68	69.3	2.73
DI-2FIQ	- 4.82	- 4.82	- 2.22	- 0.82	69.1	2.60

Table 6.2. FMO energy levels of compounds **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** calculated by B3LYP/6-31G(d,p).

The singlet and triplet energy levels of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** were calculated using TD-DFT and the calculated energies are shown in Table 6.3. To calculate the singlet and triplet energies of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** experimentally, fluorescence and phosphorescence spectra were recorded in deaerated Tol at 77 K as shown in Figure 6.6 and the calculated ΔE_{ST} values for **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** were 0.17 eV, 0.26 eV, 0.17



Figure 6.6. Normalized fluorescence and phosphorescence spectra of (a) **CBZ-IQ**, (b) **CBZ-2FIQ**, (c) **DI-IQ** and (d) **DI-2FIQ** at 77 K upon excitation at ~ 398 nm, 398 nm, 373 nm and 373 nm respectively.

eV and 0.20 eV respectively as shown in Table 6.3. These smaller ΔE_{ST} are presumably sufficient for effective RISC and TADF behaviour.

Compounds	Theoretical energy levels (eV)			Experim	Experimental energy levels (eV)			
	\mathbf{S}_1	T ₁	ΔE_{ST}	S_1	T ₁	ΔE_{ST}		
CBZ-IQ	2.63	2.28	0.35	2.54	2.37	0.17		
CBZ-2FIQ	2.55	2.27	0.27	2.63	2.37	0.26		
DI-IQ	2.44	2.25	0.19	2.51	2.34	0.17		
DI-2FIQ	2.35	2.21	0.13	2.57	2.37	0.20		

Table 6.3. Theoretical (calculated by B3LYP/6-31G(d,p)) and experimentally calculated singlet, triplet and ΔE_{ST} of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ.

6.2.4. TADF Behaviour of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ (Fluorescence Quantum Vield and Transient Photoluminescence Decay)

To confirm TADF process for **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ**, fluorescence quantum yields were determined by relative method (described in Chapter 2) using Rhodamine B as a reference dye in an aerated solution and N₂ degassed solution and the values are shown in Table 6.4-6.5. The fluorescence quantum yields of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** in aerated solution was 31.6%, 8%, 8.8% and 5.0% respectively. However, in nitrogen degassed solution

Compound	Absorbance			Integrated	$\begin{array}{c} \begin{array}{c} Quantum \\ Yield \\ \Phi = \Phi_R(I/I_R)(A_R \\ /A)(\lambda_{exR}/\lambda_{ex})(n^2 / \\ n^2_R) \end{array}$			
	1	2	3	1	2	3	Φ_{i}	Φ_{avg}
CBZ-IQ	0.047	0.074	0.1	115.54	167.99	202.39	32.2	
							32.5	31.6
							30.15	
CBZ-2FIQ	0.043	0.072	0.098	28.65	38.34	50.09	8.7	

Table 6.4. Relative quantum yields of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** using relative method and Rhodamine B as a reference dye in aerated solution.
							7.7	8
							7.6	
DI-IQ	0.045	0.089	0.09	36.14	44.67	50.84	10.74	
							7.25	8.8
							8.51	
DI-2FIQ	0.059	0.078	0.095	19.5	28.85	31.81	4.32	
							5.34	5.0
							4.98	
Rhodamine	0.033	0.065	0.105	234.7	418.24	655.36		0.50
B (EtOH)								

Table 6.5. Relative quantum yields of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ using relative method and Rhodamine B as a reference dye in N_2 degassed solution.

Compound	Absorbance Integrated Fluorescence Intensity					Integrated Fluorescence Intensity				nce Integrated Fluorescence Intensity		
	1	2	3	1	2	3	Φ_{i}	Φ_{avg}				
CBZ-IQ	0.047	0.074	0.1	212.23	259.20	311.28	59.1					
							50.2	52				
							46.4					
CBZ-2FIQ	0.043	0.072	0.098	35.71	45	76.7	10.8					
							9.1	10.5				
							11.6					
DI-IQ	0.045	0.089	0.09	62.78	72.61	88.98	18.6					
							11.8	15.1				
							14.9					
DI-2FIQ	0.059	0.078	0.095	32.7	39.27	42.35	7.2 7.3	7.0				
Rhodamine B (EtOH)	0.033	0.065	0.105	234.7	418.24	655.36	0.0	0.50				

quantum yield was significantly enhanced to 52%, 10.5%, 15.1% and 7.0% in CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ respectively. This enhancement of quantum yields in N₂ degassed solutions indicate the occurrence of TADF process in all compounds. Additionally, the transient photoluminescence decay measurements performed using 0.5 wt % ZEONEX: CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ films showed prompt components of 11.4 ns, 11.5 ns, 25 ns and 31 ns and delayed components of 36.4 ns, 36.6 ns, 1.5 µs, 0.16 µs respectively at 300 K as shown in Figure 6.7. Hence, the above experiments suggest the TADF nature³ of CBZ- IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ and could be efficiently utilized in photocatalysis reactions and OLED fabrication.



Figure 6.7. Fluorescence lifetime decays of (a) **CBZ-IQ**, **CBZ-2FIQ** and (b) **DI-IQ**, **DI-2FIQ** in 0.5 wt% of ZEONEX:TADF compound film.

6.2.5. Thermal Stability

Thermal stabilities of **CBZ-IQ**, **DI-IQ** and **DI-2FIQ** were investigated using thermogravimetric analysis (TGA) as shown in Figure 6.8. The decomposition temperature of **CBZ-IQ**, **DI-IQ** and **DI-2FIQ** were 425 °C, 495 °C and 496 °C at 7%, 8% and 15% weight loss. The higher decomposition temperatures are indicative of high thermal stabilities of these TADF compounds ascribed to the rigid and stable donor and acceptor moieties.



Figure 6.8. TGA curves of (a) CBZ-IQ, (b) DI-IQ and (c) DI-2FIQ.

6.2.6. Temperature-dependent Emission

The emission of TADF molecules (i.e., their CT-band) is sensitive towards solvent polarity and temperature. Hence, to study the effect of temperature on the emission of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ**, temperature-dependent fluorescence measurements were performed in Tol from - 5 °C up to the boiling point of the solvent. In the case of **CBZ-IQ**, upon increasing the temperature, the emission intensity increased by ~ 1.5-fold with a hypsochromic shift of ~ 18 nm. Similarly, in the case of **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ**, upon increasing the temperature, the emission intensities increased by ~ 2.5-fold, 2.1-fold and 1.9-fold with a hypsochromic shift of ~ 14 nm, 17 nm and 15 nm respectively as shown in Figure 6.9. In all cases, upon increasing



Figure 6.9. Temperature-dependent emission spectra of (a) **CBZ-IQ**, (b) **CBZ-2FIQ**, (c) **DI-IQ** and (d) **DI-2FIQ** ($\lambda_{ex} = 351 \text{ nm}$) in Tol in 10⁻⁶ M concentration.



Figure 6.10. Emission intensity ratios of (a) **CBZ-IQ**, (b) **CBZ-2FIQ**, (c) **DI-IQ** and (d) **DI-2FIQ** in Tol at different temperatures with best fit (linear) equations.

temperature, the emission intensity increased with a hypsochromic shift because the excited electron crosses the activation barrier from CT state to local excited state (LE) and hence LE states get more populated and emission occurs from LE states. The ratiometric temperature analysis^{41,42} of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** were performed and fitted with linear function as shown in Figure 6.10 and the calculated internal sensitivities were - 0.05% $^{\circ}C^{-1}$, - 0.25% $^{\circ}C^{-1}$, - 0.17% $^{\circ}C^{-1}$ and 0.19% $^{\circ}C^{-1}$ respectively.

6.2.7. Solvatochromism

The emission peaks (~ 512 nm, 527 nm, 523 nm and 546 nm) observed in the long wavelength region are assigned to CT states for all compounds, hence fluorescence solvatochromism study was performed for **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** in solvents of different polarities. In the case of **CBZ-IQ** in polar solvents such as chloroform (CHCl₃) and tetrahydrofuran (THF), the emission maximum was observed at 556 nm and 527 nm and in **CBZ-2FIQ** the emission maximum was observed at 568 nm and 549 nm respectively. While in non-polar solvents such as hexane (Hex), methylcyclohexane (MCH) and Tol, in the case of **CBZ-IQ** the emission was observed at 479 nm, 480 nm and 512 nm respectively and in **CBZ-2FIQ**, the emission was observed at 492 nm, 494 nm and 526 nm respectively. Likewise, in **DI-IQ**, in polar solvents such as CHCl₃ and THF, the emission was observed at 610 nm and 561 nm respectively and in **DI-2FIQ**



Figure 6.11. Normalized emission spectra of (a) **CBZ-IQ**, (b) **CBZ-2FIQ**, (c) **DI-IQ** and (d) **DI-2FIQ** in solvents of different polarities upon excitation at ~ 398 nm, 398 nm, 373 nm and 373 nm respectively.

in THF, the emission was observed at 600 nm while in CHCl₃, the emission was not observed due to rapid non-radiative deactivation (Figure 6.11). In non-polar solvents such as Hex, MCH and Tol, **DI-IQ** emission was observed at 484 nm, 487 nm and 523 nm and in **DI-2FIQ** the emission was observed at 486 nm, 500 nm and 546 nm respectively as shown in Figure 6.11 and Table 6.6. Hence, positive solvatochromism was observed for all compounds and the long wavelength emission peak can be attributed to CT from donor (DI and Ph-CBZ) to acceptor (IQ and 2F-IQ).

Compound	Hex	МСН	Tol	THF	CHCl ₃
CBZ-IQ	479	480	512	527	556
CBZ-2FIQ	492	494	526	549	568
DI-IQ	484	487	523	561	610
DI-2FIQ	486	500	546	600	-

Table 6.6. Emission maxima of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ in various solvents.

