

**INVESTIGATION OF INTRAMOLECULAR AGGREGATION
INDUCED FLUORESCENCE IN DIFFERENT MOLECULAR
SCAFFOLDS**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

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SUBMITTED

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*Dedicated to
Mom, Dad and
Yash*

CERTIFICATE

This is to certify that the thesis entitled, “**Investigation Of Intramolecular Aggregation Induced Fluorescence In Different Molecular Scaffolds**”, being submitted by **Ms. Shreya Juneja** 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 her. She 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.

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Prof. Siddharth Pandey

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ABSTRACT

Certain types of fluorescent materials exhibit an overall enhancement in their luminescence properties in their aggregated/condensed state—a phenomenon known as aggregation induced emission (AIE). Unlike typical fluorophores that may exhibit reduced fluorescence in aggregated states (known as aggregation caused quenching), AIE luminogens become more emissive as they aggregate. The unique properties of these intrinsically emissive aggregates open up new avenues for the development of advanced fluorescent materials with tailored functionalities. Judiciously designed AIE exhibiting systems may be developed with control/variation on the chromophoric/fluorophoric moiety(ies) as well as on the molecular backbone. A thorough exploration of AIE emanating from such systems also helps provide the understanding of the interactions present in complex fluidic systems under investigation. Deep eutectic solvents (DES) have arisen as eco-friendly alternatives to traditional solvents, showcasing distinctive properties that render them versatile in a range of chemical processes. Demonstrating the potential of AIE within DESs becomes a crucial endeavor in unraveling the practical applications of these solvent systems.

The thesis titled **‘Investigation of Intramolecular Aggregation Induced Fluorescence in Different Molecular Scaffolds’** is centrally focused on the molecular-level understanding of AIE, especially within the modern green solvents i.e. DESs. Additionally, the study extends to explore the diverse intramolecular aggregation properties afforded by novel molecular frameworks. A number of popular pyrene (Py) appended molecules are employed to study the diffusion of end groups/folding of long-chain entities (including macromolecules) in a range of

hydrophilic as well as hydrophobic DESs along with other common solvents. Notably, the thesis introduces a groundbreaking dipyranyl compound characterized by an exceptionally strong fluorescence signal for its excited-state aggregate as well as an unprecedented occurrence of intramolecular aggregation in tryptophan (Trp) containing peptidomimetics.

The thesis is structured into eight chapters. **Chapter 1 (Background and Introduction)** provides an account of evolution in the conceptualization of AIE processes, first understood as the antithesis of aggregation caused quenching effect (ACQ). It is common knowledge that Py aggregates intramolecularly post photo illumination to yield an excimer (excited-state dimer). Intramolecular excimer formation has also been utilized effectively in a variety of chemosensing applications mostly based on ratiometric measurements involving wavelengths of the monomer and excimer emissions, respectively. Moreover, intramolecular aggregation of Trp, the most abundant intrinsic fluorophore in proteins, offers an approach to study the biomolecular interactions of proteins through novel peptidomimics.

Chapter 2 titled ‘**Materials and Methodologies**’ provides an in-depth description of all the techniques and protocols involved in procurement/synthesis of chemicals as well as the investigative procedures followed. Specifically, UV-vis molecular absorbance, steady-state and time-resolved fluorescence, dynamic viscosity and dynamic density measurements have been employed to establish the findings of this thesis. Type ‘III’ hydrophilic choline chloride (ChCl)-based DESs and type V decanoic acid (DA)-based DESs constitute the major novel solvent systems employed in the study.

Chapter 3 titled ‘**Contrasting Ground- and Excited-State Intramolecular Aggregation in Choline Chloride-Based Deep Eutectic Solvents versus a Liquid Polymer**’ marks the first experimental investigation of a dipyranylalkane dissolved in choline chloride

(ChCl)-based DESs. Two specific DESs with a common hydrogen-bond acceptor, ChCl and hydrogen-bond donors urea and glycerol (Gly), respectively, in a mole ratio of 1 : 2, are utilized. The deliberate selection of relatively higher viscosity solubilizing media, with dynamic viscosities (η) of ChCl:Urea and ChCl:Gly being 1372.0 mPa.s and 473.0 mPa.s, respectively, at 293.15 K, aims to explore potential alterations or modifications in the dimerization process under these conditions. Additionally, the hydrogen-bond donor (HBD) component of one of the DESs, namely, glycerol ($\eta = 1412.0$ mPa.s at 293.15 K) and a liquid polymer, polydimethylsiloxane with number average molecular weight (MW) 2000 (PDMS2000) and η of 21.4 mPa.s at 293.15 K are investigated for the purpose of comparison. Similar to the behavior observed in common organic solvents, the two Py moieties of 1Py(3)1Py exhibit exclusive aggregation in the excited-state, forming a classical intramolecular excimer when dissolved in the liquid polymer PDMS2000. However, in contrast to several low viscosity organic solvents where two kinetically-distinguishable excimer conformations are simultaneously populated by one excited monomer, PDMS2000 displays only one detected excimer conformation. This behavior aligns with observations in other relatively viscous liquids such as liquid polyethylene glycols (PEGs). In the context of high viscosity DESs and glycerol (Gly), while intramolecular aggregation in 1Py(3)1Py does occur, it is not exclusive to the excited-state. The presence of ground-state heterogeneity is evident through both static and time-resolved fluorescence, indicating weak interactions between the two Py moieties in the ground-state that may lead to partial aggregation. The very high viscosity and/or extensive hydrogen-bonding network within the DESs/Gly are proposed as reasons for this observation.

