

Azoisoxazole Based Photoswitchable Ionic Liquids

Anees Rahman P

MS15018

*A dissertation submitted for the partial fulfilment of BS-MS dual
degree in Science*



Indian Institute of Science Education and Research Mohali

April 2020

Certificate

This is to certify that the dissertation titled “**Azoisoxazole based Photoswitchable Ionic Liquids**” submitted by Mr. Anees Rahman P (Reg. No. MS15018) for the partial fulfilment 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.

Dr. Sugumar Venkataramani

(Supervisor)

Dr. Sanchia Sengupta

(Committee member)

Dr. Rajkumar Roy

(Committee member)

Dated:

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Sugumar Venkataramani 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.

Anees Rahman P

(Candidate)

Dated:

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.

Dr. Sugumar Venkataramani

(Supervisor)

Acknowledgement

I would like to express my sincere gratitude and thanks to my supervisor **Dr. Sugumar Venkataramani** for his immense knowledge, continuous encouragement, priceless guidance and tremendous support. I would like to acknowledge members of my thesis committee, Dr. Sanchita Sengupta and Dr. Rajkumar Roy, for evaluating my work and giving me valuable suggestions throughout my project. I would like to express my sincere gratitude towards the current director Prof. Jayaraman Gowrishankar and former directors Prof. Siva Umopathy, Prof. Arvind, Prof. D. P. Sarkar and Prof. N. Sathyamurthy, for guiding us. I am also deeply thankful to Dr. S. Arulananda Babu, the Head of Department of Chemical Sciences, and Dr. K. S. Viswanathan who was the former Head of Department for all the support they have given me.

I want to express my sincere gratitude to Ankit Kumar Gaur and Debapriya Gupta for their guidance and encouragement. I am genuinely thankful to them for their help and support for completing this project. I would give my deepest love and gratitude for the support received from the Physical Organic Chemistry Group, IISER Mohali. I thank Anjali Mahadevan, Pravesh Kumar, Chitranjan Sah, Himanshu Kumar, Mayank Saraswat, Anjali Srivastava, Surbhi Grewal, Sonam Suwaisa, Sapna Singh, Amandeep Singh, Lincoln and Kaushalendra Patel for all their support and encouragement. My deepest gratitude to Sushil and Umer for helping me in doing some experiments. Special thanks to people from Dr. Samrat Mukhopadhyay's Lab and Dr. Sunil Patil's Lab for helping in this project. I would like to express my sincere thanks to all the people who helped me wherever I needed, encouraged me if I was depressed, and taught me within patience.

I would give my deepest love and gratitude to my dear parents for their unreserved loving and considerate care. I want to express my love and thanks towards my siblings, cousins and friends for their support and encouragement. None of this would be possible without their constant support.

Finally, I thank DST for INSPIRE fellowship and Department of Chemistry, IISER Mohali for all the facilities. I also express my gratitude to all other technical and non-teaching staff of IISER Mohali.

Anees Rahman

List of Figures

Fig.1.1 Most common structures of cations (A) and anions (B) used in ILs

Fig.1.2 Representative examples for the photoswitchable ILs in the literature

Fig. 1.3 General structure of Azobenzene based ionic liquid

Fig. 2.1 Reverse thermal isomerization kinetics plots for (a) **1a** and (b) **1b**

Fig. 2.2 Long-term photoswitching of compound **1b**

Fig. 2.3 UV-Vis spectra of compound **1b** for 5 cycles

Fig. 2.4 (a) & (b) Temperature dependent UV spectra of **1a** (a) before and (b) after irradiation

Fig. 2.4 Comparison of fluorescence spectra of (a) Compound **1a** and (b) **1b** in DMSO

Fig. 2.5 (a) & (b) Fluorescence lifetime decay plots of **1a** (a) and **1b** (b) in DMSO

Fig. 2.6 Fluorescence spectra after heating the compound **1a** in DMSO

Fig. 2.7 Plots depicting the fluorescence intensity changes as a function of temperature

Fig. 2.8 Conductivity versus concentration plot in **1b**

List of Schemes

Scheme 2.1 General scheme for reactions

List of Tables

Table 2.1 UV-Vis absorption data

Table 2.2 Fluorescence lifetime analysis of molecules at their emission maxima

Abbreviations

CH₃CN – Acetonitrile

DMSO – Dimethyl sulfoxide

CHCl₃ – Chloroform

CH₃OH – Methanol

EtOH – Ethanol

NaNO₂ – Sodium nitrite

NaOAc – Sodium acetate

Na₂CO₃ – Sodium carbonate

HCl – Hydrochloric acid

Me₂SO₄ – Dimethyl sulphate

Et₂SO₄ – Diethyl sulphate

NH₂OH.HCl – Hydroxylamine hydrochloride

Et₂O – Diethyl ether

ATR – Attenuated Total Reflectance

ESI – Electron Spray Ionization

TLC – Thin Layer Chromatography

MS – Mass Spectrometry

NMR – Nuclear Magnetic Resonance

¹H NMR – Proton NMR

¹³C NMR – Carbon-13 NMR

FT-IR – Fourier Transform Infrared Spectroscopy

HRMS – High Resolution Mass Spectrometry

TCSPC – Time Correlated Single Photon Counting

LED – Light Emitting Diode

Contents

List of Figures	i
List of Schemes	ii
List of Tables	iii
Abbreviations	iv
Abstract	vii
Chapter 1: Introduction	1
1.1 Ionic Liquids (ILs)	1
1.2 Photoswitchable Ionic Liquids (PILs)	2
1.3 Azobenzene based Ionic Liquids (Azo-ILs)	2
1.4 Properties and application of Photoswitchable Ionic Liquids	4
1.5 Motivation and Design	5
1.6 Tools and Techniques for experiments	5
Chapter 2: Results and Discussion	6
2.1 Synthesis	6
2.2 Analysis of photoswitching in the targets 1a and 1b using UV-Vis spectroscopy	7
2.3 Fluorescence Studies	11
2.4 Conductivity Experiments	17
Chapter 3: Conclusions and Discussion	19
Chapter 4: Materials and Methods	20
4.1 General	20
4.2 Synthesis	21
References	23
Appendix 5A	25

Appendix 5B	27
Appendix 5C	28
Appendix 5D	29
Appendix 5E	30
Appendix 5F	31

Abstract

Ionic Liquids (ILs) are salts with very low melting point (typically $< 100\text{ }^{\circ}\text{C}$). Ionic liquids are unique compared to other molecular species since their properties are tunable and peculiar. Ionic liquids have low vapour pressure, excellent thermal stability and good electrical conductivity. Such ILs have been investigated with a wide range of molecules to incorporate additional properties. In this current investigation, ILs incorporated photoswitchable molecules have been considered as targets towards making them photoswitchable ILs. Azobenzenes are molecules with two phenyl groups separated by N=N double bond got significant attraction due to their high optical sensitivity. Azobenzene compounds with light switchable properties have been widely examined in several fields based on their photoresponsive reversible isomerization.

Azobenzene based ionic liquids have attracted considerably due to the possibility of light modulated properties change. In earlier reports, azobenzene has been incorporated as a separate entity to impart photoresponsive character into the ionic liquid structure to produce photoresponsive functions to ionic liquids. However, due to the recent progress in azoheteroarene based switches, in particular, the advantages such as high *Z*-isomers stability and better photoisomerization in both directions, provide opportunities in utilizing them in the ILs. Besides that, the heterocyclic moieties can be used for direct incorporation of both IL part, as well as photoswitching part at a proximal position in making novel designs of photoswitchable ILs.

In this regard, we used alkylated azoisoxazole as the target photoswitchable ILs. Through this contribution, we present the alkylation of azoheteroarene based photoswitches to synthesize the targets, and investigations on their stability, photoswitching aspects and conductivity properties.

Chapter 1: Introduction

1.1 Ionic Liquids (ILs)

Presence of a molten salt, ethyl ammonium nitrate $[\text{EtNH}_3][\text{NO}_3]$ with a melting point below room temperature was reported by Walden in 1914, which led to the discovery of Ionic liquids (ILs)¹. Since then, ILs received moderate attention of many research groups. However, the study about ILs got manifolded when pyridinium or imidazolium cations were used. Ionic Liquids (ILs) have begun a green revolution in chemistry, physics and materials science in the form of both technological advancements and conceptual innovations in the past two decades². Ionic Liquids (ILs) are salts with a shallow melting point. In some context, the term is limited to salts whose melting point is below 100 °C. Ionic liquids are unique compared to other molecular species since their properties are tunable and peculiar. They have low vapour pressure, excellent thermal stability and good electrical conductivity and possess a large tunable electrochemical window³. These properties make them suitable for several applications like alternative solvents, electrolytes in dye-sensitized solar cells, active pharmaceutical ingredients (API) and electrodeposition of metals, etc⁴.

Ionic Liquids (ILs) are formed by intermolecular interaction between a weakly coordinating organic and inorganic anion and an organic cation of low flammability. Some of the common cations and anions that are part of the ILs are given in the following Fig. 1.1. Many ILs were produced by varying cations and anions. Most of the studies based on ILs aim to explore the relationship between their structure and properties⁴. Asymmetry among cation and anion, which leads to the low melting point of ILs and, which in turn leads to a weak crystal structure. By changing dominant forces, which in turn affect their properties, we can design ILs with desired functionality. Properties of ILs depend on an infinite number of possible combinations between cations and anions. For this reason, ILs are called designer solvents⁵.

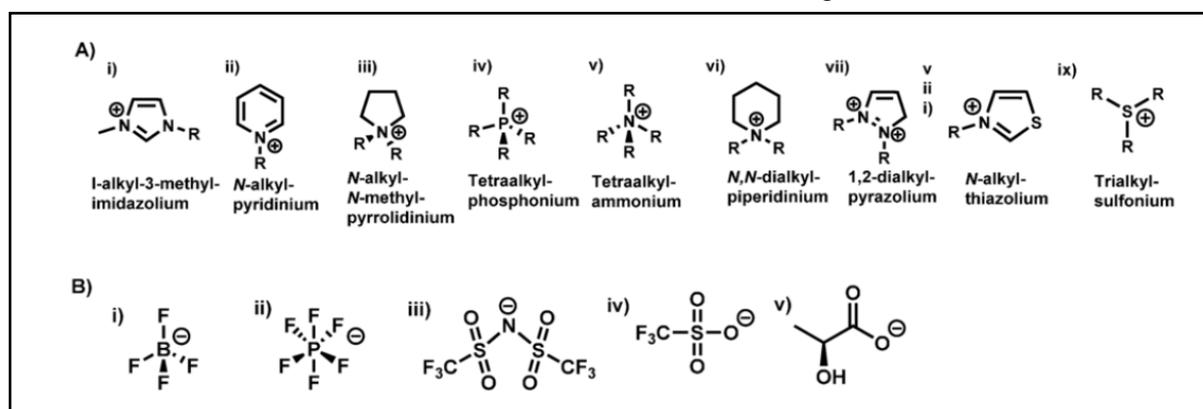


Fig.1.1 Most common structures of cations (A) and anions (B) used in ILs

1.2 Photoswitchable Ionic Liquids (PILs)

Smart materials are a class of materials whose characteristic features can be modulated by external stimuli such as pH, light, temperature etc. Photoswitchable ILs are produced by incorporating ILs with photoswitchable properties, which utilises light responsiveness along with properties of ILs⁶. Most of the photoswitchable ILs have developed by the direct merging of photoswitchable groups into anyone of the anions or cations of ILs. Photoswitchable ILs can utilise both the properties of ILs as well as the properties of photoswitchable material and their features can be modulated by merely changing the cations of this ILs⁷. Introduction of photoswitchable groups into ILs can produce photoinduced changes in their physiochemical properties. Conductivity and melting point of these ILs can be changed under irradiation with visible light and Ultraviolet (UV) sources⁸. Some of the reported photoswitchable ILs are given in Fig. 1.2.

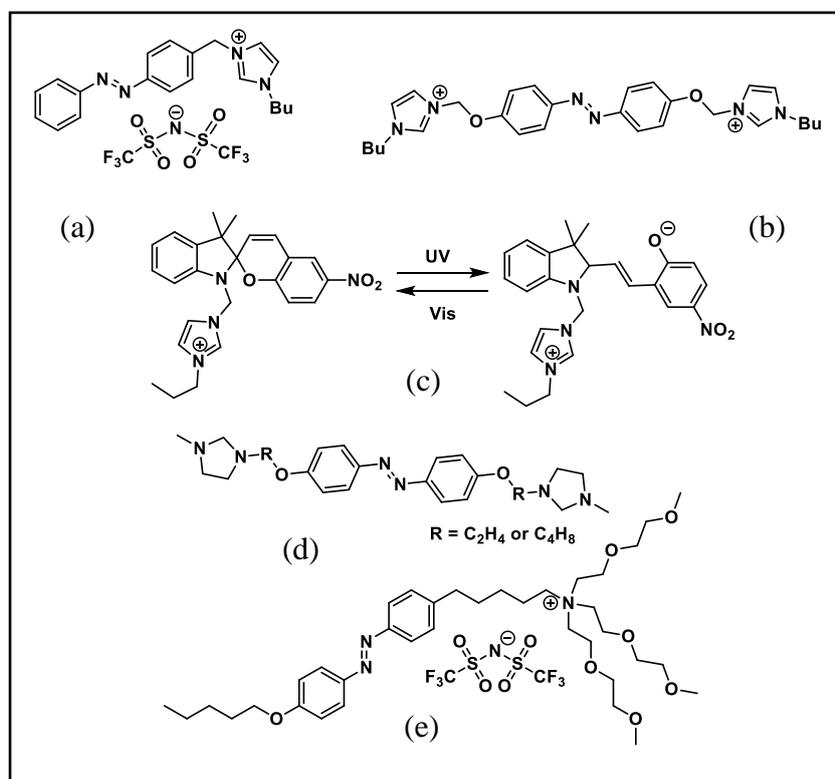


Fig.1.2 Representative examples for the photoswitchable ILs in the literature^{7, 9-11}

1.3 Azobenzene based Ionic Liquids (Azo-ILs)

Azobenzenes are molecules with two phenyl groups separated by N=N double bond got significant attraction due to their high optical sensitivity. Azobenzenes upon irradiation with UV-light of suitable wavelength, switch between two isomeric states, namely *cis* and *trans* isomers¹². Ionic liquids with reversible and stable interconversion between two different

isomeric forms were achieved by the addition of azobenzene moieties in the cationic part. Azobenzene based ILs (Azo-ILs) have also been used due to the possibility of manipulation of their properties by light¹³. In general, the *trans* isomer is the thermodynamically stable isomer, which can be switched to *cis* isomer by irradiating with UV-light. The reverse isomerisation (*cis* to *trans*) can be produced either thermally or by photoirradiation in the visible range. Nevertheless, this optical isomerisation is only possible when absorption spectra of *cis* and *trans* are significantly different. There are several mechanisms considered for isomerisation process, mainly through inversion about azo nitrogen or through rotation about the dihedral angle involving azo group¹². These mechanisms depend on numerous factors like solvents, pressure and substituents. Azo-ILs have been an excellent platform to study various applications. They can be utilised as light-controlled ion transporters. It's even shown that azobenzene-imidazolium ILs can improve drug delivery systems¹⁴. Photoswitchable abilities of ILs can be used to control their conductivity in aqueous solutions. Azo-ILs can produce reversible changes on the viscoelasticity of block copolymers¹⁵.