6.2.8. Photophysical Studies in Water/THF Mixtures

Furthermore, in order to investigate the emission behaviour of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** in water/organic solvent mixture, fluorescence studies were performed in binary mixture of THF and water. In emission spectra, in case of **CBZ-IQ** the long wavelength peak gradually disappeared with the addition of water from 0% upto 60% fraction of water and then intensity started to increase with the further addition of water from 60% to 95% due to the formation of aggregates at higher percentage of water, while in case of **CBZ-2FIQ**, the emission intensity was very weak upto 50% of water, however upon further increasing of water percentage from 50% to 95%, the emission intensity increased by 26 folds. With the further increase of water percent from 95% to upwards, the emission intensity decreased as shown in Figure 6.12. Similarly, in case of **DI-IQ**, the emission intensity dropped with the increase of water percent from 0% to 60% water however, upon further increasing of water percent from 60% to 95%, the emission intensity dropped with the increase of water percent from 0% to 60% water however, upon further increasing of water percent from 0% to 60% water however, upon further increasing of water percent from 60% to 95%, the emission intensity increased by 17 folds. Likewise in **DI-2FIQ**, the emission intensity was decreased with the addition of water from 0% to 40%, however upon further increasing of water percent from 40% to



Figure 6.12. Emission of (a) CBZ-IQ, (b) CBZ-2FIQ, (c) DI-IQ and (d) DI-2FIQ in different percentage of THF and water.

60%, the emission intensity increased by 13 folds as shown in Figure 6.12. Upon further addition of water percent from 60% to 80%, the emission intensity decreased and then increased with further addition of water percent from 80% to 95%. Figure 6.13 shows the changes in emission intensities with changes in water fraction (f_w) in the binary solvent mixture. These studies indicate that the emission of all compounds are responsive to subtle changes in solvent polarity of such binary solvent mixtures.



Figure 6.13. Changes in intensities of (a) **CBZ-IQ**, (b) **CBZ-2FIQ**, (c) **DI-IQ** and (d) **DI-2FIQ** in different fractions of water (f_w) in water/THF mixtures.

6.2.9. Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were performed for CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ in dry DCM with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte and Ag/AgCl as reference electrode to determine the HOMO and LUMO energy levels and redox potentials at ground state and excited state as shown in Figure 6.14 and Table 6.7. The first oxidation potentials (E_{ox}) for CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ were 1.25 V, 1.30 V, 0.90 V and 0.92 V and reduction potentials (E_{red}) were – 1.60 V, – 1.55 V, – 1.66

V and -1.61 V respectively. Furthermore, the excited state oxidation potentials (E_{ox}^*) and reduction potentials (E_{red}^*) were calculated using the following equation¹⁹:

$$E_{ox}^* = E_{ox} - E_{0,0},$$
 (6.1a)
 $E_{red}^* = E_{red} + E_{0,0}$ (6.1b)

where, E_{ox} and E_{red} is the half-cell oxidation potential and half-cell reduction potential respectively and $E_{0,0}$ is the energy difference of the S₀ and S₁ state and calculated by taking the intersection point of normalized absorption and emission spectra. The calculated excited state potentials are given in Table 6.7. The broad range of excited state oxidation and reduction potential of all compounds are of relevance for their role as photocatalysts in the electron transfer PET pathway (vide infra).



Figure 6.14. Cyclic voltammogram of (a) **CBZ-IQ**, (b) **CBZ-2FIQ**, (c) **DI-IQ** and (d) **DI-2FIQ** in dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) and potentials measured vs Ag/AgCl reference electrode.

Compound	Eoxonset	*HOMO	$\mathbf{E_{red}}^{onset}$	LUMO	$\mathbf{E}_{\mathbf{g}}$	E ^{ox} _{1/2}	$\mathbf{E}_{1/2}^{red}$	E _{0,0}	$\mathbf{E}_{\mathbf{ox}}^*$	$\mathbf{E}_{\mathbf{red}}^*$
	(V)	(eV)	(V)	(eV)	(eV)	(V)	(V)	(eV)	(eV)	(eV)
CBZ-IQ	1.11	-5.87	-0.89	-3.87	2.00	1.20	-1.52	2.72	-1.52	1.20
CBZ-2FIQ	1.12	-5.88	-0.91	-3.85	2.03	1.22	-1.45	2.67	-1.45	1.22
DI-IQ	0.73	-5.49	-0.89	-3.87	1.62	0.86	-1.84	2.70	-1.84	1.15
DI-2FIQ	0.76	-5.52	-0.88	-3.88	1.64	0.86	-1.80	2.67	-1.80	1.18

Table 6.7. Ground and excited state redox potentials and optical properties of CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ calculated from cyclic voltammetry.

*HOMO = $-(E_{onset}^{ox} + 4.76) \text{ eV}$, and LUMO = $-(E_{onset}^{red} + 4.76) \text{ eV}$.

6.2.10. Photocatalysis

Due to the longer lifetimes of TADF molecules, they are well known as photocatalysts (PC) in various photochemical reactions.¹⁹ Among many TADF compounds, 4CzIPN was extensively utilized in photocatalytic reactions based on photoinduced energy transfer (PEnT) and photoinduced electron transfer (PET) because of its microsecond emission lifetime and redox properties similar as Ir-based PC.^{19,20} Herein, based on the suitable triplet energies and excited state redox potentials of TADF compounds **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ**, these compounds have been utilized as photocatalysts both in PEnT and PET type mechanisms.

a) Energy transfer photocatalysis: E to Z isomerization of Stilbene

The E to Z isomerization of stilbene was utilized as model reaction of PEnT to evaluate the effectiveness of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** as photocatalysts. Furthermore, it is worth to note that these stilbenes, owing to their isomerization capabilities, have been extensively researched for their applications as molecular photoswitches, molecular motors and in the development of solar-thermal fuels. Hence, the stilbene trans-cis photoisomerization is a very valuable reaction from applications perspective. To enhance the E to Z isomerization of stilbene and to prevent the reverse isomerization of Z to E-stilbene, the triplet energy (E_T) of PC should be higher than the E_T of E-stilbene but lower than that of Z stilbene (E_T of E-stilbene = 2.2 eV and E_T of Z-stilbene = 2.5 eV). The E to Z isomerization of stilbene was performed in ACN at room temperature under blue LED irradiation using **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** as PC as shown in Scheme 6.2 and Table 6.8. In case of **CBZ-IQ** (E_T = 2.37 eV) as PC, only 20% of E-

stilbene was converted into Z-stilbene after 6 h. While after 30 h, ~ 90% of E-stilbene was converted into Z-stilbene. Similarly, in case of **CBZ-2FIQ** ($E_T = 2.37 \text{ eV}$) and **DI-2FIQ** ($E_T = 2.34 \text{ eV}$), 69% and 78% of conversion from E-stilbene to Z-stilbene were achieved respectively after 30 h (appendix page no. 297-298). In case of **DI-IQ** ($E_T = 2.34 \text{ eV}$), ~ 60% conversion was observed after 6 h and remained the same even after 30 h as shown in Table 6.8 and Figure 6.15. Thus, high conversion percentage was achieved in this work in case of **CBZ-IQ** as photocatalyst after 24 h and 30 h as reported in literature.²⁴



Scheme 6.2. Isomerization of E-stilbene to Z-stilbene using CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ as photocatalysts.

Table 6.8.	Conversion	of E-stilbene	to Z-stilbene	using	CBZ-IQ,	CBZ-2FIQ,	DI-IQ an	id DI-2FIQ	as
photocataly	ysts.								

Photocatalyst		Conversion (%) ^a			
	6 h	12 h	24 h	30 h	
CBZ-IQ	20.2	41.7	88.7	90	
CBZ-2FIQ	13.7	29.7	61.4	69	
DI-IQ	60.2	60.9	60.9	60.9	
DI-2FIQ	50.5	58.8	66.2	78	

^aConversion percentages were calculated by ¹H-NMR.

To assess the plausible mechanistic pathways of isomerization, control experiments were performed without PC and without light and no product was obtained indicating that both PC and light are essential for the conversion. On the basis of control experiments and literature reports, a plausible mechanism was proposed as shown in Figure 6.15.¹⁹ Upon photoexcitation, PC is photoexcited and the triplet state gets populated through an intersystem crossing (ISC) and then transfers energy to the substrate (E-stilbene). The formation of a triplet biradical intermediate (**5**) subsequently leads to the generation of Z-stilbene via ISC.¹⁹



Figure 6.15. (a) Conversion of E-stilbene to Z-stilbene using **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** as photocatalyst at room temperature in ACN under blue light irradiation and (b) Plausible mechanistic pathway of photocatalytic isomerization of stilbene.

b) PET catalysis: Synthesis of Arylated heteroarenes

In case of PET, we chose the arylation of heteroarenes using diazonium salts as the aryl source due to its wide-ranging applications in materials science and biomedical applications.¹⁹ This is primarily because of the interesting optical and electronic properties of the resulting compounds. The C-H arylation of heteroarenes with aryl diazonium salts was accomplished by photocatalytic method using CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ as PCs. Since the E_{ox}^* of all compounds are more negative (Table 6.7) than E_{red} of diazonium salts, all compounds can be suitably utilized for PET to diazonium salts. In the arylation of heteroarenes reaction, firstly the reaction of bromosubstituted arylation of thiophene was optimized with all TADF compounds (1 mol %) as photo redox catalyst in acetonitrile (ACN) at room temperature with blue light irradiation in argon atmosphere as shown in Scheme 6.3. The maximum of 54% and 50% product yields were obtained with the utilization of DI-IQ and CBZ-2FIQ as PC respectively as shown in Table 6.9 (entries 1-4). After optimizing the photocatalyst, we have also screened two other diazonium salts 1b and 1c, in dry ACN with 1 mol % of CBZ-2FIQ as photocatalyst for 2 h at room temperature (Table 6.9, entries 5,6). Fluorinated substrates 1b and 1c provide new substrate scope and access to fluorinated p-conjugated molecules that are air-stable and important synthons as organic semiconducting materials. Among all diazonium salts, the most electron-deficient aryl diazonium salt (1c) was found to be most efficient for product formation and delivered highest product yield of 80%. Additionally, the C-H arylation was performed for other heteroarenes such as furan, thienothiophene and 1-methylindole using CBZ-2FIQ as PC with 1a and 1c diazonium salts (Table 6.9, entries 7-10). The C-H arylation of furan using **1a** diazonium salt in ACN produced moderate yield of 55%. The C-H arylation of thienothiophene using 1a delivered mono-substituted arylation of thienothiophene with 50% yield and a similar reaction was also performed with 1c diazonium salt and produced 68% yield. The arylated products for entries 5, 6, 8, 9 in Table 3 are new compounds, not yet reported in literature. Furthermore, this photocatalytic heteroarylation method using DI based TADF compounds have provided access to heteroarylated products based on thienothiophene (entries 8 and 9) that are otherwise difficult to achieve due to difficult synthesis of monosubstituted thienothiophene. Monosubstituted thienothiophenes are very rarely reported



Scheme 6.3. Synthesis scheme of photo-arylation of various heteroarenes under blue LED using CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ as photocatalyst in ACN.