Chapter 4 titled ‘**Classifying Deep Eutectic Solvents for Polymer Solvation via Intramolecular Dimer Formation**’ is the first report on experimental investigation of

solvation characteristics of a common and useful polymer polydimethylsiloxane (PDMS) in choline chloride-based DESs. Similar to the previous chapter, DESs ChCl:Urea and ChCl:Gly are employed along with the liquid polymer PDMS2000 and glycerol. In the study, polydimethylsiloxane (PDMS) end-tagged with two pyrenyl moieties (Py-PDMS-Py) serves as a dipyrenyl fluorescence probe. The investigation reveals that the intramolecular aggregation of the two pyrenyl groups is influenced by the dissolution state of PDMS, which can be either coiled or uncoiled. The static and dynamic fluorescence behavior of Py-PDMS-Py indicates that dimerization by Py-PDMS-Py exclusively occurs in the excited-state when the solvent is PDMS2000. However, when Py-PDMS-Py is dissolved in DESs ChCl:Urea and ChCl:Gly, as well as in glycerol, clear ground-state heterogeneity, signifying the presence of Py-Py interactions in the ground-state, is revealed by the data. Based on the overall data, it is concluded that PDMS is predominantly present in coiled or tangled state in DESs and glycerol, whereas it prefers uncoiled state in liquid PDMS2000. Thus, similar to glycerol, DESs ChCl:Urea and ChCl:Gly could be characterized as the “bad” solvents for PDMS, whereas PDMS2000, due to its similarity with the polymer PDMS, acts as a “good” solvent. This straightforward spectroscopic approach proves useful for characterizing polymer solvation within complex fluidic media, providing insights into the preferred states of PDMS in different solvents.

Chapter 5 titled ‘**Probing Decanoic Acid-Based Hydrophobic Deep Eutectic Solvents for Olefin Metathesis via Excimer Formation of 6-(1-Pyrenyl)hexyl-11(1-pyrenyl)undecanoate**’ showcases the inaugural endeavor to introduce hydrophobic deep eutectic solvents (HDESs) into ring closing metathesis (RCM)-like reactions. A diene $[H_2C=CH(CH_2)_8COO(CH_2)_4CH=CH_2]$ previously studied by the Leitner and Fürstner groups has been end-labelled with pyrene to yield our fluorochrome, 6-(1-pyrenyl)hexyl-11(1-

pyrenyl)-undecanoate [1-Py(CH₂)₁₀COO(CH₂)₆1-Py]. A series of DESs composed of naturally derived constituents, namely, decanoic acid (DA), along with monoterpenoids, menthol (Men) and thymol (Thy) have been utilised to generate DESs with different pair of constituents in different molar ratios, namely, Thy : Men (1 : 1 and 1 : 2), DA : Men (1 : 1 and 1 : 2), and Thy : DA (2 : 1, 1 : 1, and 1 : 2). The studies have unveiled the formation of classical excimers, i.e., aggregates formed solely post optical stimulation in all of the eleven DESs. Time-resolved investigations reveal that for each of the DESs, the excimer formation dynamics adheres to the standard Birks' scheme at temperatures (T) ≥ 333.15 K. The estimated rate constants for intramolecular excimer formation or association (k_a) show values slightly higher as reported previously for the same probe in ionic liquids and tetraethylene glycols (TEGs). Plots of $\ln k_a$ versus $1/T$ demonstrate an excellent linear correlation between the two, clearly indicating the conformity to the empirical Arrhenius expression for each of the DESs. This research aims to assess the proficiency and tunability of HDESs for various chemical applications, particularly in the context of RCM reactions.