Azobenzene is well known for its reversible isomerisation. Due to strong π - π stacking, Azobenzene compounds are generally insoluble in ILs containing imidazolium groups¹⁶. This can be solved by incorporating azobenzene covalently to the ionic liquid. Most of the azobenzene containing ILs are in solid-state due to strong rigidity of azobenzene moieties. In order to solve this issue, higher alkyl chains are incorporated to obtain room temperature ionic liquids. Most of the reported Azo-ILs show a particular structure comprising a photoswitchable unit connected to the ionic part through a spacer group (linker) attached in between them¹³. These spacer groups are generally alkyl groups with varying chain length. Figure 1.3 gives the general structure of Azo-ILs.

With the help of azobenzene based photoresponsive unit into the ionic liquid structure photoresponsive functional ionic liquids have been generated that can control the function of ion-channels¹⁷. Ionic liquid crystals based on azobenzene have become well known for their capability to liquefy under UV irradiation since *cis*-isomer will disrupt the orderly arrangement of azobenzene units¹⁵. Ionic conductivity of azobenzene-based ILs prepared by Zhang and co-workers (with a cation containing light responsive group) has been reversibly modulated in some organic solvents under UV irradiation¹⁸. Azobenzene compounds with light-switchable

properties have been widely investigated in different areas based on their photoresponsive isomerisations, such as microfluid control, photo patterning, drug release and data storage¹⁹.

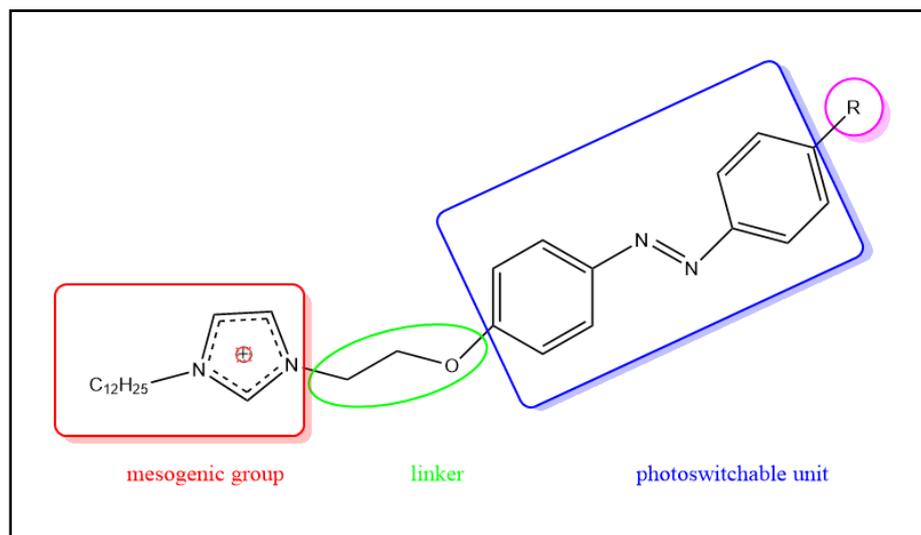


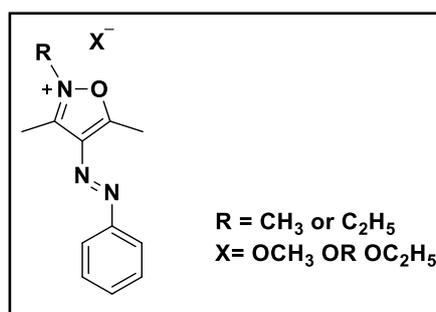
Fig. 1.3 General structure of Azobenzene based ionic liquid

1.4 Properties and Applications of Photoswitchable Ionic Liquids (PILs)

Photoswitchable Ionic Liquids (PILs) have attracted considerable attention in recent years for their unique properties and their potential high recyclability²⁰. They can be regarded as designer solvents due to the feasibility to change the cationic and anionic components within a broad range of combinations to cause changes in various physical properties such as density, viscosity, water miscibility and melting point²¹. PILs possess unique physicochemical properties such as very less vapour pressure, considerable thermal stability and good electrical conductivity, not significantly volatile. Due to their unique and favourable properties, PILs can be used for various applications²². They can be used as ion transporters controlled by light. PILs can improve the release time of drug delivery system¹⁴. The photoswitching of these ILs has also shown excellent potential in controlling the conductivity of IL in aqueous solutions. Also, when integrated into a block copolymer, Azo-ILs can induce reversible variations in viscoelasticity¹⁵. Their reversible *cis-trans* photoisomerisation process gives a broad range of applications like optical switching, data storage and polarisation holography and as a photolabile surfactant²². For these reasons, azobenzene based ionic liquids are extensively studied over the last decade.

1.5 Motivation and Design

Azoheteroarene based switches are recently known for their inherently high Z-isomers stability and better photoisomerization in both directions²³. Azothiazole, azobenzothiazole and azopyridine based *N*-alkylated photoswitches are well known for fast switching²⁴. On the other hand, several other azoheteroarenes with five-membered heterocycles such as azopyrazoles and azoisoxazoles have been proven to be more stable in Z-isomer state with exceptional photoswitching properties that can also be tuned²⁵⁻²⁹. **In this present work, our aim is to do alkylation of azoheteroarene based photoswitches and studies thermal stability, photoisomerization, aggregation behaviour.** So far there is no such report of alkylation of azoisoxazole, azopyrazole. We choose azoisoxazole for alkylation of isoxazole nitrogen by using dimethyl sulphate or diethyl sulphate as alkylating agents.



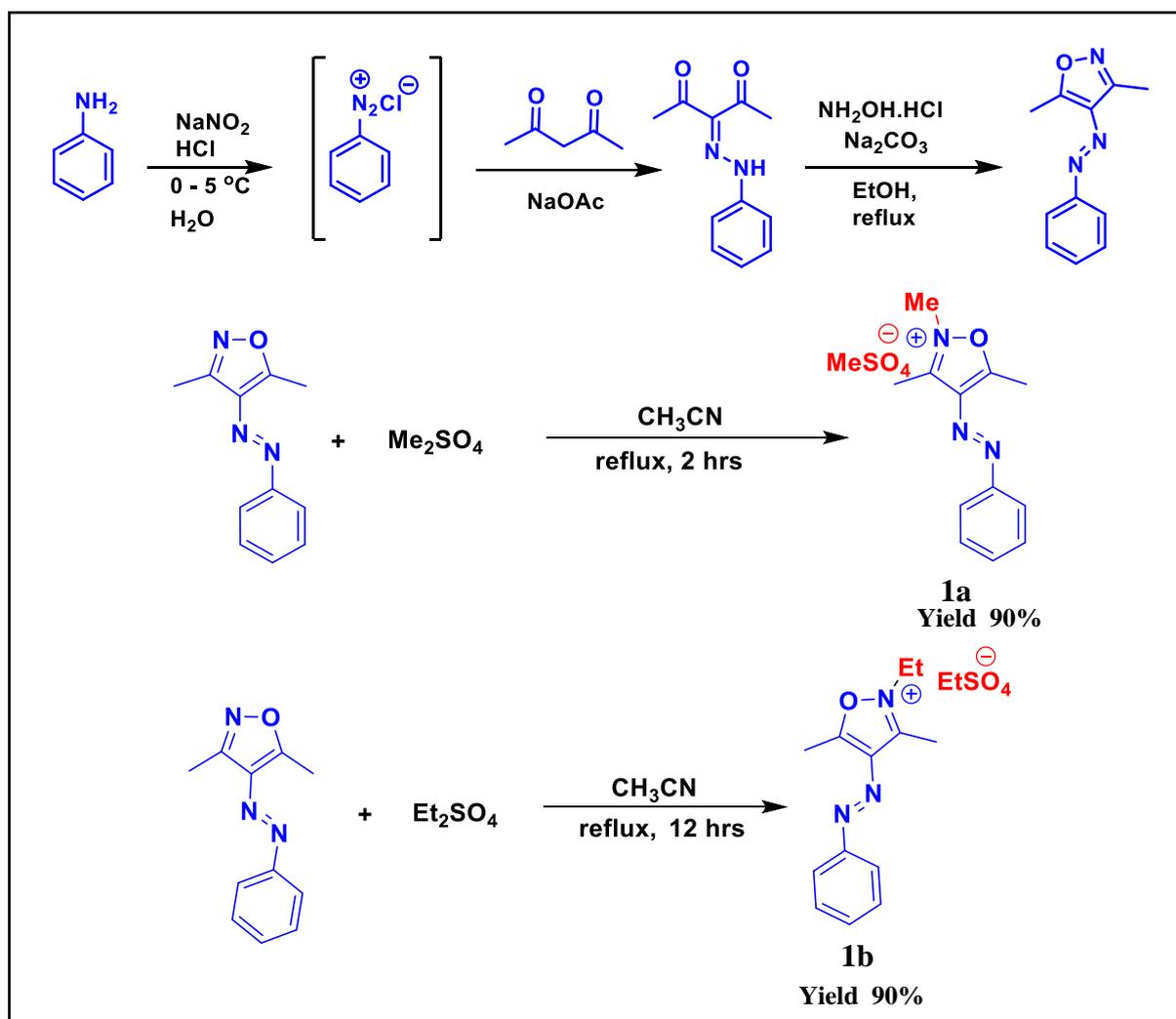
1.6 Tools and Techniques for Experiments:

To study the photoisomerisation behaviour of target molecule, we used UV-Vis and fluorescence spectroscopy. Aggregation behaviour of the target molecules was analysed mainly by conductivity measurements and fluorescence spectroscopy. Thermal stability of the desired molecules was analysed using temperature-dependent UV-Vis spectroscopy and temperature-dependent fluorescence spectroscopy. Kinetic studies were mainly carried out using UV-Vis spectroscopy. Analysing the various data obtained through different experiments were carried out using different software tools like Origin, MesterNova etc.

Chapter 2: Results and Discussion

2.1 Synthesis

The alkylated ionic salts of heteroazoarenes have been considered as the target molecules for making photoswitchable ionic liquids in this investigation. In this regard, we have synthesised two simple *N*-alkylated derivatives of phenylazo-3,5-dimethylisoxazole. Two different alkylating agents, namely, dimethyl sulfate and diethyl sulfate, have been utilised for *N*-alkylation of isoxazole nitrogen, and the optimised reaction scheme has been given (Scheme 2.1). The synthesised compounds were purified by washing the crude reaction mixture in petroleum ether multiple times, which was then dried under vacuum to yield around 90% products. All the synthesised molecules have been fully characterised by ^1H and ^{13}C -NMR, HRMS, UV-Vis and fluorescence spectroscopic techniques.



Scheme 2.1 General scheme for reactions

2.2 Analysis of photoswitching in the targets **1a** and **1b** using UV-Vis spectroscopy

The UV-Vis absorption spectra of both compounds **1a** and **1b** have been measured in DMSO. First, the absorbance spectrum was recorded after heating to ensure that the molecules are in a thermodynamically stable state (*E*-isomer). Then the compounds were irradiated with 365nm UV light, at which isomerization (switching) is maximum. The UV-Vis absorption spectra of the compounds were recorded at its PSS (photostationary state). A different wavelength of light in the visible region was used for inducing reverse isomerization (*Z* to *E* isomer).

The photoswitching studies were conducted in five different solvents for both the compounds. The solvents used for photoswitching studies were namely, DMSO, CHCl₃, CH₃OH, Water and CH₃CN. The spectroscopic data containing the percentage of conversion are summarized in the given table. 2.1. The absorption spectra corresponding to the native state (before irradiation) as well as at PSS corresponding to both forward switching (*E*-*Z*) and reverse switching (*Z*-*E*) in different solvents are given in the appendix 5A.

The switching wavelength required by our molecules ranges from 405 to 470nm. Forward and reverse switching is comparable in DMSO for both compounds (Their percentage of conversion values are almost similar). For both, the compounds in CHCl₃ forward switching is quite efficient. Conversion of *E* to *Z* is almost complete in CHCl₃ but reverse switching did not happen even under prolonged irradiation conditions. In order to get back to the native state, the sample was heated. Conversion of *Z* to *E* is more feasible in **1a** compared to **1b** on heating. Spectra of both the compounds in methanol have shown a well-separated n-π* and π-π* absorption bands, whereas, in other solvents, those were not separated well. Interestingly, the product **1b** showed a redshift in the λ_{max}, when it was switched back to *E*-isomer.

