

**A QUENCHOFLUOROMETRIC INVESTIGATION OF
ALTERNATIVE SOLVENT MEDIA**

MANISH KUMAR



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
FEBRUARY 2026**

© **Indian Institute of Technology Delhi (IITD), New Delhi, 2026**

**A QUENCHOFLUOROMETRIC INVESTIGATION OF
ALTERNATIVE SOLVENT MEDIA**

by

MANISH KUMAR

Department of Chemistry

SUBMITTED

IN FULFILLMENT OF THE REQUIREMENTS OF THE
DEGREE OF **DOCTOR OF PHILOSOPHY**

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBRUARY 2026

*Dedicated to
Mom, Dad and
brother*

CERTIFICATE

This is to certify that the thesis entitled, “**A Quenchofluorometric Investigation of Alternative Solvent Media**”, being submitted by **Mr. Manish Kumar** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Chemistry is a record of bonafide research work carried out by him. He has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results reported in the dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

Date:

Prof. Siddharth Pandey

Department of Chemistry

Indian Institute of Technology Delhi

ACKNOWLEDGEMENTS

I would like to sincerely express my heartfelt gratitude to my supervisor, Prof. Siddharth Pandey, from the Department of Chemistry, IIT Delhi, for his unwavering support and constant encouragement throughout the course of my research. His exceptional expertise and insightful guidance have been instrumental in making this journey both smooth and fruitful. His deep interest, enthusiasm, and passion for research have consistently inspired me to improve both my skills and work ethic. Above all, his punctuality, strong professional commitment, and exceptional time management have been truly motivating. His trust in granting academic freedom has greatly contributed to the production of high-quality research. I feel both proud and honored to be a part of the Pandey Research Group. I would also like to thank my SRC members, Prof. Shashank Deep, Prof. Pravin P. Ingole and Prof. J. P. Singh, for their invaluable time, insightful reviews and suggestions for the improvement of my work.

I am deeply grateful for the unconditional support my family has shown in helping me pursue my goals. I would especially like to thank my parents, Mrs. Santosh and Mr. Prakash Chand, for their steadfast belief in me. This journey is not mine alone—it's a testament to your patience and sacrifices. You stood by every decision I made and consistently encouraged me to chase my dreams without limits. Your love and unshakable faith in me have been the light that guided me through the darkest moments of my doctoral journey, giving me the strength to keep moving forward. My achievements would be nothing without your belief you held in me, even when I doubted myself. I carry deep gratitude for the values you've instilled in me—they've been my anchor and guiding light through every step of my academic journey. My father has always been the embodiment of hard work, my mother a shining example of incredible strength, and my brother Sumit the very definition of pure love. This endeavor would have been rather impossible to achieve without the love and support of my family.

This journey would not have been complete without the emotional support of my friends, who have witnessed my growth from the very beginning to where I stand today. Their constant presence has lifted my spirits and helped me navigate the challenges of this path with ease. I am both grateful and proud to have had the opportunity to mentor two exceptionally talented and ambitious M.Sc. students, Mr. Abhishek Kumar and Mr. Rajat Chauhan, with whom I shared a truly heartfelt bond. Their warmth and positivity never failed to uplift me, and I am deeply moved to say that they stood as the strongest pillars of support throughout my Ph.D. journey.

I would also like to acknowledge all my past and present lab members of the Pandey Research Group, Dr. Bhawna, Dr. Divya, Dr. Meena, Dr. Gagandeep, Dr. Vaishali, Dr. Shreya, Anjali, Anushis, Siddharth, Avika, Vikash, Lipika, Himanshu, Tarun, Deepanshi, Ratnakar, Sudhanshu, Deepti, Shailee, Love and Harshwardhan, for their constant presence and encouragement. They all have shaped my Ph.D. journey, and with them, I heartedly enjoyed the very precious 5 years of my life.

I would like to express my heartfelt gratitude to all the past and present Heads of the Department, DRC Chairs, SRC committee members, as well as the academic and administrative staff of our Department for their assistance and advice throughout my research journey. I am also deeply thankful to the Council of Scientific and Industrial Research (CSIR), India, for their financial support, and to IIT Delhi for providing the necessary infrastructure and facilities that enabled the smooth execution of my research work.

Manish Kumar

ABSTRACT

From decades of inventions, researchers have developed some novel solvents, as the conventional organic solvents are believed to not just affect the environment but also living beings. These novel solvent systems have an immense potential to act as green solvents, and in turn, can replace hazardous organic solvents. Throughout the years, many of their properties have been discovered; however, an ample scope is still left. This thesis is devoted to the identification of unique solvation behavior and solute-solvent interactions that persist in different novel media.

The thesis titled '**A Quenchofluorometric Investigation of Alternative Solvent Media**' targets information concerning molecular-level dynamics within newly developed solvent systems, such as renewable solvents, deep eutectics solvents (DESs), and perfluorinated solvents, utilizing spectroscopic techniques, mainly fluorescence quenching among others. A comprehensive study is undertaken to explore the recently discovered anomalous behavior of pyrene fluorescence quenching by an efficient fluorescence quencher nitromethane within lithium salt-added DES/ionic liquid (IL). This is extended to various other DESs by undertaking detailed and rigorous analysis. A thorough investigation of the DESs constituting lithium salt and number of H-bond donors (HBDs) is carried out to reveal their physicochemical properties as well as solute dynamics therein. The thesis further continues with less explored perfluorinated media and focuses upon their distinct solvent features by comparing them with their hydrocarbon counterparts.

Chapter 1 (Background and Introduction) not only provides introduction to the work, it also lists up-to-date literature in the area. Although water's prospective qualities as a medium are still unrivalled, many compounds remain partially or completely insoluble in water due to its high dielectric strength. The discovery of volatile organic solvents (VOCs) has overcome some of the drawbacks of water, but their high toxicity and bio-incompatibility have prompted

researchers to create new classes of solvent media that have the potential to replace hazardous organic solvents and dissolve a variety of substances.

DESs have emerged as an important alternative for various synthetic, electroanalytical, and separation processes. They can be prepared by simple mixing and continuous heating/stirring at fairly low temperatures. Recently, peculiar diffusion dynamics of choline chloride (ChCl)-based DESs have been studied using fluorescence techniques which have garnered the attention of the scientific community. Apart from DESs, perfluorinated solvents are another emerging class of solvents whose distinctive solvation characteristics afford many interesting outcomes. They are extremely non-polar and have high thermal as well as chemical stability. Renewable solvents have also emerged as media of utmost importance recently. Overall, this work explores the physicochemical properties of these solubilizing media and provides a critical explanation of solute diffusion and solvation.

Chapter 2 titled ‘**Materials and Methodologies**’ provides an in-depth description of all the techniques and protocols involved in the procurement/synthesis of chemicals as well as the investigative procedures followed. Specifically, steady-state, time-resolved fluorescence and UV-Vis molecular absorbance, dynamic viscosity (η) and density (ρ) measurements have been employed to establish the findings of this thesis. All the hygroscopic chemicals used in the work are stored in an Auto Secador desiccator cabinet. They are further dried under vacuum for at least 24 hours to expel traces of moisture before use. A freshly prepared LiCl-added glycerol solution is kept tightly covered with Teflon tape to avoid contact with moisture. Required amount of water is then added after monitoring the total moisture content using Karl-Fischer titrator. The type III hydrophilic DESs used are ChCl-based DESs including Glyceline (ChCl : glycerol) along with other HBDs, such as, ethylene glycol (EG), methyl urea (MeU) and phenol (Ph) in 1 : 2 mole ratios. The hydrophilic type IV DESs have been prepared using lithium *bis*(trifluoromethylsulfonyl)imide (LiTf₂N) salt in combination with monoamides – acetamide and 2,2,2-trifluoroacetamide, and

diamide urea with varying constituents and molar ratios, namely, LiTf_2N : acetamide (1 : 2, 1 : 3 and 1 : 4), LiTf_2N : 2,2,2-trifluoroacetamide (1 : 2, 1 : 3 and 1 : 4), and LiTf_2N : urea (1 : 2, 1 : 3 and 1 : 4). *n*-Perfluorooctane (PFO) and *n*-octane are obtained in highest purity available and used as such. Due to their high volatility, they are kept in a refrigerator. Solvents with varying polarity, e.g., acetonitrile (ACN), ethanol (Eth), cyclohexane (Cyc) and ethylbenzene (EtB) are also utilized for comparison purposes. Popular fluorophore pyrene (Py), along with different electron-withdrawing fluorescence quenchers, such as, nitromethane and nitrobenzene and amide-based electron-donating materials, *N,N*-dimethylaniline (DMA) and triethylamine (TEA), are employed to determine bimolecular diffusion properties as well other solvent characteristics. Another popular fluorophore perylene is used to investigate rotational diffusion dynamics at different temperatures. Solvatochromic probes, such as, Reichardt's betaine dye 33, *N,N*-diethylaniline (DENA) and 4-nitroaniline (NA) are used to estimate dipolarity/polarizability and H-bond donating/accepting strength of the media investigated in the work.

Chapter 3 titled ‘**Effect of Lithium Salt on Fluorescence Quenching in Glycerol: A Comparison with Ionic Liquid/Deep Eutectic Solvent**’ aims to study the influence of added LiCl on the solute diffusion *via* detailed fluorescence quenching analysis of fluorophore pyrene with a well-established fluorescence quencher nitromethane within a judiciously selected 1 wt% water in glycerol solution. The results are then compared with those of previously reported lithium salt-added IL $[\text{C}_2\text{C}_1\text{im}][\text{Tf}_2\text{N}]$ ($[\text{C}_2\text{C}_1\text{im}]$: 1-ethyl-3-methylimidazolium) and DES ChCl : urea (1 : 2). The choice of system is solely based on the similarity in terms of dynamic viscosity with LiCl-added ChCl : urea (1 : 2) in the temperature range 298 – 358 K. Increasing LiCl concentration of 1 wt% water in glycerol solution from 0 to 3.0 *m* causes the dynamic viscosity to increase exponentially, a behaviour similar to both $[\text{C}_2\text{C}_1\text{im}][\text{Tf}_2\text{N}] + \text{LiTf}_2\text{N}$ and $[\text{ChCl} : \text{urea} (1 : 2) + \text{LiCl}]$ systems. However, despite of the parallel trends in dynamic

viscosity with the salt addition, trends in bimolecular quenching rate constant (k_q) [which was expected to follow Stokes-Einstein diffusion law] for the pyrene–nitromethane fluorophore–quencher pair at each investigated temperature showed a contrasting feature. In case of IL and DES, it was observed that, as the lithium salt is incrementally added, k_q , instead of decreasing monotonically, first increases, reaches a maximum and only then decreases. On the contrary, fluorescence quenching within LiCl-added 1 wt% water in glycerol solution is found to follow a simple Stokes-Einstein diffusion law. The unusual increase in k_q at initial additions of lithium salt within LiCl-added ChCl : urea (1 : 2) and LiTf₂N-added [C₂C₁im][Tf₂N] is attributed to the higher “effective” concentration of the anions Cl[−] and Tf₂N[−], respectively, since a substantial amount of Cl[−] is already present in bulk DES ChCl : urea (1 : 2) and of Tf₂N[−] in bulk IL [C₂C₁im][Tf₂N]. It is hypothesized that the anions solvate the pyrene moiety in the excited-state during the charge-transfer process which leads to stabilization and consequently to higher rate constants. No such stabilization is thought to occur in LiCl-added 1 wt% water in glycerol solution. It is thus believed that the anomalous behavior, where k_q increases even when the viscosity of the medium increases, originates from the unique structural features of the DES ChCl : urea (1 : 2) and IL [C₂C₁im][Tf₂N], respectively, in the presence of lithium salt.