Chapter 6 titled '**Highly Efficient Intramolecular Excimer Formation in a Disulfide-Linked Dipyrenyl Compound: Proton Recognition and Fluidity Assessment**' features a novel end-tagged dipyrenyl compound, named DTP, that stands out for its remarkable ability to exhibit significantly high intramolecular excimer formation efficiency, particularly in polar solvents. DTP (featuring disulfide and diamide functionalities on the linker chain) exhibits both high excimer-to-monomer intensity ratios (I_E/I_M), as well as rapid kinetics of excimer formation, as indicated by relatively higher rate constants (k_a). The presence of functional groups like -NH-(CO)- and/or -S-S- on the linking chain between the two pyrenyl groups contributes significantly to these favorable characteristics. Notably, the I_E/I_M and k_a values

exhibit a strong dependence on the nature of the solvent, whether polar-protic or polar-aprotic. This observation is corroborated by DTP's remarkable ability to recognize H^+ with high sensitivity and selectivity, making it an effective chemosensor for protons. Moreover, the scalability of both I_E/I_M and k_a with the viscosity of the solubilizing environment positions DTP as an efficient microfluidity probe. This efficacy is demonstrated through the monitoring of a mixture constituted of acetonitrile (ACN) and dimethyl sulfoxide (DMSO) and the assessment of trace amounts of water in a representative ionic liquid and DES. The strategic design of DTP, with careful consideration of its molecular structure and functional groups, contributes to its exceptional performance in promoting the formation of intramolecular excimers. This innovative compound holds promise for applications in various fields, particularly in contexts where efficient intramolecular excimer formation is of importance, such as, in fluorescence-based sensing or imaging in polar environments.

Chapter 7 titled '**Unprecedented Intramolecular Association-Induced Fluorescence in Tryptophan-Conjugated Peptidomimetics**' chronicles a breakthrough in the area of Trp-Trp intramolecular aggregate formation. A bispidine-derived bicyclic scaffold was rationally chosen to append Trp units in order to study intramolecular through-space association between the fluorophores. The studies revealed the formation of a newly established Trp-Trp dimer. UV-vis absorbance spectra were successfully able to record a low-energy absorbance band in the region 320-420 nm at concentration of probe as low as 25 μ M in each of the investigated polar [ACN and methanol (MeOH)] as well as non-polar [ethylacetate (EtOAc), toluene, and dichloromethane (DCM)] solvents. This was in addition to the characteristic band of the monomeric Trp in the region 260-300 nm. The steady-state fluorescence did not produce a representative band for the aggregate in each of the neat solvents, hinting at the existence of a

“dark aggregate”. Gradual addition of H^+ leading to a new and rising low-energy fluorescence band established the spectacle of proton-induced modulation of fluorescence in the novel scaffold. Investigations with control compounds were carried out which helped ascertain that the origin of these spectral features was in fact the dimeric Trp-Trp entity and not a manifestation of the localized excited-state. Sensing experiments with some typical ions further demonstrated the selectivity and sensitivity of the probe towards H^+ . Subsequently, the studies serve as an excellent foundation for understanding biomolecular aggregations and encourage scientists to design such superior sensor systems.

Chapter 8 titled ‘**Conclusions and Future Prospects**’ encapsulates the key findings and insights derived from the comprehensive investigations undertaken. The detailed investigation into the properties of Py and Trp-containing scaffolds serves a dual purpose. Firstly, it sheds light on the fundamental principles governing intramolecular aggregation in diverse solvents, particularly within the context of DESs. Secondly, the studies provide a roadmap for tailoring probes that exhibit responsive behavior to specific environmental cues or triggers. The findings from this thesis contribute not only to the fundamental understanding of fluorescence phenomena in unique solvents but also hold promise for the future development of advanced probes with applications in stimuli-responsive systems.

सारांश

कुछ प्रकार के फ्लोरोसेंट पदार्थ अपने संचित/संघनित अवस्था में अपने चमकदार गुणों में समग्र वृद्धि प्रदर्शित करते हैं - इसे समुच्चयन प्रेरित उत्सर्जन (एआईई) के रूप में जाना जाता है। सामान्य फ्लोरोफोर की तुलना में जो संचित अवस्थाओं में फ्लोरोसेंस में कमी दिखा सकते हैं (जिसे समुच्चयन प्रेरित मंदन कहा जाता है), एआईई ल्यूमिनोजेन्स संचित होते ही अधिक चमकदार हो जाते हैं। इन स्वाभाविक रूप से उत्सर्जक समुच्चयों के अनूठे गुण उन्नत फ्लोरोसेंट सामग्री के विकास के लिए नए रास्ते खोलते हैं जिनमें विशेष कार्यात्मकताएं होती हैं। सावधानीपूर्वक डिज़ाइन किए गए एआईई प्रदर्शित करने वाले सिस्टम को क्रोमोफोरिक/फ्लोरोफोरिक मोलिक्यूल और मॉलिक्यूलर बैकबोन पर नियंत्रण/विविधता के साथ विकसित किया जा सकता है। इस तरह के सिस्टम से उत्पन्न एआईई की पूरी तरह से जांच करना जटिल तरल प्रणालियों में मौजूद अंतःक्रियाओं को समझने में भी मदद करता है। डीप इयूटीइक सॉल्वेंट्स (डीईएस) पारंपरिक सॉल्वेंट्स के पर्यावरण-अनुकूल विकल्प के रूप में उभरे हैं, जो विशिष्ट गुण दिखाते हैं जो उन्हें रासायनिक प्रक्रियाओं की एक विस्तृत श्रृंखला में बहुमुखी बनाते हैं। डीईएस में एआईई की संभावना को प्रदर्शित करना इन सॉल्वेंट सिस्टम्स के व्यावहारिक अनुप्रयोगों को उजागर करने में एक महत्वपूर्ण प्रयास बन जाता है।

