Multichromophoric-Catalyst Systems based on Perylene and NaphthalimideTowards Artificial Photosynthesis

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A dissertation submitted for the partial

fulfillment of BS-MS dual degree in science.

Indian Institute of Science Education and Research, Mohali

May 2020

Certificate of Examination

This is to certify that the dissertation titled "**Multichromophoric-Catalyst Systems based on Perylene and NaphthalimideTowards Artificial Photosynthesis"** submitted by Nahas k. (Reg. No. MS15040) for the partial fulfillment of BS- MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Declaration

The work presented in this dissertation 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 acknowledgement of collaborative research and discussions. This thesis is a bonafide 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 project work, I certify that the above statements by the candidate are true to the best of my knowledge.

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Acknowledgement

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Contents

Listof Figures… vi

List of Table…….vii

Listof Scheme..... viii

Listof Abbreviations…..... ix

Abstract… 1

Chapter 1 Introduction… 3

Chapter 2 Result and Discussion…….20

Chapter 3 Summary and Outlook…..... 26

Chapter 4 Experimental Section…..... 28

References……...39

Appendix…….43

List of Figures

Figure 1.1. Z-Scheme of natural photosynthesis

Figure 1.2. Calvin cycle

Figure 1.3. Scheme of artificial photosynthesis

Figure 1.4. (a) Honda-Fujishimaphotoelectrochemical cell **(b)** Grätzel model of photoelectrochemical cell

Figure 1.5. Sequence of water splitting in DSPECs

Figure 1.6. Energy level diagram showing HOMO and LUMO levels of chromophore, oxidation potential of water oxidation catalyst and conduction band of TiO_2.

Figure 1.7. Co-loaded assembly of Dye sensitized photoelectrochemical cell.

Figure 1.8. A covalently linked chromophore-catalyst assembly of DSPECs.

Figure 1.9. Example for covalently linked chromophore catalyst system.

Figure 1.10. Examples for Co-loading chromophore catalyst system.

Figure 1.11. Examples of perylenediimide (PDI) based metal free chromoophores.

Figure 1.12. Example for BODIPY based metal free chromophore and Ru based WOC.

Figure 1.13. Spectral overlaps of emission of naphthalimide donor and absorption of perylene acceptor.

Figure 1.14. Chemical structure of PDI showing three different positions for substitution.

Figure 1.15. Chemical structure of naphthalimide.

Figure 1.16. Schematic representation of molecular design.

Figure 1.17. SA-N-P-N System.

Figure 1.18. SA-N-P-N catalyst system.

List of Table

Table 3.1: Summary of the work

List of Schemes

Scheme 2.1. Synthetic scheme of energy donor naphthalimide

Scheme 2.2. Synthetic scheme of **SA-N-P-N** System

Scheme 2.3. Synthetic scheme of **SA-N-P-N-catalyst**system

Scheme 4.1. Synthesis of N-(4-hydroxyphenyl)-4-bromonaphthalene-1,8-dicarboxymonoimide.

Scheme 4.2. Synthesis of (4-hydroxyphenyl)-4-(ethylhexanamine)naphthalene-1,8-dicarboxy monoimide.

Scheme 4.3. Synthesis of perylene-tetracarboxylictetrabutylester.

Scheme 4.4. Synthesis of 1,7-dibromoperylene-3,4,9,10-tetracarboxylic tetrabutyl ester.

Scheme 4.5. Synthesis of 1,7-Dibromoperylene-3,4,9,10-tetracarboxy monoanhydridedubutylester.

Scheme 4.6. Synthesis of N-(2,6-Diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxy MonoimideDibutylester.

Scheme 4.7. Synthesis of (2,6-diisopropylphenyl)-1,7-bis[N-(pphenyloxy)-(4-(2-ethyl hexanamine)-1,8-dicarboxy napthalenemonoimide)]perylene-3,4,9,10-tetracarboxy monoimidedibutylester.

Scheme 4.8. Synthesis of 2-Phenylpyridin-4-amine.

Scheme 4.9. Synthesis of N-(2-phenylpyridine-4-amine)-1,7-dibromoperylene-3,4,9,10-tetracarboxymonoimidedibutylester

Notations and abbreviations

AcOH	-	Acetic acid
AP	-	Artificial photosynthesis
ATP	-	Adenosine triphosphate
BET	-	Back electron transfer
BODIPY	-	4,4-difluoro-4-bora-3a,4a-diaza-s-indacene
Br_2	-	Bromine
BuBr	-	Bromobutane
BuOH	-	Butanol
$CDCl_3$	-	Deuterated chloroform
CH_2Cl_2	-	Dichloromethane
$CHCl_3$	-	Chloroform
CpIrCl2	-	Pentamethylcyclopentadienyliridiumdichloride
18-C-6	-	18-Crown-6
DSPEC	-	Dyesensitized Photoelectrochemical cell
DMF	-	N,N-Dimethylformamide
DBU	-	1,8-Diazabicyclo(5.4.0)undec-7-ene
FRET	-	förster resonance energy transfer
^{1}H-NMR	-	Proton NMR
HOMO	-	Highest occupied molecular orbital
H_2	-	Hydrogen
K_2CO_3	-	Potassiumcarbonate
LUMO	-	Lowest unoccupied molecular orbital
MeCN	-	Acetonitrile
NADPH	-	Nicotinamide adenine dinucleotide phosphate
$NaHCO_3$	-	Sodium Bicarbonate
Na_2SO_4	-	Sodiumsulphate
NMP	-	N-Methyl-2-Pyrrolidone

NMR	-	Nuclear magnetic resonance
O_2	-	Oxygen
PDI	-	Perylenediimide
PS I	-	Photosystem I
PS II	-	Photosystem II
PEC	-	Photoelectrochemical cell
Pt	-	Platinum
RuBP	-	Ribulose-1, 5-bisphosphate
RuBisCO	-	Ribulose-1, 5-bisphosphate carboxylase oxygenase
RT	-	Room temperature
Ru	-	Ruthenium
RuO	-	Ruthenium oxide
SA-N-P-N	-	Surface anchoring-naphthalimide-perylene-naphthalimide
TiO_2	-	Titanium dioxide
TLC	-	Thin layer chromatography
TsOH	-	p-toluene sulphonic acid
WOC	-	Water oxidation catalyst
Zr	-	Zirconium

Abstract

The aim of this work is to synthesize light harvesting antenna and incorporate them in a molecular design of artificial photosynthetic systems where multiple chromophores capture light energy and transfer the excitation energy into a central chromophore (mimic of a reaction centre) by förster resonance energy transfer (FRET). The selection of energy donor chromophore and energy acceptor chromophore will highly depend on the efficiency of light harvesting antennae. For this work, two multichromophore catalyst systems were designed and partly synthesized based on covalent attachment of a surface anchoring (SA) group to napthalimide (N) and perylene (P) chromophores: (a) SA-N-P-N system and (b) SA-N-P-N-catalyst system where a Iridum based water oxidation catalayst will be covalently attached to the SA-N-P-N system. The two molecular design of multichromophore catalyst systems are based on the strategies of: (a) Multichromophore co-loading system (SA-N-P-N), where the chromophore and water oxidation catalyst are separately functionalized by anchoring groups to bind to photoanode and perform through surface electron transfer, and (b) Covalently linked multichromophore-catalyst system (SA-N-P-N-catalyst), where the chromophores and water oxidation catalyst are covalently linked and they are functionalized with anchoring groups to bind to the photoanode. In both systems, perylene was chosen as the central energy acceptor and naphthalimides as energy donor as the near quantitative spectral overlap of emission of naphthalimide donor and absorption of perylene acceptor indicate them to form a efficient förster resonance energy transfer (FRET) Pair. Perylene was chosen as energy acceptor because these chromoophores are highly fluorescent, synthetically versatile with good photochemical and structural stability. Naphthalimide was chosen as energy donor because of their ease for synthesis and tunability of their chemical structure in order to tune the (opto) electronic properties. These dyes are highly fluorescent, and their HOMO-LUMO energy levels and absorption profiles are complementary to those of the PDI. The advantage of designing such FRET based multichromophoric systems is that the efficient FRET leads to rapid migration of excitation energy to the central chromophore from the peripheral chromophores and as a result leads to rapid charge separation and prevents back electron transfer (BET). The prevention of BET is a very important parameter in improving the overall efficiancy of such artificial photosynthetic systems.

Chapter 1

Introduction

Energy consumption around the world is increasing rapidly with the growth of population ,economic and industrial development. Fossil fuels contribute 80% of total global energy consumption.[1] So, there is a possibility of the scarcity of fossil fuels in near future. Also, combustion of fossil fuel leads to increases in the carbon foot print on earth leading to global warming and other related consequences. In order to meet global energy demands and to replace fossil fuels, it is essential to utilize renewable energy sources like solar, wind, geothermal and nuclear energy. Solar energy is the most abundant form of renewable energy sources available on earth. A good way to approach this energy demand and environmental pollution due to fossil fuel is through the design of photoelectrochemical cell.[2]

Natural photosynthesis

Natural photosynthesis is the process used by plants and other organisms where light energy (sunlight) is captured and it is transformed into chemical energy followed by storage of this energy in the form of adenosine triphosphate (ATP).[3]The solar energy driven water splitting and carbon dioxide fixation are the two main steps in natural photosynthesis. The entire natural photosynthesis can be divided into two reactions.

1) **Light dependent reaction**: In light dependent reaction, electron generation occurs by water splitting and this electron transfers through successive electron transport chains. The movement of electrons through various electron acceptors which are arranged according to their oxidation potentials makes this entire scheme resemble Z and therefore this scheme is termed as ‘’Z scheme’’. The transfer of electrons through electron transport cascade reactions lead to the formation of energy-rich molecules, i.e adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH). Figure 1.1. illustrates the Z-scheme of natural photosynthesis.[4]

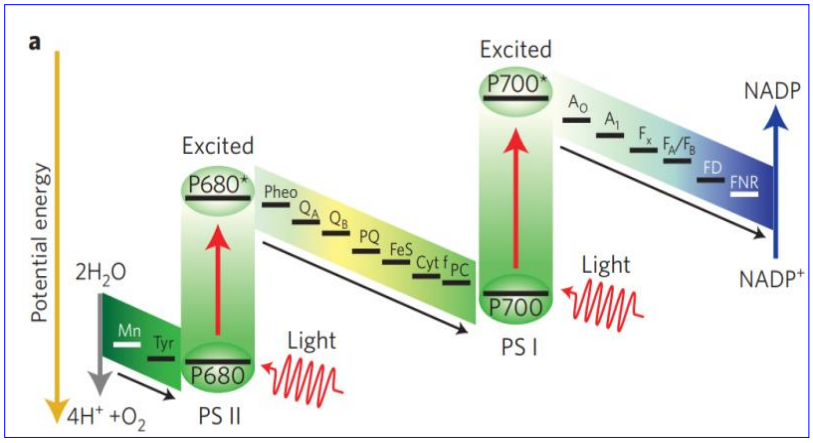


Figure 1.1. Z-scheme of natural photosynthesis showing water splitting,excitation of electron from two photosystems and elctron transport through electron transport chainelectron transport chain.Courtesy: *Nanoscale*, **2019,** *11*, 11071-11082 [5]

2) Light independent reaction: Light independent reaction is also called dark reaction in which enzyme Ribulose-1, 5-bisphosphate carboxylase oxygenase (RuBisCO) captures carbon dioxide from the atmosphere and reduces it into 3-carbon sugar molecule (Figure 1.2) which is converted into final carbohydrate molecule called glucose. Such fixation of CO_2 by enzyme RuBisCO is a cyclic process which is known as Calvin cycle.[3]

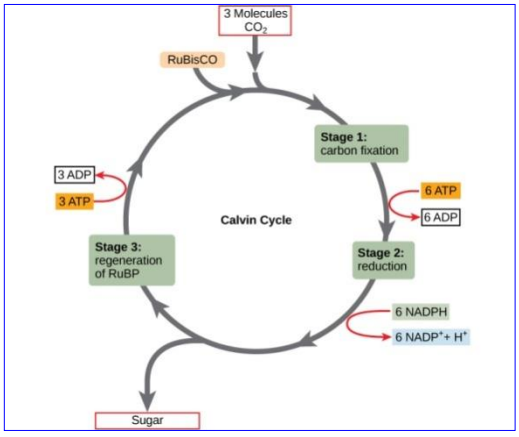


Figure 1.2. Calvin cycle showing the three steps of dark reaction.CO_2 fixation by enzyme RuBisCO, reduction, regeneration of RuBP. Courtesy: https://courses.lumenlearning.com/biology1/chapter/study-guide-energy/ [6]

Artificial photosynthesis

Conversion of solar energy into chemical energy like hydrogen fuel is a good idea to solve the current global problems on energy shortage and environmental issues. This process that imitates the natural photosynthesis to convert solar energy and water into oxygen and hydrogen efficiently is known as artificial photosynthesis (AP). The success of artificial photosynthesis is mainly dependent on the ability of artificial photosynthetic devices to collect maximum amount of incident sunlight followed by the cascade of electron transfer processes to eventually generate molecular oxygen and hydrogen from water as depicted in figure1.3. The first component in such a molecular level device is a light harvesting antenna. Artificial light harvesting antennae consist of multiple chromophoric systems with distinct chemical structures and complementary absorption features which enable them to harvest maximum amount of sunlight covering the maximum region across the visible part of the solar spectrum (i.e., 400-700 nm range). These multiple chromophores absorb light energy and if properly designed can transfer the harvested excitation energy to a central chromophore by unidirectional energy transfer, a funneling effect through an energy transfer mechanism known as förster resonance energy transfer (FRET). For this energy transfer through FRET to occur efficiently, the electronic properties of all the chromophores in light harvesting antenna should be complementary to each other. Therefore, the judicious selection of energy acceptor chromophores and energy donor chromophores will determine the efficiency of light harvesting and energy funneling from the donor to the acceptor system to a large extent. Such efficient light harvesting antennae can eventually be beneficial in the artificial photosynthetic device design as elaborated below.[7, 8]