Chapter 4 titled ‘**Lithium Salt Added (Choline Chloride : Glycerol) Deep Eutectic Solvent: Lithium Salt Recognition and Solute Diffusion**’ highlights the efficacy of Reichardt’s betaine dye 33 in recognizing the presence of LiCl salt over other methods, such as, pyrene polarity scale (Py I_1/I_3), and further extends to study the impact of LiCl on physicochemical properties and solute diffusion within Glyceline (ChCl : glycerol in 1 : 2 molar ratio) DES. Solvatochromic probes have the potential to gauge changes occurring due to additives or any other external stimuli. Herein, it is reported that the negative solvatochromism of Reichardt’s betaine dye 33 effectively manifests the changes taking place in DES Glyceline

as LiCl salt is added. From the absorbance spectra of betaine dye 33, normalized empirical scale of solvent polarity, E_T^N , is obtained which is a combination of solvent dipolarity/polarizability (π^*) and HBD acidity (α). A linearly increasing trend of E_T^N is noticed with addition of up to 3.0 *m* LiCl to Glyceline. With the help of DENA and NA (to obtain empirical Kamlet-Taft parameters), it is concluded that the addition of LiCl renders HBD acidity of the Glyceline to increase with little or no change in dipolarity/polarizability and HBA basicity (β). The interaction of lithium ions with oxygens of -OH functionalities of glycerol impart increased HBD acidity to the medium. It is important to note that the response of Py I_1/I_3 is only visible at higher concentrations of LiCl. It is noteworthy that the density of Glyceline increases linearly whereas dynamic viscosity is found to increase exponentially with increasing LiCl molality. Fluorescence quenching of pyrene with nitromethane in LiCl-added Glyceline follows simple Stern-Volmer formulation and reveals a monotonously decreasing trend of k_q as LiCl is progressively added up to 3.0 *m*. This is in contrast to the previously studied LiCl-added ChCl based DES ChCl : urea (1 : 2) where the effect of nano-heterogeneities on k_q was amply highlighted. To comprehend the observations, similar quenching studies of pyrene-nitromethane pair is performed within other LiCl-added ChCl-based DESs, namely, ChCl : EG (1 : 2), ChCl : MeU (1 : 2) and ChCl : Ph (1 : 2) at 358 K. Again, k_q is observed to decrease linearly as concentration of LiCl is increased. The contrasting behavior of LiCl-added amide-based DES and LiCl-added alcohol-based DESs is explained on the basis of higher affinity of Li^+ ions for $-\text{NH}_2$ group of urea in ChCl : urea (1 : 2) which releases more number of Cl^- to solvate and stabilize partially positively charged pyrene moiety in its excited-state. Thus, the relative translational diffusion of the solutes pyrene and nitromethane is governed simply by dynamic viscosity of the medium in case of LiCl-added alcohol-based DESs. Effect of LiCl on rotational diffusion of solute perylene again highlights the importance of dynamic viscosity in describing the solute diffusion within LiCl-added

Glyceline. The micro- and nano-heterogeneities associated with LiCl-added Glyceline reported earlier have no major role in the translational and rotational diffusion within this medium.

Chapter 5 titled ‘**Lithium *bis*(Trifluoromethylsulfonyl)imide Containing Deep Eutectic Solvents: Physicochemical Properties, Empirical Polarity Parameters, and Fluorescence Quenching Analysis**’ affords a detailed insights of the DESs prepared from LiTf₂N as HBA with three different HBDs - acetamide, 2,2,2-trifluoroacetamide and urea in their molar ratios 1 : 2, 1 : 3 and 1 : 4. It is observed that the densities of LiTf₂N-containing DESs are in between those of ChCl-based and type IV lanthanide metal-based DESs of similar mole ratios filling the gap in the density spanning DESs of various types and classes. Dynamic viscosities also vary considerably depending on the identity of the HBA and composition of the DES. Both density and dynamic viscosity show a decreasing trend as the amount of HBD is increased. However, with increasing temperature in the range 298 – 358 K, the density of DESs decreases linearly whereas dynamic viscosity decreases exponentially, irrespective of the HBD identity and their mole ratios. Composition-dependent electrical conductivity (σ), surface tension (γ) and refractive index (n_D) of LiTf₂N-based DESs are determined at 298 K with 2,2,2-trifluoroacetamide as HBD possessing the highest electrical conductivity and urea as HBD exhibiting the highest surface tension and refractive index among all the DESs. From the analysis of absorbance spectra of Reichardt’s betaine dye 33, DENA and NA, a high dipolarity/polarizability and HBD acidity of these media is estimated with relatively poor HBA basicity. Fluorescence quenching experiments with pyrene–nitromethane fluorophore-quencher pair reveal the presence of both dynamic and static components as steady-state quenching data is found to follow ‘sphere of action’ model. This is confirmed by the TCSPC data, where quenching clearly satisfies the Stern-Volmer formulation and describes the dynamic component. Preferential solvation of excited pyrene and nitromethane by Tf₂N[−] ions during the charge-transfer process can be the reason for such anomalous quenching behavior.

Chapter 6 titled '*n*-Perfluorooctane *versus* *n*-Octane: Pyrene Fluorescence to Compare and Contrast Solute Solvation' provides a comparative study of solute solvation/diffusion within PFO and its hydrocarbon analogue *n*-octane by utilising pyrene fluorescence. Due to the inherently high electronegativity of fluorine, PFO offers a considerably different solubilizing microenvironment as compared to *n*-octane. The density and dynamic viscosity of PFO is found to be much higher than that of *n*-octane owing to the bulkier fluorine atoms. Also, PFO displays more non-polar character to the cybotactic region of pyrene as observed from Py I_1/I_3 data. To study diffusional properties of PFO and *n*-octane, fluorescence quenching of pyrene is employed with electron/charge acceptor quenchers – nitrobenzene and nitromethane. Both pyrene-quencher pairs follow the Stokes-Einstein formulation in both PFO and *n*-octane. However, due to high electron affinity and aromatic π - π interactions between fluorophore and quencher, k_q of pyrene–nitrobenzene pair is significantly higher than the diffusion-controlled rate constant, k_{diff} , in both solvents. In contrast, relatively weak electron-withdrawing quencher nitromethane is able to manifest the different solvation behavior of PFO and *n*-octane, while $k_q < k_{diff}$ in *n*-octane, $k_q > k_{diff}$ in PFO. In addition to that, k_q in PFO is higher than k_q in *n*-octane, despite of the higher dynamic viscosity of PFO. This is due to the fact that highly electronegative fluorines on PFO stabilize the partial positive charge that develops on excited pyrene during electron/charge transfer to the quencher nitromethane, facilitating quenching in the process. In case of exciplex forming systems, fluorines also facilitate the development of charge on the pyrene-TEA exciplex in PFO, resulting in higher exciplex formation efficiency in PFO as compared to *n*-octane, despite $\eta_{PFO} > \eta_{n-octane}$. Exciplex formation efficiency is comparable in PFO and *n*-octane in the case of Pyrene-DMA system possibly due to charge delocalization over the benzene ring of DMA. Another striking feature in solvation is attributed to the fact that some ground-state heterogeneity is evident in the case of PFO for Pyrene-DMA exciplex-forming system whereas

n-octane does not exhibit such heterogeneities. Overall, this work highlights unusual solvation characteristics of fluoruous solvents.

Chapter 7 titled ‘**Conclusions and Future Prospects**’ encapsulates the key findings and insights derived from the comprehensive investigation undertaken. Detailed investigation into the solute solvation within alternative media is performed via different spectroscopic techniques, especially fluorescence quenching. A systematic analysis of various physicochemical properties served as the basis for the explanation of some never-seen-before phenomena. The findings from this thesis contribute not only to the fundamental understanding of fluorescence characteristics in unique solvents but also open new avenues in solvent-dependent chemical synthesis, extraction and other applications. The versatility of DESs and perfluorinated solvents as a replacement for conventional organic solvents is amply highlighted.

सारांश

दशकों के आविष्कारों से, शोधकर्ताओं ने कुछ नए सॉल्वेंट्स विकसित किए हैं, क्योंकि माना जाता है कि पारंपरिक कार्बनिक सॉल्वेंट्स न केवल पर्यावरण को बल्कि जीवित प्राणियों को भी प्रभावित करते हैं। इन नवीन विलायक प्रणालियों में हरित सॉल्वेंट्स के रूप में कार्य करने की अपार क्षमता है, और बदले में, खतरनाक कार्बनिक सॉल्वेंट्स की जगह ले सकते हैं। वर्षों के दौरान, उनकी कई संपत्तियों की खोज की गई है; हालांकि, अभी भी काफी गुंजाइश बाकी है। यह थीसिस अद्वितीय समाधान व्यवहार और विलेय-विलायक इंटरैक्शन की पहचान के लिए समर्पित है जो विभिन्न उपन्यास मीडिया में बनी रहती है।

‘ए केन्कोफ्लोरोमेट्रिक इन्वेस्टिगेशन ऑफ अल्टरनेटिव सॉल्वेंट मीडिया’ शीर्षक वाली थीसिस नए विकसित विलायक प्रणालियों के भीतर आणविक-स्तर की गतिशीलता से संबंधित जानकारी को लक्षित करती है, जैसे कि नवीकरणीय सॉल्वेंट्स, डीप यूटेक्टिक्स सॉल्वेंट्स (डीईएस), और परफ्लोरिनेटेड सॉल्वेंट्स, स्पेक्ट्रोस्कोपिक तकनीकों का उपयोग करते हुए, मुख्य रूप से प्रतिदीप्ति शमन। लिथियम नमक से जुड़े डीईएस/आयनिक तरल (आईएल) के भीतर एक कुशल प्रतिदीप्ति शमन नाइट्रोमेथेन द्वारा पाइरीन प्रतिदीप्ति शमन के हाल ही में खोजे गए विषम व्यवहार का पता लगाने के लिए एक व्यापक अध्ययन किया गया है। इसे विस्तृत और कठोर विश्लेषण करके विभिन्न अन्य डीईएस तक बढ़ाया गया है। लिथियम नमक और एच-बॉन्ड दाताओं (एचबीडी) की संख्या का गठन करने वाले डीईएस की गहन जांच की जाती है ताकि उनके भौतिक-रासायनिक गुणों के साथ-साथ उसमें विलेय गतिशीलता का पता लगाया जा सके। थीसिस आगे कम खोजे गए परफ्लोरिनेटेड मीडिया के साथ जारी है और उनके हाइड्रोकार्बन समकक्षों के साथ उनकी तुलना करके उनकी विशिष्ट विलायक विशेषताओं पर ध्यान केंद्रित करती है।

अध्याय 1 (पृष्ठभूमि और परिचय) न केवल काम का परिचय प्रदान करता है, बल्कि यह क्षेत्र में अप-टू-डेट साहित्य को भी सूचीबद्ध करता है। यद्यपि एक माध्यम के रूप में पानी के संभावित गुण

अभी भी बेजोड़ हैं, कई यौगिक इसकी उच्च ढांकता हुआ ताकत के कारण पानी में आंशिक रूप से या पूरी तरह से अघुलनशील रहते हैं। वाष्पशील कार्बनिक सॉल्वेंट्स (वीओसी) की खोज ने पानी की कुछ कमियों को दूर कर दिया है, लेकिन उनकी उच्च विषाक्तता और जैव-असंगति ने शोधकर्ताओं को विलायक मीडिया के नए वर्ग बनाने के लिए प्रेरित किया है जिसमें खतरनाक कार्बनिक सॉल्वेंट्स को बदलने और विभिन्न प्रकार के पदार्थों को भंग करने की क्षमता है। डीईएस विभिन्न सिंथेटिक, इलेक्ट्रोएनालिटिकल और पृथक्करण प्रक्रियाओं के लिए एक महत्वपूर्ण विकल्प के रूप में उभरा है। इन्हें सरल मिश्रण और काफी कम तापमान पर लगातार गर्म करके/हिलाकर तैयार किया जा सकता है। हाल ही में, कोलीन क्लोराइड (ChCl) आधारित डीईएस की अजीबोगरीब प्रसार गतिशीलता का अध्ययन प्रतिदीप्ति तकनीकों का उपयोग करके किया गया है जिसने वैज्ञानिक समुदाय का ध्यान आकर्षित किया है। डीईएस के अलावा, परफ्लोरिनेटेड सॉल्वेंट्स सॉल्वेंट्स का एक और उभरता हुआ वर्ग है जिसकी विशिष्ट सॉल्वेशन विशेषताएं कई दिलचस्प परिणाम देती हैं। वे बेहद गैर-ध्रुवीय हैं और उच्च तापीय और रासायनिक स्थिरता रखते हैं। हाल ही में नवीकरणीय सॉल्वेंट्स भी अत्यंत महत्व के मीडिया के रूप में उभरे हैं। कुल मिलाकर, यह कार्य इन घुलनशील मीडिया के भौतिक-रासायनिक गुणों की पड़ताल करता है और विलेय प्रसार और सॉल्वेशन की एक महत्वपूर्ण व्याख्या प्रदान करता है।