थीसिस जिसका शीर्षक **'विभिन्न आणविक स्कैफोल्ड्स में इंटरमोलेक्युलर एग्रीगेशन इंड्यूस्ड फ्लोरोसेंस की जांच'** है, मुख्य रूप से एआईई की आणविक-स्तरीय समझ पर केंद्रित है, विशेष रूप से आधुनिक हरे सॉल्वेंट्स यानी डीईएस में। इसके अतिरिक्त, अध्ययन नए आणविक फ्रेमवर्क्स द्वारा प्रदत्त विभिन्न इंटरमोलेक्युलर एग्रीगेशन गुणों का अन्वेषण भी करता है। कई लोकप्रिय पाइरीन (पीवाई) संलग्न अणुओं का उपयोग एंड ग्रुप्स/लंबी चेन इकाइयों (जिसमें मैक्रोमोलेक्यूल्स शामिल हैं) के फैलाव का अध्ययन करने के लिए किया जाता है, जो हाइड्रोफिलिक और

हाइड्रोफोबिक डीईएस की एक श्रृंखला के साथ अन्य सामान्य सॉल्वेंट्स में भी होते हैं। उल्लेखनीय रूप से, थीसिस एक अद्वितीय डिपाइरेनिल यौगिक को प्रस्तुत करती है, जिसे इसके उत्तेजित-राज्य समुच्चय के लिए असाधारण रूप से मजबूत फ्लोरोसेंस सिग्नल और ट्रिप्लैफैन (टीआरपी)।

शोध प्रबंध आठ अध्यायों में संरचित है। **अध्याय 1 (पृष्ठभूमि और परिचय)** एआईई प्रक्रियाओं की अवधारणा में विकास का एक विवरण प्रदान करता है, जिसे पहले एकत्रीकरण कारण शमन प्रभाव (एसीक्यू) के विपरीत के रूप में समझा गया था। यह आम ज्ञान है कि पीवाई प्रकाश उद्दीपन के बाद अंतरा-आणविक रूप से एकत्रित होकर एक एक्साइमर (उत्तेजित-अवस्था डाइमर) का उत्पादन करता है। अंतरा-आणविक एक्साइमर निर्माण का उपयोग विभिन्न केमोसेंसिंग अनुप्रयोगों में प्रभावी ढंग से किया गया है, जो मुख्य रूप से मोनोमर और एक्साइमर उत्सर्जन की तरंग दैर्ध्य से संबंधित अनुपातिक मापन पर आधारित हैं। इसके अलावा, टीआरपी का अंतरा-आणविक एकत्रीकरण, जो प्रोटीन में सबसे प्रचुर अंतर्जात फ्लोरोफोर है, नवीन पेप्टिडोमाइमिक्स के माध्यम से प्रोटीन के जैव-आणविक अंतःक्रियाओं का अध्ययन करने का एक दृष्टिकोण प्रदान करता है।

अध्याय 2 शीर्षक '**सामग्री और कार्यप्रणालियाँ**' रसायनों की खरीद/संश्लेषण के साथ-साथ अपनाई गई जांच प्रक्रियाओं में शामिल सभी तकनीकों और प्रोटोकॉल का गहन विवरण प्रदान करता है। विशेष रूप से, इस शोध प्रबंध के निष्कर्षों को स्थापित करने के लिए यूवी-विज़ आणविक अवशोषण, स्थिर-अवस्था और समय-संकल्प्य प्रतिदीप्ति, गतिशील श्यानता और गतिशील घनत्व मापन का उपयोग किया गया है। टाइप 'III' हाइड्रोफिलिक कोलीन क्लोराइड (ChCl)-आधारित डीईएस और टाइप V डेकेनोइक एसिड (DA)-आधारित डीईएस अध्ययन में उपयोग किए गए प्रमुख नवीन विलायक प्रणालियों का गठन करते हैं।

अध्याय 3 शीर्षक 'कोलीन क्लोराइड-आधारित गहरे यूटेक्टिक विलायकों बनाम एक तरल पॉलीमर में ग्राउंड- और उत्तेजित-अवस्था अंतरा-आणविक एकत्रीकरण का विरोधाभास'

