

**INVESTIGATION OF EXCITED-STATE AGGREGATION AND
COMPLEXATION WITHIN IONIC LIQUID-BASED SYSTEMS**

ANITA YADAV



**DEPARTMENT OF CHEMISTRY
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COMPLEXATION WITHIN IONIC LIQUID-BASED SYSTEMS**

by

ANITA YADAV

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



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Dedicated to
My Family

CERTIFICATE

This is to certify that the thesis entitled, “**Investigation of Excited-State Aggregation and Complexation within Ionic Liquid-Based Systems**”, being submitted by **Ms. Anita Yadav** 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.

Date:

Dr. Siddharth Pandey

Professor

Department of Chemistry

Indian Institute of Technology Delhi

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ABSTRACT

Ionic liquids with unique physicochemical properties and widespread applications in science and technology have attracted the attention of researchers worldwide. These interesting liquids with different cation/anion combinations and modified by cosolvent addition may encompass a wide variety of properties that may extend their potential in various fields. Specifically, the work presented in the thesis is concerned with the understanding of intramolecular dimerization and complexation processes within select ionic liquids and their judiciously selected cosolvent mixtures. The thesis features a detailed investigation of the key aspects of excimer (excited dimer) and exciplex (excited complex) formation in these complex fluidic systems, which provides insights into the interactions present within these systems.

The thesis comprises of six chapters. Chapter 1 (Background and Introduction) presents a compact introduction of ionic liquids and the issues that lead to this particular research work along with approaches to resolve them. Chapter 2 titled ‘Materials and Methodologies’ is about chemical procurement, purification, and storage as well as techniques used during the investigation. Chapter 3 titled ‘Excimer Formation Dynamics of 1,10-*Bis*-(1-pyrenyl)decane (BPD) in Structurally Different Ionic Liquids’ explores the alternate pathways for molecular aggregation. Intramolecular excimer formation dynamics of BPD, where the fluorophoric pyrene moieties are separated by a long decyl chain, is investigated in seven different ionic liquids in 10–90 °C temperature range. The long alkyl separator allows for ample interaction with the solubilizing milieu prior to the formation of the excimer. The ionic liquids are composed of two sets – one having four ionic liquids of 1-butyl-3-methylimidazolium cation ([bmim⁺]) with different anions and the other having four ionic liquids of

bis(trifluoromethylsulfonyl)imide anion ($[\text{Tf}_2\text{N}^-]$) with different cations. Chemical structure of the ionic liquid controls the excimer formation efficiency as excimer-to-monomer emission intensity ratio (I_E/I_M) within ionic liquids with the same dynamic viscosities are found to be significantly different. Stokes-Einstein relationship is not followed in $[\text{bmim}^+]$ ionic liquids, however, with the exception of $[\text{choline}][\text{Tf}_2\text{N}]$, it is found to be followed in $[\text{Tf}_2\text{N}^-]$ ionic liquids suggesting the cyclization dynamics of BPD to be diffusion-controlled and to depend on the viscosity of the ionic liquid irrespective of the identity of the cation.

Chapter 4 [Excimer Formation Dynamics of 1,3-*Bis*-(1-pyrenyl)propane (BPP) within Ionic Liquids Modified by Polyethylene Glycols (PEGs)] provides detail of the intramolecular excimer formation dynamics of BPP within mixtures of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate $[\text{bmim}][\text{PF}_6]$ with PEGs of varying molecular weight (MW) in the temperature range 10–90 °C. Irrespective of the composition of the medium and the temperature, excited-state intensity decay of the excimer fluorescence fits best to a three-exponential decay function suggesting the presence of one excited-state monomer and two kinetically-distinguishable excimers where both the excimers are populated simultaneously by the excited monomer with no interconversion between the two excimers. In neat PEGs for temperatures ≤ 50 °C, intensity decay data of monomer fluorescence fits best to a single-exponential decay function, whereas, at higher temperatures, the fits become better to a double exponential decay function. In neat $[\text{bmim}][\text{PF}_6]$, while a double exponential decay function is required to fit the monomer excited-state intensity decay data at lower temperatures, three exponentials are required to satisfactorily fit the data at higher temperatures. Within long-chain PEG-containing ($[\text{bmim}][\text{PF}_6] + \text{PEG}$) mixtures, PEG as opposed to $[\text{bmim}][\text{PF}_6]$ controls the excimer formation dynamics by supposedly wrapping around the excimer thus hindering

dissociation back to the monomer. The overall rate constant of the excimer formation within ([bmim][PF₆] + PEG) mixtures are found to scale better with the microviscosity rather than the bulk viscosity of the medium.