अध्याय 2 शीर्षक 'सामग्री और कार्यप्रणाली' रसायनों की खरीद/संश्लेषण में शामिल सभी तकनीकों और प्रोटोकॉल के साथ-साथ अपनाई गई जांच प्रक्रियाओं का गहन विवरण प्रदान करता है। विशेष रूप से, यूवी-विस आणविक अवशोषण, स्थिर-अवस्था और समय-हल प्रतिदीप्ति, गतिशील चिपचिपाहट (η) और घनत्व (ρ) माप को इस थीसिस के निष्कर्षों को स्थापित करने के लिए नियोजित किया गया है। काम में उपयोग किए जाने वाले सभी हिड्रोस्कोपिक रसायनों को ऑटो सेकाडोर डेसीकेटर कैबिनेट में संग्रहीत किया जाता है। उपयोग से पहले नमी के निशान को बाहर निकालने के लिए उन्हें कम से कम 24 घंटे के लिए वैक्यूम के तहत सुखाया जाता है। एक ताजा तैयार LiCl-जोड़ा ग्लिसरॉल समाधान नमी के संपर्क से बचने के लिए टेफ्लॉन टेप के साथ कसकर कवर किया जाता है। कार्ल-फिशर

टाइट्रेटर का उपयोग करके कुल नमी की मात्रा की निगरानी के बाद पानी की आवश्यक मात्रा को जोड़ा जाता है। उपयोग किए जाने वाले टाइप 'III' हाइड्रोफिलिक डीईएस ChCl -आधारित डीईएस हैं जिनमें ग्लाइसेलीन (ChCl : ग्लिसरॉल) के साथ-साथ अन्य एचबीडी, जैसे एथिलीन ग्लाइकोल (EG), मिथाइल यूरिया (MeU) और फिनोल (Ph) 1 : 2 मोल अनुपात में शामिल हैं। हाइड्रोफिलिक टाइप 'IV' DES को लिथियम *bis*(ट्राइफ्लोरोमिथाइलसल्फोनिल) imide (LiTf_2N) नमक के संयोजन में मोनोमाइड्स - एसिटामाइड और 2,2,2-ट्राइफ्लोरोएसिटामाइड, और डायमाइड यूरिया का उपयोग करके अलग-अलग दाढ़ अनुपातों में घटकों की विभिन्न जोड़ी के साथ तैयार किया गया है, अर्थात्, LiTf_2N : एसिटामाइड (1 : 2, 1 : 3 और 1 : 4), LiTf_2N : 2,2,2-ट्राइफ्लोरोएसिटामाइड (1 : 2, 1 : 3 और 1 : 4), और LiTf_2N : यूरिया (1 : 2, 1 : 3 और 1 : 4)। एन-परफ्लुओरोक्टेन (PFO) और एन-ऑक्टेन उच्चतम शुद्धता में प्राप्त किए जाते हैं और इस तरह उपयोग किए जाते हैं। उनकी उच्च अस्थिरता के कारण, उन्हें रेफ्रिजरेटर में रखा जाता है। अलग-अलग ध्रुवीयता वाले सॉल्वेंट्स, उदाहरण के लिए, एसिटोनिट्राइल (ACN), इथेनॉल (Eth), साइक्लोहेक्सेन (Cyc) और एथिलबेंजीन (EtB) का उपयोग तुलना उद्देश्यों के लिए भी किया जाता है। लोकप्रिय फ्लोरोफोर पाइरीन (Py), विभिन्न इलेक्ट्रॉन-वापस लेने वाले प्रतिदीप्ति शमन, जैसे नाइट्रोमेथेन और नाइट्रोबेंजीन और एमाइड-आधारित इलेक्ट्रॉन-दान सामग्री, डाइमिथाइलनिलिन (DMA) और ट्राइथाइलमाइन (TEA) के साथ, द्वि-आणविक प्रसार गुणों के साथ-साथ अन्य विलायक विशेषताओं को निर्धारित करने के लिए नियोजित किया जाता है। एक अन्य लोकप्रिय फ्लोरोफोर पेरिलीन का उपयोग विभिन्न तापमानों पर घूर्णी प्रसार गतिशीलता की जांच के लिए किया जाता है। सॉल्वेटोक्रोमिक जांच, जैसे, Reichardt's बीटाइन डार्क 33, एन, एन-डायथिलैनिलिन (DENA) और 4-नाइट्रोएनिलिन (NA) का उपयोग द्विध्रुवीयता/ध्रुवीकरण का अनुमान लगाने और काम में जांच किए गए मीडिया की एच-बॉन्ड दान/शक्ति को स्वीकार करने के लिए किया जाता है।

अध्याय 3 का शीर्षक 'ग्लिसरॉल में प्रतिदीप्ति शमन पर लिथियम नमक का प्रभाव: आयनिक लिक्विड/डीप यूटेक्टिक सॉल्वेंट के साथ तुलना' का उद्देश्य ग्लिसरॉल समाधान में न्यायिक

रूप से चयनित 1 wt% पानी के भीतर एक अच्छी तरह से स्थापित प्रतिदीप्ति केंचर नाइट्रोमेथेन के साथ फ्लोरोफोर पाइरीन के विस्तृत प्रतिदीप्ति शमन विश्लेषण के माध्यम से विलेय प्रसार पर अतिरिक्त LiCl के प्रभाव का अध्ययन करना है। परिणामों की तुलना पहले रिपोर्ट किए गए लिथियम नमक-जोड़ा IL $[C_2C_{1im}][Tf_2N]$ ($[C_2C_{1im}]$:1-एथिल-3-मिथाइलिमिडाज़ोलियम) और DES ChCl : यूरिया (1 : 2) से की जाती है। प्रणाली का चुनाव पूरी तरह से LiCl-added ChCl के साथ गतिशील चिपचिपाहट के संदर्भ में समानता पर आधारित है: यूरिया (1 : 2) तापमान सीमा 298 - 358 K में। ग्लिसरॉल समाधान में 0 से 3.0 m तक ग्लिसरॉल घोल में 1 wt% पानी की LiCl सांद्रता बढ़ने से गतिशील चिपचिपाहट तेजी से बढ़ने का कारण बनता है, दोनों के समान व्यवहार ($[C_2C_{1im}][Tf_2N]$ + $LiTf_2N$) और [ChCl : यूरिया (1 : 2) + LiCl] सिस्टम। हालांकि, नमक के अलावा गतिशील चिपचिपाहट में समानांतर रुझानों के बावजूद, द्वि-आणविक शमन दर स्थिर (k_q) में रुझान [जो स्टोक्स-आइंस्टीन प्रसार कानून का पालन करने की उम्मीद थी] प्रत्येक जांच किए गए तापमान पर पाइरीन-नाइट्रोमेथेन फ्लोरोफोर-केंचर जोड़ी के लिए एक विपरीत विशेषता दिखाई। IL और DES के मामले में, यह देखा गया कि, जैसे-जैसे लिथियम नमक को वृद्धिशील रूप से जोड़ा जाता है, k_q , नीरस रूप से कम होने के बजाय, पहले बढ़ता है, अधिकतम तक पहुंचता है और उसके बाद ही घटता है। इसके विपरीत, ग्लिसरॉल समाधान में LiCl-जोड़ा गया 1 wt% पानी के भीतर प्रतिदीप्ति शमन एक सरल स्टोक्स-आइंस्टीन प्रसार कानून का पालन करने के लिए पाया जाता है। k_q में असामान्य वृद्धि LiCl-added ChCl के भीतर लिथियम नमक के प्रारंभिक परिवर्धन पर ChCl : यूरिया (1 : 2) और $LiTf_2N$ -जोड़ा $[C_2C_{1im}][Tf_2N]$ को क्रमशः आयनों Cl^- और Tf_2N^- की उच्च "प्रभावी" सांद्रता के लिए जिम्मेदार ठहराया जाता है, क्योंकि Cl^- की पर्याप्त मात्रा पहले से ही थोक DES ChCl : यूरिया (1 : 2) और Tf_2N^- थोक IL $[C_2C_{1im}][Tf_2N]$ में मौजूद है। यह परिकल्पना की गई है कि आयन चार्ज-ट्रांसफर प्रक्रिया के दौरान उत्तेजित-अवस्था में पाइरीन अंश को हल करते हैं जिससे स्थिरीकरण होता है और परिणामस्वरूप उच्च दर स्थिरांक होते हैं। ग्लिसरॉल समाधान में LiCl-जोड़ा 1 wt% पानी में ऐसा कोई स्थिरीकरण नहीं माना जाता है। इस प्रकार हम मानते हैं कि विषम व्यवहार, जहां

k_q माध्यम की चिपचिपाहट बढ़ने पर भी बढ़ जाती है, DES ChCl : यूरिया (1 : 2) और IL $[\text{C}_2\text{C}_{1\text{im}}][\text{TF}_2\text{N}]$, क्रमशः, की अनूठी संरचनात्मक विशेषताओं से उत्पन्न होती है लिथियम नमक की उपस्थिति में।

अध्याय 4 शीर्षक 'लिथियम साल्ट एडेड (कोलीन क्लोराइड : ग्लिसरॉल) डीप यूटेक्टिक सॉल्वेंट: लिथियम साल्ट रिकॉग्रेशन एंड सोल्यूट डिफ्यूजन' अन्य तरीकों पर LiCl नमक की उपस्थिति को पहचानने में Reichardt's बीटाइन डाई 33 की प्रभावकारिता पर प्रकाश डालता है, जैसे कि पाइरीन पोलरिटी स्केल ($\text{Py } I_1/I_3$), और आगे ग्लाइसेलीन के भीतर भौतिक-रासायनिक गुणों और विलेय प्रसार पर LiCl के प्रभाव का अध्ययन करने के लिए विस्तारित होता है (ChCl : ग्लिसरॉल में 1 : 2 दाढ़ अनुपात) डीईएस। सॉल्वैटोक्रोमिक जांच में एडिटिव्स या किसी अन्य बाहरी उत्तेजनाओं के कारण होने वाले परिवर्तनों को मापने की क्षमता होती है। यहां, हम रिपोर्ट करते हैं कि Reichardt's बीटाइन डाई 33 का नकारात्मक सॉल्वैटोक्रोमिज्म प्रभावी रूप से डीईएस ग्लाइसेलीन में होने वाले परिवर्तनों को प्रकट करता है क्योंकि LiCl नमक जोड़ा जाता है। बीटाइन डाई 33 के अवशोषण स्पेक्ट्रा से, विलायक ध्रुवता का सामान्यीकृत अनुभवजन्य पैमाना, E_T^N , प्राप्त होता है जो विलायक द्विध्रुवीयता/ध्रुवीकरण (π^*) और एचबीडी अम्लता (α) का एक संयोजन है। E_T^N की एक रैखिक रूप से बढ़ती प्रवृत्ति। ग्लाइसेलीन में 3.0 m LiCl तक के अतिरिक्त के साथ देखा जाता है। DENA और NA (अनुभवजन्य Kamlet-Taft पैरामीटर प्राप्त करने के लिए) की मदद से, यह निष्कर्ष निकाला गया है कि LiCl के अलावा ग्लाइसेलीन की HBD अम्लता द्विध्रुवीयता/ध्रुवीकरण और HBA मूलभूतता (β) में बहुत कम या कोई बदलाव नहीं होने के साथ बढ़ता है। ग्लिसरॉल की -OH कार्यक्षमताओं की ऑक्सीजन के साथ लिथियम आयनों की बातचीत माध्यम को HBD अम्लता में वृद्धि प्रदान करती है। यह ध्यान रखना महत्वपूर्ण है कि $\text{Py } I_1/I_3$ की प्रतिक्रिया केवल LiCl की उच्च सांद्रता पर ही दिखाई देती है। यह उल्लेखनीय है कि ग्लाइसेलीन का घनत्व रैखिक रूप से बढ़ता है जबकि गतिशील चिपचिपाहट में तेजी से वृद्धि होती है। LiCl -जोड़ा ग्लाइसेलीन में नाइट्रोमेथेन के साथ पाइरीन की प्रतिदीप्ति शमन सरल स्टर्न-वोल्टमर फॉर्मूलेशन का अनुसरण करती है और k_q की