कोलीन क्लोराइड (ChCl)-आधारित डीईएस में घुले हुए एक डाइपाइरेनिलाल्केन की पहली प्रायोगिक जांच को चिह्नित करता है। एक सामान्य हाइड्रोजन-बंध स्वीकर्ता, ChCl और हाइड्रोजन-बंध दाता यूरिया और ग्लिसरॉल (Gly) के साथ क्रमशः 1 : 2 के मोल अनुपात में दो विशिष्ट डीईएस का उपयोग किया जाता है। अपेक्षाकृत उच्च श्यानता वाले घोलक माध्यम के जानबूझकर चयन का उद्देश्य, जिसमें ChCl:Urea और ChCl:Gly की गतिशील श्यानता (η) क्रमशः 1372.0 mPa.s और 473.0 mPa.s है, 293.15 K पर, इन परिस्थितियों में डाइमराइजेशन प्रक्रिया में संभावित परिवर्तन या संशोधन का पता लगाना है। इसके अतिरिक्त, डीईएस के एक हाइड्रोजन-बंध दाता (एचबीडी) घटक, अर्थात्, ग्लिसरॉल ($\eta = 1412.0$ mPa.s ; 293.15 K पर) और एक तरल पॉलीमर, पॉलीडाइमेथाइलसाइलॉक्सेन जिसका संख्या औसत आणविक भार (MW) 2000 (PDMS2000) और η 21.4 mPa.s है 293.15 K पर, तुलना के उद्देश्य से जांच की जाती है। सामान्य कार्बनिक विलायकों में देखे गए व्यवहार के समान, 1Py(3)1Py के दो पीवाई अंश तरल पॉलीमर PDMS2000 में घुलने पर केवल उत्तेजित-अवस्था में एकत्रित होते हैं, जो एक शास्त्रीय अंतरा-आणविक एक्साइमर का निर्माण करते हैं। हालांकि, कई कम श्यानता वाले कार्बनिक विलायकों के विपरीत जहां दो गतिज रूप से अलग-अलग एक्साइमर संरचनाएं एक उत्तेजित मोनोमर द्वारा एक साथ आबादित होती हैं, PDMS2000 केवल एक पता लगाए गए एक्साइमर संरचना को प्रदर्शित करता है। यह व्यवहार तरल पॉलीएथिलीन ग्लाइकॉल (PEG) जैसे अन्य अपेक्षाकृत श्यान तरल पदार्थों में अवलोकनों के अनुरूप है। उच्च श्यानता वाले डीईएस और ग्लिसरॉल (Gly) के संदर्भ में, जबकि 1Py(3)1Py में अंतरा-आणविक एकत्रीकरण होता है, यह केवल उत्तेजित-अवस्था तक सीमित नहीं है। स्थैतिक और समय-

संकल्प प्रतिदीप्ति दोनों के माध्यम से ग्राउंड-स्टेट विषमता की उपस्थिति स्पष्ट है, जो ग्राउंड-स्टेट में दो पीवाई अंशों के बीच कमजोर अंतःक्रियाओं को इंगित करती है जो आंशिक एकत्रीकरण की ओर ले जा सकती हैं। डीईएस/Gly के भीतर बहुत अधिक श्यानता और/या व्यापक हाइड्रोजन-बंधन नेटवर्क को इस अवलोकन के कारणों के रूप में प्रस्तावित किया गया है।

अध्याय 4 शीर्षक 'अंतरा-आणविक डाइमर गठन के माध्यम से पॉलीमर घुलनशीलता के लिए गहरे यूटेक्टिक विलायकों का वर्गीकरण' कोलीन क्लोराइड-आधारित डीईएस में एक सामान्य और उपयोगी पॉलीमर पॉलीडाइमेथाइलसाइलोकसेन (PDMS) की घुलनशीलता विशेषताओं की प्रायोगिक जांच की पहली रिपोर्ट है। पिछले अध्याय के समान, डीईएस ChCl:Urea और ChCl:Gly का उपयोग तरल पॉलीमर PDMS2000 और ग्लिसरॉल के साथ किया जाता है। अध्ययन में, दो पाइरेनिल अंशों (Py-PDMS-Py) के साथ अंत-टैग किए गए पॉलीडाइमेथाइलसाइलोकसेन (PDMS) एक डाइपाइरेनिल प्रतिदीप्ति जांच के रूप में कार्य करता है। जांच से पता चलता है कि दो पाइरेनिल समूहों के अंतरा-आणविक एकत्रीकरण PDMS की विघटन अवस्था से प्रभावित होता है, जो या तो कुंडलित या अकुंडलित हो सकता है। Py-PDMS-Py के स्थैतिक और गतिशील प्रतिदीप्ति व्यवहार से पता चलता है कि Py-PDMS-Py द्वारा डाइमरीकरण विशेष रूप से उत्तेजित-अवस्था में होता है जब विलायक PDMS2000 होता है। हालांकि, जब पीवाई-PDMS-पीवाई को डीईएस ChCl:Urea और ChCl:Gly के साथ-साथ ग्लिसरॉल में घोला जाता है, तो डेटा द्वारा स्पष्ट ग्राउंड-स्टेट विषमता का खुलासा किया जाता है, जो ग्राउंड-स्टेट में पीवाई-पीवाई अंतःक्रियाओं की उपस्थिति को दर्शाता है। समग्र डेटा के आधार पर, यह निष्कर्ष निकाला जाता है कि PDMS मुख्य रूप से डीईएस और ग्लिसरॉल में कुंडलित या उलझी हुई अवस्था में मौजूद है, जबकि यह तरल PDMS2000 में अकुंडलित अवस्था को प्राथमिकता देता है। इस प्रकार, ग्लिसरॉल के समान, डीईएस ChCl:Urea