Table 0.7. Optimization of reaction conditions using various photocataryst (1 C) and diazonium s	g various photocatalyst (PC) and diazonium s	photocatal	various p	ions using	condit	reaction	on of	iizati	Optim	.9. (le 6	`abl	Ί
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Entry	PC (1 mol %)	Diazonium Salt	Heteroarenes	Product	Yield [*] (%)
1	CBZ-IQ	1a	Š	Br S	46
2	CBZ-2FIQ	1 a	S	Br	50
3	DI-IQ	1 a	S	Br-	54
4	DI-2FIQ	1 a	S	Br-	43
5	CBZ-2FIQ	1b	Š	► ► ►	64



*Isolated yields after purification by column chromatography using *n*-hexane. #Confirmed by mass-spectrometry.

synthetically in literature although it is a very valuable synthon for organic (opto)electronic material design. In case of arylation of 1-methyl indole, a mixture of regioisomers 2- and 3-substituted arylated indole was obtained with 58% overall yield. Moreover, the PC could be recycled efficiently upto three times without changing in optical properties and chemical structure as shown in Figure 6.16 and ¹H NMR, thereby indicating their good cycle stability.



Figure 6.16. (a) Isolated yields obtained during recycling of **CBZ-2FIQ** in three successive photocatalytic cycles and (b) UV/Vis absorption and emission of **CBZ-2FIQ** before and after photocatalysis reactions.

To confirm the mechanistic pathway of the reactions, control experiments were performed without light, without PC or with radical scavengers such as 2,2,6,6-tetramethylpiperidinoxyl (TEMPO) using **CBZ-2FIQ** as PC with **1a** diazonium salt. Control experiments demonstrated that PC and light are both essential for efficient conversion (Table 6.9, entries 11-13). To confirm the arylation of heteroarenes through radical mechanism, the reaction of diazonium salt **1a** was conducted in presence of TEMPO. A TEMPO adduct (**9** and **10**, Scheme 6.4) was detected after 2 h of reaction irradiation in blue light and was confirmed by high resolution mass spectrometry (Table 6.9). On the basis of control experiments and literature reports, a plausible mechanism was proposed as shown in Scheme 6.4.^{30,43} After photoexcitation of PC, the photocatalysis cycle is initiated by oxidative quenching of PC due to single electron transfer (SET) from excited PC (PC^{*}) to aryl diazonium salt to generate aryl radical (**6**). The aryl radical (**6**) further reacts with heteroarene and forms intermediate **7** which can either transfer an electron to other diazonium salt molecule to initiate radical chain transfer mechanism. Finally, the carbocation intermediate **8** was deprotonated and produced the desired aryl-substituted heteroarene.



Scheme 6.4. Mechanistic pathway of photocatalytic C-H arylation of heteroarenes.

6.2.11. Electroluminescent Properties^a

To explore the potential of CBZ-IQ, DI-IQ and DI-2FIQ compounds in optoelectronic devices, OLEDs were fabricated and evaluated. Our investigation involved fabricating a series of multilayered solution-processed OLED devices using various doping concentrations and host-based strategies, to assess the electroluminescent (EL) characteristics of these compounds. The device was configured with indium tin oxide (ITO) and aluminum (Al) serving as the anode and cathode materials. respectively. Poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS)was utilized as the hole-transporting material, 4,4'-Bis(N-carbazolyl)-1,1'biphenyl(CBP) was employed as the host material, 1,3,5-tris(1-phenyl-1H-benzo[d]imidazole-2yl)beneze (TPBi) functioned as the electron-transporting material, and lithium fluoride (LiF) was used as the electron-injection material. In order to achieve optimal EL performance, a device configuration of ITO (150 nm)/ PEDOT:PSS (40 nm)/ CBP:x wt% CBZ-IQ, DI-IQ, and DI-2FIQ (x=1.0, 3.0, 5.0, 10.0 and neat film) (25 nm)/TPBi (35 nm)/LiF (1 nm)/Al (150 nm)/ TPBi (35 nm)/LiF (1.0 nm)/Al (150 nm) was adopted, as shown in Figure 6.17, to facilitate efficient charge-

^aElectroluminescence studies were performed by Mr. Prakalp Gautam of Prof. Jwo-Huei Jou's group at department of Materials Science and Engineering, National Tsing Hua University, Taiwan.

carrier and exciton generation. The non-doped devices showed inferior electroluminescent (EL) properties and brightness, which may be attributed to an imbalance in charge carrier injection and transportation within the emissive layer.^{44,45} Achieving balanced charge carriers is crucial for improving OLED performance and an effective host-guest energy transfer system can facilitate this. To this end, OLED devices were fabricated using different emitter concentrations within the host matrix. Optimizing the concentration is vital for achieving higher efficiencies, stability, and longevity of OLED devices. The decision to use a CBP host was based on several factors, including its HOMO- LUMO energy level, which are compatible with those of the emitter molecules.



Figure 6.17. (a) Energy-level diagram of the solution-processed OLED devices (b) Current density-voltage-luminance, (c) current efficiency-luminance-power efficiency and (d) electroluminescent spectra (EL) plots of the devices based on emitters **CBZ-IQ**, **DI-IQ** and **DI-2FIQ** at a different doping concentration in CBP host matrix.

Secondly, its bipolar nature helps balance the charge carriers within the emissive layer. Finally, its high triplet energy aids in preventing back-energy transfer from the dopant.⁴⁶ The OLED devices were evaluated using compounds **CBZ-IQ**, **DI-IQ** and **DI-2FIQ** as emitters, with CBP utilized as the host material. The EL spectra, current density-voltage-luminance (J-V-L), and current efficiency-luminance-power efficiency (CE-L-PE) characteristics are provided in Figures 6.17-6.20, while the detailed EL characteristics are summarized in Table 6.10. The **CBZ-IQ** based devices demonstrated excellent device performance, with a maximum current efficiency (CE_{max}) of 2.3 cd/A, external quantum efficiency (EQE_{max}) of 0.8% and luminance (L_{max}) of 3,095 cd/m². Commission Internationale de L'Eclairage (CIE) coordinates of (0.30, 0.50) were achieved,

demonstrating an efficient and stable green OLED device with a maximum EL peaked at 520 nm. Notably, the device exhibited a low turn-on-voltage (V_{on}) of 3.0 V, and even the EL spectra were well-aligned with the solid-state PL of the compound **CBZ-IQ**. This is likely due to the well-aligned energy levels between CBP and **CBZ-IQ**, resulting in efficient injection, migration and balance of charge carriers in the emissive layer (EML), leading to favourable charge-carrier and exciton generation.⁴⁶ Increasing the dopant concentration in the emissive layer of green OLED results in improving the current efficiency of the device. The results show that increasing the dopant concentration can improve the efficiency of exciton generation, leading to a greater number of photons produced per charge carrier injected.⁴⁷ This improvement in exciton generation can ultimately increase the CE_{max} of the OLED.⁴⁸ The dopant molecules in the emissive layer can act as traps for charge carriers, which increases the probability of exciton formation and subsequent radiative recombination. However, the higher dopant concentrations can promote non-radiative decay mechanisms such as quenching and triplet-triplet annihilation.⁴⁹



Figure 6.18. (a) Current density-voltage-luminance, (b) current efficiency-luminance-power efficiency and (c) CIE chromaticity plots of the **CBZ-IQ** at different doping concentrations in the CBP host matrix. The inset device image resembles the green emission of the OLED device.



Figure 6.19. (a) Current density-voltage-luminance, (b) current efficiency-luminance-power efficiency and (c) CIE chromaticity plots of the **DI-IQ** at different doping concentrations in the CBP host matrix. The inset device image resembles the green emission of the OLED device.



Figure 6.20. (a) Current density-voltage-luminance, (b) current efficiency-luminance-power efficiency and (c) CIE chromaticity plots of the **DI-2FIQ** at different doping concentrations in the CBP host matrix. The inset device image resembles the green emission of the OLED device.

Compound	Doping conc. (wt%)	Turn-on voltage ^a (V _{on})	PE _{max} / CE _{max} / EQE _{max} ^b (lm W ⁻¹ / cd A ⁻¹ / %)	PE ₁₀₀ / CE ₁₀₀ / EQE ₁₀₀ ^c (lm W ⁻¹ / cd A ⁻ ¹ / %)	CIE coordinates ^d	Max. Lum. (cd m ⁻²)
	1.0	5.0	0.5/ 1.0/ 1.8	0.3/ 0.7/ 0.8	(0.19, 0.15)	749
	3.0	3.0	0./ 2.1/ 1.0	0.5/ 1.7/ 0.7	(0.28, 0.44)	2,548
CBZ-IQ	5.0	3.0	0.6/ 2.3/ 0.8	0.4/ 1.3/ 0.5	(0.30, 0.50)	3,095
	10.0	4.0	0.6/ 2.3/ 0.7	0.4/ 1.3/ 0.4	(0.31, 0.54)	3,632
	Neat	4.5	-/ -/ -	-/ -/ -	(0.33, 0.57)	952
	1.0	5.0	0.7/ 1.7/ 0.8	0.6/ 1.6/ 0.8	(0.25, 0.33)	1,283
DLIO	3.0	4.0	0.7/ 1.7/ 0.7	0.6/ 1.6/ 0.7	(0.28, 0.40)	1,554
DI-IQ	5.0	3.0	0.8/ 2.0/ 0.8	0.8/ 2.0/ 0.8	(0.28, 0.41)	1,625
	Neat	6.5	-/ -/ -	_/ _/ _	(0.40, 0.39)	24
	1.0	3.0	0.7/ 1.4/ 0.5	0.6/ 1.4/ 0.5	(0.35, 0.48)	1,597
DI-2FIQ	3.0	3.0	0.5/ 1.1/ 0.3	0.5/ 1.1/ 0.3	(0.39, 0.53)	2,471
	5.0	3.0	0.7/ 1.3/ 0.3	0.5/ 1.0/ 0.3	(0.39, 0.54)	3,378
	Neat	4.5	-/ -/ -	-/ -/ -	(0.44, 0.52)	800

Table 6.10. Electroluminescence properties of the **CBZ-IQ**, **DI-IQ** and **DI-2FIQ** based solution-process OLED devices with different doping concentrations in the CBP host matrix.