Chapter 5 is ‘Effect of Ionic Liquids on Fluorescence of an Intramolecular Exciplex Forming Probe’. We investigate a pyrene (Py) and a tryptophan (Trp) based fluorescent probe bispidine tryptophan *tert*-butyloxycarbonylpyrene [Bisp(TrpBoc)Py], where Py and Trp groups are judiciously placed on a novel molecular scaffold namely bispidine. This probe exhibited fluorescence due to the formation of an unprecedented emissive intramolecular exciplex in polar solvents. The probe demonstrates good sensitivity, excellent selectivity, and adequate reversibility towards proton sensing. Further, the effect of structurally different ionic liquid addition on [Bisp(TrpBoc)Py] fluorescence in acetonitrile and ethanol was explored. Ionic liquid addition shows almost no effect on monomer fluorescence originating from Py but Py-Trp exciplex fluorescence decreases with an increase in ionic liquid concentration. The outcome of the analysis suggests that the chemical structure of ionic liquid controls the fluorescence from intramolecular exciplex. Further, it was observed that anions do not have much effect on intramolecular exciplex fluorescence but cations show a significant effect. Fluorescence lifetime measurements reveal no significant change in the decay times of monomer and exciplex after the addition of ionic liquid. This suggests that the quenching is not dynamic in nature within these systems. The investigation reveals that ionic liquid may form a “dark” complex with an intramolecular exciplex forming probe [Bisp(TrpBoc)Py]. Chapter 6 (Conclusions and Future Prospects) presents the conclusions drawn from the overall investigation. The work presented in this thesis will help broaden the overall utility of ionic liquids for various applications.

सार

आयनिक लिक्विड्स विथ यूनिक फेसिकोकेमिकल प्रॉपर्टीज एंड विदेशप्रद ऍप्लिकेशन्स इन साइंस एंड टेक्नोलॉजी हैवे अत्रक्टेड थे अटेंशन ऑफ रेसेअर्चेस वर्ल्डवाइड। थी इंटरस्टिंग लिक्विड्स विथ डिफरेंट कटियन/एनायन कॉम्बिनेशंस एंड मॉडिफाइड बी कोसोल्वेंट अद्वितीओं मई एनकंपास अ वाइड वैरायटी ऑफ प्रॉपर्टीज तट मई एक्सटेंड थेइर पोटेंशियल इन वेरियस फ़िल्ड्स। स्पेसिफिकल्लय, थे वर्क प्रेसैंटेड इन थे थीसिस इस कंसर्नड विथ थे अंडरस्टैंडिंग ऑफ इंटरमोलेक्युलर डिमेरिज़िऑन एंड कम्प्लेक्सेशन प्रोसेसेज वीथिन सेलेक्ट आयनिक लिक्विड्स एंड थेइर जुडीशियसली सिलेक्टेड कोसोल्वेंट मिक्सचर्स। थे थीसिस फीचर्स डिटेल्ड इन्वेस्टीगेशन ऑफ थे कीय आस्पेक्ट्स ऑफ एक्ससीमर (एक्ससिटेड डिमर) एंड एक्ससीप्लेक्स (एक्ससिटेड काम्प्लेक्स) फार्मेशन इन थी काम्प्लेक्स फ्लुइड्स सिस्टम्स, व्हिच प्रोविडेंस इनसाइट्स ईटो थे इंटरेक्शन्स प्रेजेंट वीथिन थी सिस्टम्स।