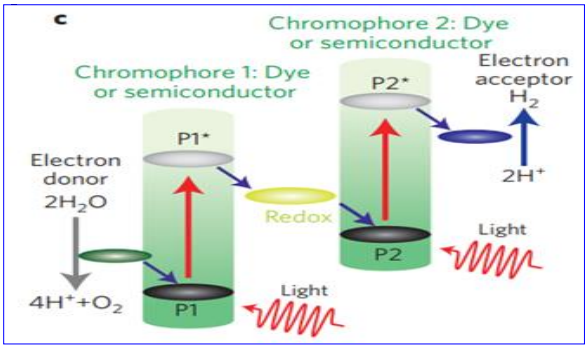


Figure 1.3. Illustration of general concept for AP showing a light harvesting antenna, photosensitizer, O_2 and H_2 evolving catalysts. Courtesy: Courtesy:*Nature photonics*, **2012**| *VOL 6* |.[9]

Multiple device design strategies have been studied for artificial photosynthesis by scientists all across the globe.[2] In this context, the first architecture which was a remarkably simple design was reported by Honda and Fujishima in 1972.This was a Photoelectrochemical (PEC) cell with platinum (Pt) cathode and titanium dioxide(TiO_2) as anode. They have reported water splitting into H_2 and O_2 when the photoanode was irradiated by ultraviolet radiation (figure1.4 A).[10] But this model had several limitations such as low efficiency, rapid electron hole recombination (also known as back electron transfer(BET)) that significantly impedes the performance of these artificial photosynthetic devices. PEC have only a single material for multiple functions such as light absorption, water oxidation catalysis and charge generation and transportation.[2,11] Gräetzel and co-workers derived a slightly modified and improved model from Honda and Fujishima. This model had a separate water oxidation catalyst ruthenium dioxide (RuO_2) along with Pt as cathode and TiO_2 as anode (figure1.4 B). Efficiency of this model was also low mainly due to significant BET and also due to photocorrosion.[2, 11]

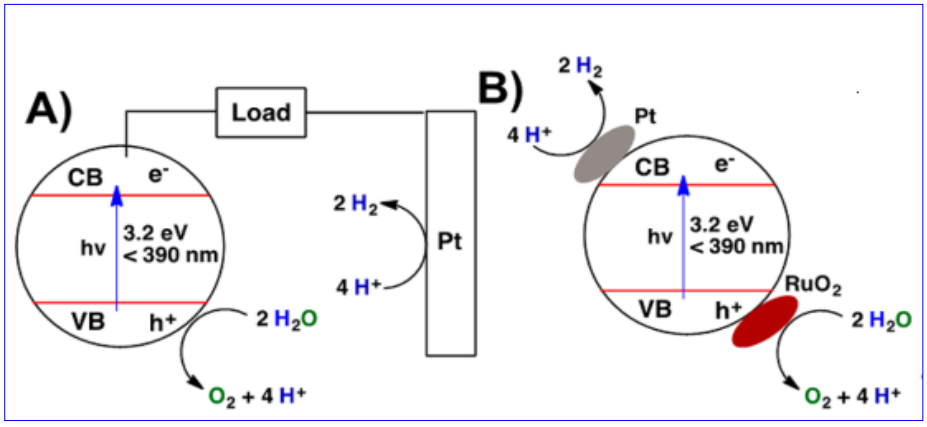


Figure 1.4. (A) Honda-Fujishima model for photoelectrochemical cell with TiO_2 as the photoanode.[10] **(B)** Grätzel model of photoelectrochemical cell illustrating semiconductor nanoparticle with RuO_2 as the water oxidation catalyst and Pt as the reduction catalyst. Courtesy: *J.Am.Chem.Soc.***1981** *103*(16), pp.4685-4690. [11]

Dye sensitized photoelectrochemical cell (DSPECs)

Dye sensitized photoelectrochemical cell (DSPECs) are photoelectrochemical cells that can drive water splitting and convert water into H_2 and O_2whereby the H_2 can be stored and used as a fuel. In comparison with normal solar cells, there is a separate light absorption and charge carrier transport components in DSPECs. Charge carrier formation occurs at the surface of chromophores and working principle of a dye sensitized photoelectrochemical cell (figure 1.5) consists of following five steps:

1) Light absorption by chromophore that is attached to a semiconductor surface (photoanode).

2) Injection of excited electrons from the chromophore into the conduction band of semiconductor.

3) Transmission of electron from semiconductor (photoanode) to Pt cathode.

4) Injection of electron from WOC to chromophore which turn on catalyst for water oxidation.

5)Steps 1−4 are repeated four times to carry out water oxidation and oxygen evolution at the WOC, followed by H_2O/H^+ reduction to H_2 at the Pt cathode.[2]

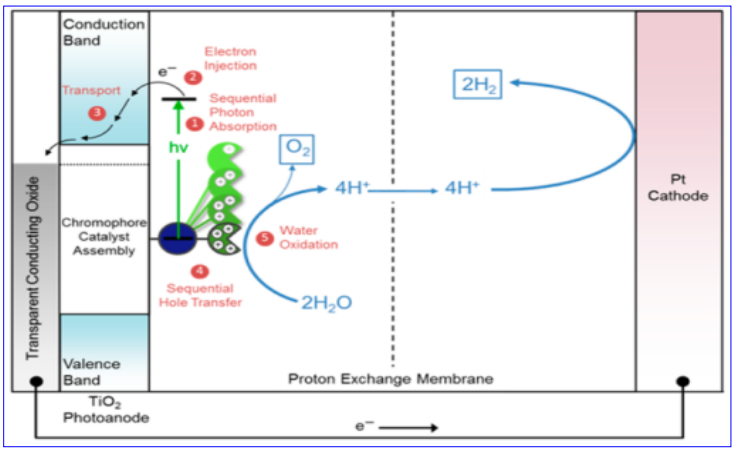


Figure 1.5. Sequence of water splitting in DSPECs into H_2 and O_2.Courtesy: *Chem. Rev*. **2015**, *115*, 13006−13049. [2]

The efficiency of DSPECs depends upon the kinetics of electron transfer which further depends on band gap engineering and methods of assembling light harvesting system and catalyst on metal oxide surface. Figure 1.6 shows the general diagram for the orientation of highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy levels of dye, conduction band of TiO_2 and WOC for efficient electron transfer. [12]

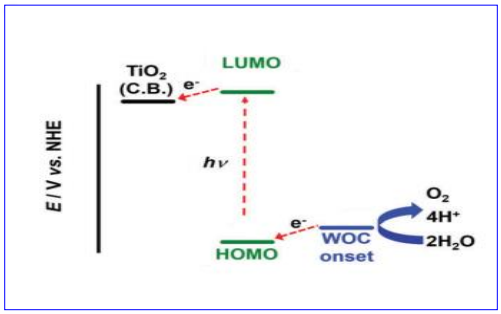


Figure 1.6. Energy level diagram showing HOMO and LUMO levels of chromophore, oxidation potential of water oxidation catalyst and conduction band of TiO_2.[12]

Chromophore-Catalyst assembly on photoanode

There are two design strategies for the chromophore catalyst assemblies:

1) **Co-adsorption**: In co-adsorption strategy as depicted in Figure 1.7, both chromophore and water oxidation catalyst are separately functionalized with anchoring groups such that they can bind to the photoanode surface separately. The electron or hole transfer in co-adsorption from catalyst to chromophore or vice versa occurs mostly through space.[2,14]

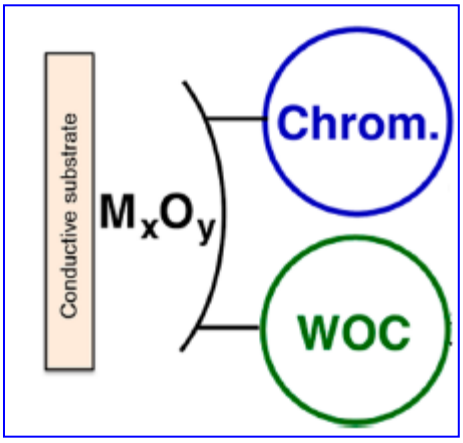


Figure 1.7. Co-loaded assembly of Dye sensitized photoelectrochemical cell. The electron or hole transfer from catalyst to chromophore occur through space. Courtesy: *Chem. Rev*. **2015**, *115*, 13006−13049. [2]

2) **Covalently linked chromophore catalyst system**: Covalently linked chromophore catalyst system: In covalently linked chromophore catalyst design as depicted in Figure 1.8, the chromophore and water oxidation catalysts are covalently linked and they are functionalized with anchoring groups that can bind to the photoanode surface. The photo anode is nanostructured and energy of conduction band is favourable for efficient electron injection. The bridging ligand which connects both chromophore and catalyst promotes rapid intra assembly electron transfer. The chromophore part has efficient electron excitation. The electron or hole transfer in the covalently linked chromophore catalyst system from catalyst to chromophore or vice versa can occur either through bond or through space. [2,14]

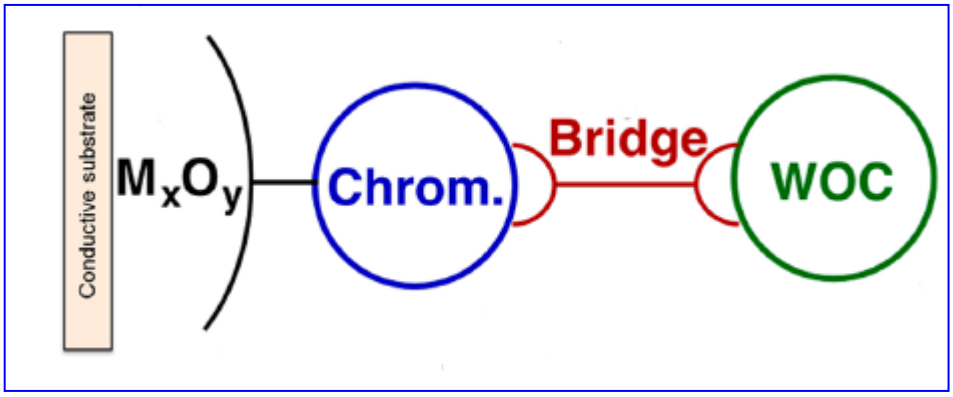


Figure 1.8. A covalently linked DSPEC chromophore-catalyst assembly. This consists of water oxidation catalyst which is linked to chromophore by a bridging ligand. This whole system functionalized with metal oxide by an anchoring group. Courtesy: *Chem. Rev*. **2015**, *115*, 13006−13049. [2]

Examples of chromophore-catalyst assemblies

Ruthenium (Ru) polypyridyl chromophore and a Ru-based WOC were synthesized in 2014 by scientist Sun and co-workers, and their terminal positions were attached with phosphoric acid anchoring groups and carboxylic acid anchoring group, respectively as shown in Figure 1.9.Here,Ru based water oxidation catalyst and Ru based chromophore is linked by a bridging group Zirconium (Zr)(IV) –phosphate bridge(figure1.9 A) and phosphate–Zr-carboxylate bridge (figure 1.9 B) linkages to construct a "layer-by-layer "model (Ru-Zr^{4+}-Ru).This whole chromophore-catalyst system is functionalized with phosphate anchoring group that can bind to the TiO_2 photoanode. [2, 13, 14]

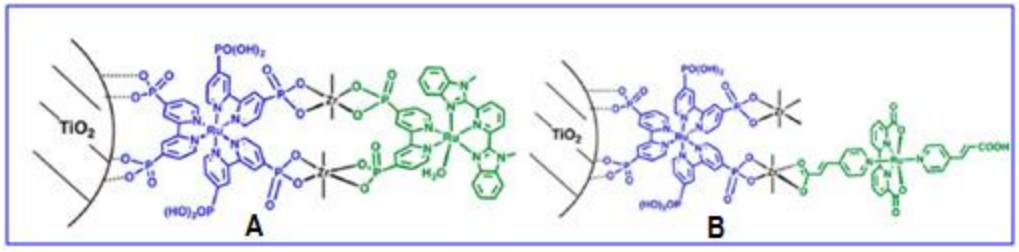


Figure 1.9. Example for co-loadedchromophore catalyst system. The "layer-by-layer" model of the dye (Ru-Zr^{4+}-Ru) connected to catalyst by **(A)** Zirconium (IV) –phosphate bridge. Courtesy: Angew. Chem., Int. Ed. 2012, 51, 12782− 12785. [13] **(B)** phosphate–Zr-carboxylate bridge. Both **A** and **B** are attached on TiO_2 by phosphoric acid anchoring group. Courtesy: ACS Catal. **2014**, *4*, 2347−2350 [14]

Figure 1.10 shows the example for co-loading chromophore catalyst system in which water oxidation catalyst and chromophore system were separately functionalized with photoanode. In figure 1.10 a), water oxidation catalyst and chromophore was functionalized with photoanode by silicate group and phosphate group, respectively while in figure 1.10 (b), water oxidation catalyst and chromophore were functionalized with photoanode TiO_2 by surface anchoring group phosphate. [9, 14, 15]

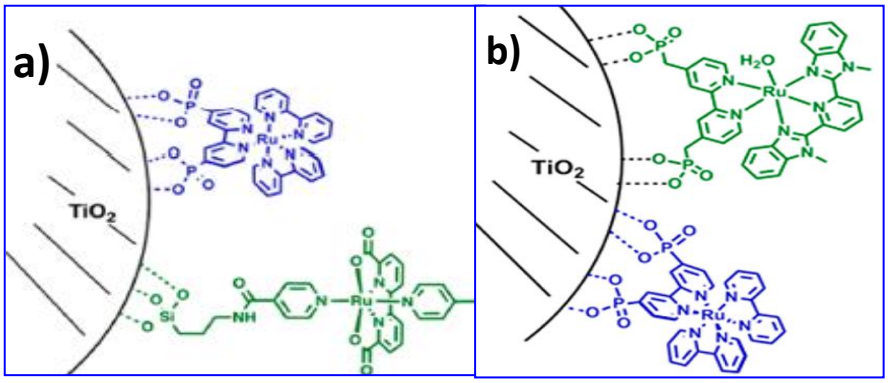


Figure 1.10. Examples for Co-loading chromophore catalyst system. Co-adsorption of **(a)** Ru dye with two phosphate groups and a [Ru-bda] WOC with a long carbon chain silane anchoring group. Courtesy:Journal of the American Chemical Society. 2013 Mar 20; 135(11):4219-22. [15] (b) Ru based photosensitizer and molecular Ru catalysts on TiO_2 film with phosphate anchoring group. Courtesy: : J.Am. Chem. Soc. **2013** 135(31), 1587-11594[16]

Gap area of research:

1) **Multichromophoric-catalyst assemblies in DSPECs are rare or not known yet:**

A single system containing multiple chromophores for efficient light harvesting, anchoring groups for binding to photoanode and WOC to facilitate water oxidation is not known to the best of my knowledge. It is really challenging to study the photocatalytic water oxidation of such a complex system.