Kinetic studies of both compounds (concentration: 100mM) were carried out in DMSO at room temperature (25 ± 2 °C). Both the kinetic plots revealed an exponential growth and followed a typical first-order rate constants. By using an exponential fit, the first-order rate constants were estimated to be 2.1 x 10⁻³ and 3.8 x 10⁻³ min⁻¹, for **1a** and **1b**, respectively (Fig. 2.1a, b). The half-lives obtained for methyl-substituted ionic liquid (**1a**) we synthesised was around 5.3 hours whereas, for ethyl substituted ionic liquid (**1b**), it was about 3.0 hours at room temperature.

Table. 2.1 UV-Vis absorption data

Compound	S. No	Solvent	λ_{\max} (nm)		Percentage of Conversion	
			Before Irradiation (<i>E</i> -isomer) (ϵ) ^a	After Irradiation (<i>Z</i> -isomer)	Forward ^c Switching	Back ^d Switching
1a	1	DMSO	353 (8190 ± 152)	346	59	70
	2	CHCl ₃	321 (5746 ± 402)	371	86	52
	3	CH ₃ CN	314 (10891 ± 190)	309	43	67
	4	Water	315 (9690 ± 226)	309	43	78
	5	CH ₃ OH	317 (7007 ± 24)	307	49	81
			387^b	388^b		
1b	1	DMSO	326 (24216 ± 725)	295	63	74
	2	CHCl ₃	321 (24216 ± 725)	368	96	36
	3	CH ₃ CN	316 (4765 ± 375)	309	49	82
	4	Water	326 (11546 ± 157)	297	63	74
	5	CH ₃ OH	316 (12057 ± 116)	310	56	65
			388^b	392^b		

^aUnit of $\epsilon - M^{-1}cm^{-1}$

^bBoth $n-\pi^*$ and $\pi-\pi^*$ peaks are well separated.

^c% of conversion of *E*-isomer = $1 - \frac{A(n-\pi^*) \text{ absorption before irradiation}}{A(n-\pi^*) \text{ absorption after irradiation at 365 nm}}$

^d% of conversion of *E*-isomer = $1 - \frac{A(\pi-\pi^*) \text{ absorption after irradiation at 365 nm}}{A(\pi-\pi^*) \text{ absorption before irradiation}}$

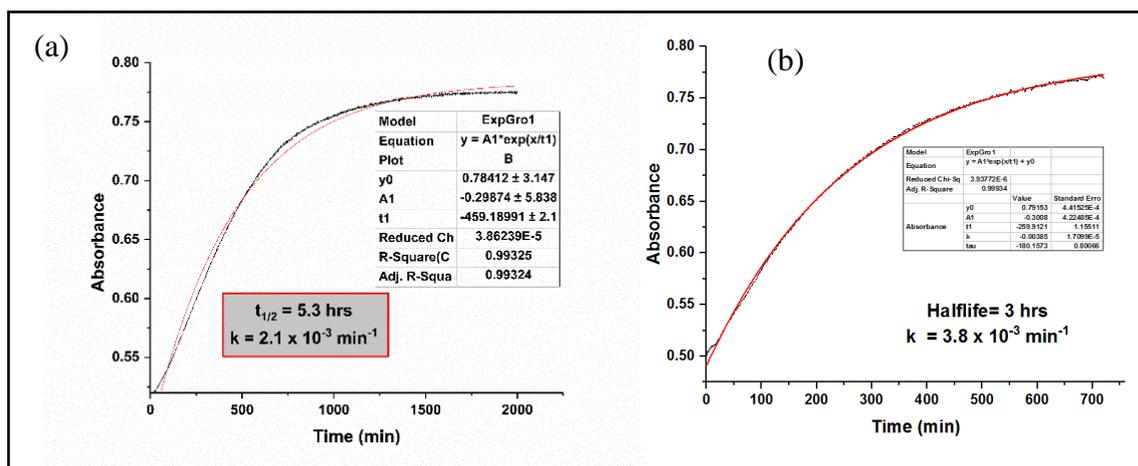


Fig. 2.1 Reverse thermal isomerization kinetics plots for (a) **1a** and (b) **1b**

Long term photoswitching studies have also been carried out for these molecules. Long term studies using compound **1b** in DMSO shows very less stability. In this regard, the sample was alternatively irradiated with 365nm (for forward isomerization) and 470nm (for reverse isomerization) over five cycles. After each cycle, the molecule exhibited lower conversion during reverse switching. This indicates that the molecule tends to stay in *cis*-isomer state, and it is not returning to original *trans*-isomeric state. This behaviour can be due to changes in the aggregation pattern of the molecule in DMSO. Long term photoswitching stability plot and UV-Vis spectra of **1b** is given in Fig. 2.2, and Fig. 2.3.

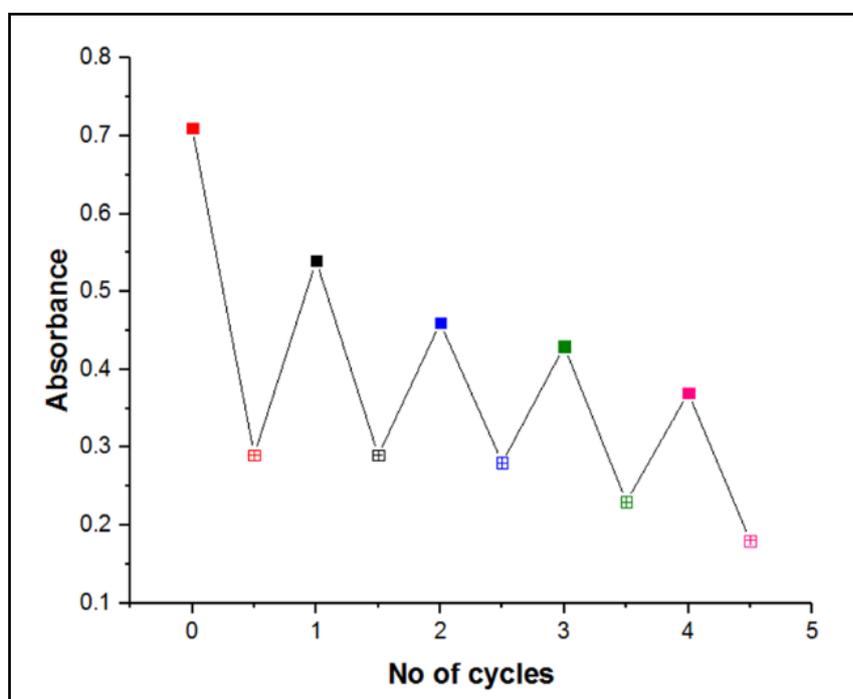


Fig. 2.2 Long-term photoswitching of compound **1b**

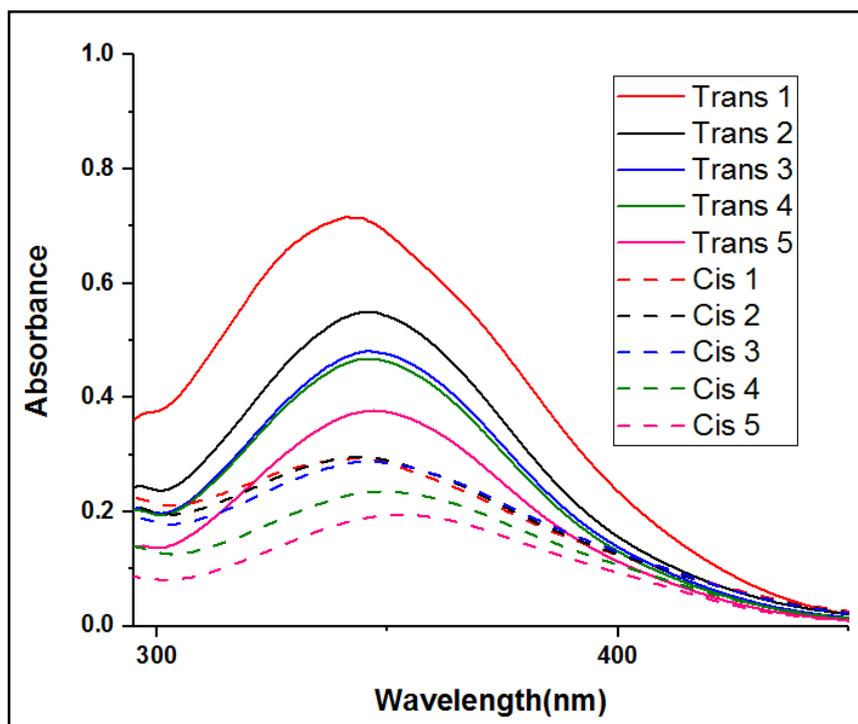


Fig. 2.3 UV-Vis spectra of compound **1b** for 5 cycles (Forward switching: 365 nm; Reverse switching: 470 nm; Solvent: DMSO; Concentration: 25.0mM)

Temperature-dependent UV-Vis spectra of compound **1a** before and after irradiating with 365nm light were also recorded in DMSO. Spectra was initially recorded at room temperature and then increased by an increment of 10 °C till 100 °C, then cooled back to room temperature at the same increment. While heating the sample towards 100 °C, we noticed that absorbance value was decreasing with the increase in temperature. On attaining 100 °C, the compound showed the least absorbance value. The absorbance value again increased upon cooling the sample back to room temperature but it did not reach the original absorption maxima, which we obtained when recording the first spectra. When the sample was subjected to cooling, there was a slight redshift in the spectra. Fig. 2.4 depicts the temperature-dependent UV-Vis spectra before irradiating (Fig.2.4 (a)) and after irradiation with 365nm light (Fig.2.4 (b)).