थीसिस में छह अध्याय शामिल हैं। अध्याय 1 (पृष्ठभूमि और परिचय) प्रेजेंट्स अ कॉम्पैक्ट इंट्रोडक्शन ऑफ आयनिक लिक्विड्स एंड थे इश्यूज तहत लीड टो थिस पार्टिकुलर रिसर्च वर्क अलॉग विथ अप्प्रोचेस टो रेसोल्वे थम। अध्याय 2 शीर्षक 'सामग्री और तरीके' रासायनिक खरीद, शोधन और भंडारण के साथ-साथ जांच के दौरान उपयोग की जाने वाली तकनीकों के बारे में है। अध्याय 3 शीर्षक 'एक्ससीमर फार्मेशन डायनामिक्स ऑफ 1,10-बिस-(1-पैरेनिल)देकने (BPD) इन स्त्रुक्चुरेल्ली डिफरेंट आयनिक लिक्विड्स' एक्सप्लोरेस थे अल्टेरनाते पठवायस फॉर मॉलिक्यूलर एग्रीगेशन। इंटरमोलेक्युलर एक्ससीमर फार्मेशन डायनामिक्स ऑफ BPD, वेयर थे फ्लुओरोफोरिक पैरेने मोईएटीएस अरे सेपरेटेड बी ए लॉन्ग डील चैन, ईस इन्वेस्टीगेटेड इन सेवन डिफरेंट आयनिक लिक्विड्स इन 10–90 °C टेम्परेचर रेंज। थी लॉन्ग अल्काइल सेपरेटर अल्लोव्स फॉर ाम्पले इंटरेक्शन विथ थी सोलुबिलीज़िंग मिलिएउ प्रायर टो थी फार्मेशन ऑफ थी एक्ससीमर। थी आयनिक लिक्विड्स अरे कंपोज्ड ऑफ ट्व सेट्स-ओने हैविंग फोर आयनिक लिक्विड्स ऑफ 1-ब्यूटाइल -3-मिथाइल

इमिडाज़ोलियम कटियन ([bmim⁺]) विथ डिफरेंट अनियन्स एंड थे इतर हैविंग फोर आयनिक लिक्विड्स ऑफ़ बिस (त्रि फ्लुओरो मिथाइल सुल्फोनिल) इमिडे एनायन ([Tf₂N⁻]) विथ डिफरेंट केशन्स। केमिकल स्ट्रक्चर ऑफ़ थे आयनिक लिक्विड कंट्रोल्स थे एक्ससीमर फार्मेशन एफिशिएंसी अस एक्ससीमर-तो-मोनोमर एमिशन इंटेसिटी रेश्यो (I_E/I_M) वीथिन आयनिक लिक्विड्स विथ शामे डायनामिक विस्कोसिटीज़ अरे फाउंड टो बे सिग्नीफिकान्तली डिफरेंट। स्टोक्स-आइंस्टीन रिलेशनशिप ईस नॉट फोल्लोवेड इन [bmim⁺] आयनिक लिक्विड्स, होवेवर, विथ थे एक्सेप्शन ऑफ़ [choline][Tf₂N], आईटी ईस फाउंड टो बे फोल्लोवेड इन [Tf₂N⁻] आयनिक लिक्विड्स सुग्गेस्टिंग थे सिकलिज़तिओन डायनामिक्स ऑफ़ BPD टो बे डिफ्फुसिओ-कंट्रोल्ड एंड तो देपेंड ऑन थे विस्कोसिटी ऑफ़ थे आयनिक लिक्विड इर्रेस्पेक्टिवे ऑफ़ थे आइडेंटिटी ऑफ़ थे कटियन।

अध्याय 4 [एक्ससीमर फार्मेशन डायनामिक्स ऑफ़ 1,3-बिस-(1-पैरेनिल)प्रोपेन (BPP) वीथिन आयनिक लिक्विड्स मॉडिफाइड बी पोलीएथीलेने गलिकल्स (PEGs)] प्रोविडेंस डिटेल् ऑफ़ थे इंटरमोलेक्युलर एक्ससीमर फार्मेशन डायनामिक्स ऑफ़ BPP वीथिन मिक्सचर्स ऑफ़ आयनिक लिक्विड 1-ब्यूटाइल-3-मिथाइल इमिडाज़ोलियम हेक्साफ्लुओरोफॉस्फेटे [bmim][PF₆] विथ PEGs ऑफ़ वारयिंग मॉलिक्यूलर वेट (MW) इन थे टेम्परेचर रेंज 10–90 °C। रैस्पेक्टिवे ऑफ़ थे कम्पोजीशन ऑफ़ थे मध्यम एंड थे टेम्परेचर, एक्ससिटेड-स्टेट इंटेसिटी देकय ऑफ़ थे एक्ससीमर फ्लुओरेसेन्स फिट्स बेस्ट तो अ थ्री-एक्सपोनेंशियल देकय फंक्शन सुग्गेस्टिंग थे प्रजेस ऑफ़ ओने एक्ससिटेड-स्टेट मोनोमर एंड ट्व कीनेटिकल्लय-डिस्टिंगुइसाब्ले एक्सकॉमेर्स वेयर बोथ थे एक्सकॉमेर्स अरे पॉपुलटेड सिमुलतानूसली बी थे एक्ससिटेड मोनोमर विथ नो इंटरकंवरसिओ बिटवीन थे ट्व एक्सकॉमेर्स। इन नेट PEGs फॉर टेम्परेचरेस ≤ 50 °C, इंटेसिटी देकय डाटा ऑफ़ मोनोमर फ्लुओरेसेन्स फिट्स बेस्ट टो अ सिंगल-एक्सपोनेंशियल देकय फंक्शन, व्हेरास, अट हायर टेम्परेचरेस, थे फिट्स बिकम बेटर टो अ डबल एक्सपोनेंशियल देकय फंक्शन। इन नेट [bmim][PF₆], व्हिले अ डबल एक्सपोनेंशियल देकय फंक्शन ईस रिक्वायर्ड टो फिट थे मोनोमर एक्ससिटेड-स्टेट इंटेसिटी देकय डाटा अट लोअर टेम्परेचरेस, थ्री एक्सपोनेंटीकल्स अरे