2) Metal free chromophores are very rare:

Till now, in most of the DSPECs, photocatalytic studies are carried out using Ru-based chromoophores and are known to have optimal performances. [16] However, Ru metal is extremely toxic and not eco-friendly and chromophores containg Ru are more expensive as compared to metal free chromophores.

3) FRET based light harvesting antenna in DSPECs are not explored yet:

The maximum light of the solar spectrum can be harvested by designing the multichromophoric FRET based systems that have complementary absorption spanning the wide range of the visible part in the solar spectrum i.e., in the range from 400 to 700

nm. FRET based systems are expected to have many advantages like rapid exciton migration and prevention of back electron transfer, fast charge injection into anode and hole injection into catalyst which will be helpful to increase the overall efficiency of the DSPECs.

Literature examples of metal free chromophores.

Perylene-based multichromophoric compounds were synthesized by condensation reaction of corresponding imide anhydride and amine functionalized 2-phenylpyridine unit. This is shown in figure 1.11(1-4).These systems showed energy transfer efficiencies up to 99.98% and may be effective components of fluorescent solar concentrator films.

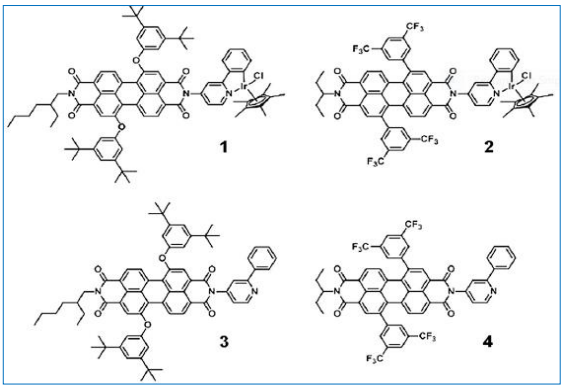


Figure 1.11. Examples of perylenediimide (PDI) based metal free chromophores.
Courtesy: *PNAS*, **2019,** *109*(39),15651-15656.[18]

4,4-difluoro-4-bora-3a,4adiaza-s-indacene (BODIPY) dye bearing a hexylthiophene conjugation and two groups based on rhodanine acetic acid was attached with a ruthenium water oxidation catalyst(figure1.12). This system at pH 7.2 showed an excellent Faradaic efficiency of hydrogen ($H_{2)}$ production of ~65.8%.[12]

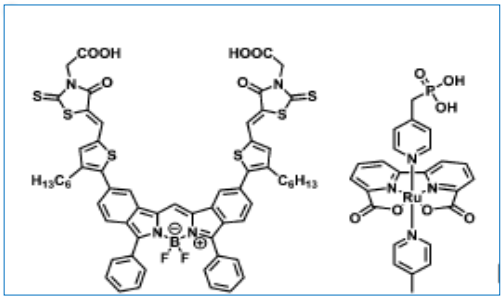


Figure 1.12. Example for BODIPY based metal free chromophore and Ru based WOC. Courtesy: *Chem. Commun.*, *53(50)*, **1981**, 6784-6787. [12]

Major challenges in this field:

1) Prevention of BET: In multichromophoric–catalyst system the central chromophore should be well engineered for rapid charge separation across the oxide interface and the distance between core antennas should be optimized through suitable spacers to prevent BET. Otherwise this BET will result in decrease in the overall efficiency of any dye sensitized Photoelectrochemical cell.

2) Stabilization of surface binding and chemical stability for long term p**erformance of DEPECs.**

The various surface anchoring groups must be chosen carefully for both the dye and catalyst molecules in order to: (i) prevent separation from the photoanode surface, (ii) successful transfer of the injected electrons, (iii) effective oxidizing conditions, and (iv) inhibit extensive solar irradiation. Carboxylic acid and phosphonic acid, two commonly used anchors are observed to have poor stability in aqueous environments that result in the surface hydrolysis and dropping of catalytic function. [20]

3) **Choice of multiple chromophores to extend absorption profile from** UV to IR region **with effective energy transfer.**

In multichromophoric systems there must be a spectral overlap between the peripheral chromophore (donor) emission and central chromophore (acceptor) absorption spectra for efficient FRET. Also transition dipoles of donor emission and acceptor absorption should aligned in a favorable way to facilitate the FRET to occur.

3) The strong tendency of PDIs to form π-π aggregates is a challenge

Perylenediimide (PDI) has a strong tendency to form π-π aggregates thus, the synthesis of perylene based light harvesting antennae needs careful design, good selection of spacers that and long alkyl chains connected to these chromophores that can impart sufficient solubility and prevent the undesirable aggregation and also suitable non-conjugated spacers can prevent electron transfer and its competition with the desired energy transfer process.

Choice of energy donor and energy acceptor components for efficient FRET to design chromophore catalyst systems according to two design strategies

FRET theory of energy transfer is helpful while choosing energy donor and acceptor systems. The rate of energy transfer (k_{FRET}) from an excited donor to an acceptor is in terms of their dipolar interaction at a given distance, R is shown in equation 1 and their Förster radius (R_0)

$$k_{FRET} = \frac{1}{\tau_D}\left(\frac{R_0}{R}\right)^6 (1)$$

Where R_0 is the Förster radius, τ_D is the intrinsic lifetime of the donor.

Förster radius is the distance at which the energy transfer efficiency is 50% and can be written as;

$$R_0^6 = \frac{9(ln\,10)k^2 Q_D}{128\Pi^5 N_A n^4} J(\lambda) (2)$$

Equation 2, is helpful for the selection of potential donor and acceptor pairs where (J (λ)), is the spectral overlap integral of the donor emission and acceptor absorption, k^2 is their orientation factor, Q_D is the donor quantum yield, N_A Avogadro's number and n is the refractive index of the medium . In order to achieve highly efficient energy transfer, it has been observed that the distance between donor and acceptor, R, must be less than R_0.[20]

Naphthalimide chromophore as energy donor and perylene as energy acceptor

PDI was chosen as energy acceptor chromophore and naphthalimide as energy donor chromophore due to their complementarity in absorption spectrum and good overlap of naphthalimide emission and perylene absorption as depicted in figure 1.13.

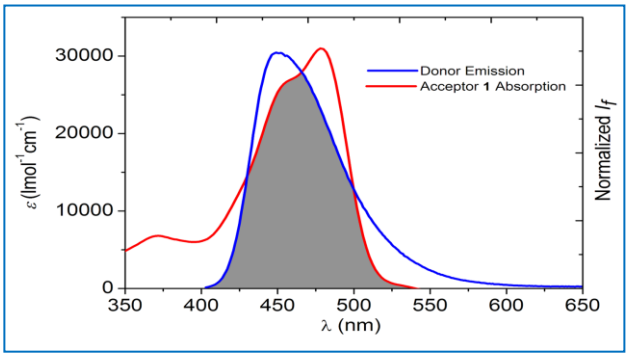


Figure 1.13. Spectral overlaps of emission of naphthalimide donor and absorption of perylene acceptor showing that they form a good FRET pair. Courtesy:*Chem sci*,**2016**,*7*, 3517-3532 [6]

Perylene dyes (energy acceptor)

Perylenes are highly fluorescent, [23] versatile compound with good photochemical and structural stability.It has strong optical absorption and high emission quantum yield. One important feature of perylene is the presence of three different positions around perylene core for the attachment of substituents. Imide, bay (1, 6, 7, 12), and the ortho (2, 5, 8, 11) are the positions for attachment of substituents. Figure 1.14 shows these three positions of perylene core. It is easier to functionalize imide and bay positions of perylene due to their straightforward synthetic schemes. The substitutions at bay position and imide position influences the optoelectronic and self assembling properties of the dye

respectively.[23]Perylene can form good energy transfer pair with naphthalimide and several other chromophores such as anthracene and naphthalene dimide (NDI).[6]

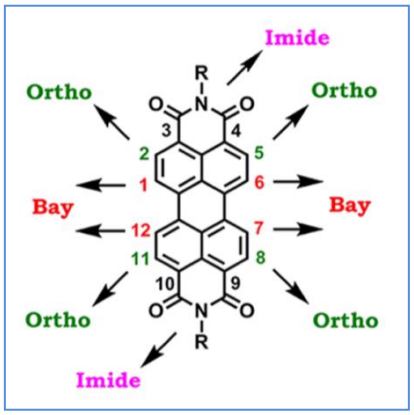


Figure 1.14. Chemical structure of PDI showing three different positions for substitution.Courtesy:*J. Org. Chem.*, **2019**, *84*, *15*, 9532-9547. [23]

Naphthalimide dyes (Energy donor)

Naphthalimide dyes possess a great ease for modification and manipulation of their structure in order to tune its optoelectronic properties. These dyes are highly fluorescent, and their HOMO-LUMO energy levels and absorption profiles are complementary to those of PDI. Naphthalimide and PDI therefore form good potential FRET pairs.[6]The chemical structure of naphthalimide is shown in figure 1.15.

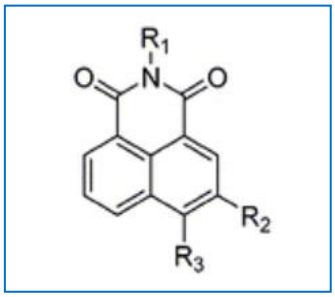


Figure 1.15. Chemical structure of naphthalimide.Courtesy:*Chem. Soc. Rev.*, **2019,** *39(10)*,3936-3953. [25]

Objective of our work

The objective of this work is to synthesize multichromophoric system and assemblies for adsorption on photoanode. Thus, we are aiming to synthesize light harvesting antenna into simpler artificial photosynthesis system where multiple chromophores capture light energy and transfer this energy into a central chromophore that mimics a reaction centre by a process called förster resonance energy transfer. The selection of energy donor chromophore and energy acceptor chromophore will highly depend on the efficiency of light harvesting antenna. For this work, perylene was chosen as energy acceptor chromophore and naphthalimide as energy donor chromophore due to their complementarity in absorption spectrum. We have designed two strategies for multichromophore catalyst system (figure 1.16).

- **Multichromophore catalyst co-loading system**: In co-adsorption strategy, both chromophore and water oxidation catalyst are separately functionalized with anchoring groups for binding to the photoanode (figure 1.16. 1).
- **Covalently linked multichromophore-catalyst system**: In this design, chromophore and water oxidation catalyst are covalently linked and they are functionalized with anchoring groups for binding to photoanode (figure 1.16. 2).

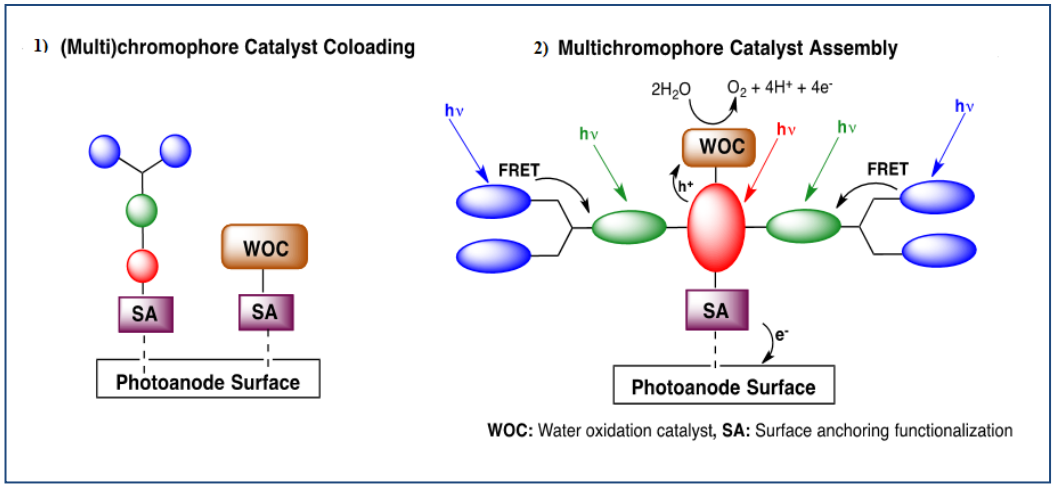


Figure 1.16. Schematic representation of molecular design: 1) Chromophore catalyst co-loading assembly involves surface anchoring functionalization of a single or multichromophores for binding to photoanode. 2) Multichromophore-catalyst system which consists of red, green and blue chromophores and functionalized with water oxidation catalyst and surface anchoring group. [12]

Compounds to be synthesized

SA-N-P-N system: This system consists of perylene (P) as energy acceptor, naphthalimide (N) as energy donor in bay position and diisopropyl aniline in peri position of perylene. Perylene can form good energy transfer pair with naphthalimide. In this system there will be efficient energy transfer. The molecule at the other peri position is functionalized with an anhydride surface anchoring (SA) group. Therefore, we abbreviate this molecule as **SA-N-P-N** system as depicted in figure 1.17.

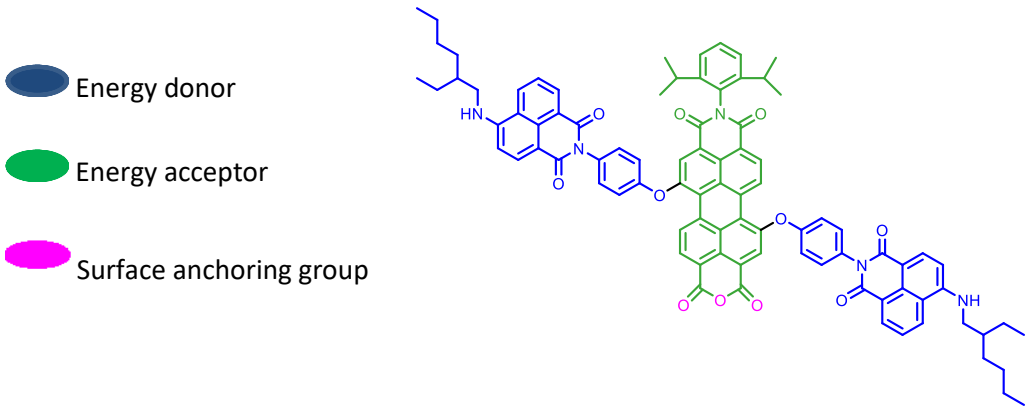


Figure 1.17. SA-N-P-N System consists of surface anchoring group, naphthalimide as energy donor, perylene diimide as energy acceptor.