और $\text{ChCl}:\text{Gly}$ को PDMS के लिए "खराब" विलायक के रूप में वर्गीकृत किया जा सकता है, जबकि PDMS2000, पॉलीमर PDMS के साथ इसकी समानता के कारण, एक "अच्छा" विलायक के रूप में कार्य करता है। यह सीधा स्पेक्ट्रोस्कोपिक दृष्टिकोण जटिल तरल माध्यमों के भीतर पॉलीमर घुलनशीलता की विशेषता बताने के लिए उपयोगी साबित होता है, जो विभिन्न विलायकों में PDMS की पसंदीदा अवस्थाओं के बारे में अंतर्दृष्टि प्रदान करता है।

अध्याय 5 शीर्षक 'जलविरोधी गहन यूटेक्टिक विलायकों का अंतरा-अणुक एक्साइमर गठन के लिए मूल्यांकन' चक्रीकरण से जुड़ी रासायनिक प्रतिक्रियाओं में जलविरोधी गहन यूटेक्टिक विलायकों (एचडीईएस) को पेश करने के पहले प्रयास को दर्शाता है। लेइटनर और फर्स्टनर समूहों द्वारा पहले अध्ययन किए गए एक डाइईन $[\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_8\text{COO}(\text{CH}_2)_4\text{CH}=\text{CH}_2]$ को पाइरीन के साथ अंत-लेबल किया गया है जिससे हमारा फ्लोरोक्रोम, 6-(1-पाइरेनिल)हेक्सिल-11(1-पाइरेनिल)-अंडेकेनोएट $[1\text{-Py}(\text{CH}_2)_{10}\text{COO}(\text{CH}_2)_6\text{1-Py}]$ बनता है। प्राकृतिक रूप से प्राप्त घटकों, यानी डेकेनोइक एसिड (DA), के साथ-साथ मोनोटर्पेनॉइड्स, मेंथॉल (Men) और थाइमोल (Thy) से बने डीईएसs की एक श्रृंखला का उपयोग विभिन्न मोलर अनुपातों में विभिन्न घटकों के जोड़े के साथ डीईएसs उत्पन्न करने के लिए किया गया है, अर्थात्, Thy : Men (1 : 1 और 1 : 2), DA : Men (1 : 1 और 1 : 2), और Thy : DA (2 : 1, 1 : 1, और 1 : 2)। अध्ययनों ने सभी ग्यारह डीईएसs में केवल ऑप्टिकल उत्तेजना के बाद बने क्लासिकल एक्साइमर्स के गठन को उजागर किया है। समय-संकल्प जांच से पता चलता है कि प्रत्येक डीईएस के लिए, एक्साइमर गठन की गतिशीलता तापमान (T) ≥ 333.15 K पर मानक बर्क्स योजना का पालन करती है। अंतरा-अणुक एक्साइमर गठन या संगठन (k_a) के लिए अनुमानित दर स्थिरांक आयनिक तरल पदार्थों और टेट्राएथिलीन ग्लाइकॉल (TEGs) में इसी जांच के लिए पहले बताए गए मूल्यों से थोड़े अधिक दिखाते हैं। $\ln k_a$ बनाम $1/T$ के प्लॉट दोनों

के बीच एक उत्कृष्ट रैखिक संबंध दर्शाते हैं, जो स्पष्ट रूप से प्रत्येक डीईएस के लिए अनुभवजन्य अरहेनियस व्यंजक के अनुरूपता को दर्शाता है। यह शोध विभिन्न रासायनिक अनुप्रयोगों के लिए Hडीईएसs की दक्षता और ट्यूनेबिलिटी का मूल्यांकन करने का लक्ष्य रखता है, विशेष रूप से चक्रीकरण प्रतिक्रियाओं के संदर्भ में।