^aDevice voltage at luminance >1 cdm⁻², ^bMaximum PE, CE, and EQE, ^cPE, CE, and EQE at 100 cdm⁻², ^dCIE coordinates at 100 cdm⁻² Note: the device fabrication was done for three compounds only due to insufficient amount of **CBZ-2FIQ**.

6.3. Conclusions

We have successfully designed and synthesized four new D-A compounds, **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** based on DI and Ph-CBZ donors and IQ derivatives as acceptors. All the molecules exhibited reasonably small ΔE_{ST} , therefore showed efficient TADF properties. The positive solvatochromic study of all compounds indicated that the emission bands in long

wavelength regions arose due to CT from donor to acceptor. All TADF molecules showed efficient solid-state emission and showed enhancement of emission intensity with the formation of aggregates due to an increase in water percentage in THF solution. Green OLED devices were fabricated using **CBZ-IQ DI-IQ** and **DI-2FIQ** TADF molecules as emitters. Additionally, all the molecules **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** were utilized as efficient photocatalysts in PEnT and photoredox reactions. The isomerization of stilbene has been utilized as PEnT and the conversion of \sim 90% after 30 h was achieved from E to Z-stilbene. And the C-H arylation of heteroarenes has been utilized as photoredox reaction where the oxidative quenching of PC occurred and the formed aryl radical reacted with heteroarene and a maximum of 80% product was observed after 2 h using blue light in ACN. Further applications of these compounds in other types of photocatalytic reactions and improvement in device design are envisaged as future directions of this work.

6.4. Experimental Section



Synthesis of IQ and 2F-IQ:

Scheme 6.5. Synthesis scheme of compound IQ and 2F-IQ.37

A mixture of 5-bromoisatin (1 g, 4.42 mmol) and *o*-phenylenediamine or 1,2-Diamino-4,5difluorobenzene (500 mg, 2.43 mmol) in acetic acid was refluxed for 24 h. Then the reaction mixture was cooled and added in ice-cold water. The formed solid precipitate was filtered off and washed with water. Then the precipitate was dried and used for further reaction.

Synthesis of IQ: In a solution of **1** (100 mg, 0.335 mmol) and potassium carbonate (186 mg, 1.342 mmol) in anhydrous 10 mL DMF, 1-bromohexane (0.1 mL, 0.67 mmol) was added and then heated at 140 °C overnight. Subsequently, the reaction mixture was cooled and stirred for 2 h in binary

mixture of H₂O:MeOH (1:1). The yellow precipitate was formed and filtered via suction filtration and washed with water and then dried. A yellow color solid was obtained with 70% yield.

¹**H NMR (400 MHz, CDCl₃) (IQ):** δ (ppm) 8.58 (d, J = 4 Hz, 1 H), 8.28 (dd, J = 8 Hz, 1.1 Hz, 1 H), 8.13 (dd, J = 8 Hz, 1.1 Hz, 1 H), 7.81 – 7.74 (m, 2 H), 7.69 (td, J = 8 Hz, 8 Hz, 1.3 Hz, 1 H), 7.34 (d, J = 8 Hz, 1 H), 4.44 (t, J = 8 Hz, 2 H), 1.96 – 1.89 (m, 2 H), 1.42 – 1.27 (m, 6 H), 0.88 (t, J = 8 Hz, 3 H).

Synthesis of 2F-IQ: In a solution of **2** (100 mg, 0.3 mmol) and potassium carbonate (166 mg, 1.2 mmol) in anhydrous 10 mL DMF, 1-bromohexane (0.09 mL, 0.6 mmol) was added and then heated at 140 °C overnight. Then the reaction mixture was cooled and stirred for 2 h in binary mixture of H₂O:MeOH (1: 1). A yellow precipitate was formed and filtered via suction filtration and washed with water and then dried. A yellow color solid was obtained with 68% yield.

¹**H** NMR (400 MHz, CDCl₃) (IQ): δ (ppm) 8.51 (d, J = 4 Hz, 1 H), 7.97 (dd, J = 8 Hz, 8 Hz, 1 H), 7.83 (dd, J = 8 Hz, 8 Hz, 1 H), 7.76 (dd, J = 8 Hz, 1.7 Hz, 1 H), 7.34 (d, J = 8 Hz, 1 H), 4.41 (t, J = 8 Hz, 2 H), 1.94-1.87 (m, 2 H), 1.38 – 1.28 (m, 6 H), 0.86 (t, J = 8 Hz, 3 H).

Synthesis of 10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (3):



Scheme 6.6. Synthesis scheme of compound 3.³⁸

A solution of 2-indolinone (2 g, 15 mmol) in POCl₃ (10 mL) was heated at 100 °C for overnight. Then, the reaction mixture was poured into ice and neutralized carefully with KOH. After neutralization, the precipitate was filtered and dried. The compound was separated by column chromatography using ethyl acetate and hexane (20/80, v/v) as eluent. Further, the compound was purified by recrystallization in acetone and hexane mixture and pale-yellow solid was obtained with 60% yield.

¹**H NMR (400 MHz, DMSO):** *δ* (ppm) 11.88 (s, 3 H), 8.67 (d, *J* = 8 Hz, 3 H), 7.72 (d, *J* = 8 Hz, 3 H), 7.41-7.31 (m, 6 H).

5,10-Bis(4-(tert-butyl)phenyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (DI):



Scheme 6.7. Synthesis scheme of DI.³⁹

Compound **3** (200 mg, 0.579 mmol) and 4-tert-butyliodobenzene (316 mg, 1.216 mmol) were dissolved in 1,4-dioxane and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, $Pd(OAc)_2$ (5.2 mg, 0.023 mmol), tri-tert-butylphosphine tetrafluoroborate (25 mg, 0.087 mmol) and potassium tert-butoxide (260 mg, 2.316 mmol) were taken and simultaneously DI and compound **3** were added and heated at 100 °C for 18 h. The reaction was cooled and diluted with DCM and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using ethyl acetate and hexane (5/95, v/v) as eluent and off-white solid was obtained with 30% yield.

¹**H NMR (400 MHz, DMSO**): δ (ppm) 11.95 (s, 1 H), 8.83 (d, *J* = 8.0 Hz, 1 H), 7.74 (dd, *J* = 4 Hz, 4 Hz, 4 H), 7.65 (t, *J* = 8 Hz, 3 H), 7.58 (d, *J* = 8 Hz, 2 H), 7.49 – 7.37 (m, 3 H), 7.22 – 7.11 (m, 3 H), 6.66 – 6.56 (m, 2 H), 5.76 (d, *J* = 8 Hz, 1 H), 5.54 (d, *J* = 8 Hz, 1 H), 1.48 (s, 18 H).

Synthesis of 3,6-dibromo-9H-carbazole (4) and 3,6-diphenyl-9H-carbazole (Ph-CBZ):



Scheme 6.8. Synthesis scheme of compound 4 and Ph-CBZ.⁴⁰

To a stirred solution of carbazole (1 g, 0.005 mmol) in dry dimethylformamide (DMF) (25 mL), a solution of N-bromosuccinimide (2.31 g, 0.012 mmol) in dry DMF (20 mL) was added slowly at 0 °C. The mixture was stirred for 24 h at room temperature. The reaction mixture was then poured into water and extracted with dichloromethane (DCM). Subsequently, the organic layer was washed three times with water and dried over anhydrous sodium sulphate (Na₂SO₄). After filtration and evaporation, the crude product was purified by silica gel chromatography using hexane/DCM (5:1, v/v), recrystallization from ethanol and then dried under vacuum to afford compound **4** as a grey solid in 80% yield.

¹**H NMR (400 MHz, DMSO**) δ (ppm): 11.61 (s, 1 H), 8.43 (d, *J* = 4 Hz, 2 H), 7.54 (d, *J* = 4 Hz, 1 H), 7.52 (d, *J* = 4 Hz, 1 H), 7.48 (s, 1 H), 7.46 (s, 1 H).

Synthesis of 3,6-diphenyl-9H-carbazole (Ph-CBZ):

Compound **4** (500 mg, 1.538 mmol) and phenylboronic acid (470 mg, 3.846 mmol) were dissolved in 20 mL dry 1,4-dioxane and the solution was subjected to three cycles of freeze-pump-thaw. In a two-neck round-bottomed flask, Pd(PPh₃)₄ (72 mg, 0.061 mmol) was taken and the degassed solution was added to the flask and simultaneously 2 M solution of K₂CO₃ was added and stirred for 24 h at 80 °C. The reaction mixture was cooled and diluted with ethyl acetate and washed with saturated brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using ethyl acetate and hexane (10/90, v/v) as eluent. The white solid was obtained from the column which was further dissolved in minimum amount of DCM and recrystallized by adding *n*-hexane and white solid was obtained with 60% yield.

¹**H** NMR (400 MHz, CDCl₃) δ (ppm): 8.35 (d, J = 4 Hz, 2 H), 8.13 (s, 1 H), 7.74-7.69 (m, 6 H), 7.50 (q, J = 8 Hz, 6 H), 7.37 – 7.33 (m, 2 H).

Synthesis of DI-IQ and DI-2FIQ:



Scheme 6.9. Synthesis scheme of compound DI-IQ.¹⁶

DI-IQ: Compounds **DI** (317 mg, 0.52 mmol) and **IQ** (200 mg, 0.52 mmol) were dissolved in Tol and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, $Pd_2(dba)_3$ (24 mg, 0.026 mmol), tri-tert-butylphosphine tetrafluoroborate (23 mg, 0.078 mmol) and sodium tert-butoxide (250 mg, 2.6 mmol) were taken and simultaneously **DI** and **IQ** were added and heated at 110 °C for 12 h. The reaction was cooled and diluted with ethyl acetate and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using ethyl acetate and hexane (10/90, v/v) as eluent. Yellow color solid was obtained with 60% yield.