SA-N-P-N-catalyst system: This system consists of perylene (P) as energy acceptor, naphthalimide (N) as energy donor in bay position and Iridium (Ir) based WOC (catalyst) in peri position of perylene. The Ir based complexes containing pentamethylcyclopentadiene (Cp*) ligand and phenyl pyridine are highly active and robust WOCs as reported by Crabtree, Brudvig, and co-workers.[26, 27] The unsaturated first coordination sphere functions as active site for the substrate water molecule and catalyst allows the accumulation of multiple charges to form a high-valent metal–oxo intermediate which is essential for water oxidation process.[28] The other peri position is functionalized with a anhydride surface anchoring (SA) group. Therefore, we abbreviate this molecule as SA-N-P-N- catalyst system as depicted in figure 1.18.

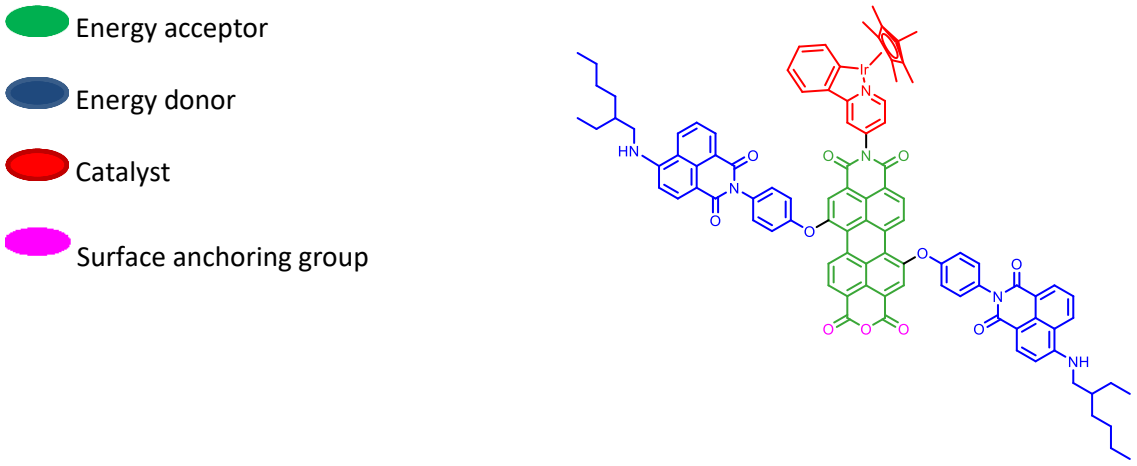


Figure 1.18. SA-N-P-N-catalyst system consist of surface anchoring group, naphthalimide as energy donor, perylene diimide as energy acceptor and a water oxidation catalyst part.

Chapter 2

Result and Discussion

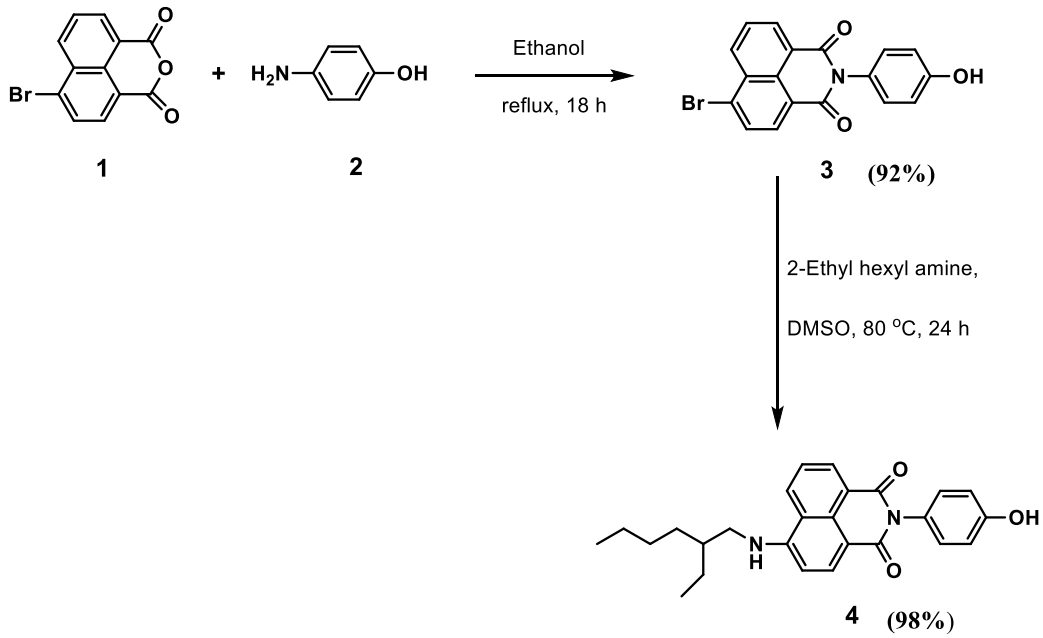
As discussed in the introduction section (Chapter 1), the intention of this project was to design and synthesize multichromophore-catalyst compounds according to the following two design strategies:

1) Multichromophore catalyst co-loading system: In co-adsorption strategy, both chromophore and water oxidation catalyst are separately functionalized by anchoring groups so that they can bind to the photoanode surface accordingly. We have termed such system as **SA-N-P-N** system.

2) Covalently linked multichromophore catalyst system: In this design, multichromophoric system will be synthesized first followed by covalent attachment of water oxidation catalyst to one end of the multichromophoric system and covalent attachment of the anchoring group at the other end of the multichromophoric system such that it can bind to the photoanode surface. We term such system as **SA-N-P-N-catalyst** as discussed in chapter 1.

In both of the above design strategies, SA indicates the surface anchoring group which is the anhydride terminus of the central chromophore, P indicates perylene central chromophore that is an energy acceptor and N indicates napthalimide as the peripheral energy donor chromophore. The main intention of utilizing P and N in the multichromophoric system design is based on that fact that P and N form an efficient FRET pair with energy transfer efficiencies of 80-90% and ultrafast energy transfer from N to P in picoseconds timescale.[6] Furthermore, it is relatively straight forward to introduce an anhydride end in the perylene chromophore and it has been shown that anhydride binds effectively to the TiO_2 photoanode [29] that we intend to use in our final artificial photosynthetic device design. Therefore, an anhydride functionality in our molecular design serves as the effective binding unit i.e., surface anchoring group.

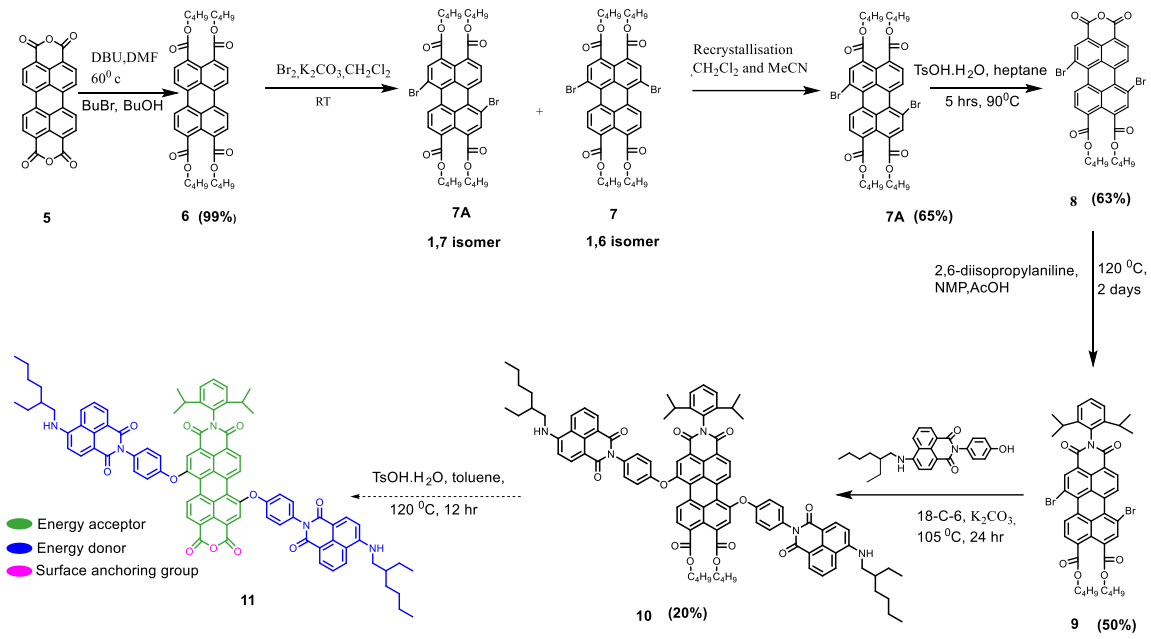
Accordingly, we started the project with the synthesis of the naphthalimide subchromophore (Scheme 1) that serves as the energy donor unit of the multichromophore unit in both the design strategies.



Scheme 2.1. Synthetic scheme of energy donor naphthalimide

Scheme 2.1.shows the two step synthetic route of energy donor naphthalimide where the first step is the amination of 4-bromo-1,8-naphthalic anhydride (**1**) with p-aminophenol which is commercially available to obtain compound **3**.The first step was an18 hour reaction with ethanol as solvent used under reflux condition. Subsequently, simple substitution reaction of the bromo functionality was carried out to obtain compound **4** where the bromo group of **3** was substituted by 2-ethylhexylaminein the presence of dimethylsulphoxide (DMSO) as solvent and temperature of 80 ^{o}C for about 24 hours.

Followed by the synthesis of naphthalimide energy donor subchromophore, we proceeded with the synthesis of the perylene energy acceptor subchromophore as depicted in the scheme 2.2 below.



Scheme 2.2. Synthetic scheme of **SA-N-P-N** System

The synthetic scheme of SA-N-P-N system is outlined in the scheme 2.2. The synthesis of all compounds in scheme 2.2 started with the commercially available perylene-3, 4,9,10 tetracarboxylic dianhydride. In the first step, perylene-3, 4, 9, 10-tetrabutylester (**6**) has been synthesized from compound **5** with high yield by opening up of the anhydride ring using basic reagents DBU and DMF as solvent. The dibromination of compound **6** in DCM at room temperature was performed using Br_2 in presence of K_2CO_3 as base to obtain a mixture of 1,7-isomer and 1,6-isomer. The desired compound was 1, 7 isomer (**7A**) that was achieved by the recrystallisation from a mixture of two isomers (i.e., 1,7- and 1,6-isomers) using a solvent mixture of DCM and acetonitrile in a ratio of 9:1. After the crystallization, we were able to obtain a mixture **7** and **7A** in a 10:1 ratio.

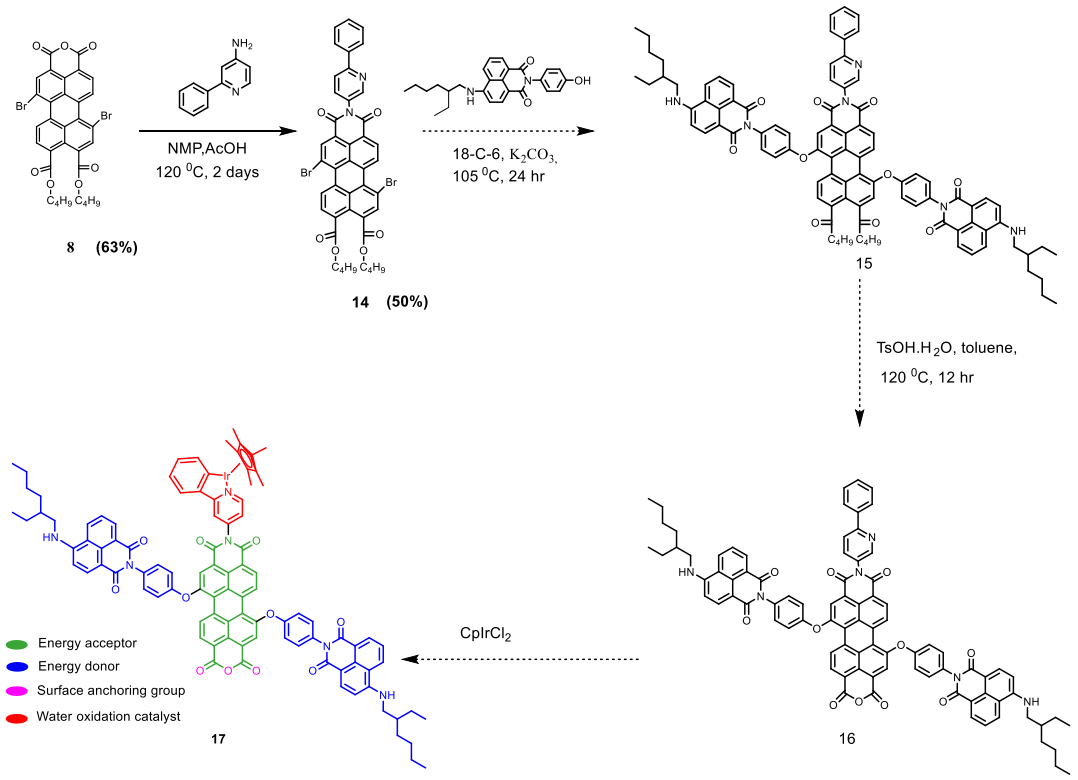
After one more crystallization the pure 1,7-isomer was achieved. The purification process was monitored by ^{1}H NMR spectroscopy.

The conversion of compound **7A** to compound **8** (one ring closed perylene system i.e., perylenemonoanhydride) was achieved by an acid-catalyzed (p-toluenesulphonic acid monohydrate) removal of two ester moieties in heptane as solventat 90 °C for 5 hours. This reaction also led to the formation of the bisanhydride side product (perlyenebisanhydride). Therefore, a DCM washing was performed because the desired compound **8** (monoanhydride) was soluble in DCM while the side product (bisanhydride) was insoluble in DCM. Thus, based on the differential solubility of the monoanhydride and bisanhydride, the latter could be selectively removed and the monoanhydride compound thus could be obtained in a pure form after DCM washing.