नीरस रूप से घटती प्रवृत्ति का पता चलता है। चूंकि LiCl को उत्तरोत्तर 3.0 m तक जोड़ा जाता है। यह पहले अध्ययन किए गए LiCl-added ChCl आधारित DES ChCl के विपरीत है, ChCl : यूरिया (1 : 2) जहां नैनो-विषमताओं का k_q प्रभाव पर्याप्त रूप से हाइलाइट किया गया था। अवलोकनों को समझने के लिए, पाइरीन-नाइट्रोमेथेन जोड़ी के समान शमन अध्ययन अन्य LiCl-जोड़े गए ChCl-आधारित DES के भीतर किए जाते हैं, अर्थात्, ChCl : EG (1 : 2), ChCl : MeU (1 : 2) और ChCl : Ph (1 : 2) 358 K पर फिर से, k_q LiCl की सांद्रता में वृद्धि के रूप में रैखिक रूप से कम करने के लिए मनाया जाता है। LiCl-जोड़ा एमाइड-आधारित DES और LiCl-जोड़ा अल्कोहल-आधारित DES के विपरीत व्यवहार को ChCl में यूरिया के $-NH_2$ समूह के लिए Li^+ आयनों की उच्च आत्मीयता के आधार पर समझाया गया है ChCl : यूरिया (1 : 2) जो अपनी उत्तेजित-अवस्था में आंशिक रूप से सकारात्मक रूप से चार्ज पाइरीन अंश को हल करने और स्थिर करने के लिए Cl^- की अधिक संख्या जारी करता है। इस प्रकार, विलेय पाइरीन और नाइट्रोमेथेन का सापेक्ष ट्रांसलेशनल प्रसार केवल LiCl-जोड़ा अल्कोहल-आधारित DES के मामले में माध्यम की गतिशील चिपचिपाहट द्वारा नियंत्रित होता है। विलेय पेरिलीन के घूर्णी प्रसार पर LiCl का प्रभाव फिर से LiCl-जोड़ा ग्लाइसेलीन के भीतर विलेय प्रसार का वर्णन करने में गतिशील चिपचिपाहट के महत्व पर प्रकाश डालता है। पहले रिपोर्ट किए गए LiCl-added ग्लाइसेलीन से जुड़ी सूक्ष्म और नैनो-विषमताओं की इस माध्यम के भीतर ट्रांसलेशनल और रोटेशनल प्रसार में कोई प्रमुख भूमिका नहीं है।

अध्याय 5 में लिथियम बीस (ट्राइफ्लोरोमिथाइलसल्फोनील) इमाइड युक्त डीप यूटेक्टिक सॉल्वेंट्स: फिजिकोकेमिकल गुण, अनुभवजन्य ध्रुवीयता पैरामीटर्स, और प्रतिदीप्ति शमन विश्लेषण शीर्षक से तीन अलग-अलग एचबीडी - एसिटामाइड, 2,2,2-ट्राइफ्लोरोएसिटामाइड और यूरिया के साथ एचबीए के रूप में एलआईटीएफ 2 एन से तैयार डीईएस की विस्तृत जानकारी प्रदान करता है। यह देखा गया है कि $LiTf_2N$ युक्त DES का घनत्व समान मोल अनुपात के ChCl-आधारित और टाइप 'IV' लैंथेनाइड धातु-आधारित DES के बीच होता है, जो विभिन्न प्रकार और वर्गों के DES में फैले घनत्व में अंतर को भरता है। गतिशील चिपचिपाहट भी एचबीए की पहचान और डीईएस की संरचना

के आधार पर काफी भिन्न होती है। घनत्व और गतिशील चिपचिपाहट दोनों ही घटती प्रवृत्ति दिखाते हैं क्योंकि एचबीडी की मात्रा बढ़ जाती है। हालांकि, 298 - 358 K की सीमा में बढ़ते तापमान के साथ, डीईएस का घनत्व रैखिक रूप से कम हो जाता है जबकि गतिशील चिपचिपाहट तेजी से कम हो जाती है, भले ही एचबीडी पहचान और उनके मोल अनुपात कुछ भी हों। LiTf_2N -आधारित DES की संरचना-निर्भर विद्युत चालकता (σ), सतह तनाव (γ) और अपवर्तक सूचकांक (n_D) 298 K पर निर्धारित की जाती है, जिसमें HBD के रूप में उच्चतम विद्युत चालकता और यूरिया HBD के रूप में सभी DES के बीच उच्चतम सतह तनाव और अपवर्तक सूचकांक प्रदर्शित करता है। Reichardt's बीटाइन डाई 33, DENA और NA के अवशोषण स्पेक्ट्रा के विश्लेषण से, इन मीडिया की उच्च द्विध्रुवीयता/ध्रुवीकरण और एचबीडी अम्लता का अनुमान अपेक्षाकृत खराब एचबीए मूलभूतता के साथ लगाया जाता है। पाइरीन-नाइट्रोमेथेन फ्लोरोफोर-कैंचर जोड़ी के साथ प्रतिदीप्ति शमन प्रयोगों से गतिशील और स्थिर दोनों घटकों की उपस्थिति का पता चलता है क्योंकि स्थिर-अवस्था शमन डेटा 'कार्वाई के क्षेत्र' मॉडल का पालन करने के लिए पाया जाता है। इसकी पुष्टि टीसीएसपीसी डेटा द्वारा की जाती है, जहां शमन स्पष्ट रूप से स्टर्न-वोल्मर फॉर्मूलेशन को संतुष्ट करता है और गतिशील घटक का वर्णन करता है। चार्ज-ट्रांसफर प्रक्रिया के दौरान Tf_2N^- आयनों द्वारा उत्तेजित पाइरीन और नाइट्रोमेथेन का अधिमान्य समाधान इस तरह के विषम शमन व्यवहार का कारण हो सकता है।

अध्याय 6 शीर्षक 'एन-परफ्लुओरोक्टेन बनाम एन-ऑक्टेन: पाइरीन फ्लोरेसेंस टू कंपेयर एंड कंट्रास्ट सोल्यूट सॉल्वेशन' पाइरीन प्रतिदीप्ति का उपयोग करके PFO और इसके हाइड्रोकार्बन एनालॉग एन-ऑक्टेन के भीतर विलेय सॉल्वेशन/प्रसार का तुलनात्मक अध्ययन प्रदान करता है। फ्लोरीन की स्वाभाविक रूप से उच्च इलेक्ट्रोनगेटिविटी के कारण, PFO एन-ऑक्टेन की तुलना में काफी अलग घुलनशील माइक्रोएन्वायरमेंट प्रदान करता है। भारी फ्लोरीन परमाणुओं के कारण PFO का घनत्व और गतिशील चिपचिपाहट एन-ऑक्टेन की तुलना में बहुत अधिक पाया जाता है। इसके अलावा, PFO पाइरीन के साइबोटेटिक क्षेत्र में अधिक गैर-ध्रुवीय चरित्र प्रदर्शित करता है जैसा कि $P_y I_1/I_3$ डेटा से देखा गया

है। PFO और एन-ऑक्टेन के प्रसार गुणों का अध्ययन करने के लिए, पाइरीन की प्रतिदीप्ति शमन को इलेक्ट्रॉन/चार्ज स्वीकर्ता शमन - नाइट्रोबेंजीन और नाइट्रोमेथेन के साथ नियोजित किया जाता है। दोनों पाइरेन-केंचर जोड़े PFO और एन-ऑक्टेन दोनों में स्टोक्स-आइंस्टीन फॉर्मूलेशन का पालन करते हैं। हालांकि, फ्लोरोफोर और शमन के बीच उच्च इलेक्ट्रॉन आत्मीयता और सुगंधित π - π बातचीत के कारण, k_q पाइरीन-नाइट्रोबेंजीन जोड़ी दोनों सॉल्वेंट्स में प्रसार-नियंत्रित दर स्थिरांक, k_{diff} की तुलना में काफी अधिक है। इसके विपरीत, अपेक्षाकृत कमजोर इलेक्ट्रॉन-वापस लेने वाला शमन नाइट्रोमेथेन PFO और एन-ऑक्टेन के विभिन्न समाधान व्यवहार को प्रकट करने में सक्षम है, जबकि, $k_q < k_{diff}$ एन-ऑक्टेन में, $k_q > k_{diff}$, PFO में। इसके अलावा, k_q पीएफओ में एन-ऑक्टेन से अधिक है पीएफओ की उच्च गतिशील चिपचिपाहट के बावजूद। यह इस तथ्य के कारण है कि पीएफओ पर अत्यधिक विद्युत ऋणात्मक फ्लोरीन आंशिक धनात्मक आवेश को स्थिर करते हैं जो इलेक्ट्रॉन/चार्ज के दौरान उत्तेजित पाइरीन पर विकसित होता है, जिससे इस प्रक्रिया में शमन की सुविधा मिलती है। एक्सिप्लेक्स बनाने की प्रणाली के मामले में, फ्लोरीन पीएफओ में पाइरीन-TEA एक्सिप्लेक्स पर चार्ज के विकास की सुविधा भी प्रदान करते हैं, जिसके परिणामस्वरूप एन-ऑक्टेन की तुलना में PFO में उच्च एक्सिप्लेक्स गठन दक्षता होती है, $\eta_{PFO} > \eta_{n-Octane}$ के बावजूद पाइरीन-डीएमए प्रणाली के मामले में PFO और एन-ऑक्टेन में एक्सिप्लेक्स गठन दक्षता तुलनीय है, संभवतः DMA के बेंजीन रिंग पर चार्ज डेलोकलाइज़ेशन के कारण। सॉल्वेशन में एक और उल्लेखनीय विशेषता को इस तथ्य के लिए जिम्मेदार ठहराया जाता है कि पाइरीन-DMA एक्साइप्लेक्स-फॉर्मिंग सिस्टम के लिए पीएफओ के मामले में कुछ ग्राउंड-स्टेट विषमता स्पष्ट है, जबकि एन-ऑक्टेन ऐसी विषमताओं को प्रदर्शित नहीं करता है। कुल मिलाकर, यह काम फ्लोरस सॉल्वेंट्स की असामान्य सॉल्वेंट्स विशेषताओं पर प्रकाश डालता है।

अध्याय 7 शीर्षक 'निष्कर्ष और भविष्य की संभावनाएं' व्यापक जांच से प्राप्त प्रमुख निष्कर्षों और अंतर्दृष्टि को समाहित करता है। वैकल्पिक मीडिया के भीतर विलेय समाधान में विस्तृत जांच विभिन्न स्पेक्ट्रोस्कोपिक तकनीकों, विशेष रूप से प्रतिदीप्ति शमन के माध्यम से की जाती है। विभिन्न भौतिक-