¹**H** NMR (400 MHz, CDCl₃) (DI-IQ): δ (ppm) 8.88 (d, J = 2.0 Hz, 1 H), 8.27 (dd, J = 8 Hz, 1.1 Hz, 1 H), 8.21 (dd, J = 8, 1.0 Hz, 1 H), 7.87 – 7.79 (m, 2 H), 7.72 – 7.60 (m, 10 H), 7.39 (dd, J = 8 Hz, 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 1 H), 7.20 – 7.13 (m, 2 H), 7.04 – 7.00 (m, 1 H), 6.75 – 6.70 (m, 2 H), 6.45 (td, J = 8 Hz, 1 H), 6.07 (d, J = 8 Hz, 1 H), 5.91 (dd, J = 8 Hz, 4 Hz, 2 H), 4.74- 4.67 (m, 1 H), 4.60 – 4.53 (m, 1 H), 2.10- 2.03 (m, 2 H), 1.51 (d, J = 4 Hz, 18 H), 1.46 – 1.28 (m, 6 H), 0.90 (t, J = 8 Hz, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 151.81, 146.26, 141.47, 139.64, 139.50, 138.07, 138.04, 137.90, 134.36, 129.49, 129.22, 128.82, 127.95, 126.91, 126.87, 126.32, 122.98, 122.90, 122.79, 122.69, 122.29, 122.23, 120.32, 119.62, 110.71, 109.92, 109.89, 109.86, 35.00, 35.00, 31.60, 28.48, 26.79, 22.61, 14.11.

MS (**HRMS-ESI**): Calculated for C₆₄H₅₈N₆ [M+H]⁺: 911.4778; found 911.4758.



Scheme 6.10. Synthesis scheme of compound DI-2FIQ.¹⁶

DI-2FIQ: Compound **DI** (70 mg, 0.115 mmol) and compound **2F-IQ** (48 mg, 0.115 mmol) were dissolved in Tol and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, $Pd_2(dba)_3$ (5 mg, 0.005 mmol), tri-tert-butylphosphine tetrafluoroborate (5 mg, 0.017 mmol) and sodium tert-butoxide (55 mg, 0.575 mmol) were taken and simultaneously **DI** and **2F-IQ** were added and heated at 110 °C for 12 h. The reaction was cooled and diluted with ethyl acetate and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using ethyl acetate and hexane (10/90, v/v) as eluent and a yellow solid was obtained with 55% yield.

¹**H NMR (400 MHz, CDCl₃):** δ (ppm) 8.83 (d, J = 1.9 Hz, 1 H), 8.02 – 7.87 (m, 3 H), 7.69- 7.61 (m, 9 H), 7.37 (t, J = 8 Hz, 2 H), 7.31 (d, J = 8 Hz, 1 H), 7.16 (m, 2 H), 7.03 (t, J = 8 Hz, 1 H), 6.75 – 6.71 (m, 2 H), 6.46 (t, J = 8 Hz, 1 H), 6.05 (d, J = 8 Hz, 1 H), 5.91 (dd, J = 4 Hz, 2 H), 4.71-4.63 (m, 1 H), 4.57-4.50 (m, 1 H), 2.05 (m, 2 H), 1.57 (s, 4 H), 1.51 (d, J = 2.8 Hz, 18 H), 1.37 – 1.32 (m, 2 H), 0.90 (t, J = 7.2 Hz, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 151.97, 138.24, 138.18, 138.12, 134.79, 131.85, 128.93, 127.04, 127.02, 126.99, 126.96, 126.93, 123.13, 123.09, 122.98, 122.95, 122.89, 122.85, 122.23,

120.14, 120.06, 119.78, 119.64, 110.98, 110.11, 110.00, 109.90, 42.01, 35.14, 31.73, 31.66, 28.59, 26.90, 22.73, 14.22.

MS (**HRMS-ESI**): Calculated for $C_{64}H_{56}F_2N_6$ [M+H]⁺: 947.4578; found 947.4551.

Synthesis of CBZ-IQ and CBZ-2FIQ:



Scheme 6.11. Synthesis scheme of compound CBZ-IQ.¹⁶

CBZ-IQ: Compound **Ph-CBZ** (166 mg, 0.52 mmol) and compound **IQ** (200 mg, 0.52 mmol) were dissolved in Tol and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, Pd₂(dba)₃ (24 mg, 0.026 mmol), tri-tert-butylphosphine tetrafluoroborate (23 mg, 0.078 mmol) and sodium tert-butoxide (250 mg, 0.26 mmol) were taken and simultaneously **Ph-CBZ** and **IQ** were added and heated at 110 °C for 12 h. The reaction was cooled and diluted with ethyl acetate and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using ethyl acetate and hexane (10/90, v/v) as eluent. Yellow color solid was obtained with 60% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.74 (d, *J* = 1.9 Hz, 1 H), 8.45 (d, *J* = 1.4 Hz, 2 H), 8.30 (dd, *J* = 8 Hz, 1.9 Hz, 1 H), 8.20 (d, *J* = 8 Hz, 1.9 Hz, 1 H), 7.90 (dd, *J* = 8 Hz, 2.0 Hz, 1 H), 7.81 (td, *J* = 8 Hz, 1.9 Hz, 1 H), 7.75 (t, *J* = 8 Hz, 5 H), 7.71 – 7.68 (m, 3 H), 7.53 – 7.48 (m, 6 H), 7.37 (t, *J* = 8 Hz, 2 H), 4.60 (t, *J* = 8 Hz, 2 H), 2.10 – 2.02 (m, 2 H), 1.54 – 1.33 (m, 6 H), 0.91 (t, *J* = 8 Hz, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 145.61, 143.00, 140.98, 139.50, 138.75, 133.45, 129.56, 129.24, 128.00, 126.32, 125.51, 121.19, 113.61, 111.08, 41.69, 31.58, 28.52, 26.82, 22.67, 14.16.
MS (HRMS-ESI): Calculated for C₄₄H₃₆N₄ [M+H]⁺: 621.2978; found 621.2902.



Scheme 6.12. Synthesis scheme of compound CBZ-2FIQ.¹⁶

CBZ-2FIQ: Compound **Ph-CBZ** (50 mg, 0.156 mmol) and compound **2F-IQ** (65 mg, 0.156 mmol) were dissolved in Tol and degassed by freeze-pump-thaw method. In a two-neck round bottomed flask, Pd₂(dba)₃ (7 mg, 0.007 mmol), tri-tert-butylphosphine tetrafluoroborate (7 mg, 0.023 mmol) and sodium tert-butoxide (75 mg, 0.78 mmol) were taken and simultaneously **Ph-CBZ** and **IQ** were added and heated at 110 °C for 12 h. The reaction was cooled and diluted with ethyl acetate and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using ethyl acetate and hexane (10/90, v/v) as eluent. Yellow color solid was obtained with 55% yield.

¹**H** NMR (400 MHz, CDCl₃): δ (ppm) 8.72 (d, J = 2.0 Hz, 1 H), 8.45 (d, J = 1.5 Hz, 2 H), 8.03 (dd, J = 8 Hz, 8 Hz, 1 H), 7.96 – 7.91 (m, 2 H), 7.78 – 7.75 (m, 5 H), 7.73 – 7.69 (m, 2 H), 7.54 – 7.49 (m, 6 H), 7.39 (t, J = 8 Hz, 2 H), 4.58 (t, J = 8 Hz, 2 H), 2.05 (p, J = 8 Hz, 2 H), 1.53 – 1.34 (m, 6 H), 0.93 (t, J = 8 Hz, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 143.25, 142.01, 141.48, 133.86, 130.41, 128.96, 127.47, 126.78, 125.87, 124.11, 121.75, 120.46, 119.08, 111.07, 110.18, 42.01, 31.63, 28.71, 26.93, 22.74, 14.21.

MS (**HRMS-ESI**): Calculated for C₄₄H₃₄F₂N₄ [M+H]⁺: 657.2878; found 657.2781.

Synthesis aryl diazonium tetrafluoroborates

General procedure for the preparation of aryl diazonium tetrafluoroborates.³⁰

To the solution of appropriate aniline (5 mmol) in 2 mL distilled water 50% hydrofluoroboric acid (1.5 mL) was added and then after cooling the reaction mixture at 0 °C, sodium nitrite (0.35 g in 1 mL water) solution was added dropwise in 5 min. interval of time. The reaction mixture was stirred

for 30-40 minutes at same temperature and then the formed precipitate was collected by filtration. The precipitate was re-dissolved in minimum amount of acetone and then diethyl ether was added to the solution until the formation of precipitation of diazonium salt. The formed precipitate was washed several times by diethyl ether and dried under vacuum.

Synthesis scheme of 1a:



¹**H NMR (400 MHz, DMSO-***d*₆): δ (ppm) 8.58 (d, J = 9.0 Hz, 2 H), 8.26 (d, J = 9.0 Hz, 2 H).

Synthesis scheme of 1b:



¹**H NMR (400 MHz, DMSO-***d*₆) δ (ppm) 8.64 (dd, J = 5.7, 2.4 Hz, 2 H), 8.44 (tt, J = 8 Hz, 2.4 Hz, 2.4 Hz, 2 H)

Hz, 1 H).

Synthesis scheme of 1c:



¹**H NMR (400 MHz, DMSO-***d*₆) δ (ppm) 9.51 (s, 2 H), 9.18 (s, 1 H).

Synthesis of 1-methyl indole (1d):



Sodium hydride (60% in mineral oil, 15 mmol, 1.5 equiv.) was added to a solution of indole (10 mmol, 1.0 equiv.) in THF at 0 °C and then the reaction mixture was allowed to room temperature and stirred for 30 minutes. Then the reaction mixture was again cooled to 0 °C and methyl iodide (12 mmol, 1.2 equiv.) was added dropwise and then reaction mixture was stirred at room temperature until the reaction was completed. After monitoring by TLC, the reaction mixture was cooled to 0 °C and quenched with saturated ammonium chloride solution and extracted by diethyl ether. The compound was purified by column chromatography using ethyl acetate and hexane (10/90, v/v) as eluent and an oily compound was obtained with 90% yield.