The next step was the amination reaction of compound **8**that was performed with 2,6-diisopropylaniline, in N-methyl-2-pyrrolidone (NMP) as solvent and acetic acid as catalyst. The reaction was kept at 120 ^{o}C for duration of reaction was 2 days and followed by the reaction, the product formation was monitored by thin layer chromatography at regular intervals and finally was obtained by extraction (work up) method. Followed by the amination, we proceeded to attach the energy donor naphthalimide subchromophore at the bay positions of the perylene central chromophore.

The attachment of naphthalimide group (**10**) on bay position of perylene core was achieved by simple substitution of the 1,7-bromo substituents with the phenoxy functionalized naphthalimide subunits. The reaction was carried out in dry toluene at 90 ^{0}C in presence of K_2CO_3 as a mild base and 18-crown-6 as a phase transfer catalyst. The desired compound was obtained in pure form after column chromatography and characterized by NMR spectroscopy. Compound **10** was to be further subjected to one-sided ring closure using p-TsOH in presence of toluene as solvent to obtain compound **11**as and discussed earlier, the anhydride terminus of compound **11** (**SA-N-P-N**) will serve as the surface anchoring that will bind to the TiO_2 photoanode. In our group, further work is being carried out to design an Ir based water oxidation catalyst functionalized with surface anchoring group that can be used along with compound **11** for the co-adsorption studies as outlined in our molecular design strategy 1.

Next, we proceeded with synthesis of the **SA-N-P-N-catalyst** system according to design strategy 2 as depicted in the below scheme 2.3.



Scheme 2.3. Synthetic scheme of **SA-N-P-N-Catalyst** system

The synthetic scheme of **SA-N-P-N-catalyst**system is outlined in scheme 2.3. We started synthesis of **SA-N-P-N-catalyst** system from compound **8**. The first step was the amination of the reaction of compound **8** with an amine functionalized pyridine that will act as the precursor for attaching an Iridium water oxidation catalyst in the final step of the synthetic scheme. The amination reaction was performed with 2-phenylpyridin-4-amine in NMP and acetic acid at 120 ^{o}C for duration of 2 days. The 2-phenylpyridin-4-amine was synthesized starting from 4-amino-2-chloropyridine that was subjected to Palladium catalyzed Suzuki coupling with phenyl boronic acid. The dotted arrows are the synthesis work still remaining to be done in the project and will be pursued in the future

but the descriptions of the steps are summarized as follows. The aminated compound **14** will be subjected alkylation at 1,7-positions with naphthalimide functionalized with phenol moieties in presence of K_2CO_3 as base and 18-C-6 as the phase transfer catalyst to obtain the multichromophore –catalyst system**15**. Subsequently, **15** will be subjected to one-sided ring closure to obtain the monoanhydride compound **16**, where the anhydride functionality serves as the surface anchoring group for binding to the TiO_2photoanode. Finally, compound **16** will be subjected to a reaction with $IrCpCl_2$, the water oxidation catalyst precursor in presence of NMP as solvent at 120 ^oC for two days and the pyridine moiety in compound **16** chelates the Ir to finally give the product compound **17** which will be the target compound **SA-N-P-N-catalyst** system. In all the above synthetic steps, purifications of the compounds were performed mostly by column chromatography and by recrystallization in one of the steps and the correct structures were deduced by ^1H NMR spectroscopy as detailed in the experimental section (Chapter 4).

Chapter 3

Summary and Outlook

The objective of this thesis was to synthesize multichromophoric system and assemblies for adsorption on photoanode in order to design artificial photosynthetic device based on dye sensitized photoelectrochemical cell. The main goal was to synthesize light harvesting antenna into simpler artificial photosynthesis system where multiple chromophores capture light energy and transfer this energy into a central chromophore that mimics a reaction centre by a process called förster resonance energy transfer (FRET). The judicious selection of energy donor chromophore and energy acceptor chromophore determines the energy transfer efficiency of light harvesting antennae. For this work, perylene was chosen as energy acceptor chromophore and naphthalimide as energy donor chromophore due to their complementarity in absorption spectrum and they form an excellent FRET pair as known from literature. We adopted two strategies for the design of multichromophore-catalyst system (figure 1.16).

- **Multichromophore catalyst co-loading system**: In the co-adsorption strategy, both chromophore and water oxidation catalyst are separately functionalized with anchoring groups for binding to the photoanode (See table 3.1).We have termed multichromophore co-loading system as **SA-N-P-N** system where thechromophorewill be functionalized with anhydride anchoring group for binding to photoanode. The design and synthesis of aIr based water oxidation catalyst functionalized with anchoring for photoanode binding is being separately pursued in our group at present.
- **Covalently linked multichromophore catalyst system (SA-N-P-N-catalyst)**: In this design, chromophore and water oxidation catalyst are covalently linked and they are functionalized with anchoring groups for binding to photoanode(Table 3.1).

Energy donor and energy acceptor subchromophores have been successfully synthesized and characterized by ^{1}H NMR and the synthesis of the **SA-N-P-N** system was complete till the penultimate step. The remaining steps of **SA-N-P-N** and **SA-N-P-N-catalyst** will be pursued in the future and studies regarding their photophysical studies and eventual integration into an artificial photosynthetic device will be taken up.

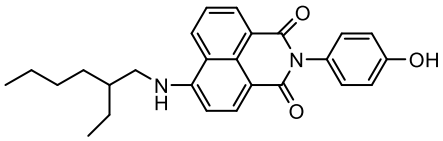
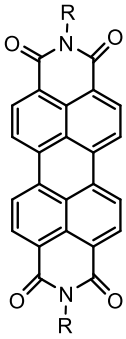
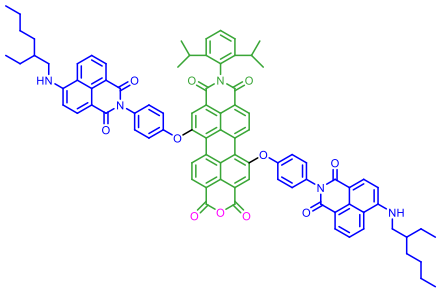
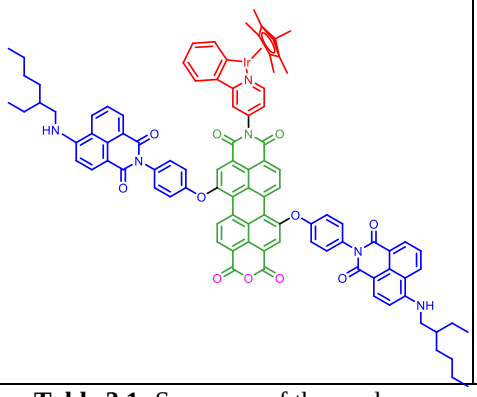
	Chemical structures	Important characteristics
Donor		• Highly fluorescent • Synthetic versatility • Complimentary absorption to perylenes
Acceptor		• High photochemical stability. • High fluorescence quantum yield. • Perylene and naphthalimide is a good FRET pair.
SA-N-P-N system		Energy donor Energy acceptor Surface anchoring group
SA-N-P-N Catalyst system		Energy acceptor Energy donor Catalyst Surface anchoring group

Table 3.1: Summary of the work

Chapter 4

Experimental section

General information:

4.1. Materials

All chemicals and solvents were purchased from Sigma Aldrich, Merck and Himedia. Solvents like dichloromethane (DCM) were distilled using standard distillation setup. Toluene was dried by heating over sodium and using benzophenone as indicator. DCM was dried over phosphorus pentoxide and distilled prior to use. Column chromatography was carried out using silica gel of mesh size 60-120 as well as extraction of desired compounds after reaction were directly used without any further distillation. Reactions were monitored by checking thin layer chromatography (TLC) using TLC plates which were visualized under UV lamp (excitation wavelengths of 254 nm and 365 nm).

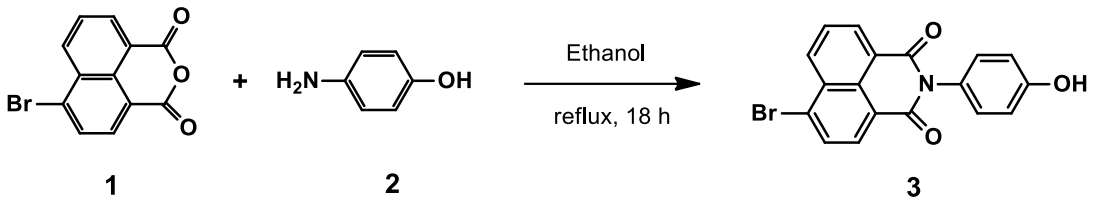
4.2. Measurements

The ^{1}H NMR spectra were recorded on a 400 MHz Bruker Biospin Avance IIIFT-NMR and 500 MHz Avance Neo (Bruker) FT NMR spectrometer with TMS as standard at room temperature. $CDCl_3$ and DMSO-D_6 were the solvents used for doing NMR. Column chromatography was performed with silica gel of mesh size (60-120).

4.3. Synthesis

Synthesis of donor precursor

4.3.1 Synthesis of N-(4-hydroxyphenyl)-4-bromonaphthalene-1,8-dicarboxymonoimide

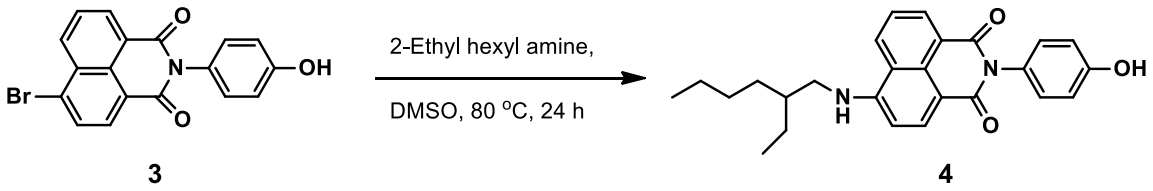


Scheme 4.1. Synthesis of N-(4-hydroxyphenyl)-4-bromonaphthalene-1,8-dicarboxymonoimide. [7]

A mixture of 4-bromo-1,8-naphthalic anhydride (1 g, 3.61mmol) and 4-aminophenol (0.4690 g, 4.30mmol) in ethanol (120 mL) was refluxed for 18 hours (h). Subsequently, reaction mixture was cooled to room temperature and filtered. After filtration the residue was washed with pure ethanol and dried in vacuum oven to obtain compound **3** as an off-white solid compound with a yield of 92%.[7]

^{1}H NMR (400 MHz, DMSO-d$_6$) : δ (ppm) = 9.69 (s, 1 H), 8.57 (t, J = 8 Hz, 2 H), 8.33 (d, J = 8 Hz, 1 H), 8.24 (d, J = 8 Hz, 1H), 8.02 (t, J = 8 Hz, 1 H), 7.14 (d, J = 8 Hz, 2 H), 6.87 (d, J = 8 Hz, 2 H).

4.3.2 Synthesis of (4-hydroxyphenyl)-4-(ethylhexanamine)naphthalene-1,8-dicarboxy monoimide



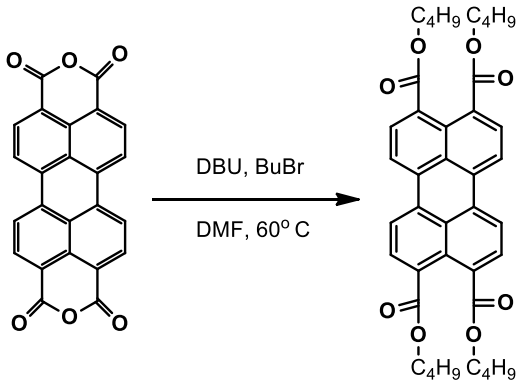
Scheme 4.2. Synthesis of (4-hydroxyphenyl)-4-(ethylhexanamine)naphthalene-1,8-dicarboxy monoimide. [7]

Mixture of N-(4-hydroxy phenyl)- 4-bromonaphthalene-1,8-dicarboxy monoimide (852 mg, 2.32mmol), ethyl hexane amine (4.472g, 34.60 mmol) and DMSO (30 mL)were taken in a 50 mL round-bottomed (RB) flask. Later, the reaction mixture was stirred for 24 h at 80 ^{o}C. Subsequently, the solution was poured in 200 mL of water to form precipitate. But the precipitate was not formed, then extraction was performed using DCM and water, organic layer was passed through sodium sulphate and the solvent was removed using the rotary evaporator under vacuum and the solid was dried in a vacuum oven to obtain orange solid compound **4** with a yield of 98%.[7]

^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm)= 9.60 (s, 1 H), 8.77 (d, *J* = 4 Hz, 1 H), 8.42 (d, *J* = 8Hz, 1 H), 8.25 (d, *J* = 12 Hz, 1 H), 7.80 (t, *J* = 4 Hz, 1H), 7.70 (t, *J* = 8 Hz, 1H), 7.05 (d,*J*= 8H, 2 H), 6.84 (d, *J* = 8 Hz, 2 H), 3.29 (t, J=8Hz, 2 H), 1.83-1.80 (m, 1 H), 1.45-1.31 (m, 8 H), 0.93-0.89 (m, 3 H), 0.86-0.83 (m, 3 H).