रिक्वायर्ड टो सटिस्फैक्टरीली फिट थे डाटा अट हायर टेम्परेचरस वीथिन लॉन्ग -चैन PEG-कोन्टाइनिंग ([bmim][PF₆] + PEG) मिक्सचर्स, PEG अस ओप्पोसेड टो [bmim][PF₆] कंट्रोलस थे एकससीमर फार्मेशन डायनामिक्स बी सुप्पुसेडली रैपिंग अराउंड थे एकससीमर थुश हिन्डरिंग दिसोसिएशन बैक टो थे मोनोमर। थे ओवरआल रेट कांस्टेंट ऑफ़ थे एकससीमर फार्मेशन वीथिन ([bmim][PF₆] + PEG) मिक्सचर्स ईस फाउंड टो स्केल बेटर विथ थे मिक्रोविस्कोसिटी राथर थान थे बल्क विस्कोसिटी ऑफ़ थे मेडियम।

अध्याय 5 'इफ़ेक्ट ऑफ़ आयनिक लिक्विड्स ऑन फ्लुओरेसेन्स ऑफ़ अन इंटरमोलेक्युलर एकससीप्लेक्स फॉर्मिंग प्रोब'। वी इन्वेस्टीगेट अ पयरेने (Py) एंड अ ट्रीप्टोफन (Trp) बेस्ड फ्लोरोसेंट प्रोब बिस्पिडिने ट्रीप्टोफन टेरट-बुटीलोकसीकार्बोनैलपैरेने [Bisp(TrpBoc)Py], वेयर Py and Trp गुप्स आर जुडीशियसली प्लेस्ड ऑन अ नावेल मॉलिक्यूलर स्कैफ़ोल्ड नामेली बिस्पिडिने। थिस प्रोब एकसहिबिटेड फ्लुओरेसेन्स डुए टो थे फार्मेशन ऑफ़ अन उनपरेसडेंटेड एमईसीवे इंटरमोलेक्युलर एकससीप्लेक्स इन पोलर सॉल्वेंट्स। थे प्रोब डेमॉस्ट्रेट्स गुड सेंसिटिविटी, एकसीलेंट सेलेक्टिविटी, एंड अडकते रेवेर्सिबिलिटी टुवर्ड्स प्रोटोन सेंसिंग। फरदर, थे इफ़ेक्ट ऑफ़ स्ट्रुक्चुरेल्ली डिफरेंट आयनिक लिक्विड अद्वितीओं ऑन [Bisp(TrpBoc)Py] फ्लुओरेसेन्स इन असतोनिटरीले एंड इथेनॉल वास् एकसप्लोरेड। आयनिक लिक्विड अद्वितीओं शोज ऑलमोस्ट नो इफ़ेक्ट ऑन मोनोमर फ्लुओरेसेन्स ओरिगिनाटिंग फ्रॉम Py बट Py-Trp एकससीप्लेक्स फ्लुओरेसेन्स डिक््रीसेस विथ इनक्रीस इन आयनिक लिक्विड कंसंट्रेशन। थे आउटकम ऑफ़ थे एनालिसिस सुग्गेस्ट्स तट केमिकल स्ट्रक्चर ऑफ़ आयनिक लिक्विड कंट्रोलस थे फ्लुओरेसेन्स फ्रॉम इंटरमोलेक्युलर एकससीप्लेक्स। फरदर, इट वास् ऑब्सेर्वेड तट अनियन्स डॉ नॉट हैवे मच इफ़ेक्ट ऑन इंटरमोलेक्युलर एकससीप्लेक्स फ्लुओरेसेन्स बट केशन्स शो सिग्नीफिकेंट इफ़ेक्ट। फ्लुओरेसेन्स लाइफटाइम मासुरेमेन्ट्स रेवेअल नो सिग्नीफिकेंट चेंज इन थे देकय टाइम्स ऑफ़ मोनोमर एंड एकससीप्लेक्स आफ्टर अद्वितीओं ऑफ़ आयनिक लिक्विड। थिस सुग्गेस्ट्स तट थे केंचींग इस नॉट डायनामिक इन नेचर वीथिन थेसे सिस्टम्स। थे इन्वेस्टीगेशन रेवेल्स तट आयनिक लिक्विड