अध्याय 6 शीर्षक 'डाइसल्फाइड-लिंकड डाइपाइरेनिल यौगिक में अत्यधिक कुशल अंतरा-अणुक एक्साइमर गठन: प्रोटॉन पहचान और तरलता मूल्यांकन' एक नए अंत-टैग किए गए डाइपाइरेनिल यौगिक, जिसे DTP नाम दिया गया है, को प्रस्तुत करता है, जो विशेष रूप से ध्रुवीय विलायकों में उल्लेखनीय रूप से उच्च अंतरा-अणुक एक्साइमर गठन दक्षता प्रदर्शित करने की अपनी असाधारण क्षमता के लिए उल्लेखनीय है। DTP (जिसमें लिंकर श्रृंखला पर डाइसल्फाइड और डायामाइड कार्यात्मकताएं हैं) उच्च एक्साइमर-से-मोनोमर तीव्रता अनुपात (I_E/I_M) के साथ-साथ एक्साइमर गठन की तीव्र गतिकी भी प्रदर्शित करता है, जैसा कि अपेक्षाकृत उच्च दर स्थिरांकों (k_a) द्वारा संकेतित किया गया है। दो पाइरेनिल समूहों के बीच लिंकिंग श्रृंखला पर $-NH-(CO)-$ और/या $-S-S-$ जैसे कार्यात्मक समूहों की उपस्थिति इन अनुकूल विशेषताओं में महत्वपूर्ण योगदान देती है। उल्लेखनीय रूप से, I_E/I_M और k_a मान विलायक की प्रकृति पर मजबूत निर्भरता प्रदर्शित करते हैं, चाहे वह ध्रुवीय-प्रोटिक हो या ध्रुवीय-अप्रोटिक। यह अवलोकन DTP की उच्च संवेदनशीलता और चयनात्मकता के साथ H^+ को पहचानने की उल्लेखनीय क्षमता द्वारा समर्थित है, जो इसे प्रोटॉन के लिए एक प्रभावी केमोसेंसर बनाता है। इसके अलावा, विलायक वातावरण की श्यानता के साथ I_E/I_M और k_a दोनों की मापनीयता DTP को एक कुशल सूक्ष्म तरलता जांच के रूप में स्थापित करती है। यह प्रभावशीलता एसीटोनाइट्राइल (एसीएन) और डाइमिथाइल सल्फॉक्साइड (डीएमएसओ) के मिश्रण की निगरानी और एक प्रतिनिधि आयनिक तरल और डीईएस में पानी की न्यूनतम मात्रा के

मूल्यांकन के माध्यम से प्रदर्शित की गई है। DTP के रणनीतिक डिजाइन में, इसकी आणविक संरचना और कार्यात्मक समूहों पर सावधानीपूर्वक विचार करना, अंतरा-अणुक एक्साइमरों के गठन को बढ़ावा देने में इसके असाधारण प्रदर्शन में योगदान देता है। यह नवीन यौगिक विभिन्न क्षेत्रों में अनुप्रयोगों के लिए आशाजनक है, विशेष रूप से उन संदर्भों में जहां कुशल अंतरा-अणुक एक्साइमर गठन महत्वपूर्ण है, जैसे, ध्रुवीय वातावरण में प्रतिदीप्ति-आधारित संवेदन या इमेजिंग में।

अध्याय 7 शीर्षक 'ट्रिफ्लैकैन-संयुग्मित पेप्टिडोमिमेटिक्स में अभूतपूर्व अंतरा-अणुक संघ-प्रेरित प्रतिदीप्ति' टीआरपी-टीआरपी अंतरा-अणुक समुच्चय गठन के क्षेत्र में एक महत्वपूर्ण खोज का वर्णन करता है। फ्लोरोफोर के बीच अंतरा-अणुक अंतर-स्थान संघ का अध्ययन करने के लिए टीआरपी इकाइयों को जोड़ने के लिए एक बिस्पिडीन-व्युत्पन्न द्विचक्रीय ढांचे को तर्कसंगत रूप से चुना गया था। अध्ययनों ने एक नव स्थापित टीआरपी-टीआरपी डाइमर के गठन को प्रकट किया। UV-vis अवशोषण स्पेक्ट्रा सफलतापूर्वक जाँच के संकेन्द्रण को $25\mu\text{M}$ जितना कम रखते हुए भी 320-420 nm क्षेत्र में एक निम्न-ऊर्जा अवशोषण बैंड को दर्ज करने में सक्षम थे, यह ध्रुवीय [एसीएन और मेथनॉल (एमईओएच)] के साथ-साथ अध्रुवीय [एथिल एसीटेट (ईटीओएसी), टॉल्यूईन, और डाइक्लोरोमीथेन (डीसीएम)] विलायकों में किया गया। यह 260-300 nm क्षेत्र में एकल टीआरपी के विशिष्ट बैंड के अतिरिक्त था। स्थिर-अवस्था प्रतिदीप्ति ने प्रत्येक शुद्ध विलायक में समुच्चय के लिए एक प्रतिनिधि बैंड उत्पन्न नहीं किया, जो एक "अंधकार समुच्चय" के अस्तित्व का संकेत देता है। H^+ के क्रमिक संयोजन से एक नया और बढ़ता हुआ निम्न-ऊर्जा प्रतिदीप्ति बैंड स्थापित हुआ, जो नवीन ढांचे में प्रोटॉन-प्रेरित प्रतिदीप्ति परिवर्तन का दृश्य स्थापित करता है। नियंत्रण यौगिकों के साथ जांच की गई जिसने यह सुनिश्चित करने में मदद की कि इन स्पेक्ट्रल विशेषताओं का स्रोत वास्तव में द्विअणुक टीआरपी-टीआरपी इकाई थी और स्थानीयकृत उत्तेजित-अवस्था का प्रकटीकरण नहीं।