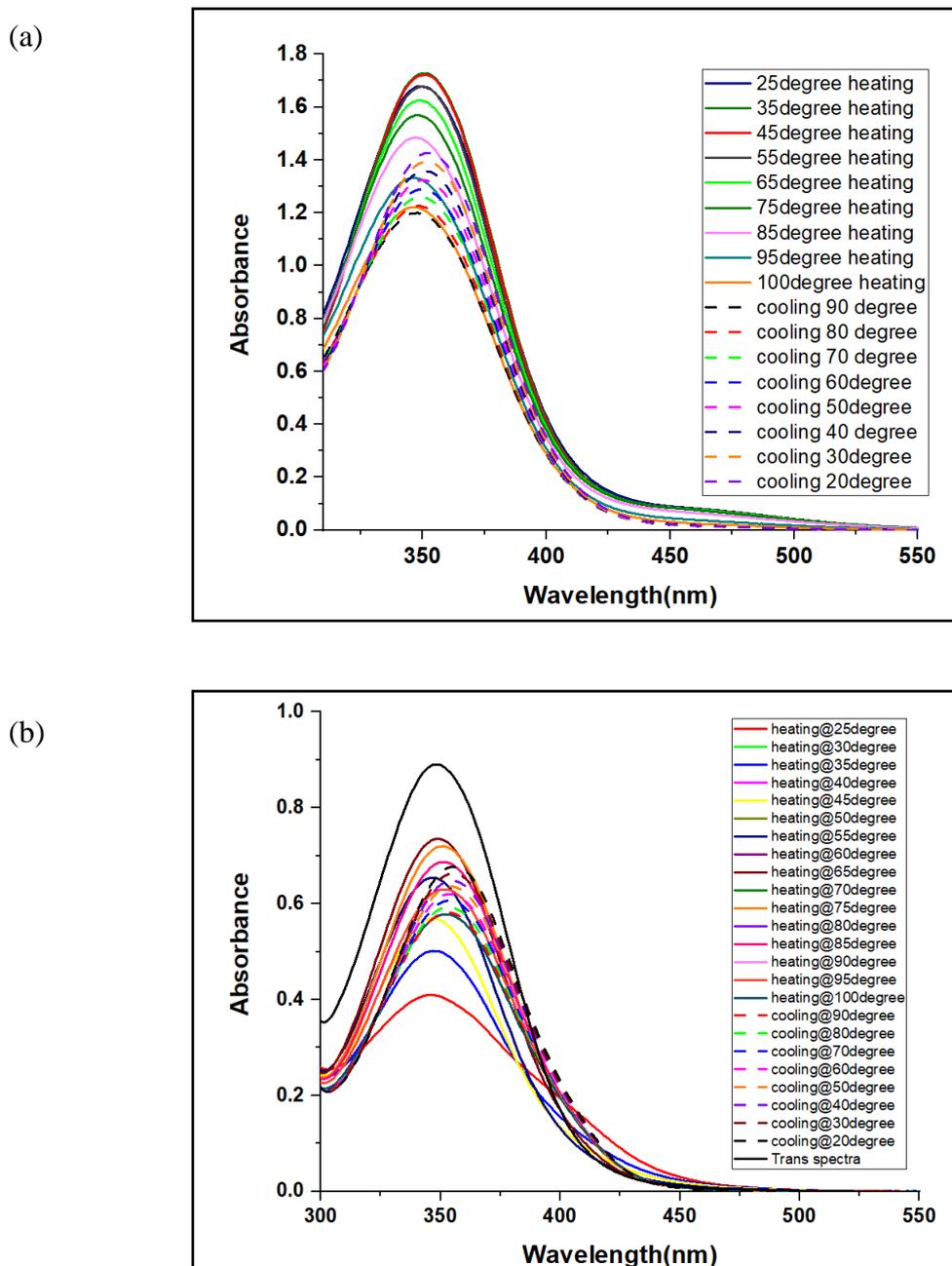


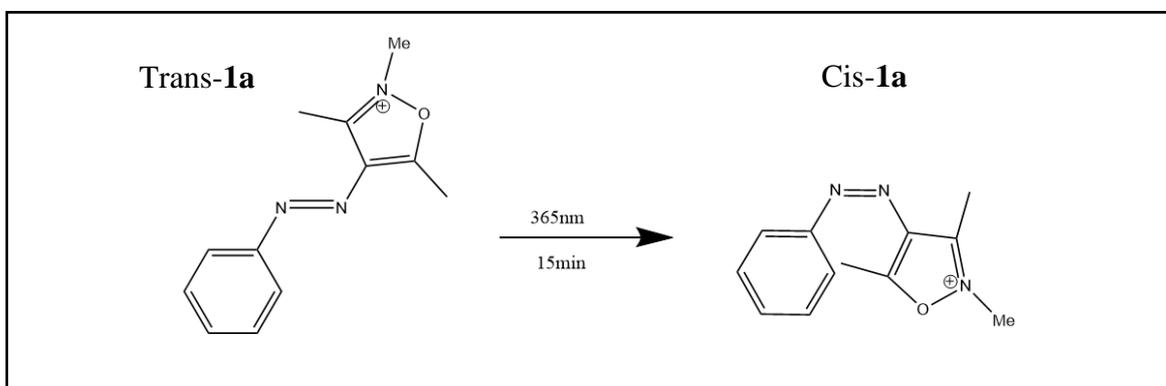
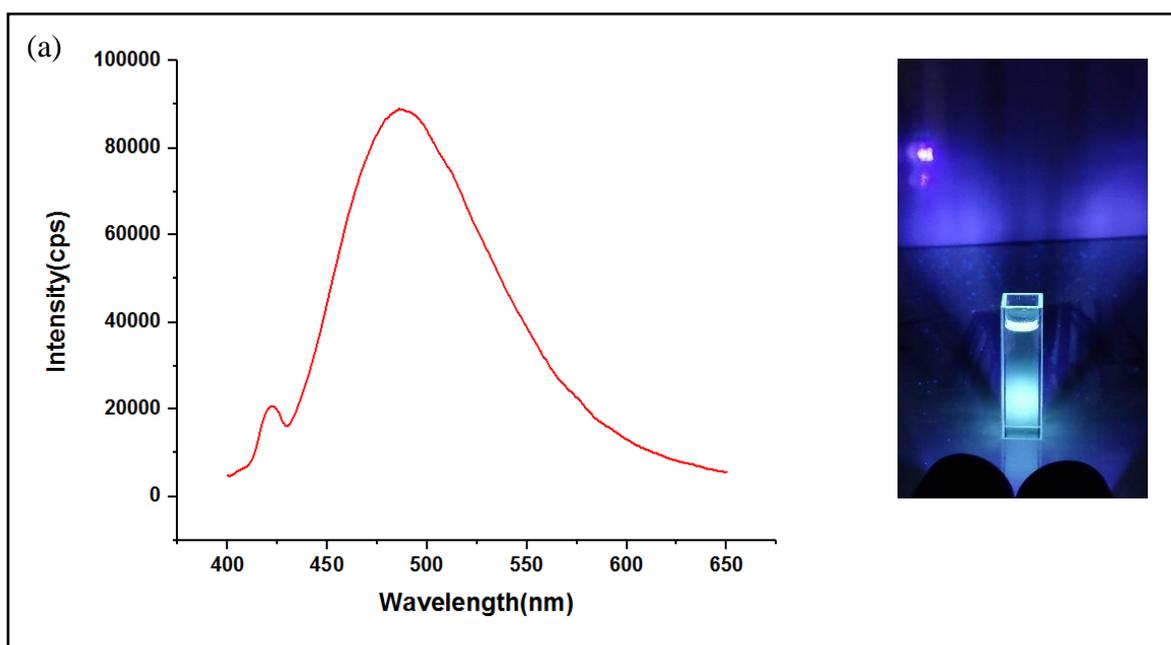
Fig. 2.4 (a) & (b) Temperature-dependent UV spectra of **1a** (a) before and (b) after irradiation

2.3 Fluorescence Studies:

While performing the solution phase photoswitching studies of both the target molecules, we observed a green light emanating from the solution after irradiating at 365nm light for about 15-20 minutes (Fig. 2.4). We realized that the molecules must be showing fluorescence in the *cis* form. The intensity of the emitted green light got increased as more molecules get converted from *E* to *Z* isomer. The intensity gets saturated when all the molecules are get converted to *Z*-

isomer. Both the molecules showed this property in almost all solvents that we used to record UV-Vis spectra.

To gain more information, fluorescence spectroscopic studies for both the molecules have been carried out in DMSO. Both molecules were showing a broad emission when excited with a light of 365nm. Both of the molecules emitted in the green light region of the spectra with emission maxima around 475nm and 490nm for **1a** (Fig. 2.4 (a)) and **1b** (Fig. 2.4 (b)), respectively. Presumably, there could be some form of aggregation happening to molecules at the concentration in which these experiments are performed (100 μ M) when they get converted to *Z*-isomer due to which they were showing fluorescence behaviour in solution, and the molecules were non-fluorescent in *E*-isomeric state. The understanding of the exact reason for this behaviour is currently underway.



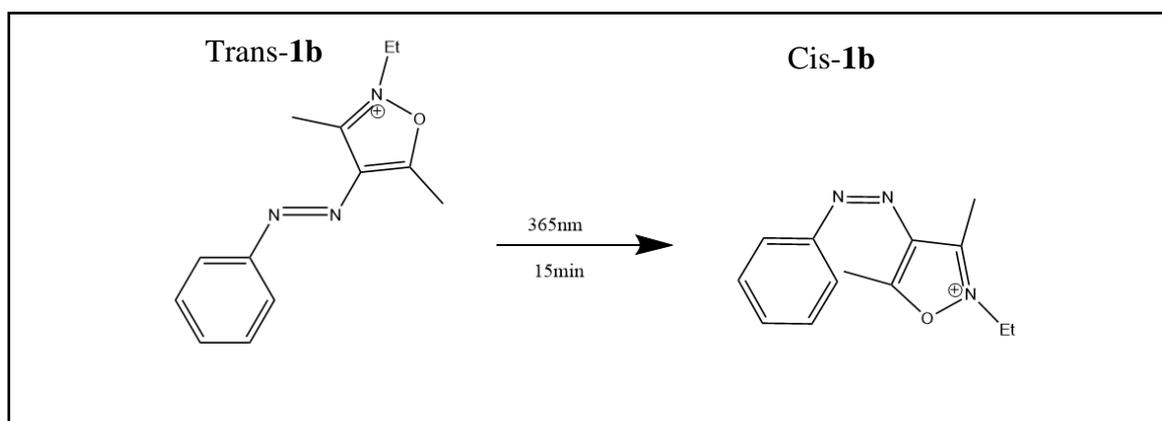
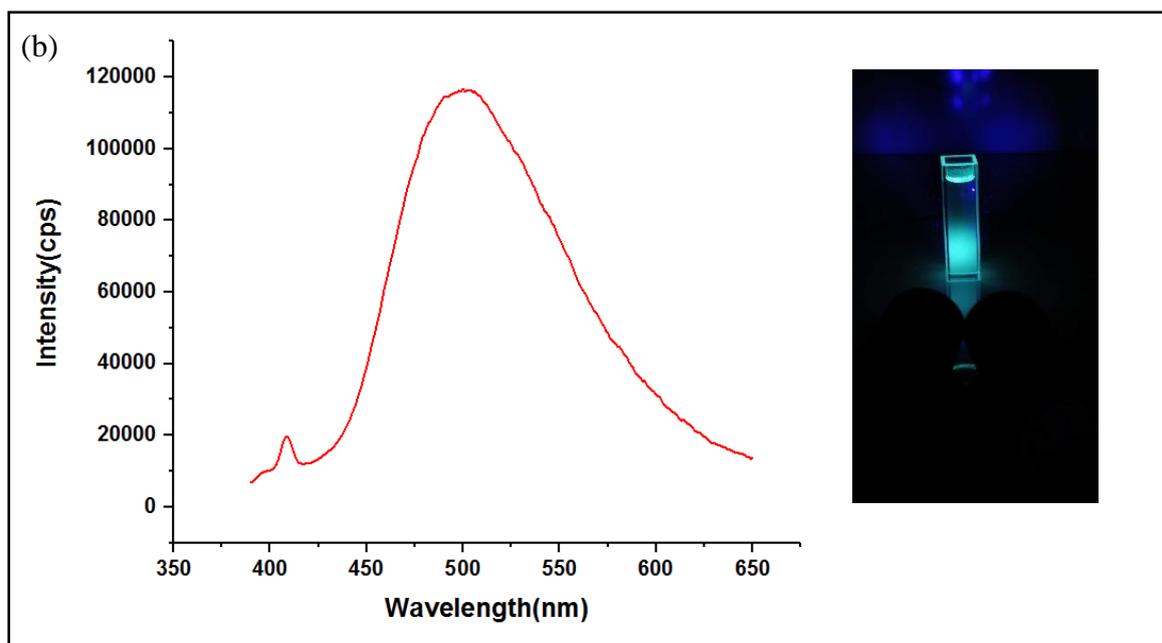


Fig. 2.4 Comparison of fluorescence spectra of (a) Compound **1a** and (b) **1b** in **DMSO**
(Concentration: 100.0 μM)

To understand more about this fluorescence behaviour, we performed TCSPC experiments. Fluorescence lifetime measurements were performed for both **1a** and **1b** in DMSO using time-correlated single-photon counting (TCSPC) technique. The fluorescence lifetimes of **1a** and **1b** were measured upon excitation at 375 nm with a laser diode. Decay profiles at emission wavelengths of 475 nm (corresponding to **1a**) and 490 nm (corresponding to **1b**) were studied. Fig. 2.5 shows the fluorescence decays along with fitted plots. Fitting parameters and lifetimes are given in Table 2.2.

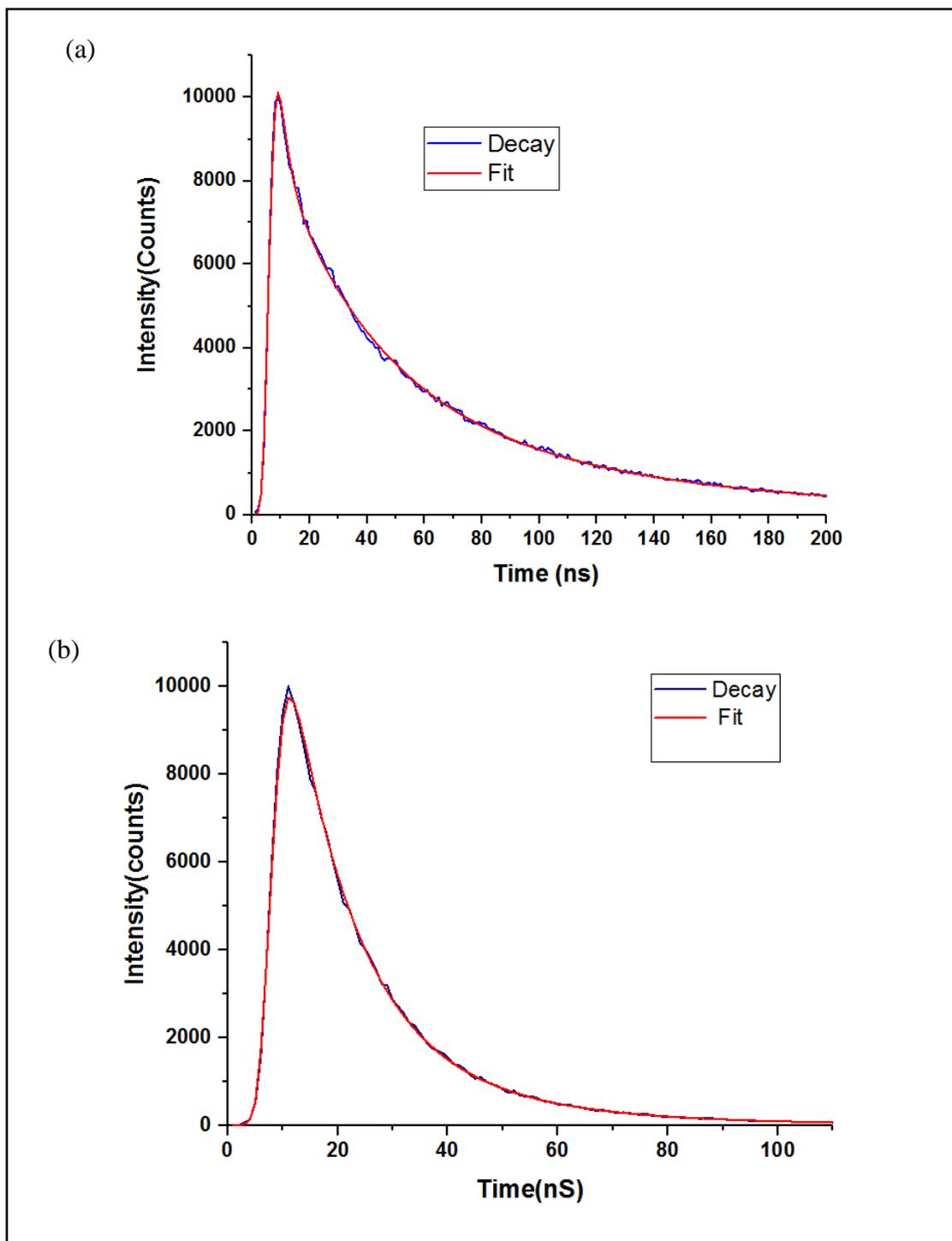


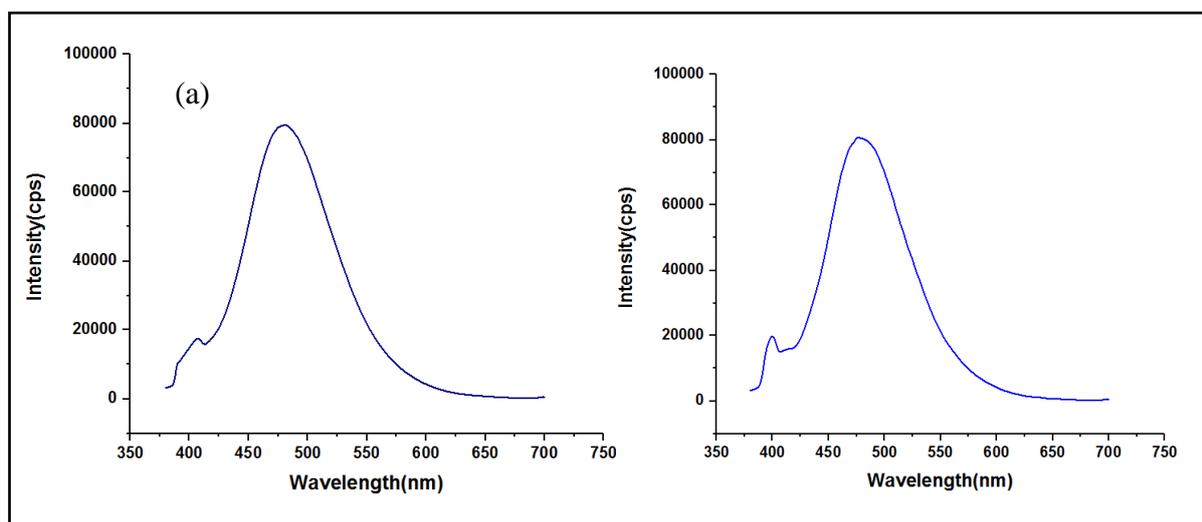
Fig. 2.5 (a) & (b) Fluorescence lifetime decay plots of **1a** (a) and **1b** (b) in **DMSO**