Synthesis of acceptor precursor

4.3.3 Synthesis of perylene-tetracarboxylic tetrabutyl ester



5 **6**

Scheme 4.3. Synthesis of perylene-tetracarboxylictetrabutylester. [30]

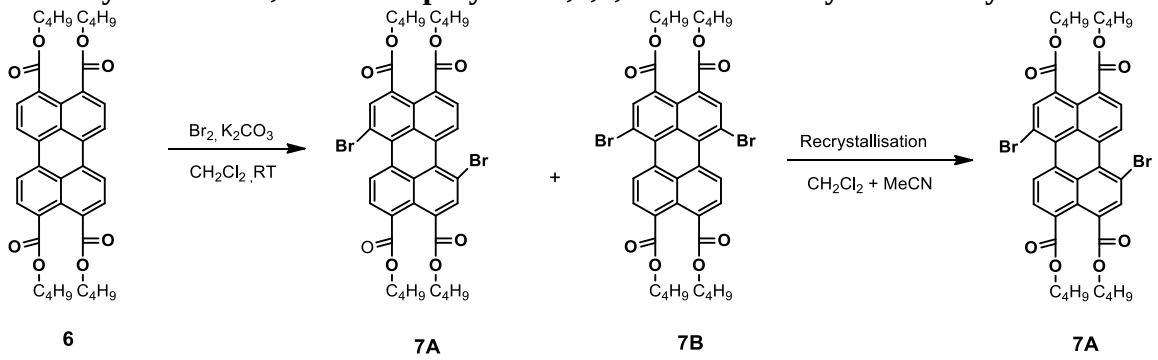
A mixture of Perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) (**5**) (1.96 g, 4.98 mmol), 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) (3.032 g,19.92 mmol), n-butanol (3.702 mL, 0.4mol) was charged in 250 mL round- bottomed (RB) flask. Then, 12 mL was added to RB and subjected to stirring for 0.5 h at 60 °C. Subsequently,1-bromobutane (2.74 g, 0.0398 mmol) was added to the reaction mixture followed by the addition of another 9 mL of DMF and further kept for stirring for 3 h. Subsequently

reaction mixture was allowed to reach at room temperature. Then, resulting solution was added into 100 mL of water and kept for stirring for another 15 min. Subsequently the mixture was filtered to get the crude product. The crude compound after the filtration process was subjected to purification process by column chromatography on silica gel, eluted with DCM to obtain golden orange solid compound with a yield of 99%.[30]

This same reaction was performed by using double amount of each reactant for scaling up the desired compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.05 (d, J = 8 Hz, 4 H), 7.91 (d, J = 8 Hz, 4 H), 4.35 (t, J = 8 Hz, 8 H), 1.84-1.77 (m, 8 H), 1.55-1.48 (m, 8H), 1.01 (t, J = 8 Hz, 12 H).

4.4.4. Synthesis of 1,7-dibromoperylene-3,4,9,10-tetracarboxylictetrabutyleste



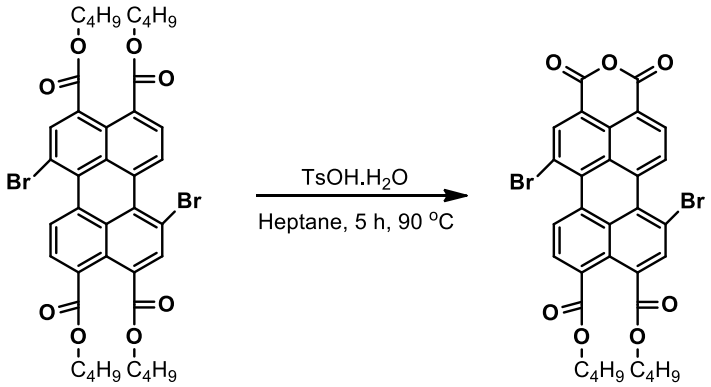
Scheme 4.4. Synthesis of 1,7-dibromoperylene-3,4,9,10-tetracarboxylic tetrabutyl ester.[31]

A mixture of perylene-tetracarboxylictetrabutylester (**6**) (0.500 g, 0.76mmol) and K_2CO_3 (0.250 g, 1.81 mmol) was taken in a 50 mL round-bottomed (RB) flask and DCM (10 mL) was added to the reaction mixture. Subsequently, bromine (0.500 mL, 9.70 mmol) was subjected to the RB which contains reaction mixture and kept for stirring at RT for 24 h. Then sodium metabisulphite (aquous solution) was added dropwise to the reaction mixture, a while stirring. Extraction was performed using DCM and water and the combined organic layers were dried over sodium sulphate and the solvent was evaporated using rotary evaporator under vacuum. The resultant crude product consisted of a mixture of 1,7- and 1,6-dibromo isomers. The mixture was subjected to double recrystallization for one week in 9:1 mixture of dichloromethane and acetonitrile respectively. But after checking NMR mixture of both the isomers was there. So, again reaction mixture was subjected to recrystallization for another one week to obtain desired compound and the

yield was 65%. The same procedure was repeated with 1 g of the compound **6** for scaling up the reaction.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.93 (d, J = 8 Hz, 2 H), 8.28 (s, 2 H), 8.08 (d, J = 8 Hz, 2H), 4.34 (t, J = 8 Hz, 8 H), 1.78 (t, J = 8 Hz, 8 H), 1.51-1.46 (m, 8 H), 0.99 (t, J = 8 Hz, 12 H).

4.4.5 Synthesis of 1,7-Dibromoperylene-3,4,9,10-tetracarboxy monoanhydride Dibutylester



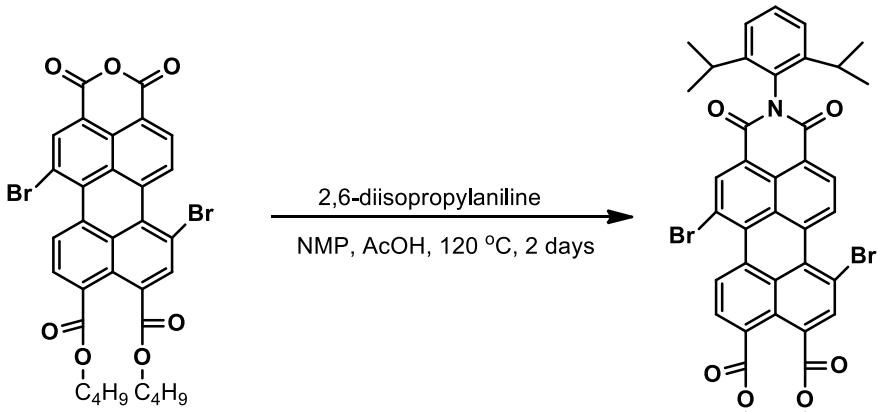
Scheme 4.5. Synthesis of 1,7-Dibromoperylene-3,4,9,10-tetracarboxy monoanhydridedubutylester. [31]

Compound **7A** (200 mg, 0.25mmol) and p-toluene sulfonic acid monohydrate (p-TsOH·H_2O) (61 mg,0.32 mmol) were taken in 50 mL round-bottomed (RB) flask and then 2 mL of heptane was subjected into the reaction mixture. Then the reaction mixture was stirred at 90 °C for 5 h. After some time, color change was noticed. The reaction mixture's color was changing from orange to red with the formation of precipitate. After 5 h, the reaction mixture was allowed for cooling to RT. Subsequently, the product was subjected to filtration and washed with small portion of water and methanol. Then the precipitate was dried in vacuum oven. This precipitate was taken in 100 mL methanol and kept for refluxing for another 3 h. Subsequently, reaction mixture was cooled to room temperature and subjected to filtration to remove the starting reagents. Then the residue was kept for drying and washed with small amount of DCM in order to remove the

insoluble perylenebisimide side product. The solvent was evaporated by using rotary evaporator to get the desired compound. Then compound was subjected to silica gel column chromatography for purification of the desired compound first with DCM/hexane (1:1) then with pure DCM to obtain red solid compound **8** with a yield of 63%.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.30-9.24 (m, 2 H), 8.90 (s, 1 H), 8.68 (d, J = 8 Hz, 1H), 8.35 (s, 1H), 8.16 (d, J = 8 Hz, 1 H), 4.38-4.34 (m, 4 H), 1.84-1.76 (m, 4 H), 1.53-1.47 (m, 4 H), 1.03-0.98 (m, 6 H).

4.4.6 Synthesis of N-(2,6-Diisopropylphenyl)-1,7-dibromoperylene- 3,4,9,10-tetracarboxy Monoimide Dibutylester.



8 **9**

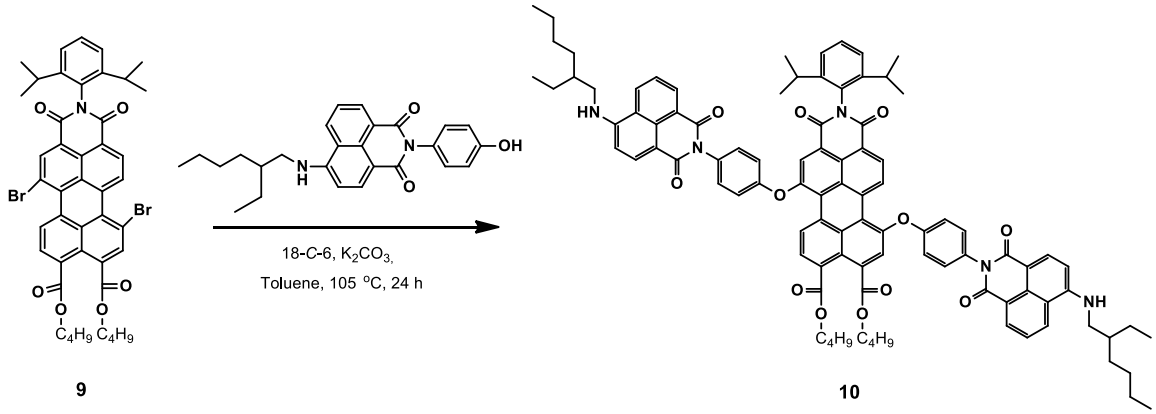
Scheme 4.6. Synthesis of N-(2,6-Diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxy MonoimideDibutylester.[31]

Dibromo perylene dibutylester monoanhydride (50 mg, 0.73mmol) was taken in a 100 mL RB flask and added 2,6-diisopropylaniline (28.7mg, 1.58mmol), acetic acid (0.023 mL, 0.40 mmol) and NMP (5 mL) into the RB flask. Subsequently, reaction mixture was stirred for two days at 120 °C under nitrogen atmosphere. The reaction mixture was kept at RT. After it reaches room temperature, the reaction mixture was added into distilled water to obtain the precipitate. Then the remaining NMP is removed by washing

precipitate with large amount of water. The same reaction was performed using 110 mg of the starting compound. But in this reaction precipitate was not formed when reaction mixture was poured to water. So, extraction was performed using DCM and water and the organic layers were dried over sodium sulphate and the solvent was evaporated using rotary evaporator under vacuum. Then the crude product was subjected for purification by column chromatography using DCM as eluent to obtain purple solid compound **9** with a yield of 50%.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.28 (d, *J*= 8 Hz, 1 H), 9.24 (d, *J* = 8 Hz, 1 H), 8.95 (s, 1 H), 8.73 (d, *J* = 8 Hz, 1 H), 8.36 (s, 1 H), 8.16 (d, *J* = 8 Hz, 1 H), 7.51 (t, *J*= 8 Hz, 1 H), 7.36 (d, *J*= 8 Hz, 2 H), 4.37 (t, *J*= 8 Hz, 4 H), 2.76-2.71 (m, 2 H), 1.83-1.77 (m, 4 H), 1.54-1.48 (m, 4 H), 1.19 (s, 6 H), 1.17 (s, 6 H), 1.01 (t, *J* = 8 Hz, 6 H).

4.4.7. Synthesis of (2,6-diisopropylphenyl)-1,7-bis[N-(pphenyloxy)-(4-(2-ethylhexanamine)-1,8-dicarboxynapthalenemonoimide)]perylene-3,4,9,10-tetracarboxymonoimidedibutylester



Scheme 4.7. Synthesis of (2,6-diisopropylphenyl)-1,7-bis[N-(pphenyloxy)-(4-(2-ethyl hexanamine)-1,8-dicarboxy napthalenemonoimide)]perylene-3,4,9,10-tetracarboxy monoimidedibutylester. [7]

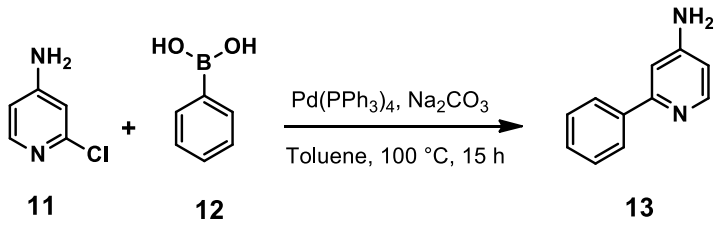
Compound **4**(77 mg, 0.1842mmol) was taken in a 50 mL RB flask and K_2CO_3 (48 mg, 0.35 mmol) and 18-crown-6 (123 mg, 0.46 mmol) were added into the RB flask followed by addition of 20 mL of dry toluene into the reaction mixture. The reaction mixture was

stirred at room temperature for 30 minutes. Temperature slightly increased upto 50 ^{o}C and stirring was continued for another 20 minutes under nitrogen atmosphere. Subsequently, compound **9** (49 mg, 0.058mmol) was added to reaction mixture and stirred for 24 h at 105 ^{o}C. After 24 h, the reaction mixture was cooled to RT and toluene was evaporated using rotary evaporation. Extraction was performed using DCM and water. Then the residue was refluxed with methanol for 3 h. Methanol was removed by rotary evaporation to obtain reddish-brown crude product with a yield of 20%. Subsequently, the crude product was subjected to column chromatography using DCM/Chloroform (3:1) as eluent for purification. This reaction was repeated several times due to low yield. [7]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.42 (d, *J* = 10 Hz, 1 H), 9.37 (d, *J* = 5 Hz, 1 H), 8.68 (d, *J* = 10 Hz, 1 H), 8.62 (d, *J* = 10 Hz, 2 H), 8.56 (s,1 H), 8.50 (d, *J* = 5 Hz, 2 H), 8.12-8.10 (m, 3 H), 7.97 (s, 1 H), 7.72-7.70 (m, 1 H), 7.67-7.64 (m, 2 H), 7.54-7.52(m, 1H), 7.47 (s, 1 H), 7.38-7.31 (m, 7 H), 6.76 (d, *J* = 10 Hz, 2 H), 6.58 (s, 1 H), 4.37-4.31 (m, 4 H), 3.35-3.33 (m,4 H), 2.78-2.73 (m, 2 H), 2.06-2.02 (m, 4 H), 1.81-1.78 (m, 8 H), 1.54-1.52 (m, 8 H), 1.19-1.14 (m, 18 H), 1.03-0.94 (m, 18 H).