कुछ विशिष्ट आयनों के साथ संवेदन प्रयोगों ने H^+ के प्रति जांच की चयनात्मकता और संवेदनशीलता को और अधिक प्रदर्शित किया। तदुपरांत, ये अध्ययन जैव-आणविक समुच्चयन को समझने के लिए एक उत्कृष्ट आधार के रूप में कार्य करते हैं और वैज्ञानिकों को ऐसी श्रेष्ठ संवेदक प्रणालियों को डिजाइन करने के लिए प्रोत्साहित करते हैं।

अध्याय 8 शीर्षक 'निष्कर्ष और भविष्य की संभावनाएं' किए गए व्यापक अन्वेषणों से प्राप्त प्रमुख निष्कर्षों और अंतर्दृष्टियों को संक्षेपित करता है। पीवाई और टीआरपी-युक्त ढांचों के गुणों की विस्तृत जांच एक दोहरा उद्देश्य पूरा करती है। सबसे पहले, यह विभिन्न विलायकों में अंतरा-अणुक समुच्चयन को नियंत्रित करने वाले मौलिक सिद्धांतों पर प्रकाश डालती है, विशेष रूप से डीईएसs के संदर्भ में। दूसरा, ये अध्ययन विशिष्ट पर्यावरणीय संकेतों या ट्रिगर्स के प्रति उत्तरदायी व्यवहार प्रदर्शित करने वाली जांचों को तैयार करने के लिए एक रोडमैप प्रदान करते हैं। इस शोध प्रबंध के निष्कर्ष न केवल अद्वितीय विलायकों में प्रतिदीप्ति घटनाओं की मौलिक समझ में योगदान देते हैं, बल्कि उत्तेजना-उत्तरदायी प्रणालियों में अनुप्रयोगों के साथ उन्नत जांचों के भविष्य के विकास के लिए भी आशाजनक हैं।

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LIST OF ABBREVIATIONS

Abbreviation	Full Form
[bmim][PF ₆]	1-Butyl-3-Methylimidazolium Hexafluorophosphate
[emim][Tf ₂ N]	1-Ethyl-3-Methylimidazolium <i>Bis</i> (Trifluoromethylsulfonyl)Imide
1-MePy	1-Methylpyrene
1Py(3)1Py	1,3- <i>Bis</i> (1-Pyrenyl)Propane
ACN	Acetonitrile
ACQ	Aggregation Caused Quenching
AIE	Aggregation Induced Emission
CD	Circular Dichroism
ChCl	Choline Chloride
DA	Decanoic Acid
DCM	Dichloromethane
DES	Deep Eutectic Solvent
DMSO	Dimethyl Sulfoxide
EG	Ethylene Glycol
EtOAc	Ethylacetate
EtOH	Ethanol
Gly	Glycerol
HBA	Hydrogen Bond Acceptor
HBC	Hexabenzocoronene
HBD	Hydrogen Bond Donors
HDES	Hydrophobic Deep Eutectic Solvents
IAIF	Intramolecular Association Induced Fluorescence
IL	Ionic Liquid

IRF	Instrument Response Function
LEC	Light-Emitting Electrochemical Cells
Men	Menthol
MeOH	Methanol
NADES	Natural Deep Eutectic Solvents
NMR	Nuclear Magnetic Resonance
OLED	Organic Light-Emitting Diodes
OPV	Organic Photovoltaics
PAH	Polycyclic Aromatic Hydrocarbons
PDMS	Polydimethylsiloxane
PEG	Polyethylene Glycol
PMT	Photomultiplier Tube
Py	Pyrene
RCM	Ring-Closing Metathesis
RIR	Intramolecular Rotation
SCF	Supercritical Fluids
TCSPC	Time-Correlated Single Photon Counting
TEG	Tetraethyleneglycol
Thy	Thymol
TICT	Twisted Intramolecular Charge Transfer
TPE	Tetraphenylethene
Trp	Tryptophan
UV	Ultraviolet
Vis	Visible
VOC	Volatile Organic Compound