Table 2.2 Fluorescence lifetime analysis of molecules at their emission maxima

Compound ($\lambda_{\text{ex}}=375\text{nm}$)	$\lambda_{\text{em}}(\text{nm})$	τ_1 (α_1)(ns)	τ_2 (α_2)(ns)	τ_3 (α_3)(ns)	τ_{avg}^* (ns)	χ^2
1a	475	0.70 (0.86)	1.60 (0.14)	-	0.80	1.29
1b	490	1.90 (0.38)	5.40 (0.19)	0.17 (0.43)	1.80	1.35

A slower decay was observed for compound **1a** emission at 475nm with a lifetime of 0.70ns than the compound **1b** emission at 490nm with a lifetime 0.17ns (given in figure 2.4(a) and 2.4(b) respectively). The average lifetimes of the decay for both **1a** and **1b** were obtained to be 0.80ns and 1.80ns, respectively.

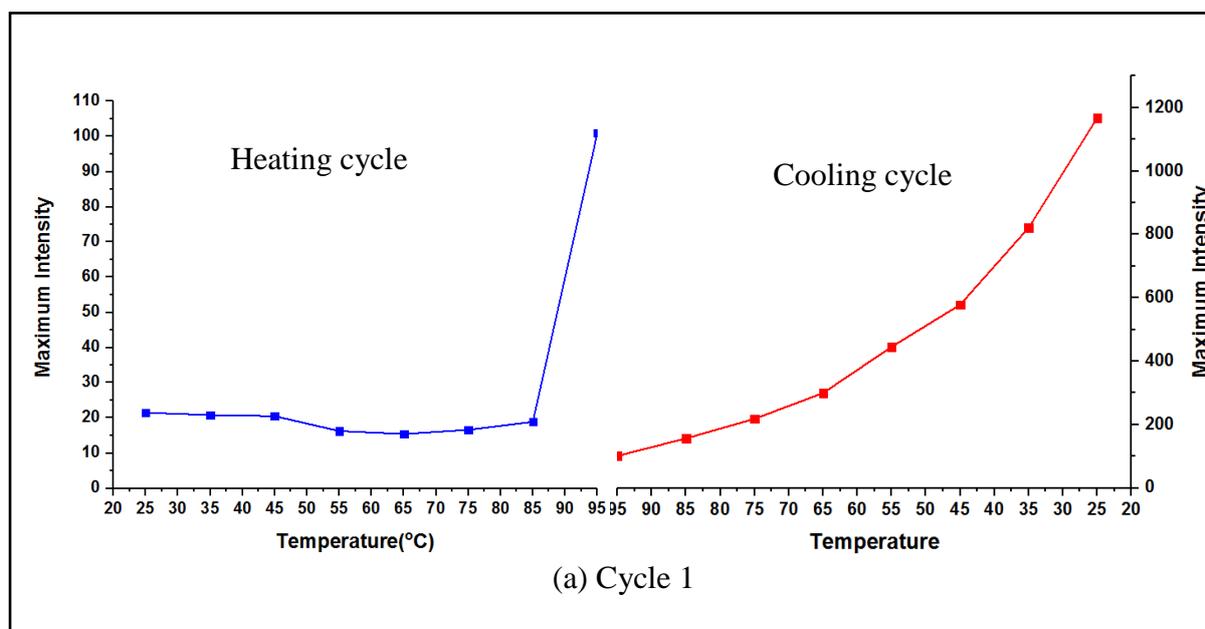
Compound **1a** is showing fluorescence property even in *E*-isomeric state after heating it in DMSO. This behaviour is only observed when the solvent used is DMSO, and it is not observed in any other solvents. Heated sample also shows fluorescence even after irradiating with 365nm light. Fluorescence spectra of heated sample before and after irradiation with 365nm light is given in Fig. 2.6. Both spectra's are similar to each other with λ_{ex} at 475nm.

**Fig. 2.6** Fluorescence spectra after heating the compound **1a** in DMSO (a) *E*-isomer after heating in DMSO and (b) *Z*-isomer after heating in DMSO

To understand more about this behaviour of our compound **1a**, which shows fluorescence property in *E*-isomeric state on heating, we recorded temperature-dependent fluorescence

spectra in DMSO. We recorded the fluorescence spectra for two heating cycles, starting with room temperature up to 100 °C with an increment of 10 °C. Then the sample was cooled down to room temperature in the same way. Similarly, fluorescence spectra recording was continued for the second cycle. Compound **1a** did not show fluorescence behaviour until 95 °C. On cooling back to room temperature, the fluorescence intensity increased again and reached a maximum value at room temperature. During heating again in the second cycle, fluorescence intensity was decreasing with the increase in temperature. During the second cooling cycle, fluorescence intensity keeps on increasing with the decrease in temperature and reaches the maximum value, which is higher than the first cycle. Individual spectra of each, cycle as well as combined spectra of both heating cycles, are given in Appendix 5B.

The maximum intensity of each fluorescence spectra was plotted against the corresponding temperature. The combined plots were found to obtain a hyperbolic form. From the plots of the first cycle, we can clearly see that **1a** is showing fluorescence only beyond 85 °C. On cooling intensity is further increasing and reaches a maximum intensity of around 1200 at room temperature. In the second cycle, both heating and cooling cycles showed a hyperbolic curve with an intensity decreases on heating, whereas intensity increases on cooling and reaches a maximum value around 1800 at room temperature. The plots of maximum intensity against temperature are given in Fig. 2.7.



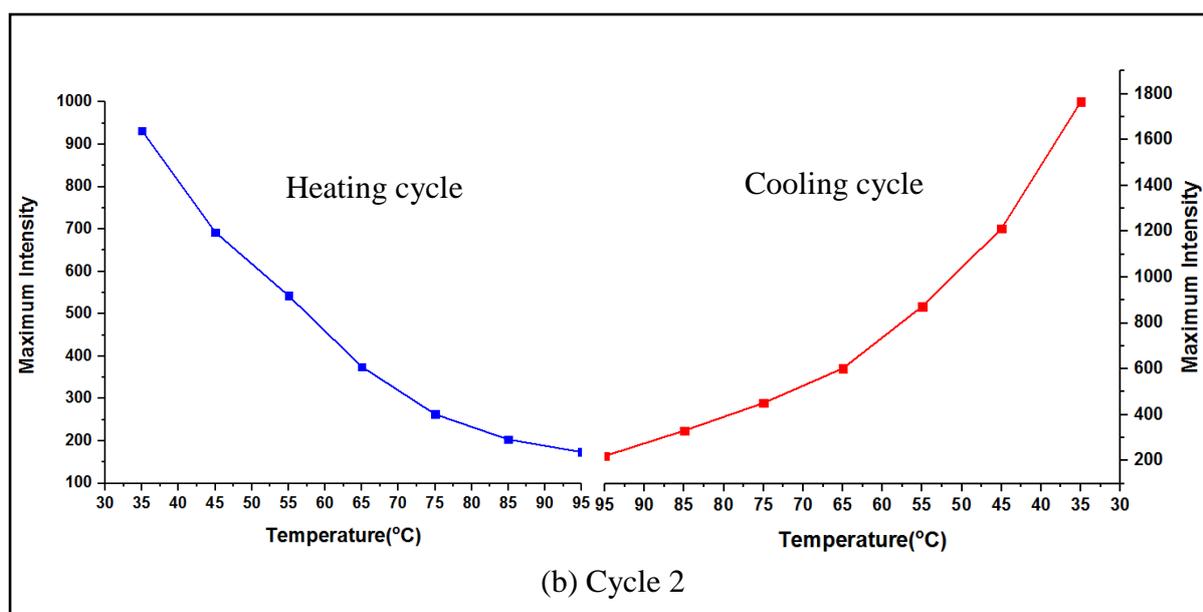


Fig. 2.7 Plots depicting the fluorescence intensity changes as a function of temperature (a) First cycle and (b) Second cycle (the intensity corresponds to the emission maxima was utilized for both the cycles)

2.4 Conductivity Studies:

Conductivity studies were performed to understand the difference in conductivity values in both *cis* and *trans* isomeric states. Conductivity studies were performed for **1b** in distilled water before and after irradiating with 365nm light. We found that after irradiating with 365 nm light, conductivity values are slightly higher compared to the conductivity before irradiation. Plots of conductivity against concentration are given in figure 2.8. This indicates that *Z*-isomer is showing more conductivity than *E*-isomer, which might be due to higher mobility as a result of the change in the shape and size upon irradiation. However, this phenomenon may also be due to the aggregation of molecules upon converting into *cis*-isomer due to which the conductivity value gets increased slightly. These preliminary studies need more studies for understanding the exact reason for this behaviour.

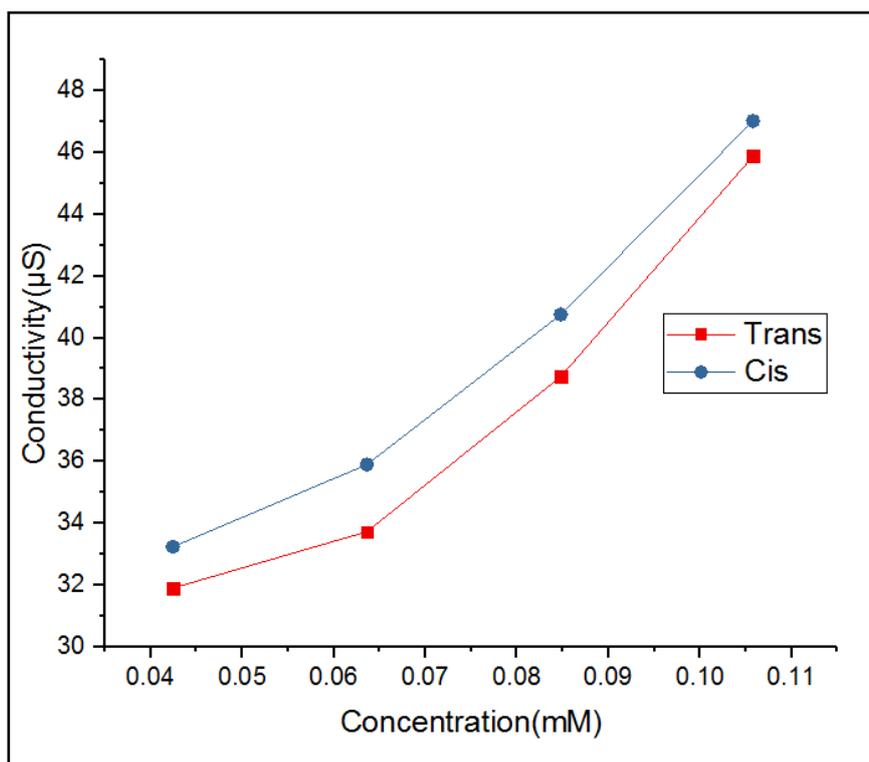


Fig. 2.8 Conductivity versus concentration plot in **1b**.

Chapter 3: Conclusions and Discussions

The goal of our project was to synthesise room temperature photoswitchable ionic liquids. Towards this goal, we designed two target molecules having phenylazo-3,5-dimethylisoxazole as a photoswitchable unit quartered with alkyl groups at the isoxazole nitrogen atom. Both the target molecules were successfully synthesised and fully characterised by NMR and HRMS. UV-Vis studies were performed for understanding their photoswitching behaviour. Target molecules **1a** and **1b** showed quantitative photoswitching in different solvents used. Interestingly, both molecules did not undergo reverse switching in chloroform upon irradiation with varying wavelengths of light or under prolonged irradiation condition. In these cases, reverse switching was only possible through heat. Both molecules were exhibited fluorescence behaviour when irradiated with 365nm light in *cis* isomeric form. Compound **1a** showed fluorescence property even in *trans* isomeric state after heating it in DMSO. This behaviour was only observed when DMSO was used as the solvent, whereas such emission behaviour was not observed in any other solvents. Temperature-dependent fluorescence studies showed an interesting result of increasing fluorescence intensity with cooling, whereas it gets decreased on heating. Although aggregate induced emission phenomenon can be considered for explaining this, the reversal of such emission in the presence of light and also the dependence of temperature makes these phenomena more interesting—more studies needed to be performed to understand this behaviour.