Synthesis of SA-N-P-N-catalyst system

4.4.8. Synthesis of 2-Phenylpyridin-4-amine



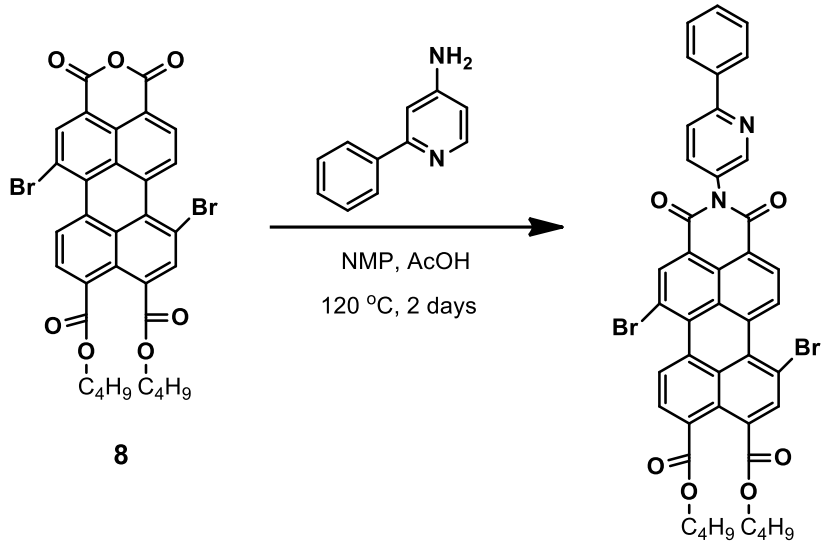
Scheme 4.8. Synthesis of 2-Phenylpyridin-4-amine. [32]

4-amino-2-chloropyridine (500.0 mg, 3.89 mmol) was taken in schlenk tube and added 3 mL of toluene and dissolved the compound. Then phenyl boronic acid (570.0 mg, 4.67 mmol) was taken in another schlenk tube and added 3 mLof toluene and both the schlenk tubes were subjected to four cycles of freeze-pump-thaw degassing process. Subsequently, sodium carbonate solution was purged in separate schlenk tube and

$Pd(PPh_3)_4$ (225.0 mg, 0.19 mmol) was added in schlenk RB under nitrogen atmosphere. Then 4-amino-2-chloropyridine, phenyl boronic acid and sodium carbonate solution were mixed in schlenk RB under N_2 atmosphere. The mixture was stirred for 15 h at 100 °C. After cooling the reaction mixture to room temperature, the reaction mixture was extracted using ethyl acetate for three times and water, the excess water in organic layer was removed by passing organic layer over sodium sulphate. After removal of the solvent by rotary evaporator, white oily crude product was obtained and column chromatography was performed with petroleum ether/ethyl acetate (1:2) to get desired compound. Yield was 30%. Some extra peaks were found in NMR from 7.69-7.48 ppm. [32]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=8.31 (d, J = 4 Hz, 1 H), 7.88 (d, J = 4 Hz, 2 H), 7.43-7.36 (m, 3H), 6.92 (s, 1 H), 6.48 (d, J = 8 Hz, 1H), 4.39 (br, 2 H).

4.4.9. Synthesis of N-(2-phenylpyridine-4-amine)-1,7-dibromoperylene-3,4,9,10-tetracarboxymonoimidedibutylester



Scheme 4.9. Synthesis of N-(2-phenylpyridine-4-amine)-1,7-dibromoperylene-3,4,9,10-tetracarboxymonoimidedibutylester [31]

Dibromo perylene dibutylester monoanhydride (**8**)(47 mg, 0.0700mmol) was taken in a 50 mL RB and added 2-Phenylpyridin-4-amine(25.7mg, 0.1509mmol), acetic acid (0.023 mL, 0.4021 mmol) and NMP (4 mL) into the round-bottomed (RB) flask. Subsequently, the reaction mixture was stirred at 120 ^{o}C for two days under inert atmosphere. The reaction mixture was then kept at RT. Subsequently, reaction mixture was added to distilled water to get the precipitate of crude product and dried in vacuum oven to obtain dark purple solid. Column chromatography was performed using DCM/Chloroform (1:2) for the purification of compound **14**.

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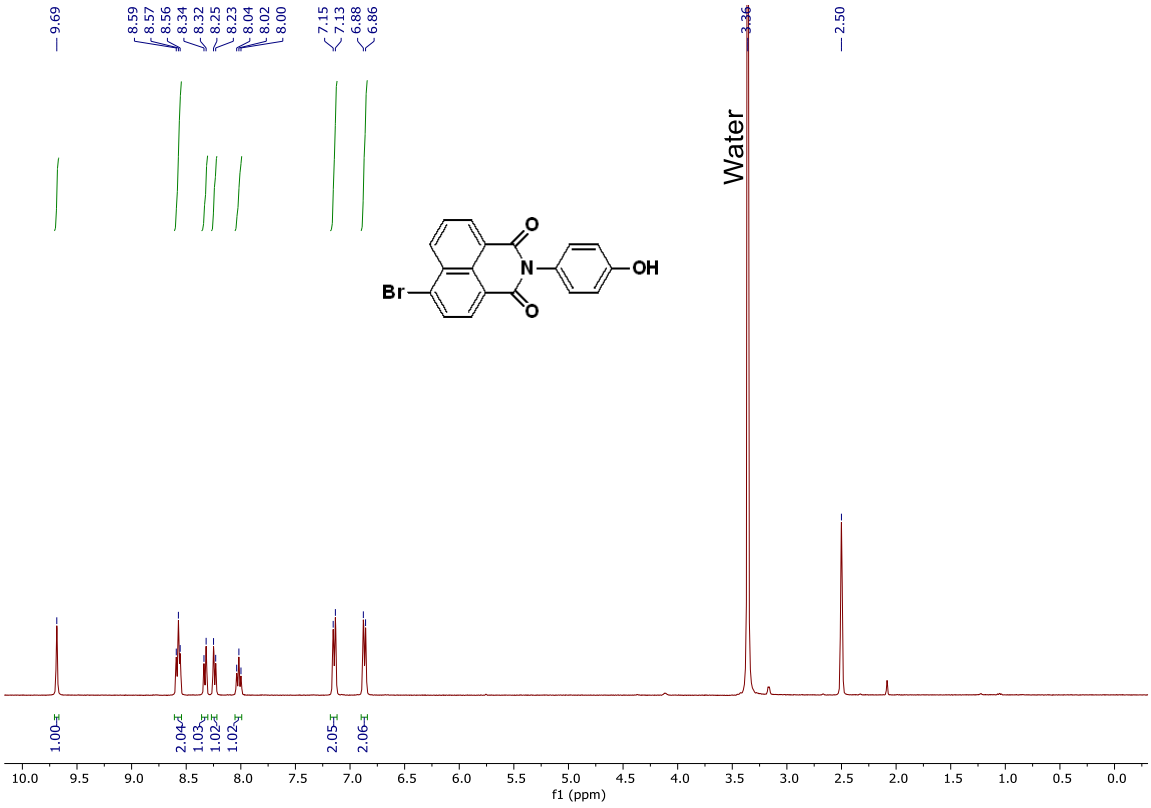
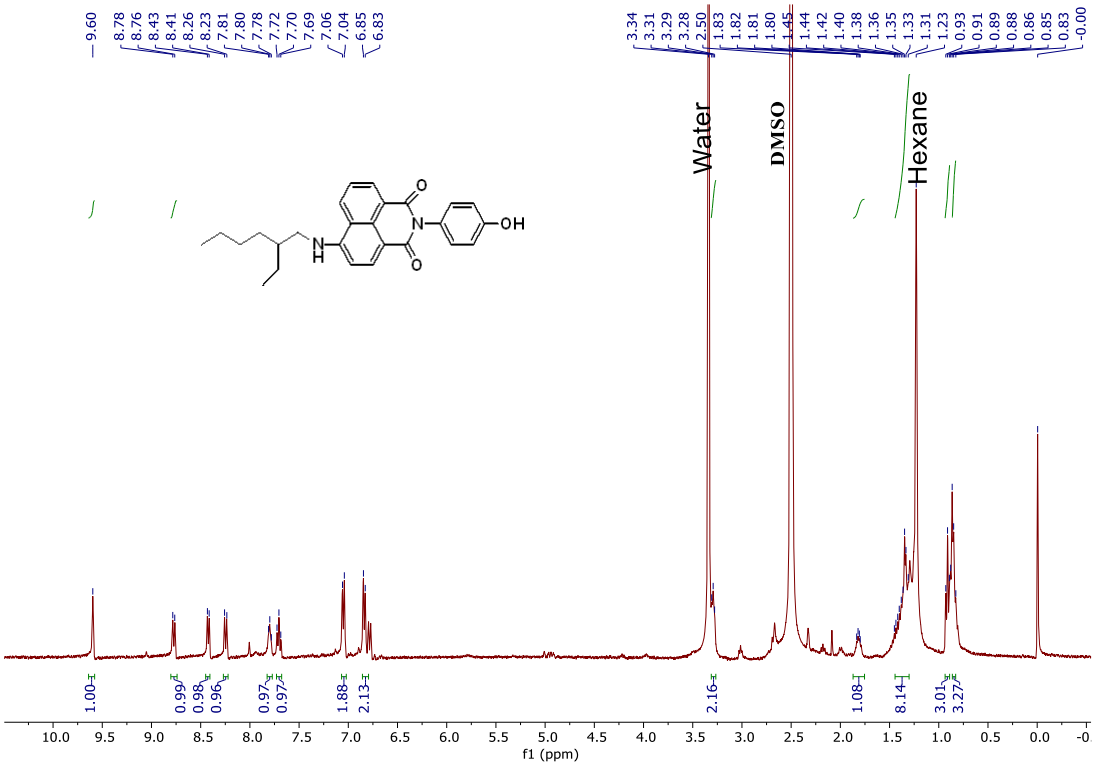
APPENDIX

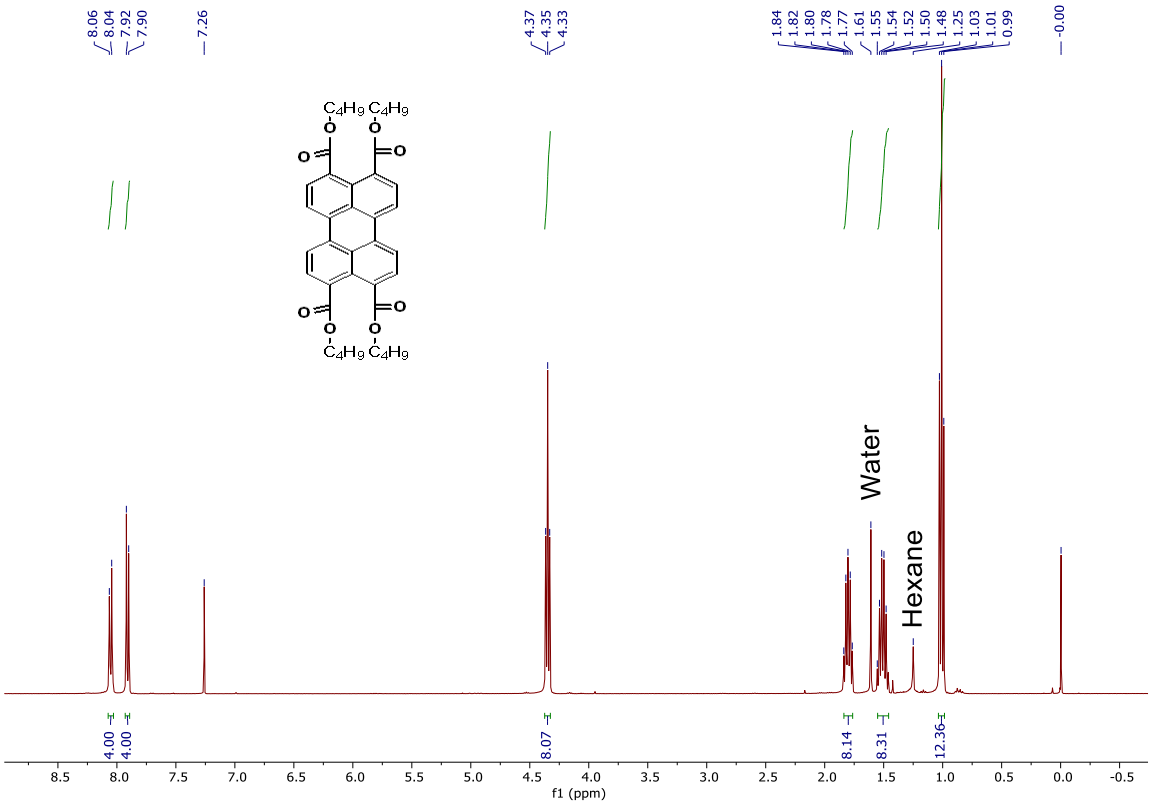
N-(4-hydroxyphenyl)-4-bromonaphthalene-1,8-dicarboxymonoimide(3), ^{1}H NMR, DMSO-d_6, 400 MHz



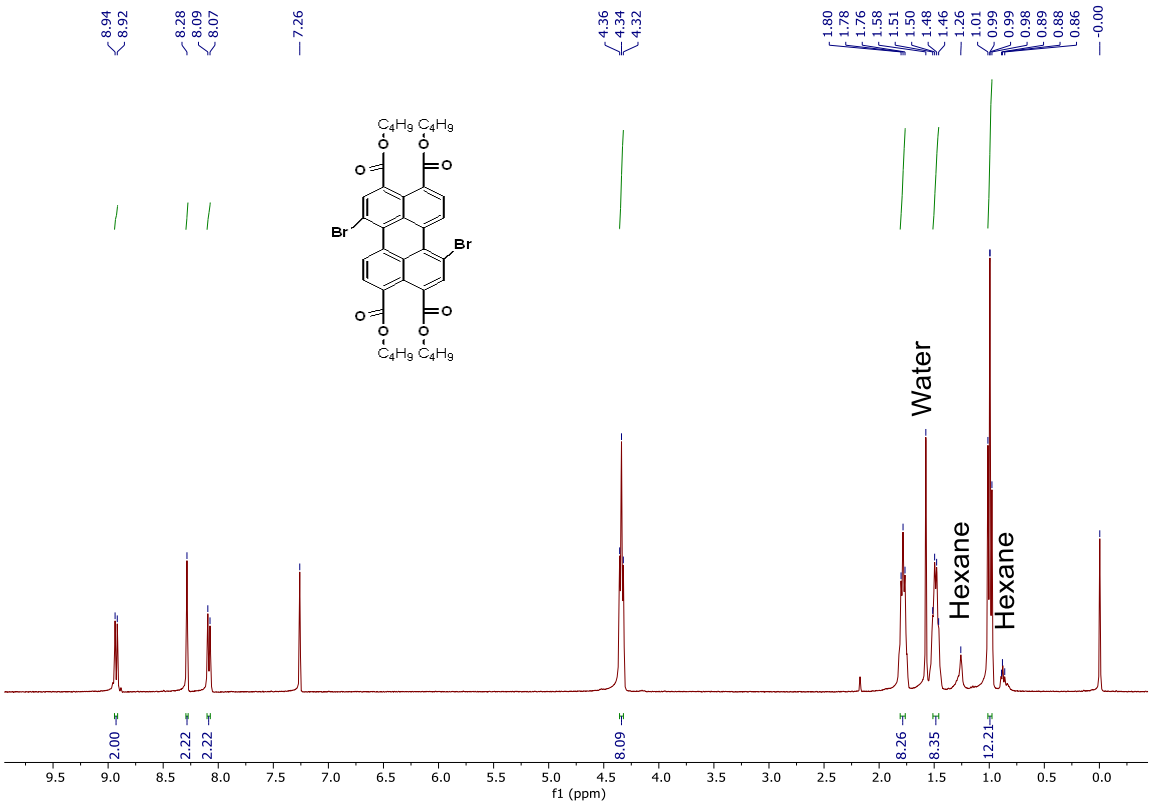
4-hydroxyphenyl)-4-(ethylhexanamine)naphthalene-1,8-dicarboxymonoimide(4), ^{1}H NMR, DMSO-d_6, 400 MHz