¹**H NMR (400 MHz, CDCl₃)** δ (ppm) 7.73 (d, *J* = 7.9 Hz, 1 H), 7.43 – 7.38 (m, 1 H), 7.35 – 7.29 (m, 1 H), 7.20 (td, *J* = 7.5 Hz, 7.1 Hz, 1.0 Hz, 1 H), 7.11 (d, *J* = 3.1 Hz, 1 H), 6.59 – 6.56 (m, 1 H), 3.83 (s, 3 H).

General procedure for the reaction of aryl diazonium tetrafluoroborates with heteroarene:

The compounds aryl diazonium tetrafluoroborate (1 equiv.), photocatalyst (0.01 equiv.) and thiophane or furan (5 equiv.) were dissolved in dry ACN in a Schlenk tube and the resulting mixture was degassed by freeze-pump-thaw method. The reaction mixture was irradiated by blue LED light and stirred at room temperature for 2 h in N₂ atmosphere. Then the reaction mixture was diluted with ethyl acetate and washed with brine solution. The organic layer was dried over sodium sulphate and concentrated at rotary evaporator. The compound was purified by column chromatography using *n*-hexane as eluent.

2-(4-bromophenyl)thiophene (1P):



¹**H NMR (400 MHz, CDCl**₃) δ (ppm) 7.51 (d, *J* = 4 Hz, 4 H), 7.32 (d, *J* = 4 Hz, 2 H), 7.11 (t, *J* = 4 Hz, 1 H).

2-(3,5-difluorophenyl)thiophene (2P):



¹**H NMR (400 MHz, CDCl**₃) δ (ppm) 7.34 (t, J = 4 Hz, 2 H), 7.11 (t, J = 8 Hz, 3 H), 6.72 (t, $J = 10^{-1}$

8 Hz, 1 H).

2-(3,5-bis(trifluoromethyl)phenyl)thiophene (3P):



¹**H NMR (400 MHz, CDCl₃)** δ (ppm) 8.00 (s, 2 H), 7.77 (s, 1 H), 7.43 (dd, J = 8 Hz, 4 Hz, 2 H),

7.15 (t, J = 4 Hz, 1 H).

2-(4-bromophenyl)furan (4P):



¹**H NMR (400 MHz, CDCl**₃) δ (ppm) 7.52 (q, J = 8 Hz, 4 H), 7.47 (m, J = 4 Hz, 1 H), 6.65 (d, J = 4 Hz, 1 H), 6.48 (dd, J = 4 Hz, 1 H).

2-(4-bromophenyl)thieno[3,2-b]thiophene (5P):



¹**H NMR (400 MHz, CD₂Cl₂)** δ (ppm) 7.53 (s, 5 H), 7.42 (d, *J* = 5.0 Hz, 1 H), 7.28 (d, *J* = 4.8 Hz, 1 H).

2-(3,5-bis(trifluoromethyl)phenyl)thieno[3,2-b]thiophene (6P):



¹**H** NMR (400 MHz, CD₂Cl₂) δ (ppm) 8.01 (s, 2H), 7.78 (s, 1H), 7.64 (s, 1H), 7.49 – 7.43 (m, 1H), 7.29 (d, J = 4.7 Hz, 1H).

3-(4-bromophenyl)-1-methyl-1H-indole (7P):



¹**H** NMR (400 MHz, CD₂Cl₂) δ (ppm) 8.63 (d, J = 8 Hz, 1 H), 7.63 (dd, J = 12 Hz, 8 Hz, 3 H), 7.50 (dd, J = 12 Hz, 8 Hz, 6 H), 7.37 (dt, J = 12 Hz, 8 Hz, 4 H), 7.25 – 7.17 (m, 3 H), 6.57 (d, J = 8 Hz, 1 H), 3.96 (s, 3 H), 3.85 (s, 3 H).

TEMPO Adducts (8P and 9P):



HRMS: Calculated for **8P**: 312.0962; found: 312.1136 and calculated for **9P**: 396.0996; found: 396.2120.

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Appendix of Chapter 6

a. ¹H and ¹³C NMR spectra

¹H NMR spectra of IQ





¹H NMR spectra of DI



¹H NMR spectra of 4



¹H NMR spectra of Ph-CBZ



¹H NMR spectra of DI-IQ



¹³C NMR spectra of DI-IQ




¹³C NMR spectra of DI-2FIQ





¹³C NMR spectra of CBZ-IQ



150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 f1 (ppm)



¹³C NMR spectra of CBZ-2FIQ







¹H-NMR spectra of isomerization of stilbene using CBZ-2FIQ as PC



^{7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60 6.55 6.50 6.45 6.40 6.35 6.30} f1 (ppm)



¹H-NMR spectra of isomerization of stilbene using DI-IQ as PC

¹H-NMR spectra of isomerization of stilbene using DI-2FIQ as PC



^{7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60 6.55 6.50 6.45 6.40 6.35 6.30} f1 (ppm)

¹H-NMR spectra of arylation of heteroarenes (electron transfer reactions)

¹H NMR spectra of 1a







¹H NMR spectra of 1c



¹H NMR spectra of 1d





¹H NMR spectra of 1P







¹H NMR spectra of 3P









¹H NMR spectra of 6P

R 8.01 **R** 7.47 **R** 7.47 7.47 7.47 7.47 7.47 7.45 7.46 7.46 7.46 7.46 7.29





¹H NMR spectra of CBZ-2FIQ, Before and After Photocatalysis



b. Frequencies and Coordinates of DFT Optimized Geometries

Table	6.11.	Results	of	first	three	frequencies	and	molecular	symmetries	calculated	from	geometry
optimi	zation	of CBZ-	IQ	, CBZ	2-2FI(), DI-IQ and	DI-	2FIQ.				

		Compounds	Symmetry	First Three	e Frequencies		
	_			9	0.97	-	
		CBZ-IQ	C_1	15	5.77		
				25	5.57		
				8	3.73		
		CBZ-2FIQ	C_1	14	4.52		
				24	4.12		
			~	1(0.50		
		DI-IQ	C_1	1:	5.16		
				10	0.97		
		DI-2FIO	\mathbf{C}_{1}	14	4 44		
		21 2		1:	5.90		
	_					-	
Coo	rdinates	of geometry	optimized	С	3.43214	-1.44704	-1.58818
stru	cture of CB	Z-IQ		Ν	4.80239	-1.66516	-1.71952
С	8.89036	0.60864	2.02337	С	1.86935	-0.27997	-0.11731
С	7.94029	1.27265	2.83880	C	0.82291	-0.74084	-0.92057
С	6.59745	1.19046	2.54855	C C	1 08978	-1 54578	-2 04564
С	6.14640	0.44138	1.43142	C	2 20072	1.01914	2.04504
С	7.11341	-0.23337	0.60303	C	2.30073	-1.91014	-2.38013
С	8.48808	-0.12744	0.93087	С	5.45309	-2.45077	-2.74906
N	4 80398	0 38335	1 17537	Ν	-0.52193	-0.39569	-0.60966
C	1 16855	0.32067	0 12458	С	-1.55652	-1.29592	-0.34030
C	4.40055	-0.52907	0.12430	С	-2.74943	-0.57155	-0.09141
C	5.45208	-1.00095	-0.69681	С	-2.41621	0.83414	-0.20863
Ν	6.74370	-0.97227	-0.48936	С	-1.03776	0.90157	-0.53205
С	3.17593	-0.62389	-0.45992	a	0 1 55 40	a 01101	0.00010

С

-3.15768

2.01181

-0.08810

С	-2.54144	3.25335	-0.28922	Н	-8.44194	-5.36216	1.45756
С	-1.16621	3.28404	-0.61967	С	-3.31449	4.51534	-0.16157
С	-0.40439	2.12770	-0.74663	С	-3.08812	5.59599	-1.03145
С	-1.52962	-2.69067	-0.26974	С	-4.29726	4.66404	0.83229
С	-2.71504	-3.34967	0.03742	С	-3.81497	6.77930	-0.91167
С	-3.92505	-2.65850	0.28083	Н	-2.35287	5.49628	-1.82443
С	-3.92574	-1.25929	0.21568	С	-5.02806	5.84515	0.94941
Н	5.84734	1.68796	3.15472	Н	-4.47003	3.85393	1.53457
Н	9.20058	-0.64274	0.29492	С	-4.78987	6.90974	0.07868
Н	1.66939	0.32839	0.75796	Н	-3.62602	7.59768	-1.60078
Н	0.25729	-1.87429	-2.65889	Н	-5.77755	5.93771	1.73042
Н	2.57357	-2.54228	-3.25377	Н	-5.35723	7.83112	0.17132
Н	5.11158	-3.49118	-2.72158	Н	-2.71670	-4.43474	0.06846
Н	5.25264	-2.03675	-3.74319	Н	-0.61681	-3.24690	-0.45306
Н	6.52628	-2.42113	-2.55887	Н	-4.83615	-0.70896	0.43349
Н	-4.21971	1.96534	0.13343	Н	9.94656	0.68271	2.26495
Н	-0.68144	4.24587	-0.75422	Н	8.27761	1.84780	3.69559
Н	0.64972	2.18229	-0.99546	Coord	linates of	geometry	optimized
С	-5.16798	-3.40528	0.60327	struct	ure of CBZ-	2FIQ	
С	-6.41346	-2.98621	0.10442	C	-8.49637	0.27727	-1.34614
С	-5.13579	-4.55025	1.41801	C	-7.62029	1.00616	-2.18822
С	-7.58160	-3.68203	0.41121	C	-6.26699	0.97278	-1.98964
Н	-6.46010	-2.12100	-0.55025	C	-5.72991	0.19885	-0.92718
С	-6.30286	-5.24954	1.72105	C	-6.62249	-0.54259	-0.07086
Н	-4.18965	-4.87842	1.83810	С	-8.01885	-0.48133	-0.31037
С	-7.53231	-4.81839	1.22023	Ν	-4.37639	0.18318	-0.75129
Н	-8.53117	-3.34154	0.00789	С	-3.95331	-0.55452	0.25106
Н	-6.25252	-6.12743	2.35908	C	-4.86180	-1.29206	1.10060
				Ν	-6.16484	-1.30453	0.96733