मय फॉर्म अ “डार्क ” काम्प्लेक्स विथ इंटरमोलेक्युलर एक्ससीप्लेक्स फॉर्मिंग प्रोब [Bisp(TrpBoc)Py]। अध्याय 6 (निष्कर्ष और भविष्य की संभावनाएँ) प्रेजेंट्स थे कन्क्लूसिऑस ड्रान फ्रॉम थे ओवरआल इन्वेस्टीगेशन। थे वर्क प्रेसैंटेड इन थिस थीसिस विल हेल्प ब्रोएडेन थे ओवरआल यूटिलिटी ऑफ़ आयनिक लिक्विड्स फॉर वेरियस ऍप्लिकेशन्स।

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LIST OF ABBREVIATIONS

| Abbreviation | Full form |
|------------------------------|---|
| [bmim][PF ₆] | 1-Butyl-3-methylimidazolium hexafluorophosphate |
| [bmim][BF ₄] | 1-Butyl-3-methylimidazolium tetrafluoroborate |
| [bmim][Tf ₂ N] | 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide |
| [bmpyrr][Tf ₂ N] | 1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide |
| [dmpim][Tf ₂ N] | 1,2-Dimethyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide |
| [choline][Tf ₂ N] | <i>N,N,N</i> -trimethylethanolammonium bis(trifluoromethanesulfonyl)imide |
| [pmpip][Tf ₂ N] | 1-Methyl-1-propylpiperidinium bis(trifluoromethanesulfonyl)imide |
| [emim][Tf ₂ N] | 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide |
| [bpy][Tf ₂ N] | <i>N</i> -butylpyridinium bis(trifluoromethanesulfonyl)imide |
| [bmim][OTf] | 1-Butyl-3-methylimidazolium trifluoromethylsulfonate |
| [bmim][EtSO ₄] | 1-Butyl-3-methylimidazolium ethylsulfate |
| LiTf ₂ N | Lithium bis(trifluoromethanesulfonyl)imide |
| ACN | Acetonitrile |
| BPP | 1,3- <i>Bis</i> (1-pyrenyl)propane |
| BPD | 1,10- <i>Bis</i> (1-pyrenyl)decane |
| [BispBoc] | Bispidine <i>tert</i> -butyloxycarbonyl |
| [Bisp(LeuBoc)Py] | Bispidine leucine <i>tert</i> -butyloxycarbonylpyrene |
| [Bisp(TrpBoc)Py] | Bispidine tryptophan <i>tert</i> -butyloxycarbonylpyrene |
| CCC | Countercurrent chromatography |
| CE | Capillary electrophoresis |

| | |
|----------|---|
| CNT | Carbon nanotube |
| E_T^N | Normalized E_T values |
| EtOH | Ethanol |
| FTIR | Fourier transform infra red |
| HPLC | High performance liquid chromatography |
| HBD | Hydrogen-bond donating acidity |
| HBA | Hydrogen-bond accepting basicity |
| IRF | Instrument response function |
| IL | Ionic Liquid |
| LMPE | Liquid-phase microextraction |
| LED | Light emitting diode |
| MePy | 1-Methylpyrene |
| MW | Molecular weight |
| MALDI-MS | Matrices-assisted laser-desorption/ionization mass spectrometry |
| OLED | Organic light emitting diode |
| Py | Pyrene |
| PEG | Poly(ethylene glycol) |
| PAHs | Polycyclic aromatic hydrocarbons |
| PMT | Photomultiplier tube |
| PL | Photoluminescence |
| QCM | Quartz crystal microbalance |
| RCM | Ring closing metathesis |

| | |
|-------|--|
| SCF | Supercritical fluid |
| Trp | Tryptophan |
| TEG | Tetraethylene glycol |
| TCSPC | Time-correlated single photon counting |
| uv | Ultraviolet |
| vis | Visible |
| VOC | Volatile organic compound |
| VTF | Vogel-Tammann-Fulcher |