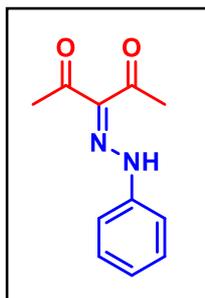
Preliminary conductivity experiments showed that *cis* isomer had higher conductivity than *trans* isomer. For explaining the aggregation property, conductivity experiments before and after irradiating with 365nm light and varying concentrations have to be performed. DSC experiments have to be performed to determine the phase transition temperature. The following of photoswitching behaviour using NMR spectroscopic studies and also the determination of the exact percentage of photoisomerisation, in particular at different concentration, are highly desired in understanding such phenomena.

Chapter 4: Materials and Methods

4.1 General

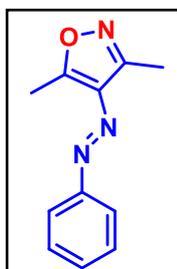
All commercially available reagents and solvents were purchased either from Sigma Aldrich, TCI, Alfa Aesar or Avra and were used without purifications unless otherwise mentioned. Purification of the products was carried out either by column chromatography on silica gel (Merk) mesh size 100-200 μ m or on neutral alumina. Merck Silica gel 60 F254 TLC plates were used to perform thin-layer chromatography. Waters Synapt G2-SiQ-TOF mass spectrometer was used to record high-resolution mass spectra. HRMS spectra were gotten from a TOF mass analyser by utilising electrospray ionisation (ESI) in both positive and negative modes. FT-IR spectra were recorded on Perkin-Elmer ATR spectrometer. UV-Vis photoswitching and kinetics studies have been performed utilizing quartz cuvettes on an Agilent Cary 5000 UV-Vis NIR spectrophotometer, whereas temperature-dependent UV-Vis experiments have been performed in Agilent Cary 60 UV-Vis spectrophotometer. Fluorescence spectra were recorded on Horiba Scientific Spectrofluorometer using four-sided quartz cuvette, whereas temperature-dependent spectra were recorded using Hitachi F-7000 spectrofluorometer. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 (Sigma-Aldrich) in Bruker Avance-III 400MHz spectrometer (operational frequencies 400 and 100 MHz, respectively). Chemical shift values (δ) are reported in parts per million (ppm), and Coupling constants (J) are reported in Hz. Signal of residual CDCl_3 (7.26 ppm) has been used for internal calibration. Fluorescence lifetime measurements were recorded using the Horiba Scientific TCSPC instrument with 370nm laser source. Photoexcitation experiments were conducted using commercial 365nm laser light source or commercial LED light source from Applied Photophysics. Conductivity measurements were recorded using PICO pH and conductivity meter. NMR data were processed using MesterNova software, whereas UV-Vis, Fluorescence and TCSPC data were processed using Origin 9.0. Molecular structures and reactions schemes were drawn using ChemDraw professional 15.0.

4.2 Synthesis



In a 50ml RB flask, aniline or substituted aniline (5.0mmol) is added into distilled water and cooled to 0°C. Concentrated HCl (37%, 1.6ml) was added dropwise to the mixture with continuous stirring to get a clear solution. A cold aqueous solution of NaNO₂ (5.5mmol) dissolved in 5ml distilled water was added dropwise to the reaction mixture. The reaction mixture was stirred for 30 minutes at 0 °c till diazonium salt intermediate is formed. In a conical flask, a solution of sodium acetate (17.5mmol) and acetylacetone (5.0mmol) was dissolved in 25ml of distilled water, and 3ml of methanol was added to it and cooled to 0 °c. This reaction mixture was charged with diazonium intermediate dropwise and stirred for 2 hours in room temperature. Completion of the reaction was monitored through TLC. A yellow to orange precipitate obtained was filtered and washed with water and dried in vacuum to get the desired product²⁵.

(E)-3,5-dimethyl-4-(phenyldiazenyl)isoxazole

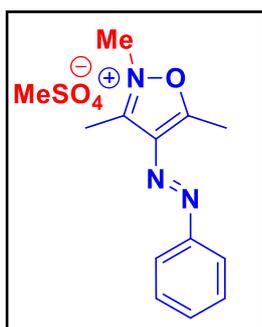


A mixture of arylazoacetylacetone derivative (1.0mmol), hydroxylamine hydrochloride (1.5mmol) and sodium carbonate (1.5mmol) was refluxed in 10ml ethanol. The reaction mixture was monitored by TLC. After completion of the reaction, the solvent was evaporated and purified by column chromatography (1:50) ethyl acetate/hexane mixture²⁵.

Colour: yellow solid, Yield: 88% Melting point: 55-57 °C ¹H NMR (400 MHz, CDCl₃) δ 2.53 (s, 3H), 2.75 (s, 3H), 7.44-7.51 (m, 3H), 7.80-7.82 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.77, 12.23, 122.27, 129.14, 130.80, 132.52, 152.93, 153.78, 169.52; HRMS-ESI: [M+H]⁺ 202.0980, found 202.0973²⁵.

IR (ATR, cm⁻¹) 3041, 2923, 1613, 1411, 1061, 763²⁵.

(E)-2,3,5-trimethyl-4-(phenyldiazenyl)isoxazol-2-ium methyl sulfate

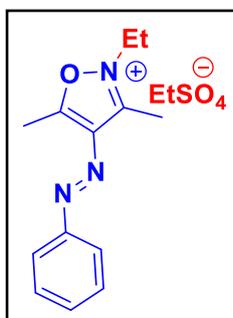


A mixture of Arylazo-3,5-dimethylisoxazole (0.5mmol) and dimethyl sulphate (0.75mmol) was refluxed in 4-6ml of ACN for two hours. The reaction mixture was washed in diethyl ether 3-4 times and dried in vacuum to get the desired product.

Colour: yellowish orange, Yield: 90% $^1\text{H NMR}$ (400MHz, $\text{CD}_3\text{OD-d}_4$) δ 2.97(s, 3H), 2.99(s, 3H), 4.37(s, 3H), 7.62(m, 3H), 7.97-7.99(m, 2H) $^{13}\text{C NMR}$ (100MHz, CD_3OD) δ 12.25, 12.33, 20.70, 39.03, 117.11, 123.99, 130.57, 134.11, 153.64, 170.07 **HRMS-ESI**: m/z: 2016.1109.

IR (ATR, cm^{-1}): 858, 1032, 1152, 1554, 1612, 2509, 2853, 3042, 3417.

(E)-2-ethyl-3,5-dimethyl-4-(phenyldiazenyl)isoxazol-2-ium methyl sulfate



A mixture of Arylazo-3,5-dimethylisoxazole (1mmol) and diethyl sulphate (1mmol) was refluxed in 4-6 ml of ACN for 12 hours. The reaction mixture was washed in diethyl ether 3-4 times and dried in vacuum to get the desired product.

Colour: orange, Yield: 90% $^1\text{H NMR}$ (400MHz, $\text{CD}_3\text{OD-d}_4$) δ 1.49-1.52(t, $J = 7.2$, 3H), 2.82(s, 3H), 2.83(s, 3H), 4.37(q, $J = 7.2$, 2H), 7.62(m, 3H), 7.97-7.99(m, 2H) **HRMS-ESI**: m/z: 230.168.

IR (ATR, cm^{-1}): 862, 1032, 1151, 1424, 1643, 2366, 2940, 3059, 3408.

References

1. B. Wang, L. Quin, T. Mu, Z. Xue, G. Gao, *Chem. Rev.* **2017**, 117, 10, 7113-7131.
2. P. Denis, M. Anja-Verena, *Coordination Chemistry Reviews* **2018**, 363, 1–16.
3. J. Zheng, C. Wang, Y. Yamaguchi, M. Miyamoto, A. Goto, *Angew. Chem.* **2015**, 127, 1552–1556.
4. S. Kathrin, M. Johanna, T. S. Eike, M. Anja-Verena, *Cryst. Growth Des.* **2015**, 15, 9, 4701-4712.
5. J. Dupont, *Journal of the Brazilian Chemical Society*, **2004**, 15, 341.
6. P. A. Hunt, I. R. Gould, B. Kirchner, *Aust. J. Chem.* **2007**, 60, 9.
7. S. Coleman, R. Byrne, N. Alhashimy, K. J. Fraser, D. R. MacFarlanec, D. Diamond, *Phys. Chem. Chem. Phys.*, **2010**, 12, 7009-7017.
8. J. G. Huddleston, A. E. Visser, W. M. Reichert, *Green chem.* **2001**, 3, 156.
9. K. Ishiba, M. Morikawa, C. Chikara, T. Yamada, K. Iwase, M. Kawakita, N. Kimizuka, *Angew. Chem. Int. Ed.* **2015**, 54, 1532–1536.
10. C. Wang, K. Hashimoto, R. Tamate, H. Kokubo, M. Watanabe, *Angew. Chem. Int. Ed.* **2018**, 57, 227–230.
10. C. Wang, K. Hashimoto, R. Tamate, H. Kokubo, K. Morishima, X. Li, M. Shibayama, F. Lu, T. Nakanishi, M. Watanabe, *Chem. Commun.* **2019**, 55, 1710–1713.
11. A. Abbaszad Rafi, N. Hamidi, A. Bashir-Hashemi, M. Mahkam, *ACS Biomater. Sci. Eng.* **2018**, 4, 184–192.
12. H. L. Ngo, K. Le Compte, L. Hargens, *Thermochimica Acta*, **2000**, 357, 97.
13. E. D. Bates, R. D. Mayton, I. Ntai, *J. Am. Chem. Soc.* **2002**, 124, 926.
14. A. João, L. Cunha-Silva, J. C. Lima, A. J. Parola, *Org. Lett.* **2014**, 16, 10, 2582-2585.
15. L. C. Branco, F. Branco, *Chem. Commun.* **2009**, 41, 6204.
16. Q. Zhang, C. Shan, X. Wang, *Liq. Cryst.* **2008**, 35, 1299.
17. K. Nobuoka, S. Kitaoka, T. Yamauchi, T. Harran, and Y. Ishikawa, *Chem. Lett.* **2016**, 45, 433–435.
18. S. Zhang, S. Liu, Q. Zhang, Y. Deng, *Chem. Commun.* **2011**, 47, 6641.
19. C. L. Forber, E. C. Kelusky, N. J. Bunce, M. C. Zerner, *J. Am. Chem. Soc.* **1985**, 107, 5884–5890.
20. R. D. Rogers, G. A. Voth, *Acc. Chem. Res.* **2007**, 40, 1077–1078.
21. R. Hagiwara, Y. J. Ito, *Fluorine Chem.* **2000**, 105, 221–227.

22. A. R. Abdolrahim, H. Nazila, A. Bashir-Hashemi, M. Mehrdad, *ACS Biomater. Sci. Eng.* **2018**, 4, 1, 184-192.
23. Z. Li, X. Yuan, Y. Feng, Y. Chen, Y. Zhao, Wang, Q. Xu, J. Wang, *Phys. Chem. Chem. Phys.* **2018**, 20 (18), 12808–12816.
24. R. Oliver, M. Guillaume, *Cryst. Growth Des.* **2020**, 20, 1, 214-225.
25. P. Kumar, A. Srivastava, C. Sah, S. Devi and S. Venkataramani* *Chem. Eur. J.*, **2019**, 25, 11924 – 11932.
26. C. E. Weston, R. D. Richardson, P. R. Haycock, A. J. P. White, M. J. Fuchter, *J. Am. Chem. Soc.* **2014**, 136, 11878–11881.
27. S. Devi, M. Saraswat, S. Grewal, S. Venkataramani*, *J. Org. Chem.* **2018**, 83, 4307–4322.
28. J. Calbo, A. R. Thawani, R. S. L. Gibson, A. J. P. White, M. J. Fuchter, *Beilstein J. Org. Chem.* **2019**, 15, 2753–2764.
29. S. Grewal, D. Gupta, A. K. Gaur, M. Saraswat, and S. Venkataramani*, *Photoisomerization: Causes, Behavior and Effects* Ed. Diego Sampedro, Nova Publishers, USA, **2019**.