रासायनिक गुणों का एक व्यवस्थित विश्लेषण कुछ पहले कभी न देखी गई घटनाओं की व्याख्या के आधार के रूप में कार्य करता है। इस थीसिस के निष्कर्ष न केवल अद्वितीय सॉल्वेंट्स में प्रतिदीप्ति विशेषताओं की मौलिक समझ में योगदान करते हैं, बल्कि विलायक-निर्भर रासायनिक संश्लेषण, निष्कर्षण और अन्य अनुप्रयोगों में नए रास्ते भी खोलते हैं। पारंपरिक कार्बनिक सॉल्वेंट्स के प्रतिस्थापन के रूप में डीईएस और परफ्लोरिनेटेड सॉल्वेंट्स की बहुमुखी प्रतिभा पर पर्याप्त रूप से प्रकाश डाला गया है।

CONTENTS

	Page No.
Certificate	I
Acknowledgements	III
Abstract	V
Contents	XIV
List of Figures	XX
List of Tables	XXXIV
List of Schemes	XLIV
List of Abbreviations	XLV

Chapter 1: Introduction

1. Introduction	4
1.A. Deep Eutectic Solvents: Fundamentals and Synthesis	9
1.A.1. Types of DESs	11
1.A.2. Physicochemical Properties of DESs	13
1.A.3. Application of DESs	15
1.B. Perfluorinated Solvents: Properties and Applications	17
1.C. Renewable Solvents	19
1.D. Quenchofluorometry	20
1.D.1. Dynamic Quenching	22
1.D.2. Static Quenching	23

1.D.3. Combination of Static and Dynamic Quenching	24
1.D.4. Quenching Sphere of Action	25
1.E. Motivation for the Current Work	25
1.E.1. Objectives	26
1.E.2. Specific Objectives	26
1.F. Relevance in the Current Scenario	27
1.G. References	29
 Chapter 2: Materials and Methodologies	
2. Introduction	40
2.A. Instrumentation	41
2.B. Materials	43
2.B.1. Solvents Investigated	43
2.B.2. Fluorescence Probes, Quenching Agents and Other Materials Used	46
2.C. Methodology	48
2.C.1. Brief Description of Pyrene	48
2.C.2. Sample Preparation	49
2.C.3. Data Acquisition	49
2.C.4. Data Analysis	50
2.D. References	51
 Chapter 3: Effect of Lithium Salt on Fluorescence Quenching in Glycerol: A Comparison with Ionic Liquid/ Deep Eutectic Solvent	
3. Introduction	56
3.A. Developing the Appropriate Solvent System	58

3.B. Density and Dynamic Viscosity	60
3.C. Pyrene Emission Intensity Ratio (Py I_1/I_3)	62
3.D. Pyrene Excited-State Intensity Decay	64
3.E. Fluorescence Quenching of Pyrene by Nitromethane	69
3.F. Conclusions	82
3.G. References	84

Chapter 4: Lithium Salt Added (Choline Chloride : Glycerol) Deep Eutectic Solvent: Lithium Salt Recognition and Solute Diffusion

4. Introduction	90
4.A. Determination of Polarity, Acidity and Basicity of LiCl-added Glyceline	92
4.A.1. Response of Reichardt's Betaine Dye 33	93
4.A.2. Estimation of Kamlet-Taft Parameters	95
4.A.3. Response of Pyrene as Polarity Probe	98
4.B. Density and Dynamic Viscosity	99
4.C. Fluorescence Quenching of Pyrene by Nitromethane	103
4.D. Rotational Reorientation Dynamics of Perylene	130
4.E. Conclusions	136
4.F. References	138

Chapter 5: Lithium *bis*(Trifluoromethylsulfonyl)imide Containing Deep Eutectic Solvents: Physicochemical Properties, Empirical Polarity Parameters, and Fluorescence Quenching

5. Introduction	144
5.A. Determination of Physicochemical Properties	147

5.A.1. Temperature and Composition Dependence of Density	147
5.A.2. Dynamic Viscosity and Its Temperature and Composition Dependence	153
5.A.3. Electrical Conductivity, Surface Tension and Refractive Index	158
5.B. Determination of Polarity	162
5.B.1. E_T^N and Kamlet-Taft Parameters	162
5.B.2. Pyrene Band 1-to-Band 3 Emission Intensity Ratio (Py I_1/I_3)	171
5.C. Excited-State Intensity Decay of Pyrene	175
5.D. Fluorescence Quenching of Pyrene	180
5.D.1. Lifetime Data Analysis	180
5.D.2. Steady-State Intensity Analysis	191
5.E. Deviation from Theoretical Rate Constants	201
5.F. Conclusions	205
5.G. References	207

Chapter 6: *n*-Perfluorooctane versus *n*-Octane: Pyrene Fluorescence to Compare and Contrast Solute Solvation

6. Introduction	216
6.A. Density and Dynamic Viscosity	218
6.B. Photophysical Properties of Pyrene	220
6.B.1. Absorption and Emission Spectra	220
6.B.2. Comparison of Solvent Polarity	221
6.B.3. Excited-State Emission Intensity Decay	223

6.C. Fluorescence Quenching of Pyrene	225
6.C.1. Pyrene – Nitrobenzene Pair	225
6.C.2. Pyrene – Nitromethane Pair	232
6.D. Exciplex Formation by Pyrene	237
6.D.1. Pyrene – Triethylamine Pair	237
6.D.2. Pyrene – Dimethylaniline Pair	252
6.E. Conclusions	269
6.F. References	270
Chapter 7: Conclusions and Future Prospects	276
Bio-Data	284

LIST OF FIGURES

Figure No.	Figure Caption	Page No.
1.1.	Evolution of different solvent systems.	5
1.2.	Desirable properties of alternative solvents.	7
1.3.	A representative phase diagram illustrating the eutectic point resulting from the mixture of components A and B.	9
1.4.	Examples of some commonly used HBDs and HBAs.	10
1.5.	A triphasic system showing immiscibility of perfluorocarbon with both aqueous phase and organic phase, as demonstrated by Giuseppe Resnati and co-workers.	17
1.6.	A comparison between dynamic and static quenching.	21
2.1.	Structure of the components used to prepare DESs.	45
2.2.	Structure of the perfluorinated solvent utilized in the study.	46
2.3.	Structures of the fluorescence probes used.	47
2.4.	Structures of the absorbance probes used.	47
2.5.	Structures of the fluorescence quenchers and other materials employed in the work.	48
3.1.	Plots of $\ln \eta$ vs $1/T$ for LiCl-added 1 wt% water in glycerol solution. Solid lines exhibit a linear fit to the data, which is in agreement with the empirical Arrhenius law. The recovered parameters - activation energy ($E_{a,\eta}$) and $\ln A$ (where A is the pre-exponential factor) - as function of m_{LiCl} are shown in the inset.	59
3.2.	Plots of density (ρ) vs T (K) (panel A) at different concentrations of LiCl and density (ρ) vs m_{LiCl} (panel B) at different temperatures	

- in the range 298 – 358 K. Error associated with ρ is $< \pm 0.005$ g.cm⁻³. 61
- 3.3. Plots of dynamic viscosity (η) vs m_{LiCl} for 1 wt% water in glycerol solution (represented by solid lines) and ChCl : urea (1 : 2) (represented by dashed lines) at different temperatures. Error associated with η is $< \pm 2\%$. 62
- 3.4. Py I_1/I_3 vs T (K) plots for varying concentrations of LiCl in 1 wt% water in glycerol solution (panel A) and Py I_1/I_3 vs m_{LiCl} plots at different temperatures in 1 wt% water in glycerol solution (panel B). Slopes obtained from linear regression analysis for each plot are represented as insets in their respective panels. 63
- 3.5. Representative plots of fit to a double exponential decay function of excited-state intensity decay of pyrene (10 μM , $\lambda_{\text{em}} = 373$ nm) dissolved in 0.0 m_{LiCl} (panel A) and 3.0 m_{LiCl} (panel B) at 343 K. Longer of the recovered decay times is also shown in both cases. Residuals are provided below each panel. Excitation is achieved using a 341 nm nano LED. 65
- 3.6. Plots of τ (ns) vs T (K) at a given concentration of LiCl in 1 wt% water in glycerol solution (panel A) and that of τ (ns) vs m_{LiCl} at a given temperature (panel B). The insets represent the slopes obtained from the respective plots. 68
- 3.7. Representative plots of fit to a double-exponential decay function of the excited-state intensity decay of pyrene (10 μM , $\lambda_{\text{em}} = 373$ nm) dissolved in 1.0 m_{LiCl} in the absence of nitromethane (panel A) and presence of 0.37 M nitromethane (panel B) at 343 K.

- Longer of the recovered decay times is also shown in both cases. Residuals are provided below each panel. Excitation is achieved using a 341 nm nano LED. 70
- 3.8. Plots of $\frac{\tau_0}{\tau}$ vs $[\text{CH}_3\text{NO}_2]$ for LiCl-added 1 wt% water in glycerol at a given temperature. Solid lines show fit to the simple Stern-Volmer equation. 77
- 3.9. Plots of $\ln k_q$ vs $1/T$ for LiCl-added 1 wt% water in glycerol solution. Solid lines show a linear fit of the data, which is in agreement with the empirical Arrhenius law. The recovered parameters - activation energy (E_a) and $\ln A$ (where A is the pre-exponential factor) - as function of m_{LiCl} are shown in the inset. 79
- 3.10. Bimolecular quenching rate constant (k_q) plotted as a function of m_{LiCl} at different temperatures for 1 wt% water in glycerol (panel A) and that for ChCl : urea (1 : 2) and $[\text{C}_2\text{C}_{1\text{im}}][\text{Tf}_2\text{N}]$ (panel B). k_q (ChCl : urea (1 : 2)) vs m_{LiCl} and k_q ($[\text{C}_2\text{C}_{1\text{im}}][\text{Tf}_2\text{N}]$) vs $x_{\text{LiTf}_2\text{N}}$ are plotted in the same graph for comparison. 81
- 4.1. Absorbance spectra of Reichardt's betaine dye 33 [50 μM] in Glyceline and LiCl-added Glyceline under ambient conditions (panel A) and variation in E_T^N with a mole fraction of LiCl (x_{LiCl}) (panel B). The solid straight line is the best fit obtained from the linear regression analysis. Error in E_T^N is $\leq \pm 0.007$. 94
- 4.2. UV-visible absorbance spectra of *N,N*-diethylnitroaniline (DENA, 20 μM) and 4-nitroaniline (NA, 20 μM) (panel A) and variation in α , β and π^* with mole fraction of LiCl (x_{LiCl}) within Glyceline

- (panel B) under ambient conditions. Errors in α, β and π^* are $\leq \pm 0.005$. 97
- 4.3. Fluorescence emission spectra of pyrene within Glyceline in the absence and presence of LiCl ($\chi_{\text{LiCl}} = 0.24$) at 298 K (panel A) and at 298 K and 358 K at $\chi_{\text{LiCl}} = 0.24$ (panel B). Band-1-to-3 emission intensity ratio of pyrene (Py I_1/I_3) within LiCl-added Glyceline for temperatures ranging between 298 and 358 K (panel C) and for different LiCl mole fractions at all investigated temperatures (panel D). Error in Py I_1/I_3 is $\leq \pm 0.02$. 98
- 4.4. Density (ρ) of LiCl-added Glyceline as a function of temperature (T) (panel A) and molality of LiCl (m_{LiCl}) (panel B); solid lines are obtained from the linear regression analysis of the data. Plot of $\ln \eta$ vs $1/T$ (panel C; solid curves denote fit to VFT model) and variation of estimated activation energy of viscous flow ($E_{a,\eta}$) vs m_{LiCl} at 298 K (inset of panel C). $\ln \eta$ is plotted as a function of m_{LiCl} (panel D; solid lines indicate result of linear regression) at different temperatures with extent of change of $\ln \eta$ with m_{LiCl} at different temperatures shown in the inset of panel D. 101
- 4.5. Representative plots of double exponential fit to the excited-state intensity decay data of pyrene (10 μM , $\lambda_{\text{em}} = 373$ nm) in the absence of LiCl at 298 K and 358 K (panels A and B, respectively) and in the presence of 3.0 m LiCl at 298 K and 358 K (panels C and D, respectively). Residuals are provided below each panel. Excitation is achieved using a 341 nm Nano-LED. 104