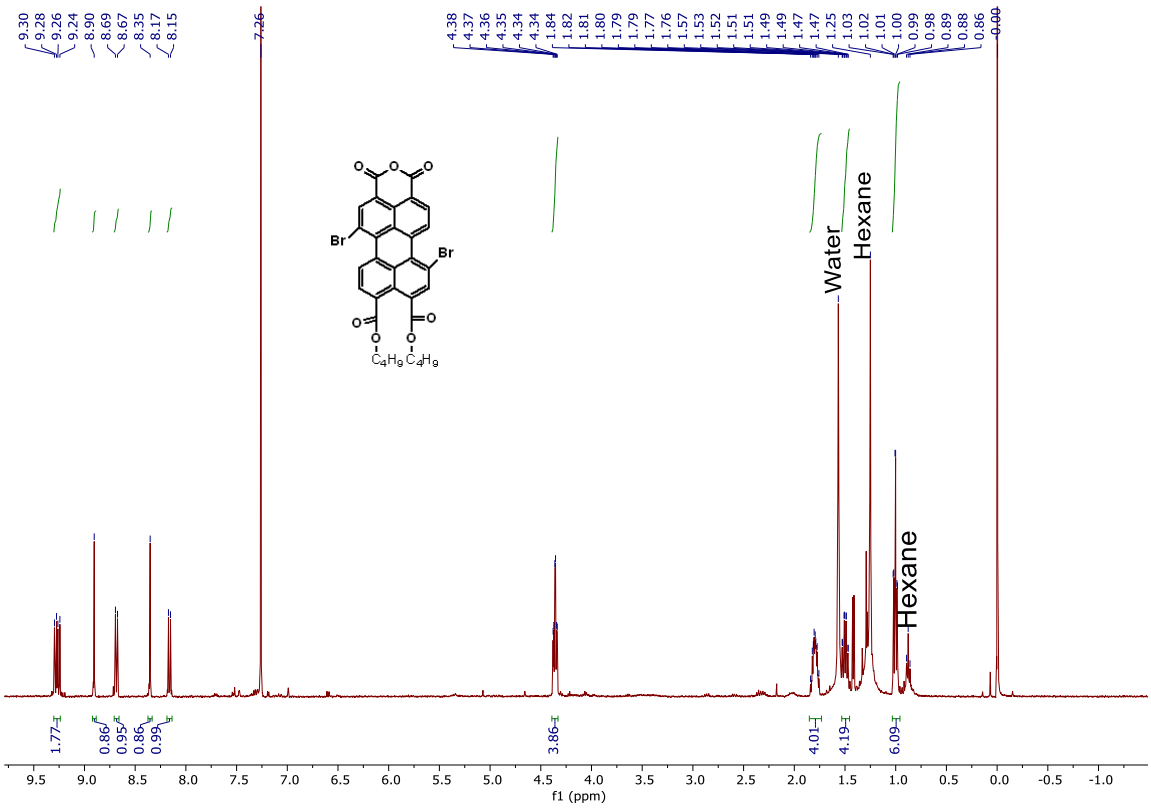
Perylene-tetracarboxylictetrabutyl ester (6), ^{1}H NMR, $CDCl_3$, 400 MHz



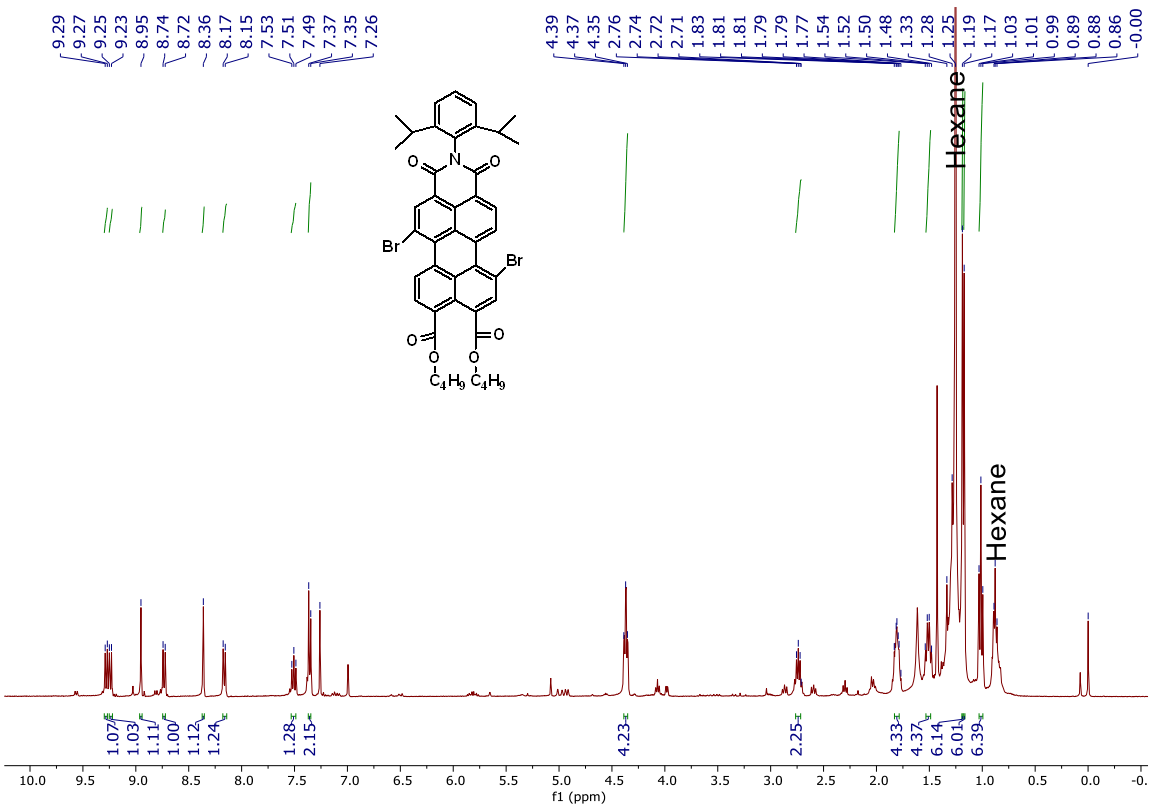
1,7-dibromoperylene-3,4,9,10-tetracarboxylic tetrabutyl ester(7A), ^{1}H NMR, $CDCl_3$, 400 MHz



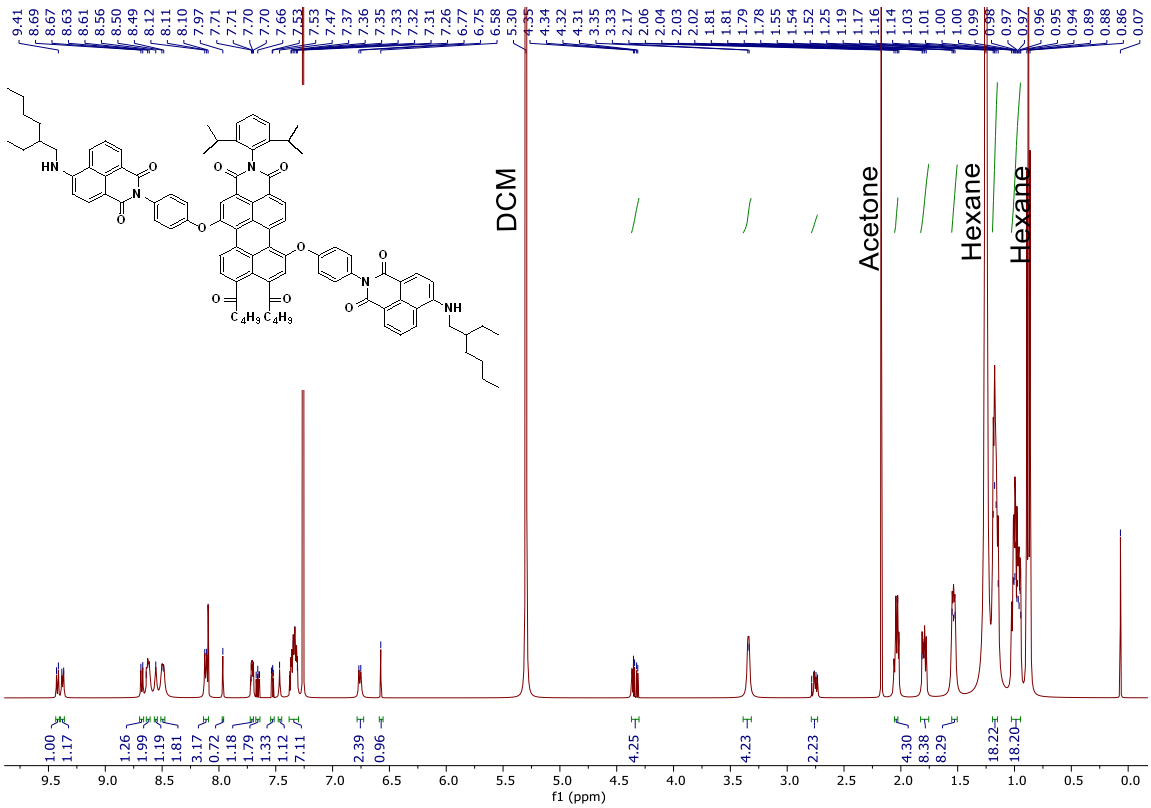
1,7-Dibromoperylene-3,4,9,10-tetracarboxymonoanhydride Dibutylester (8), ^{1}H NMR, $CDCl_3$, 400 MHz



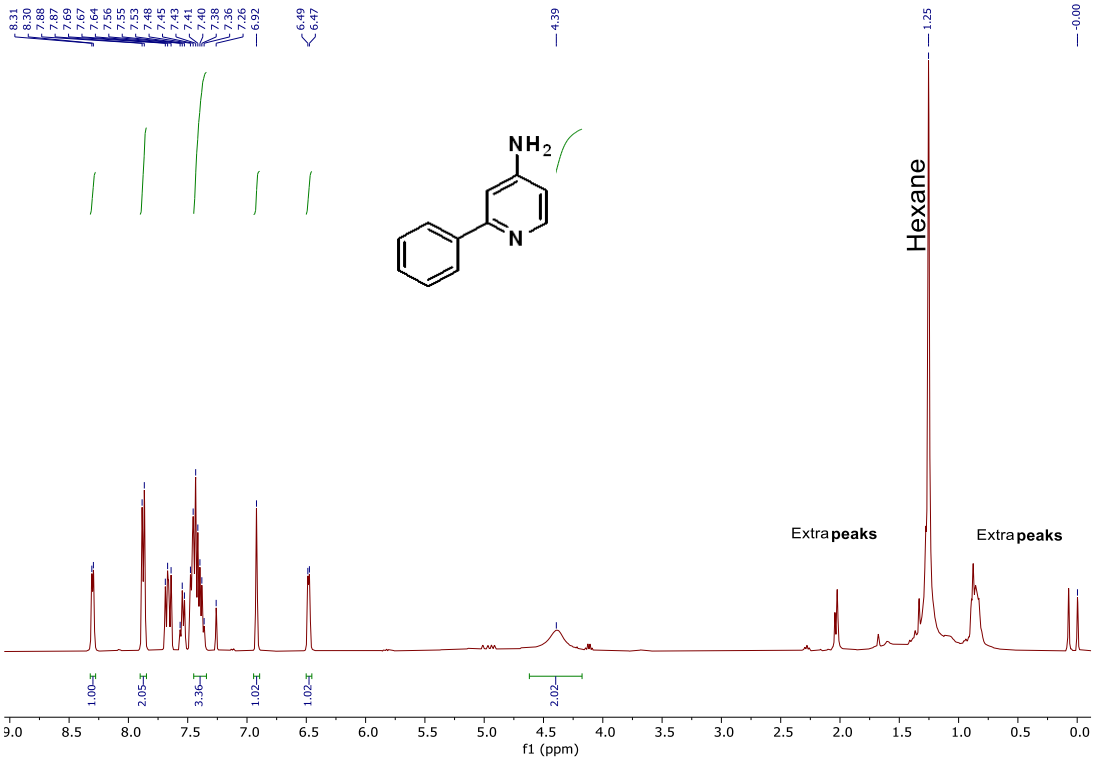
N-(2,6-Diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxy MonoimideDibutylester (9), ^{1}H NMR, $CDCl_3$, 400 MHz



(2,6-diisopropylphenyl)-1,7-bis[N-(pphenyloxy)-(4-(2-ethyl hexanamine)-1,8-dicarboxy napthalenemonoimide)]perylene-3,4,9,10-tetracarboxy monoimidedibutylester (10), ^{1}H NMR, $CDCl_3$, 500 MHz



2-Phenylpyridin-4-amine (13), ^{1}H NMR, $CDCl_3$, 400 MHz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8.30
7.88
7.87
7.69
7.67
7.64
7.56
7.55
7.53
7.48
7.45
7.43
7.41
7.40
7.38
7.36
7.26
6.92
6.49
6.47
4.39
1.25
-0.00
NH2
N
Hexane
Extra peaks
Extra peaks
1.00
2.05
3.36
1.02
1.02
2.02
f1 (ppm)