Appendix- 5A

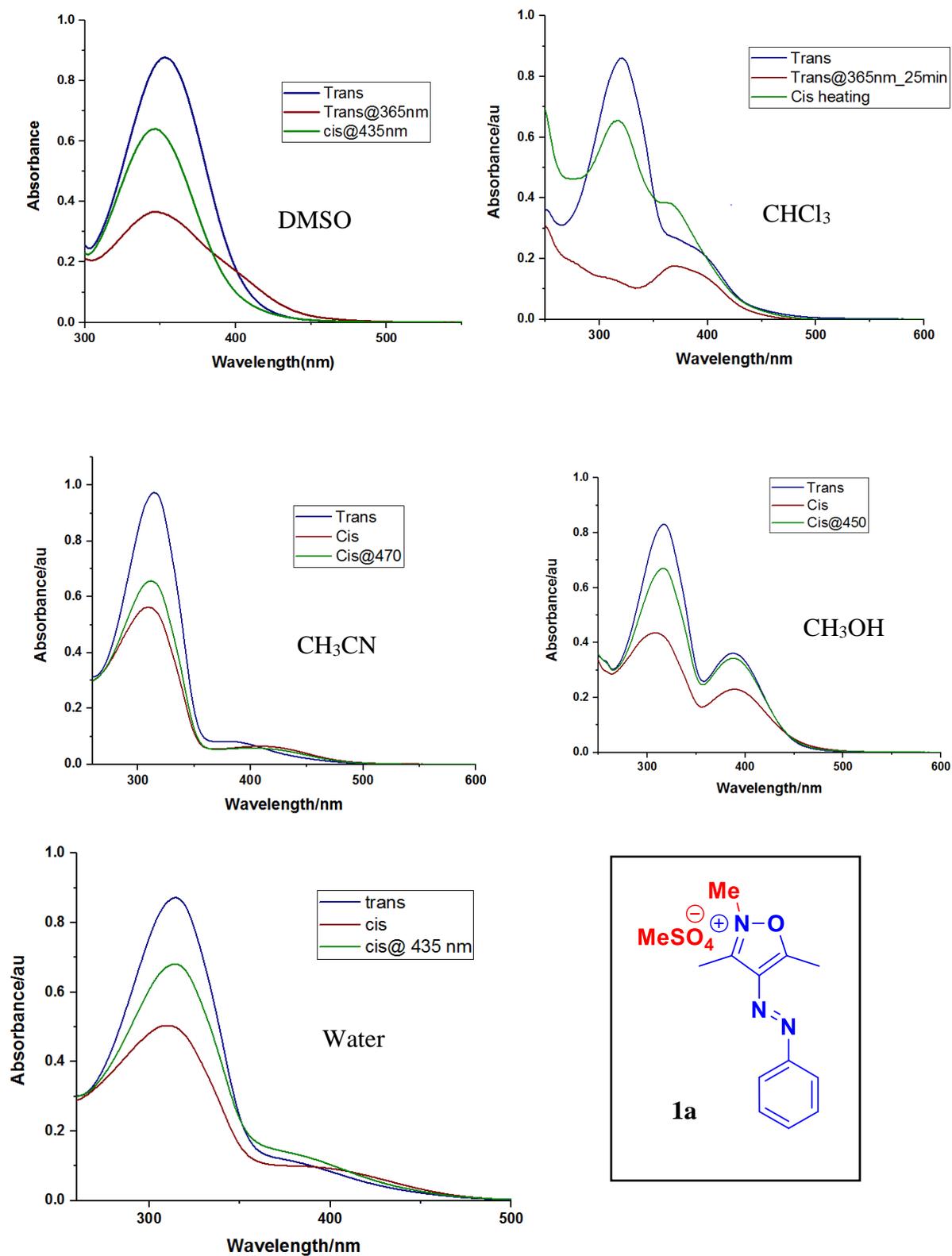


Fig. 5A.1 Analysis of photoswitching behaviour of **1a** using UV-Vis spectroscopic studies in different solvents

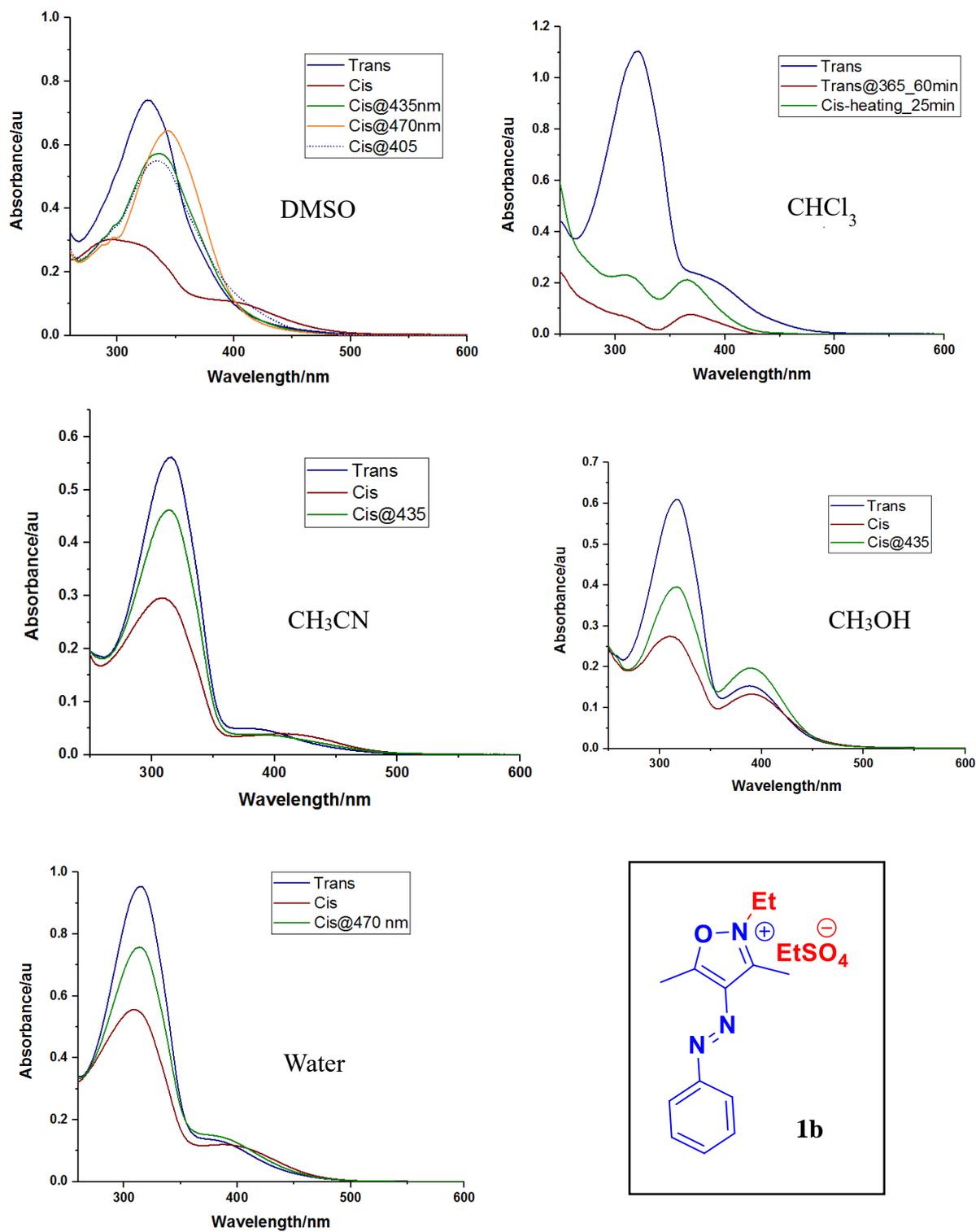


Fig. 5A.2 Fig. 5A.1 Analysis of photoswitching behaviour of **1b** using UV-Vis spectroscopic studies in different solvents

Appendix-5B

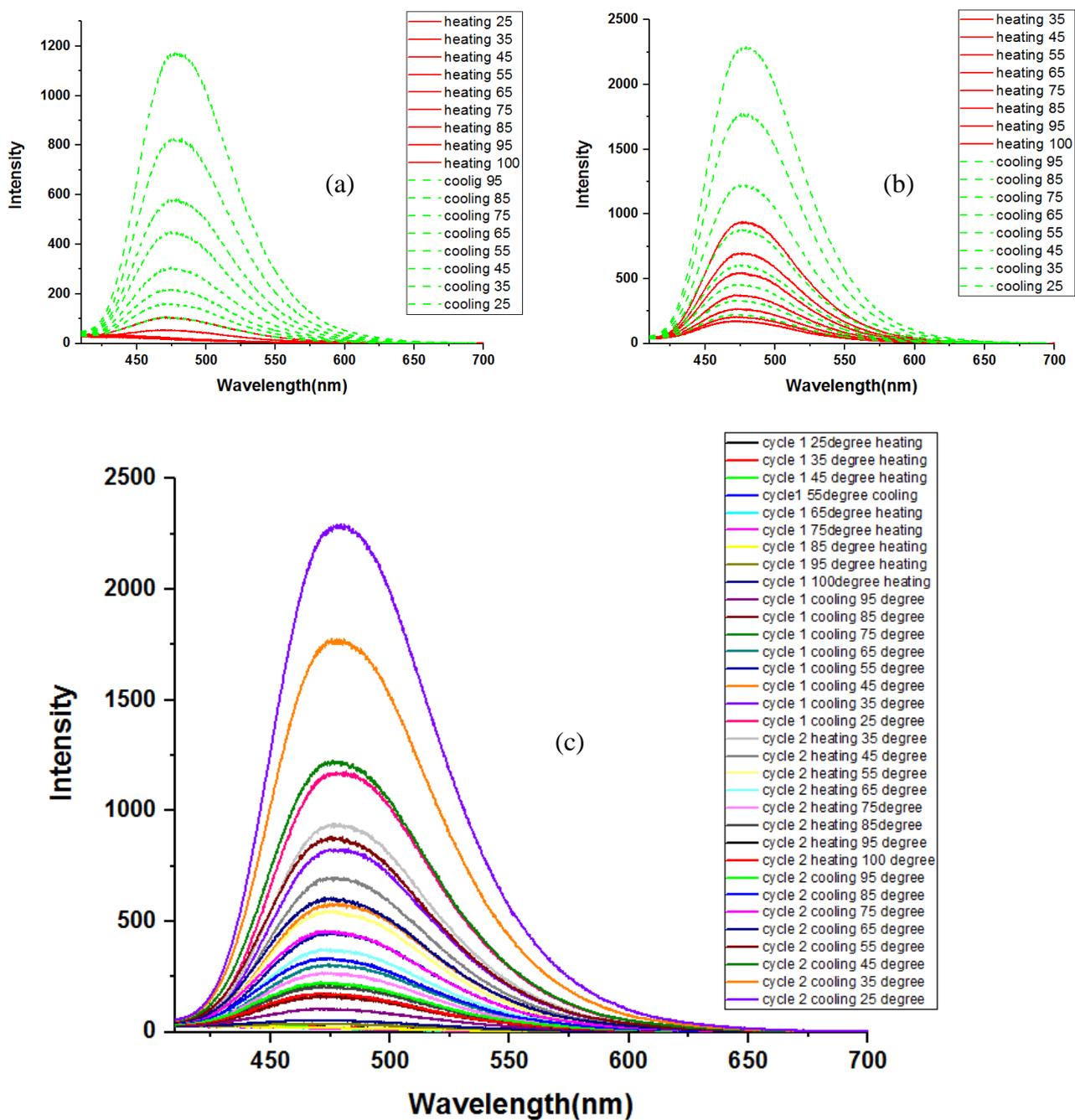


Fig. 5B Temperature dependent fluorescence spectra of **1a**: (a) first cycle (b) second cycle (c) both cycles combined