- 4.6. Plot of $\ln(1/\tau_o)$ vs $1/T$ for pyrene in LiCl-added Glyceline with the inset showing corresponding activation energies for radiative transition ($E_{a,rad}$) for different LiCl concentrations. 106
- 4.7. Plot of τ_o (ns) vs m_{LiCl} for pyrene in LiCl-added Glyceline at investigated temperatures (inset shows the slopes obtained from the linear regression analysis). Relative error associated with decay time is $\leq \pm 2\%$. 107
- 4.8. Plots of τ_o/τ vs $[CH_3NO_2]$ for pyrene in LiCl-added Glyceline at different temperatures. Solid lines show fit to the simple Stern-Volmer equation. 116
- 4.9. Plot of $\ln k_q$ vs $1/T$ for pyrene-nitromethane in LiCl-added Glyceline system. Solid lines indicate good agreement with the empirical Arrhenius law. Recovered parameters, activation energy (E_a) and $\ln A$ (where A is the pre-exponential factor), as functions of m_{LiCl} are shown in the inset. 119
- 4.10. Estimated k_q as function of LiCl concentration for pyrene-nitromethane in LiCl-added Glyceline system (panel A) and for LiCl-added DES systems [Glyceline, ChCl : EG (1 : 2), ChCl : MeU (1 : 2), ChCl : Ph (1 : 2)] at 358 K (panel B) (insets present slopes recovered from the linear regression analysis of the data). 121
- 4.11. Plot of k_q vs T/η for pyrene-nitromethane in LiCl-added Glyceline system showing adherence to Stokes-Einstein relation (plot of k_q vs $1/\eta$ in the inset also exhibits satisfactory linear behavior). 129
- 4.12. Representative plots of single exponential fit to the excited-state anisotropy decay data of perylene (5 μ M, $\lambda_{em} = 445$ nm) in the

- absence of LiCl at 298 K and 358 K (panels A and B, respectively) and in the presence of 3.0 *m* LiCl at 298 K and 358 K (panels C and D, respectively). Residuals are provided below each panel. Excitation is achieved using a 405 nm Nano-LED. 131
- 4.13. Variation of rotational reorientation times (θ) of perylene with temperature and LiCl concentration in LiCl-added Glyceline system. 133
- 4.14. θ as functions of η/T (panel A) and η (inset of panel A) for perylene in all LiCl-added Glyceline systems and for individual LiCl-added Glyceline systems, respectively (panel B). Solid lines represent the linear regression analysis of the data. Standard uncertainties associated with θ are $\leq \pm 0.05$ ns. 134
- 5.1. Variation of density with temperature for the investigated DESs. The solid lines represent fit to the equation $\rho/(\text{g.cm}^{-3}) = \rho_0/(\text{g.cm}^{-3}) + aT/(\text{K})$. 149
- 5.2. Densities of LiTf₂N-based DESs as a function of HBD per mole of LiTf₂N at 298 K. Inset represents the degree of change evaluated as the difference between density of mole ratios 1 : 2 and 1 : 4. 151
- 5.3. Variation of dynamic viscosity of LiTf₂N-based DESs as a function of temperature (panel A). Solid lines fit best according to the VFT equation; $\ln \eta/(\text{mPa.s}) = A + \frac{B}{T-T_0}$. Panel B shows comparison of activation energy of the viscous flow ($E_{a,\eta}$) at 298 K for these DESs. 155
- 5.4. Variation of dynamic viscosity with moles of HBD per mole of LiTf₂N for the DESs LiTf₂N : acetamide, LiTf₂N : 2,2,2-

trifluoroacetamide and LiTf ₂ N : urea (panels A, B and C, respectively) in the temperature range 288 K to 358 K.	157
5.5. Electrical conductivity (panel A), surface tension (panel B) and refractive index (panel C) of the investigated DESs as a function of LiTf ₂ N : HBD mole ratio at 298 K.	161
5.6. Absorbance spectra of Reichardt's betaine dye 33 (50 μM) in LiTf ₂ N : acetamide (1 : 2), LiTf ₂ N : 2,2,2-trifluoroacetamide (1 : 2) and LiTf ₂ N : urea (1 : 2) (panels A, B and C, respectively) DESs in the temperature range 298 K to 358 K.	164
5.7. Plots of E_T^N as a function of temperature for LiTf ₂ N : HBD (1 : 2) DESs. Slopes obtained for each DES systems are compared in the inset.	166
5.8. Absorbance spectra of DENA (20 μM) in LiTf ₂ N : acetamide (1 : 2), LiTf ₂ N : 2,2,2-trifluoroacetamide (1 : 2) and LiTf ₂ N : urea (1 : 2) (panels A, B and C, respectively) DESs in the temperature range 298 K to 358 K.	169
5.9. Absorbance spectra of NA (20 μM) in LiTf ₂ N : acetamide (1 : 2), LiTf ₂ N : 2,2,2-trifluoroacetamide (1 : 2) and LiTf ₂ N : urea (1 : 2) (panels A, B and C, respectively) DESs in the temperature range 298 K to 358 K.	170
5.10. Band 1-to-band 3 emission intensity ratio of pyrene (Py I_1/I_3) within various investigated LiTf ₂ N-based DESs at 298 K.	171
5.11. Py I_1/I_3 plotted as a function of T (K) for different LiTf ₂ N-based DESs at a molar ratio 1 : 2 (panel A) and for LiTf ₂ N/acetamide	

- DES system at three different compositions (panel B). Error in I_1/I_3 is $\leq \pm 0.02$. 173
- 5.12. Representative plots of double-exponential fit to the excited-state emission intensity decay of pyrene ($10\ \mu\text{M}$) in different LiTf₂N-based DESs (panels A-E) at 298 K and 358 K. Residuals are provided for each decay below decay plots. Excitation is achieved using a 341 nm Nano-LED. 176
- 5.13. Plots of $\ln(1/\tau_{0,L})$ as a function of $1/T$ for pyrene dissolved in LiTf₂N-based DESs at a molar ratio 1 : 2 (panel A) and for LiTf₂N/acetamide DES system in the composition range 1 : 2 to 1 : 4 (panel B). Solid lines indicate an excellent agreement of the experimental data to the Arrhenius-type equation. Errors associated with decay times are $\leq \pm 2\%$. 179
- 5.14. Representative plots of double-exponential fit to the excited-state emission intensity decay of pyrene ($10\ \mu\text{M}$) in different LiTf₂N-based DESs (panels A-E) in the absence and presence of 0.27 M nitromethane at 298 K. Residuals are provided for each decay below decay plots. Excitation is achieved using a 341 nm Nano-LED. 181
- 5.15. Plots of $\tau_{0,L}/\tau_L$ vs $[\text{CH}_3\text{NO}_2]$ for pyrene-nitromethane fluorophore-quencher pair in different LiTf₂N-based DESs (panels A-E) at different temperatures in the range 298 – 358 K. Solid lines show good agreement to the simple Stern-Volmer equation. Errors associated with decay times are $\leq \pm 2\%$. 187

- 5.16. Plots of $\ln k_q$ vs $1/T$ for investigated LiTf₂N-based DESs at a molar ratio 1 : 2 (panel A) and for different compositions of LiTf₂N/acetamide DES system. Solid lines show good fit to the empirical Arrhenius expression. 189
- 5.17. Steady-state fluorescence quenching of pyrene (10 μ M) with varying concentration of nitromethane within LiTf₂N : urea (1 : 2) at different temperatures in the range 298 – 358 K. 192
- 5.18. Steady-state fluorescence quenching of pyrene (10 μ M) with varying concentration of nitromethane within LiTf₂N : 2,2,2-trifluoroacetamide (1 : 2) at different temperatures in the range 298 – 358 K. 193
- 5.19. Steady-state fluorescence quenching of pyrene (10 μ M) with varying concentration of nitromethane within LiTf₂N : acetamide (1 : 2) at different temperatures in the range 298 – 358 K. 194
- 5.20. Steady-state fluorescence quenching of pyrene (10 μ M) with varying concentration of nitromethane within LiTf₂N : acetamide (1 : 3) at different temperatures in the range 298 – 358 K. 195
- 5.21. Steady-state fluorescence quenching of pyrene (10 μ M) with varying concentration of nitromethane within LiTf₂N : acetamide (1 : 4) at different temperatures in the range 298 – 358 K. 196
- 5.22. F_0/F vs $[\text{CH}_3\text{NO}_2]$ plots for pyrene-nitromethane fluorophore-quencher pair in different LiTf₂N-based DESs at the investigated temperatures in the range 298 – 358 K. Solid curves represent fit to a quenching sphere-of-action model combined with dynamic quenching. 197

- 5.23. Modified Stern-Volmer plots obtained from the linear regression of the data acquired from the steady-state fluorescence quenching within LiTf₂N : acetamide (1 : 2) DES. 198
- 5.24. k_q as functions of T/η (panel A) for pyrene-nitromethane fluorophore quencher pair in all LiTf₂N-based DES systems investigated and for the individual LiTf₂N-based DES systems (panel B). Solid lines represent the linear regression analysis of the data. 204
- 6.1. Density (ρ) of PFO and *n*-octane as a function of T (K) (panel A). The slopes (α) of ρ vs T for both the solvents are compared in the inset of panel A. $\ln \eta$ of PFO and *n*-octane as a function of $1/T$ (panel B) and corresponding activation energy of the viscous flow ($E_{a,\eta}$) (inset of panel B). Errors associated with ρ and η of PFO are $< \pm 0.005 \text{ g.cm}^{-3}$ and $< 2\%$, respectively. 219
- 6.2. Absorbance spectra, normalized at λ_{max} (panel A), and fluorescence emission spectra [λ_{ex} (PFO/*n*-Octane) = 328/335 nm, excitation/emission slit = 2/2 nm], normalized at I_1 (panel B), of pyrene (10 μM) acquired within PFO and *n*-octane at 298 K. 221
- 6.3. Band 1-to-band 3 emission intensity ratio of pyrene (Py I_1/I_3) within various investigated solvents at 298 K. Slopes of Py I_1/I_3 as a function of T (K) are shown in the inset. 222
- 6.4. Representative plots of single-exponential fit to the excited-state emission intensity decay of pyrene (10 μM) in PFO (panel A) and *n*-octane (panel B) at 288 K and 318 K. Residuals are provided for