С	-2.61958	-0.81943	0.74830	Н	-4.31448	-3.83869	3.00456
С	-2.77961	-1.69201	1.85671	Н	-4.44802	-2.42870	4.08781
Ν	-4.13195	-1.96711	2.05754	Н	-5.77496	-2.82004	2.96626
С	-1.34825	-0.41346	0.34470	Н	4.62668	2.07118	-0.17757
С	-0.24097	-0.86256	1.06880	Н	1.05912	4.18364	0.96993
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н н н н	-5.79907 -7.10474 2.28446 0.64013	-0.11693 -1.06355 4.05231 5.82700	4.24870 3.49252 -1.34019 -1.73862	Coor struc C C	dinates of ture of DI-21 10.07544 9.40785	geometry FIQ -0.20545 0.24972	optimized 0.85206 2.01580
н н н н	-5.79907 -7.10474 2.28446 0.64013 -1.77570	-0.11693 -1.06355 4.05231 5.82700 5.44289	4.24870 3.49252 -1.34019 -1.73862 -1.31400	Coor struc C C C	dinates of ture of DI-21 10.07544 9.40785 8.05485	geometry FIQ -0.20545 0.24972 0.45373	optimized 0.85206 2.01580 2.01374
н н н н н н	-5.79907 -7.10474 2.28446 0.64013 -1.77570 -2.57593	-0.11693 -1.06355 4.05231 5.82700 5.44289 3.21844	4.24870 3.49252 -1.34019 -1.73862 -1.31400 -0.56025	Coor struc C C C C	dinates of ture of DI-21 10.07544 9.40785 8.05485 7.30693	geometry FIQ -0.20545 0.24972 0.45373 0.20721	optimized 0.85206 2.01580 2.01374 0.83226
н Н Н Н Н Н	-5.79907 -7.10474 2.28446 0.64013 -1.77570 -2.57593 1.12979	-0.11693 -1.06355 4.05231 5.82700 5.44289 3.21844 -5.42686	4.24870 3.49252 -1.34019 -1.73862 -1.31400 -0.56025 0.14899	Coor struc C C C C C	dinates of ture of DI-21 10.07544 9.40785 8.05485 7.30693 7.98744	geometry FIQ -0.20545 0.24972 0.45373 0.20721 -0.25590	optimized 0.85206 2.01580 2.01374 0.83226 -0.35160
н Н Н Н Н Н Н	-5.79907 -7.10474 2.28446 0.64013 -1.77570 -2.57593 1.12979 -1.30358	-1.80732 -0.11693 -1.06355 4.05231 5.82700 5.44289 3.21844 -5.42686 -5.91430	4.24870 3.49252 -1.34019 -1.73862 -1.31400 -0.56025 0.14899 0.03214	Coor struc C C C C C C C	dinates of ture of DI-21 10.07544 9.40785 8.05485 7.30693 7.98744 9.39082	geometry FIQ -0.20545 0.24972 0.45373 0.20721 -0.25590 -0.45491	optimized 0.85206 2.01580 2.01374 0.83226 -0.35160 -0.30790
н Н Н Н Н Н Н Н	-5.79907 -7.10474 2.28446 0.64013 -1.77570 -2.57593 1.12979 -1.30358 -2.94413	-1.80732 -0.11693 -1.06355 4.05231 5.82700 5.44289 3.21844 -5.42686 -5.91430 -4.05660	4.24870 3.49252 -1.34019 -1.73862 -1.31400 -0.56025 0.14899 0.03214 -0.11145	Coor struc C C C C C C C N	dinates of ture of DI-21 10.07544 9.40785 8.05485 7.30693 7.98744 9.39082 5.95846	geometry FIQ -0.20545 0.24972 0.45373 0.20721 -0.25590 -0.45491 0.41880	optimized 0.85206 2.01580 2.01374 0.83226 -0.35160 -0.30790 0.85802
н Н Н Н Н Н Н Н	-5.79907 -7.10474 2.28446 0.64013 -1.77570 -2.57593 1.12979 -1.30358 -2.94413 -2.20275	-1.80732 -0.11693 -1.06355 4.05231 5.82700 5.44289 3.21844 -5.42686 -5.91430 -4.05660 -1.72351	4.24870 3.49252 -1.34019 -1.73862 -1.31400 -0.56025 0.14899 0.03214 -0.11145 -0.12589	Coor struc C C C C C C C N C	dinates of ture of DI-21 10.07544 9.40785 8.05485 7.30693 7.98744 9.39082 5.95846 5.33360	geometry FIQ -0.20545 0.24972 0.45373 0.20721 -0.25590 -0.45491 0.41880 0.16914	optimized 0.85206 2.01580 2.01374 0.83226 -0.35160 -0.30790 0.85802 -0.27113
н Н Н Н Н Н Н Н Н	-5.79907 -7.10474 2.28446 0.64013 -1.77570 -2.57593 1.12979 -1.30358 -2.94413 -2.20275 6.73925	-1.80752 -0.11693 -1.06355 4.05231 5.82700 5.44289 3.21844 -5.42686 -5.91430 -4.05660 -1.72351 2.16128	4.24870 3.49252 -1.34019 -1.73862 -1.31400 -0.56025 0.14899 0.03214 -0.11145 -0.12589 0.17484	Coor struc C C C C C C C N C C	dinates of ture of DI-21 10.07544 9.40785 8.05485 7.30693 7.98744 9.39082 5.95846 5.33360 6.03153	geometry FIQ -0.20545 0.24972 0.45373 0.20721 -0.25590 -0.45491 0.41880 0.16914 -0.29435	optimized 0.85206 2.01580 2.01374 0.83226 -0.35160 -0.30790 0.85802 -0.27113 -1.45066
н Н Н Н Н Н Н Н Н Н	-5.79907 -7.10474 2.28446 0.64013 -1.77570 -2.57593 1.12979 -1.30358 -2.94413 -2.20275 6.73925 8.33854	-1.80752 -0.11693 -1.06355 4.05231 5.82700 5.44289 3.21844 -5.42686 -5.91430 -4.05660 -1.72351 2.16128 0.35762	4.24870 3.49252 -1.34019 -1.73862 -1.31400 -0.56025 0.14899 0.03214 -0.11145 -0.12589 0.17484 0.78249	Coor struc C C C C C C N C N C N	dinates of ture of DI-21 10.07544 9.40785 8.05485 7.30693 7.98744 9.39082 5.95846 5.33360 6.03153 7.32197	geometry FIQ -0.20545 0.24972 0.45373 0.20721 -0.25590 -0.45491 0.41880 0.16914 -0.29435 -0.50978	optimized 0.85206 2.01580 2.01374 0.83226 -0.35160 -0.30790 0.85802 -0.27113 -1.45066 -1.51811
н Н Н Н Н Н Н Н Н Н Н Н	-5.79907 -7.10474 2.28446 0.64013 -1.77570 -2.57593 1.12979 -1.30358 -2.94413 -2.20275 6.73925 8.33854 7.53243	-1.80732 -0.11693 -1.06355 4.05231 5.82700 5.44289 3.21844 -5.42686 -5.91430 -4.05660 -1.72351 2.16128 0.35762 -1.96587	4.24870 3.49252 -1.34019 -1.73862 -1.31400 -0.56025 0.14899 0.03214 -0.11145 -0.12589 0.17484 0.78249 1.11796	Coor struc C C C C C C C N C N C N C	dinates of ture of DI-21 10.07544 9.40785 8.05485 7.30693 7.98744 9.39082 5.95846 5.33360 6.03153 7.32197 3.93578	geometry FIQ -0.20545 0.24972 0.45373 0.20721 -0.25590 -0.45491 0.41880 0.16914 -0.29435 -0.50978 0.26971	optimized 0.85206 2.01580 2.01374 0.83226 -0.35160 -0.30790 0.85802 -0.27113 -1.45066 -1.51811 -0.63423

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Summary

Twisted organic donor-acceptor (D-A) fluorescent molecular rotors (FMRs) are of great importance because of their photophysical properties that are tunable by variations in solvent polarity, temperature, viscosity, and pH. Another class of twisted D-A molecules are characterized by their small singlet-triplet energy gaps that facilitate reverse intersystem crossing (RISC). Such molecules as a result of RISC can exhibit long-lived delayed fluorescence components and show thermally activated delayed fluorescence (TADF) process. This thesis titled "*Twisted Donor-Acceptor Fluorescent Molecular Rotors and Conjugates for Sensing, Photocatalytic and Electroluminescence Applications*" involves the design, synthesis and photophysical studies of organic D-A rotor molecules with twisted intramolecular charge transfer (TICT) and conjugates with TADF properties. The key findings of this thesis are in the following directions:

- Design and synthesis of twisted D-A TICT rotors based on BODIPY and benzodithiophene (BDT) chromophores and TADF conjugates based on diindolocarbazole (DI) electron donors with various acceptors such difluorodibenzophenazine (PF), phenanthroimidazole (PI) and indoloquinoxaline (IQ).
- Photophysical and electrochemical characterization of D-A rotors and conjugates using various steady-state spectroscopic techniques, transient absorption spectroscopy and validation of the results using density functional theory (DFT) and time-dependent DFT calculations.
- Investigation of ratiometric temperature and viscosity sensing, pH sensing, bio-imaging and photocatalysis reactions of the synthesized D-A rotor molecules.
- Utilization of DI based TADF conjugates in energy and electron transfer photocatalysis and in organic light-emitting diodes (OLEDs).

The thesis is divided into seven chapters and the details of each chapter are as follows:

Chapter 1 presents a discussion on the importance and advantages of D-A rotor molecules over heavy atom-free organic chromophores and the different excited state processes involved in such molecules upon photoexcitation. The mechanisms of various photophysical processes such as TICT, aggregate-induced emission (AIE) and TADF have been discussed. Subsequently, structural and optical features of the chromophores that have been used in this thesis are presented. Lastly, literature examples based on some of these chromophores in the areas of sensing, imaging, photocatalysis and OLED applications are discussed. **Chapter 2** provides information on materials used for the synthesis and characterization techniques with the details of these methods used for the characterization of all molecules in this work.