Appendix-5C

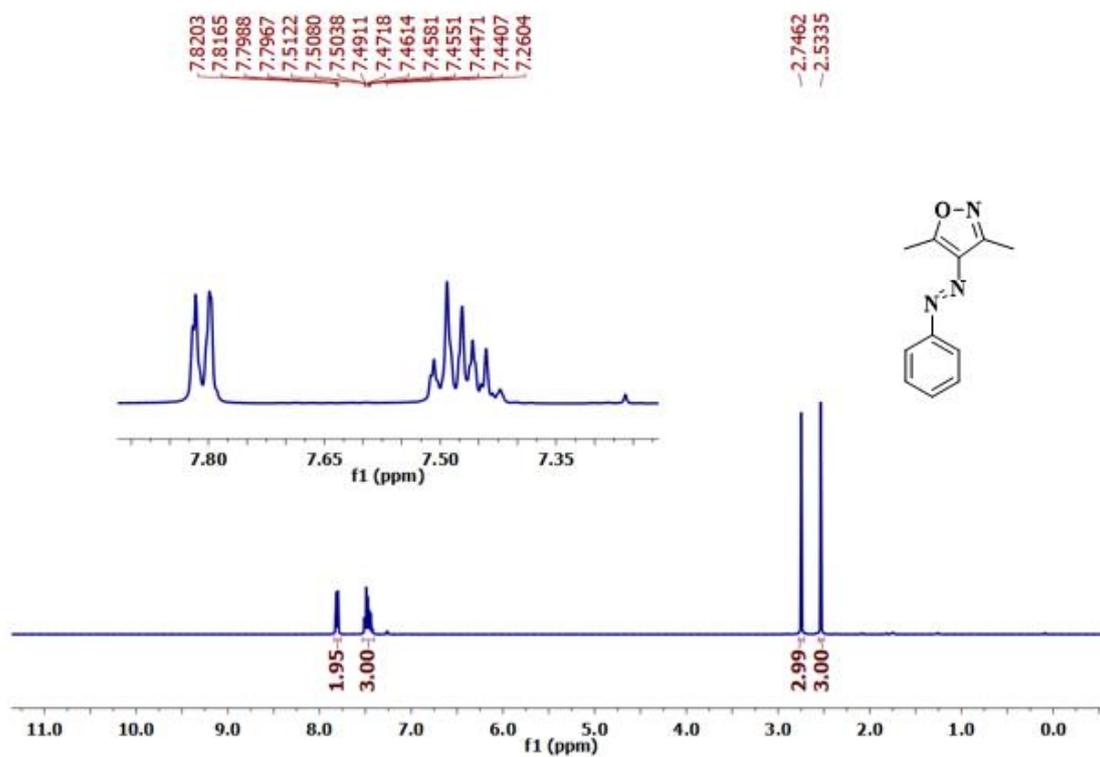


Fig.5C.1 ¹H NMR spectrum of (*E*)-3,5-dimethyl-4-(phenyldiazenyl)isoxazole

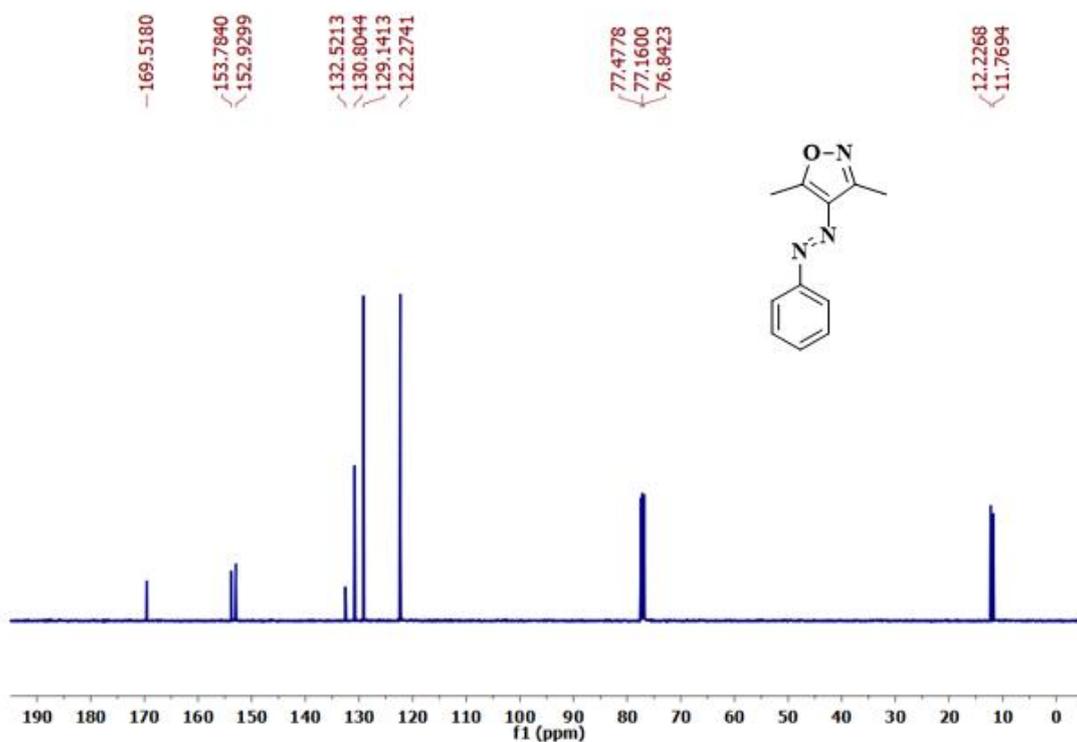


Fig. 5C.2 ¹³C NMR spectrum of (*E*)-3,5-dimethyl-4-(phenyldiazenyl)isoxazole

Appendix-5D

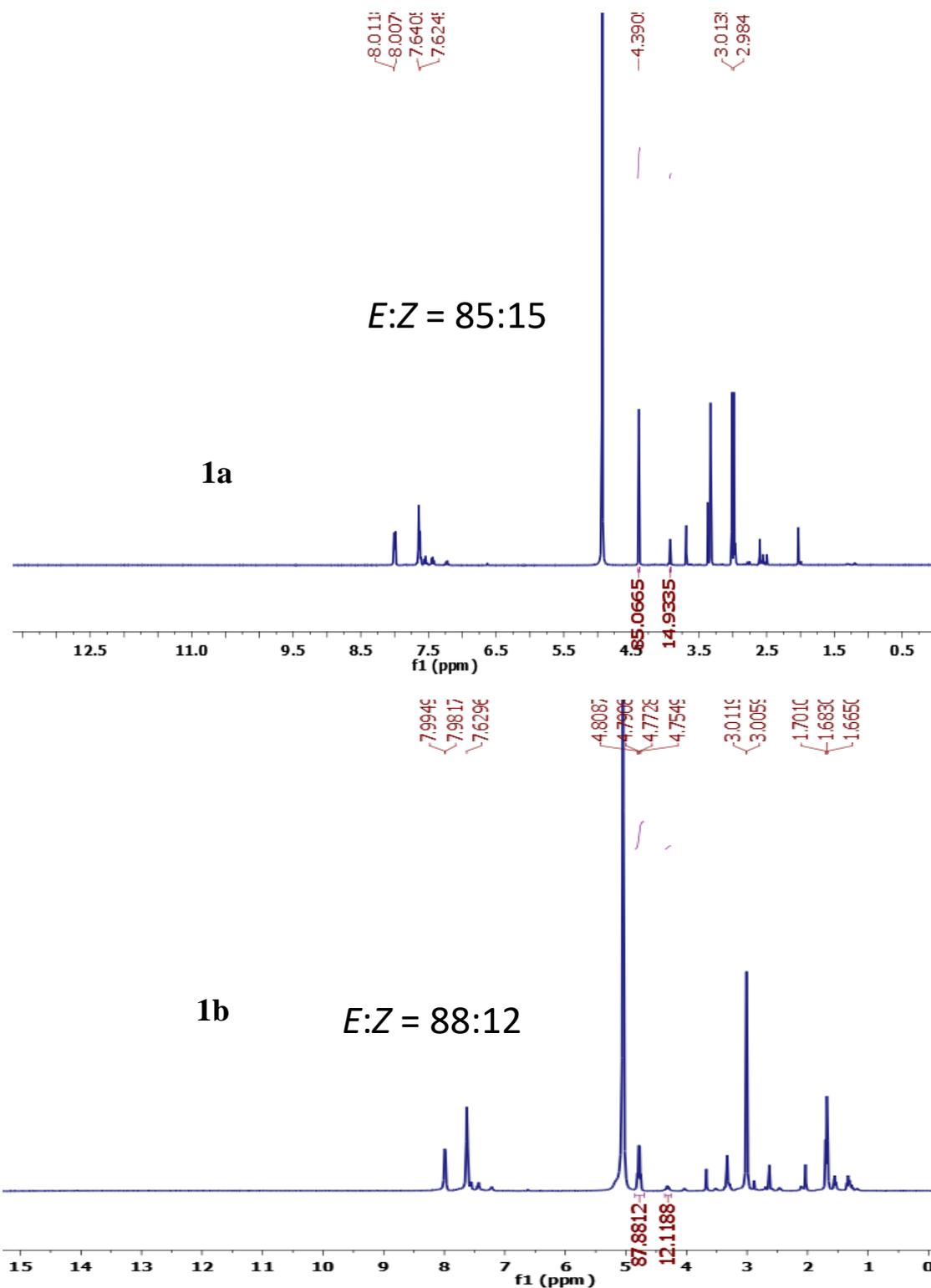


Fig. 5D ¹H NMR spectrum of 1a & 1b

Appendix-5F

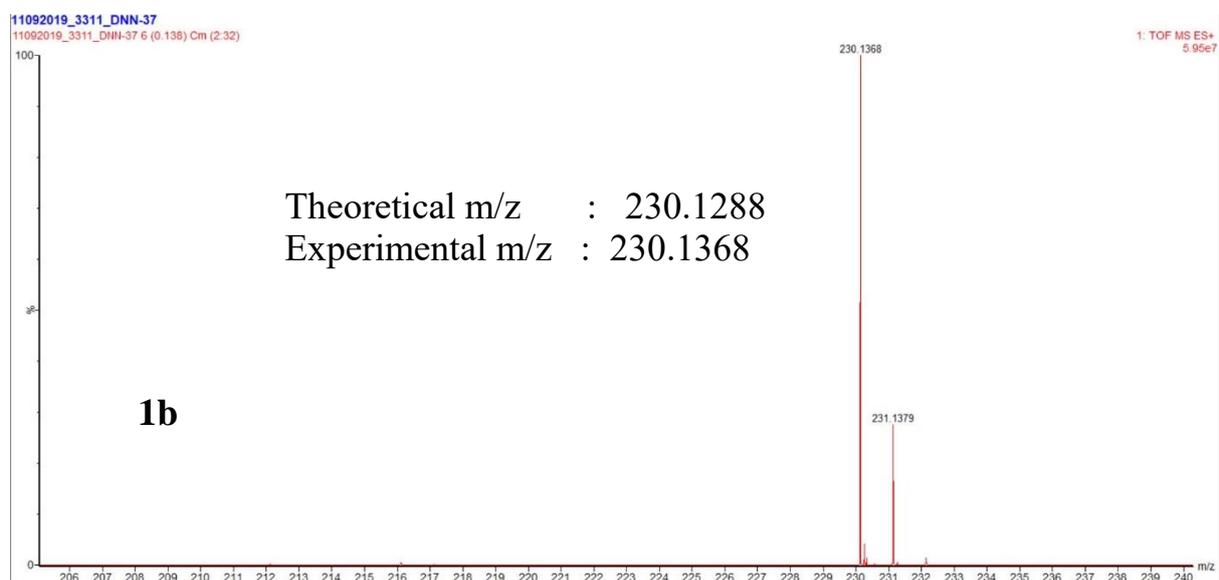
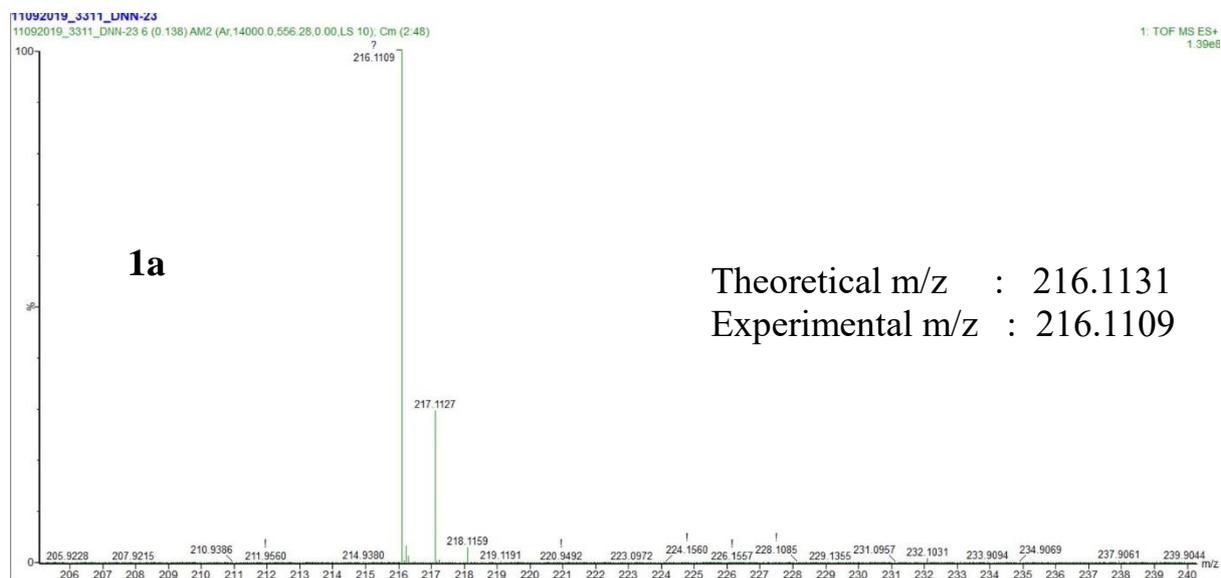


Fig. 5F HRMS spectra of both **1a** and **1b**

Anees Rahman P

Education

2015–2020* [BS-MS Dual Degree Program in Chemical Sciences](#), Indian Institute of Science Education and Research (IISER) Mohali, Current CPI: 7.7*.

Expected graduation date - May 2020, currently pursuing 10th Semester.

2012–2014 **Higher Secondary Education**, Chennamangallur Higher Secondary School, Kozhikode, Marks aggregate: 95.6%.

2010–2012 **Secondary Education**, Chennamangallur Higher Secondary School, Kozhikode, Marks aggregate: 95%.

Field of Interest

Photochemistry

Functional Organic Materials

Photoswitchable Functional Materials

Physical Organic Chemistry

Research Experience

Master thesis

August 2019-
April 2020 [Azaisoxazole based photoswitchable Ionic Liquids](#)

My current work focuses on the synthesis of Photoswitchable Room Temperature Ionic Liquids (RTILs). The main objective of the project is to study the photophysical properties of such RTILs using different Spectroscopic Techniques.

Supervisor: Dr. Sugumar Venkataramani, IISER Mohali

Summer Internships

May–July
2019 **Synthesis and photoswitching studies of Azohetroarene based Ionic Liquids.**

Supervisor: Dr. Sugumar Venkataramani, IISER Mohali

May–July
2018 **Effect of solvents and modifiers on mechanical strength of Polyethersulphone(PES) membrane.**

Supervisor: Dr. V Sivasubramanian, NIT Calicut

May–July 2017 **Synthesis and characterization of p-hydroxybenzaldehyde isonicotinichydrazone and its complexes.**
Supervisor: Dr. M.R.Prathapachandra Kurup, Cochin University of Science and Technology (CUSAT), Kochi.

May–July 2015 **Synthesis of Transition Metal Complexes and study their structure using various spectroscopic techniques.**
Supervisor: Dr. M.R.Prathapachandra Kurup, Cochin University of Science and Technology (CUSAT), Kochi.

Research Skills+

Analytical skills

Spectroscopic Techniques FTIR, ATR, AAS, UV-VIS, Fluorescence, NMR, Mass Spectrometry, Polarimeter, Potentiometer, Conductometer, TCSPC.

Computer Skills

Programming Python, Sage.

Languages

Tools Origin, ChemDraw, Mesternova, Scifinder.

Conferences and Workshops

- **1st CRIKC CHEMISTRY SYMPOSIUM (CCS-2019)**
Attended the conference on 2nd and 3rd November 2019, IISER Mohali
- **Academic Publishing for Quality Research: How to Get Published and Avoid Pitfalls**
Workshop organized by Wiley at IISER Mohali on 7th December 2019

Fellowships, Credentials

- **DST Inspire research fellowships:** Aug 2015 to May 2020.
- Among top 1% in Higher Secondary Examinations conducted by Kerala Board of Higher Secondary Education.
- Received Scholarship funded by DST, Government of India for doing Summer Internships.
- Participated in “Kerala School Sasthrolsavam-2013” (State level science fair).

Languages

English Fluent in reading, writing and speaking.

Malayalam Mother Tongue.

Reference

Dr. Sugumar Venkataramani

Assistant Professor

Department of Chemical Sciences, IISER Mohali

E-mail: sugumarv@iisermohali.ac.in

Website: <https://sites.google.com/site/sugumarvenkataramani/home>