- each decay below decay plots. Excitation is achieved using a 308 nm Nano-LED. 224
- 6.5. Plots of $\ln(1/\tau)$ as a function of $1/T$ for pyrene dissolved in PFO and *n*-octane. Solid lines indicate an excellent agreement of the experimental data to the Arrhenius-type equation. Estimated activation energy for radiative transition ($E_{a,rad}$) is shown in the inset. Errors associated with decay times are $\leq \pm 2\%$. 225
- 6.6. Representative plots of single-exponential fit to the excited-state emission intensity decay of pyrene (10 μ M) in PFO (panel A) and *n*-octane (panel B) in the absence and presence of 3.33 mM nitrobenzene at 298 K. Residuals are provided for each decay below decay plots. Excitation is achieved using a 308 nm Nano-LED. 226
- 6.7. Plots of τ_0/τ vs $[C_6H_5NO_2]$ for pyrene-nitrobenzene fluorophore-quencher pair in PFO and *n*-octane at 288 K and 318 K. Solid lines show good agreement with the simple Stern-Volmer equation. 228
- 6.8. Plot of k_q vs T/η for pyrene-nitrobenzene fluorophore-quencher pair in PFO and *n*-octane showing adherence to Stokes-Einstein relation (panel A). Plot of $\ln k_q$ vs $1/T$ showing good fit to the empirical Arrhenius expression (panel B). Activation energy (E_a) for the bimolecular quenching process is shown in the inset of panel B. 231
- 6.9. Representative plots of single-exponential fit to the excited-state emission intensity decay of pyrene (10 μ M) in PFO (panel A) and *n*-octane (panel B), in the absence and presence of 56 mM

nitromethane under ambient conditions. Residuals are provided for each decay below decay plots. Excitation is achieved using a 308 nm Nano-LED.	233
6.10. Plot of τ_0/τ vs $[\text{CH}_3\text{NO}_2]$ for pyrene-nitromethane fluorophore-quencher pair in PFO and <i>n</i> -octane under ambient conditions. Experimentally-observed (Exp) ratio of k_q in PFO to that in <i>n</i> -octane and the same ratio obtained from Stokes-Einstein (SE) formulation is shown in the inset.	235
6.11. Fluorescence spectra of pyrene (excitation/emission slit = 2/2 nm) dissolved in PFO with incremental additions of TEA at different temperatures. Insets show variation in monomer intensity at λ_{max} (nm) = 370 and exciplex intensity at λ_{max} (nm) = 480 with increase in [TEA].	238
6.12. Normalized fluorescence spectra [at λ_{max} (nm) = 370] of pyrene in the presence of up to 0.41 M TEA in PFO at different temperatures. Insets show a linear dependence of $I_{\text{Ex}}/I_{\text{M}}$ on [TEA].	239
6.13. Fluorescence spectra of pyrene (excitation/emission slit = 2/2 nm) dissolved in <i>n</i> -octane with incremental additions of TEA at different temperatures. Insets show variation in monomer intensity at λ_{max} (nm) = 372 and exciplex intensity at λ_{max} (nm) = 480 with increase in [TEA].	240
6.14. Normalized fluorescence spectra [at λ_{max} (nm) = 372] of pyrene in the presence of up to 0.41 M TEA in <i>n</i> -octane at different temperatures. Insets show a linear dependence of $I_{\text{Ex}}/I_{\text{M}}$ on [TEA]	241

- 6.15. Slopes of $I_{\text{Ex}}/I_{\text{M}}$ vs [TEA] obtained from the linear regression analysis in PFO and *n*-octane vs temperature. Representative $I_{\text{Ex}}/I_{\text{M}}$ vs [TEA] plot at 298 K is shown in the inset. 242
- 6.16. Representative plots of double-exponential fit to the excited-state emission intensity decay of pyrene (10 μM) in PFO and *n*-octane (panels A and B, respectively), in the presence of 0.41 M TEA at λ_{em} (nm) = 480 at 288 K. Residuals are provided for each decay below decay plots. Excitation is achieved using a 308 nm Nano-LED. 249
- 6.17. Fluorescence excitation spectra (excitation/emission slit = 2/2 nm) of pyrene (10 μM) dissolved in PFO in the presence of 0.41 M TEA at different temperatures. 250
- 6.18. Fluorescence excitation spectra (excitation/emission slit = 2/2 nm) of pyrene (10 μM) dissolved in *n*-octane in the presence of 0.41 M TEA at 288 K and 293 K. 251
- 6.19. Fluorescence spectra of pyrene (excitation/emission slit = 2/2 nm) dissolved in PFO with incremental additions of DMA at different temperatures. Insets show variation in monomer intensity at λ_{max} (nm) = 370 and exciplex intensity at λ_{max} (nm) = 438 with increase in [DMA]. 252
- 6.20. Normalized fluorescence spectra [at λ_{max} (nm) = 370] of pyrene in the presence of up to 5.62 mM DMA in PFO at different temperatures. Insets show a linear dependence of $I_{\text{Ex}}/I_{\text{M}}$ on [DMA]. 253

6.21.	Fluorescence spectra of pyrene (excitation/emission slit = 2/2 nm) dissolved in <i>n</i> -octane with incremental additions of DMA at different temperatures. Insets show variation in monomer intensity at λ_{max} (nm) = 372 and exciplex intensity at λ_{max} (nm) = 438 with increase in [DMA].	254
6.22.	Normalized fluorescence spectra [at λ_{max} (nm) = 372] of pyrene in the presence of up to 5.62 mM DMA in <i>n</i> -octane at different temperatures. Insets show a linear dependence of $I_{\text{Ex}}/I_{\text{M}}$ on [DMA].	255
6.23.	Slopes of $I_{\text{Ex}}/I_{\text{M}}$ vs [DMA] obtained from the linear regression analysis in PFO and <i>n</i> -octane vs temperature.	256
6.24.	Representative plots of double-exponential fit to the excited-state emission intensity decay of pyrene (10 μM) dissolved in PFO and <i>n</i> -octane (panels A and B, respectively), in the presence of 5.62 mM dimethylaniline at λ_{em} (nm) = 438 at 288 K. Residuals are provided for each decay below decay plots. Excitation is achieved using a 308 nm Nano-LED.	265
6.25.	Fluorescence excitation spectra (excitation/emission slit = 2/2 nm) of pyrene (10 μM) dissolved in PFO in the presence of 5.62 mM DMA at different temperatures.	267
6.26.	Fluorescence excitation spectra (excitation/emission slit = 2/2 nm) of pyrene (10 μM) dissolved in <i>n</i> -octane in the presence of 5.62 mM DMA at different temperatures.	268

LIST OF TABLES

Table No.	Table Caption	Page No.
3.1.	Comparison of experimental dynamic viscosities ($\eta/\text{mPa.s}$) of 1 wt% water in glycerol solution with the literature values of DES ChCl : urea (1 : 2) at pressure (p) = 0.101 MPa at different temperatures. Error in η is $\leq 2\%$.	58
3.2.	Comparison of experimental dynamic viscosities ($\eta/\text{mPa.s}$) of 1 wt% water in glycerol solution with the literature values at pressure (p) = 0.101 MPa at different temperatures.	59
3.3.	Recovered excited-state intensity double-exponential decay parameters for pyrene (10 μM ; excitation wavelength at 341 nm using nano LED source; emission wavelength collected at 373 nm) dissolved in the investigated system comprising of 1 wt% water in glycerol solution at varying concentration of LiCl in the temperature range 298 – 358 K. Error associated with decay times is $\leq 2\%$.	66
3.4.	Recovered excited-state intensity double-exponential decay parameters for pyrene (10 μM ; excitation wavelength at 341 nm using a nano LED source; emission collected at 373 nm) dissolved in the investigated system comprising of 1 wt% water in glycerol solution at varying concentrations of quencher (CH_3NO_2) and LiCl concentrations at different temperatures in the range 298 – 358 K. Error associated with decay times is $\leq 2\%$.	71

- 3.5. Estimated bimolecular quenching rate constant, k_q ($\text{M}^{-1} \text{s}^{-1}$), for quenching of pyrene in LiCl-added 1 wt% water in glycerol solution by CH_3NO_2 at varying concentrations of LiCl at different temperatures. 78
- 4.1. Absorbance maxima for Reichardt's betaine dye 33 ($\lambda_{\text{max},33}$), DENA ($\lambda_{\text{max},\text{DENA}}$) and NA ($\lambda_{\text{max},\text{NA}}$) and corresponding estimated Kamlet–Taft empirical solvent parameters, at different mole fractions of LiCl (χ_{LiCl}) in Glyceline under ambient conditions. Error in λ_{max} are $\leq \pm 1$ nm. Error in E_T^N is $\leq \pm 0.007$ and errors in α , β and π^* are $\leq \pm 0.005$. 96
- 4.2. Density ($\rho/\text{g.cm}^{-3}$) and dynamic viscosity ($\eta/\text{mPa.s}$) for LiCl-added Glyceline system with varying concentration of LiCl at pressure (p) = 0.101 MPa and at different temperatures in the range 298 – 358 K. Standard uncertainty in density (ρ) is $< \pm 0.005 \text{ g.cm}^{-3}$ and standard uncertainty in dynamic viscosity (η) is $< \pm 2 \%$. 100
- 4.3. Recovered empirical VFT parameters from the analysis of $\ln(\eta/\text{mPa.s})$ vs $1/T$ for LiCl-added Glyceline mixtures and corresponding activation energy of viscous flow ($E_{a,\eta}$) at 298 K. 102
- 4.4. Recovered excited-state intensity decay parameters for pyrene (10 μM ; excitation with 341 nm Nano-LED; emission collected at 373 nm) dissolved in LiCl-added Glyceline. Errors associated with decay times are $\leq \pm 2\%$. 105
- 4.5. Recovered excited-state intensity decay parameters for pyrene (10 μM ; excitation with 341 nm Nano-LED; emission collected at 373

- nm) dissolved in the LiCl-added Glyceline at varying quencher (CH_3NO_2) concentration. Errors associated with decay times are $\leq \pm 2\%$. 108
- 4.6. Stern-Volmer dynamic quenching constant, K_D (M^{-1}), obtained from the linear regression analysis of $\frac{\tau_0}{\tau}$ vs $[\text{CH}_3\text{NO}_2]$ data and estimated bimolecular quenching rate constant, k_q ($\text{M}^{-1}.\text{s}^{-1}$), for pyrene-nitromethane fluorophore-quencher pair in LiCl-added Glyceline at different temperatures. 117
- 4.7. Linear regression analysis of k_q ($\text{M}^{-1}.\text{s}^{-1}$) vs m_{LiCl} (mol.kg^{-1}) data for pyrene in LiCl-added Glyceline. 122
- 4.8. Recovered excited-state intensity decay parameters for pyrene (10 μM ; excitation with 341 nm Nano-LED; emission collected at 373 nm) dissolved in the LiCl-added ChCl : EG (1 : 2) DES at varying quencher (CH_3NO_2) concentration at 358 K. Errors associated with decay times are $\leq \pm 2\%$. 122
- 4.9. Stern-Volmer dynamic quenching constant, K_D (M^{-1}), obtained from the linear regression analysis of $\frac{\tau_0}{\tau}$ vs $[\text{CH}_3\text{NO}_2]$ data and estimated bimolecular quenching rate constant k_q ($\text{M}^{-1}.\text{s}^{-1}$) for pyrene-nitromethane fluorophore-quencher pair in ChCl : EG (1 : 2) DES at different LiCl concentrations and 358 K. 124
- 4.10. Recovered excited-state intensity decay parameters for pyrene (10 μM ; excitation with 341 nm Nano-LED; emission collected at 373 nm) dissolved in the LiCl-added ChCl : MeU (1 : 2) DES at varying

quencher (CH_3NO_2) concentration at 358 K. Errors associated with decay times are $\leq \pm 2\%$.	125
4.11. Stern-Volmer dynamic quenching constant, K_D (M^{-1}), obtained from the linear regression analysis of $\frac{\tau_0}{\tau}$ vs $[\text{CH}_3\text{NO}_2]$ data and estimated bimolecular quenching rate constant k_q ($\text{M}^{-1}.\text{s}^{-1}$) for pyrene-nitromethane fluorophore-quencher pair in ChCl : MeU (1 : 2) DES at different LiCl concentrations and 358 K.	126
4.12. Recovered excited-state intensity decay parameters for pyrene (10 μM ; excitation with 341 nm Nano-LED; emission collected at 373 nm) dissolved in the LiCl-added ChCl : Ph (1 : 2) DES at varying quencher (CH_3NO_2) concentration at 358 K. Errors associated with decay times are $\leq \pm 2\%$.	127
4.13. Stern-Volmer dynamic quenching constant, K_D (M^{-1}), obtained from the linear regression analysis of $\frac{\tau_0}{\tau}$ vs $[\text{CH}_3\text{NO}_2]$ data and estimated bimolecular quenching rate constant k_q ($\text{M}^{-1}.\text{s}^{-1}$) for pyrene-nitromethane fluorophore-quencher pair in ChCl : Ph (1 : 2) DES at different LiCl concentrations and 358 K.	128
4.14. Recovered anisotropy decay parameters for perylene (5 μM ; excitation with 405 nm Nano-LED; emission collected at 445 nm) dissolved in the LiCl-added Glyceline system at different temperatures and LiCl concentrations.	131
4.15. Linear regression analysis of θ (ns) of perylene vs η/T data of LiCl-added Glyceline.	135