Chapter 3A describes the design and synthesis of three D- π -A molecular rotors/non-rotors, *pp*-**AD** and *pp*-**ADA**, **Me**-*pp*-**ADA** based on BDT donor and BODIPY acceptor (Figure 1) and a biphenyl spacer and explored the influence of π -spacer length and methyl substituents at specific positions in the acceptor backbone on TICT behaviour of these molecules. TICT rotors *pp*-**AD** and *pp*-**ADA** showed near-infrared (NIR) emission (~ 712 nm, ~ 725 nm respectively) with considerably high (pseudo) Stokes shift of upto ~ 208 nm and ~ 221 nm respectively, these values being the highest known for any BODIPY-based compound so far. However, compound **Me**-*pp*-**ADA** with methyl substituents did not show TICT due to the impeded free rotation of the mesophenyl group of the BODIPY and instead exhibited excitation energy transfer with a transfer efficiency of ~ 88% as revealed by steady-state emission and transient absorption spectroscopy. Furthermore, the ratiometric temperature and viscosity sensing and rigidochromic behaviour of these rotors were also analyzed.



Figure 1. Chemical structures of dyad *pp*-AD, triads *pp*-ADA and Me-*pp*-ADA studied in Chapter 3A with their key photophysical features.

and (b) pp-BODIPY, mp-BODIPY, mm-BODIPY, T-BODIPY and T-ADA studied in Chapter 3B.

Chapter 3B describes the synthesis of biphenyl functionalized regioisomeric BODIPYs such as *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY and **T-BODIPY** (thiophene at meso-position) and a triad rotor **T-ADA** (BDT as donor and BODIPY as acceptor, (Figure 2)). Subsequently, photophysical studies and investigation of these rotors as organic photosensitizers (PSs) were

performed. Among all PSs, **T-ADA** showed charge transfer (CT) band at ~ 650 nm and exhibited AIE phenomenon. The singlet oxygen quantum yields (SOQY) for all molecules were calculated and **T-BODIPY** showed SOQY of ~ 77% due to the presence of heavy atom (Br atom at thiophene ring) and CT mediated intersystem crossing (ISC). However, rotor **T-ADA** showed SOQY of ~ 35% due to CT-mediated ISC and such observations were substantiated by transient absorption spectroscopic studies. Due to the efficient generation of ¹O₂ for all compounds, *pp*-BODIPY, *mp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, **T-BODIPY** and **T-ADA** were utilized as photocatalysts in the aerobic photooxidation of thioanisole to methyl phenyl sulfoxide with high selectivity of 99%.



Figure 2. Chemical structures of *pp*-BODIPY, *mp*-BODIPY, *mm*-BODIPY, T-BODIPY and T-ADA studied in Chapter 3B with their key photophysical features and photocatalysis.

Chapter 4 describes the synthesis and investigation of three rotor molecules **AIN**, **AINP** and **F**-**AINP** (Figure 3) based on aminoindole (AI) donor and naphthalimide acceptor. Photophysical and solvatochromic studies for all compounds indicated the formation of a longer wavelength emission band attributed to charge transfer (CT) from AI to naphthalimide. The emission of all rotors was highly sensitive to temperature and viscosity of the solvent and their ratiometric temperature sensing and viscosity sensing properties were analyzed. All rotors were AIE active except **F**-**AINP** due to intramolecular hydrogen bonding between NH- and F at the 7-position of the indole that led to restricted intramolecular rotation and hence distinct photophysical properties. Furthermore, all rotors serve as colorimetric pH sensors where upon lowering of pH (protonation), the intensity of CT band decreased indicating the weakening of CT interactions due to protonation on donor and the spectral changes could be reverted by base addition. Accordingly, rotors **AINP** and **F**-**AINP**

were utilized for live cell imaging on A549 (lung cancer) and L929 (fibroblast) cell lines. The live cell fluorescence microscopic studies therefore revealed the localization of **AINP** and **F-AINP** dyes in the cytoplasmic space of A549 cells.



Figure 3. Chemical structures of the rotors AINP and F-AINP studied in Chapter 4 with their properties and applications.

Chapter 5 describes the synthesis and investigation of two new twisted D-A TADF conjugates **DI-PF** and **DI-PI** (Figure 4) based on DI donor and PF and PI derivatives as acceptors. Triads **DI-PF** and **DI-PI** showed CT bands at ~ 590 nm and at 519 nm with a large Stokes shift of 196 nm and 126 nm respectively. Fluorescence and phosphorescence studies at 77 K for **DI-PF** and **DI-PI** revealed very small to modest ΔE_{ST} values of 0.01 eV and 0.34 eV respectively. Transient photoluminescence decay profiles of **DI-PF** and **DI-PI** showed shorter prompt components of 40



Figure 4. Chemical structures of the TADF conjugates **DI-PF** and **DI-PI** studied in Chapter 5 with their key photophysical features and applications in photocatalysis.

ns and 13.38 ns and longer delayed components of 6.15 μ s and 2.05 μ s respectively confirming the TADF nature for **DI-PF** and **DI-PI**. These combined properties of **DI-PF** and **DI-PI** make them suitable photocatalysts in reactions involving energy transfer and electron transfer pathways. Accordingly, these compounds were employed as photocatalysts in E to Z isomerization of stilbene with a maximum of 66% conversion based on their triplet energy levels and in arylation of various heteroarenes with excellent isolated yields of up to 86% in acetonitrile (ACN).

Chapter 6 describes the synthesis of four twisted D-A TADF conjugates **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** (Figure 5) based on phenyl carbazole (Ph-CBZ) and DI donor and IQ and difluoro-substituted indoloquinoxaline (2FIQ) act as an acceptor. The molecules **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** showed CT bands at ~ 512 nm, 527 nm, 523 nm and 546 nm respectively. Fluorescence and phosphorescence studies at 77 K for **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** revealed ΔE_{ST} values of 0.17 eV, 0.26 eV, 0.17 eV and 0.20 eV respectively. Transient photoluminescence decay profiles of **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** showed shorter prompt components (11.4 ns to 31 ns) and longer delayed components (36.4 ns to 1.5 µs) confirming the TADF nature of all molecules.



Figure 5. Chemical structures of the TADF conjugates CBZ-IQ, CBZ-2FIQ, DI-IQ and DI-2FIQ studied as photocatalysts and emitters for OLEDs in Chapter 6.

Compounds **CBZ-IQ**, **CBZ-2FIQ**, **DI-IQ** and **DI-2FIQ** were employed as photocatalysts in E to Z isomerization of stilbene with up to 90% yield of products and in arylation of various heteroarenes with excellent substrate scope and isolated yields of 80% in ACN. Additionally, solution-processable OLEDs were fabricated using green emitters **CBZ-IQ**, **DI-IQ** and **DI-2FIQ**.

Future Perspective

The thesis involves the design, synthesis, and characterization of D-A fluorescent molecules for sensing, photocatalysis and OLEDs. In Chapters 3 and 4, we have utilized D-A rotor molecules for sensing and imaging. The future advancement of this work will be in the direction of synthesis of new D-A NIR rotors with specific organelle binding groups having sensitivity towards multiple stimuli such as viscosity, temperature, and pH. Such rotors could localize at particular cell organelles and can detect slight changes in the cellular systems. Chapters 5 and 6 involve the design and synthesis of TADF molecules for photocatalysis and OLEDs. The work has provided fundamental understanding of the photophysical properties of TADF molecules that served as efficient photocatalysts for photoinduced electron transfer and photoinduced energy transfer mediated reactions. The future perspectives of this work could be the exploration of newer reactions where these compounds can be utilized as PET or PEnT photocatalysts for reactions such as C-C and C-X bond formation, halogenation, dual photocatalysis, and photopolymerization. Additionally, the incorporation of TADF conjugates as emitters in OLED design and optimization to obtain high device performances are envisaged. Based on this work, design of new TADF materials with better efficiencies and stabilities for TADF-based OLED fabrication devices is expected.

List of Publications

- S. Sharma and S. Sengupta, Twisted organic TADF triads based on a diindolocarbazole donor for efficient photoisomerization of stilbene and photoarylation of heteroarenes. *Org. Chem. Front.*, 2023, 10, 6087-6095. (Featured in 2023 Organic Chemistry Frontiers Hot articles)
- S. Sharma, and S. Sengupta, Diindolocarbazole-based rigid donor-acceptor TADF molecules for energy and electron transfer photocatalysis *Chem. Eur. J.*, 2023, e202303754.
- S. Sharma, S. Chawla, V. Gupta, A. K. De and and S. Sengupta, BODIPY-based regioisomers and donor-acceptor rotor as organic photosensitizers for maximizing singlet oxygen quantum yield and for photooxidation of thioanisole. (*Manuscript under review*, 2023).
- A. Kumari, <u>S. Sharma</u>, and S. Sengupta, Molecular rotors of naphthalimide and benzodithiophene as effective solvent polarity probes, temperature sensors and for g-C₃N₄ sensitization. (*Manuscript under revision*, 2023).
- S. Sharma, S. Srinivas, S. Rakshit, and S. Sengupta, Aminoindole and naphthalimide based charge transfer fluorescent probes for pH sensing and live cell imaging. *Org. Biomol. Chem.*, 2022, 20, 9422-9430.
- R. De, <u>S. Sharma</u>, S. Sengupta, S. K. Pal, Discs to a 'bright' future: exploring discotic liquid crystals in organic light emitting diodes in the era of new-age smart materials. *The Chemical Record*, **2022**, *22*, e202200056.
- Zimu Wei, <u>S. Sharma</u>, Abbey M. Philip, S. Sengupta, and F. C. Grozema, *Phys. Chem. Chem. Phys.*, 2021, 23, 8900-8907.
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- Aswathy P. R.[#], <u>S. Sharma[#]</u>, N. P. Tripathi, S. Sengupta, Regioisomeric BODIPYbenzodithiophene dyads and triads with tunable red emission as ratiometric temperature and viscosity sensors. *Chem. Eur. J.*, **2019**, *25*, 14870-14880. ([#]Equal contribution) (Hot Paper)