5.1.	Density ($\rho/\text{g.cm}^{-3}$) of LiTf ₂ N-based DESs at pressure (p) = 0.1 MPa and temperature 288 K to 358 K.	147
5.2.	Comparison of density ($\rho/\text{g.cm}^{-3}$) and dynamic viscosity ($\eta/\text{mPa.s}$) of LiTf ₂ N-based DESs studied in this work with other common DESs reported in the literature at pressure (p) = 0.1 MPa and temperature T (K) = 298.	148
5.3.	Result of the regression analysis of density ($\rho/\text{g.cm}^{-3}$) vs temperature data according to equation: $\rho/(\text{g.cm}^{-3}) = \rho_o/(\text{g.cm}^{-3}) + a(T/\text{K})$ for the investigated LiTf ₂ N-based DESs over the temperature range 288 K to 358 K.	150
5.4.	Summary of estimated physicochemical property values associated with density for LiTf ₂ N-based DESs at Pressure (p) = 0.1 MPa and Temperature T (K) = 298.	152
5.5.	Dynamic viscosity ($\eta/\text{mPa.s}$) of LiTf ₂ N-based DESs at different mole ratios at Pressure (p) = 0.1 MPa and temperature 288 K to 358 K.	154
5.6.	Summary of parameters associated with dynamic viscosity of DESs according to the VFT Model: $\ln \eta/(\text{mPa.s}) = A + \frac{B}{T-T_o}$.	156
5.7.	Electrical conductivity ($\sigma/\text{mS.cm}^{-1}$), surface tension ($\gamma/\text{mN.m}^{-1}$) and refractive index (n_D) of LiTf ₂ N-based DESs at Pressure (p) = 0.1 MPa and temperature T (K) = 298.	160
5.8.	Absorption wavelength maxima of Betaine dye 33 ($\lambda_{\text{max},33}/\text{nm}$), DENA ($\lambda_{\text{max},\text{DENA}}/\text{nm}$) and NA ($\lambda_{\text{max},\text{NA}}/\text{nm}$), along with the	

estimated $E_T(30)$ parameter in LiTf ₂ N-based DESs at temperatures 298 K to 358 K.	165
5.9. Estimated parameters E_T^N , π^* , α and β for LiTf ₂ N-based DESs at temperatures 298 K to 358 K.	165
5.10. Results of linear regression analysis of E_T^N vs temperature data for the three DESs.	167
5.11. Py I_1/I_3 Data collected within investigated LiTf ₂ N-based DES systems in the temperature range 298 – 358 K. Error in Py I_1/I_3 is $\leq \pm 0.02$.	172
5.12. Linear regression analysis of plots of Py I_1/I_3 vs T (K) for the investigated DESs.	174
5.13. Recovered parameters for the excited-state emission intensity decay from the double-exponential fit to the data for pyrene (10 μ M; Excitation with 341 nm nano-LED) dissolved in the investigated DES systems ($\lambda_{em} = 372$ nm), at different temperatures in the range 298 – 318 K. Errors associated with decay times are $\leq \pm 2\%$.	178
5.14. Recovered linear regression parameters according to the Arrhenius expression and corresponding activation energy of radiative transition ($E_{a,rad}$) for the investigated DES systems.	180
5.15. Recovered parameters for the excited-state emission intensity decay from the double-exponential fit to the data for pyrene (10 μ M; excitation with 341 nm nano-LED; emission collected at 372 nm) at varying quencher (CH ₃ NO ₂) concentration in the LiTf ₂ N-	

- based DESs, in the temperature range 298 – 358 K. Errors associated with decay times are $\leq \pm 2\%$. 182
- 5.16. Estimated bimolecular quenching rate constants, k_q ($M^{-1}.s^{-1}$) $\times 10^{-8}$, obtained from the regression analysis of $\tau_{0,L}/\tau_L$ vs $[CH_3NO_2]$ and F_0/F vs $[CH_3NO_2]$ data, respectively, for pyrene-nitromethane fluorophore-quencher pair in LiTf₂N-Based DESs at different temperatures. 188
- 5.17. Recovered linear regression parameters according to the Arrhenius expression and corresponding activation energy of fluorescence quenching (E_a) for the investigated DES systems are correlated with activation energy of viscous flow ($E_{a,\eta}$). 190
- 5.18. Quenching ‘sphere-of-action’ volume, V (M^{-1}), and associated radii, r (Å), obtained for pyrene-nitromethane fluorophore-quencher pair within various LiTf₂N-based DESs at different temperatures. 200
- 5.19. Diffusion coefficients, D ($cm^2.s^{-1}$), of pyrene (Py) and nitromethane (NM), and calculated bimolecular diffusional rate constants, k_{Smol} ($M^{-1}.s^{-1}$) and k_{diff} ($M^{-1}.s^{-1}$), along with experimental bimolecular quenching rate constant, k_q ($M^{-1}.s^{-1}$), of pyrene-nitromethane fluorophore-quencher pair obtained within different LiTf₂N-based DESs in the temperature range 298 – 358 K. 202

5.20.	Linear regression analysis of k_q ($M^{-1}.s^{-1}$) of pyrene-nitromethane fluorophore quencher pair vs T/η within different investigated DES systems.	205
6.1.	Density (ρ) and dynamic viscosity (η) of PFO and <i>n</i> -octane at pressure (p) = 0.101 MPa and at different temperatures in the range 288-318 K. Errors in ρ and η of PFO are $< \pm 0.005 \text{ g.cm}^{-3}$ and $< \pm 2\%$, respectively.	220
6.2.	Linear regression analysis of plots of density (ρ) and dynamic viscosity (η) of PFO and <i>n</i> -octane as a function of temperature according to the equations: $\rho = \rho_0 + \alpha T$; $\ln \eta = \ln A + \frac{E_a}{RT}$.	220
6.3.	Py I_1/I_3 data collected within some investigated solvents in the temperature range 288–338 K. Error in Py I_1/I_3 is $\leq \pm 0.02$.	223
6.4.	Linear regression analysis of plots of Py I_1/I_3 vs T (K) for the investigated solvents.	223
6.5.	Recovered excited-state emission intensity decay parameters from the single-exponential fit to the data for pyrene (10 μM ; excitation with 308 nm Nano-LED) dissolved in PFO ($\lambda_{\text{em}} = 370 \text{ nm}$) and <i>n</i> -octane ($\lambda_{\text{em}} = 372 \text{ nm}$) at different temperatures in the range 288-318 K. Errors associated with decay times are $\leq \pm 2\%$.	224
6.6.	Recovered excited-state emission intensity decay parameters from the single-exponential fit to the data for pyrene (10 μM ; excitation with 308 nm Nano-LED); dissolved in PFO/ <i>n</i> -octane at varying quencher ($\text{C}_6\text{H}_5\text{NO}_2$) concentration. Errors associated with decay times are $\leq \pm 2\%$.	227

- 6.7. Diffusion coefficients, D ($\text{cm}^2.\text{s}^{-1}$), of pyrene (Py) and nitrobenzene (NB), and calculated bimolecular diffusional rate constants, k_{Smol} ($\text{M}^{-1}.\text{s}^{-1}$) and k_{diff} ($\text{M}^{-1}.\text{s}^{-1}$), along with experimental bimolecular quenching rate constant, k_{q} ($\text{M}^{-1}.\text{s}^{-1}$), of pyrene-nitrobenzene fluorophore-quencher pair obtained within PFO and *n*-octane in the temperature range 288-318 K. 229
- 6.8. Recovered excited-state emission intensity decay parameters from the single-exponential fit to the data for pyrene (10 μM ; excitation with 308 nm Nano-LED; emission collected at 370 nm (PFO) and 372 nm (*n*-octane)) at varying quencher (CH_3NO_2) concentration under ambient conditions. Errors associated with decay times are $\leq \pm 2\%$. 234
- 6.9. Diffusion coefficients, D ($\text{cm}^2.\text{s}^{-1}$), of pyrene (Py) and nitromethane (NM), and calculated bimolecular diffusional rate constants, k_{Smol} ($\text{M}^{-1}.\text{s}^{-1}$) and k_{diff} ($\text{M}^{-1}.\text{s}^{-1}$), along with experimental bimolecular quenching rate constant, k_{q} ($\text{M}^{-1}.\text{s}^{-1}$), of pyrene-nitromethane fluorophore-quencher pair obtained within PFO and *n*-octane at 298 K. 236
- 6.10. Recovered excited-state emission intensity decay parameters from the single and double-exponential fit to the data for pyrene (10 μM ; excitation with 308 nm Nano-LED; emission collected at 370 nm and 480 nm) at varying quencher (TEA) concentration in PFO/*n*-octane, in the temperature range 288-318 K. Errors associated with decay times are $\leq \pm 2\%$. 243

- 6.11. Recovered excited-state emission intensity decay parameters from the single and double-exponential fit to the data for pyrene (10 μ M; excitation with 308 nm Nano-LED; emission collected at 370 nm and 480 nm) at varying quencher (DMA) concentration in PFO/*n*-octane, in the temperature range 288-318 K. Errors associated with decay times are $\leq \pm 2\%$. 257
- 6.12. Recovered excited-state emission intensity decay parameters from the global fit analysis of the data for pyrene (10 μ M; excitation with 308 nm Nano-LED; emission collected at 370 nm and 480 nm) at varying quencher (DMA) concentration in PFO/*n*-octane, in the temperature range 288-318 K. Errors associated with decay times are $\leq \pm 2\%$. 261

LIST OF SCHEMES

Scheme No.	Scheme Caption	Page No.
6.1.	Birk's scheme for pyrene-dimethylaniline (Py-DMA) exciplex formation.	266

LIST OF ABBREVIATIONS

Abbreviation	Full Form
[C ₂ C ₁][Tf ₂ N]	1-Ethyl-3-Methylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide
ACN	Acetonitrile
Ce	Cerium
ChCl	Choline Chloride
Cyc	Cyclohexane
DENA	<i>N,N</i> -Diethylaniline
DES	Deep Eutectic Solvent
DMA	<i>N,N</i> -Dimethylaniline
EG	Ethylene Glycol
EtB	Ethylbenzene
Eth	Ethanol
FT-IR	Fourier Transform Infrared
Gd	Gadolinium
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
HPLC	High Performance Liquid Chromatography
IC	Internal Conversion
IL	Ionic Liquid
IRF	Instrument Response Function
ISC	Intersystem Crossing
La	Lanthanum
LED	Light Emitting Diode
LiTf ₂ N	lithium <i>bis</i> (trifluoromethylsulfonyl)imide
MeU	Methyl Urea
NA	4-nitroaniline
NADES	Natural Deep Eutectic Solvent
NB	Nitrobenzene
NM	Nitromethane
NMR	Nuclear Magnetic Resonance

PAH	Polycyclic Aromatic Hydrocarbon
PFO	Perfluorooctane
Ph	Phenol
PMT	Photomultiplier Tube
Py	Pyrene
RTIL	Room Temperature Ionic Liquid
SV	Stern-Volmer
TCSPC	Time-Correlated Single Photon Counting
TEA	Triethylamine
TMS	Trimethyl Silane
UV	Ultraviolet
VFT	Vogel-Fulcher-Tammann
Vis	Visible
VOC	Volatile Organic Compound