

Room Temperature Ionic Liquids as Media for Photophysical Studies

Prasun K. Mandal, Aniruddha Paul and Anunay Samanta*
School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

In this article, we first present a brief introduction on room temperature ionic liquids based on substituted imidazolium salts that have been the focus of extensive studies in recent years. Subsequently, we summarize some of the photophysical studies made in these ionic liquids. Finally, we discuss the suitability of the imidazolium ionic liquids in optical studies taking into consideration their absorption and fluorescence behavior.

Keywords: Room temperature ionic liquids; Imidazolium salts; Green solvent; Fluorescence; Photophysical behavior.

INTRODUCTION

A significant effort in recent years has been directed towards finding suitable replacements for the conventional solvents as these are volatile liquids used in large quantities for various purposes and are difficult to contain. The growing concern for increasing air and water pollution by these chemicals has given birth to 'green chemistry'¹ and has led to the realization of the importance of solvent free synthesis² and the use of water, supercritical carbon dioxide³ or room temperature ionic liquids^{4,5} as the reaction media.

Room temperature ionic liquids are organic salts, which in their pure state are liquids at ambient temperature.^{4,5} While molten organic substances such as tetraalkylammonium and tetraalkylphosphonium salts were considered seriously for some time as likely solvent systems because of their relatively low melting points (between 50-250 °C) and ability to dissolve a wide variety of organic compounds, the instability in acids and thermal decomposition of these salts have made their usage significantly restricted.⁶

The discovery of air and water stable ionic liquids based on substituted imidazolium cation in 1992 has given a boost to the research activities on the ionic liquids.⁷ The sudden spurt in this activity can be understood when taking into consideration that these salts are low melting, thermally stable, highly conducting, less reactive, less sensitive towards moisture, possess a wide liquid range, and are able to dissolve a wide variety of inorganic and organic substances.^{4,5} However, the property of the imidazolium ionic

liquids that is considered most attractive from the viewpoint of the environment is their negligible vapour pressure. The nonvolatility, nonflammability and nontoxic nature of the imidazolium ionic liquids has made them environmentally benign 'green' media for carrying out various chemical reactions.^{4,5} The structures of some of the most commonly used imidazolium salts are given in Chart 1, and some of the solvent properties are collected in Table 1. It is evident from the data collected in Table 1 that the halide salts are solid at room temperature, whereas those with larger anions are low melting and are suitable as solvent systems at ambient temperatures. Among the imidazolium salts, those involving [bmim] and [emim] cations and [PF₆], [BF₄] and [Tf₂N] anions are most commonly studied. These salts are fairly stable at ambient conditions and the properties are suitable for various studies. The syntheses of these salts are straightforward.^{13,15} In the first step of a 2-step synthesis, a halide salt is prepared by reaction of the appropriate imidazole derivative and the alkyl halide. The second step involves the replacement of the anion. The commonly used imidazolium ionic liquids are also available from commercial sources, though not in a very pure form.

Chart 1

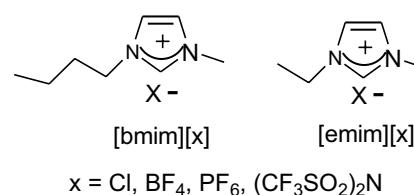


Table 1. Some physical properties of RTILs mentioned in the text

RTIL	m.p. (°C)	η (cP)	ρ (g/cc)	σ	$E_T(30)$
[emim][Cl]	87 ^a	s	s	-	-
[bmim][Cl]	65 ^a	s	s	-	-
[emim][BF ₄]	6 ^a	66.5 ^b	1.25 ^b	13 ^c	49.1 ^d
[bmim][BF ₄]	-81 ^e	154 ^b	1.2 ^b	-	48.9 ^d
[emim][PF ₆]	60 ^f	s	s	5.2 ^c	s
[bmim][PF ₆]	-61 ^e	371 ^b	1.37 ^b	1.5 ^c	52.3 ^g
[emim][Tf ₂ N]	-3 ^h	34 ^h	1.52 ^h	8.8 ^h	47.7 ⁱ
[bmim][Tf ₂ N]	-4 ^h	52 ^h	1.43 ^h	3.9 ^h	47.2 ⁱ

s: solid; η : viscosity; ρ : density; σ : Specific conductivity (mS/cm); $E_T(30)$: microscopic solvent polarity parameter (see: Reichardt, C. In *Solvents and Solvent Effects in Organic Chemistry*; VCH, Weinheim, Germany, 1988; p. 378)

a) Ref 5d; b) at 20 °C, ref 4b; c) at 25 °C, ref 8; d) ref 9; e) ref 10; f) ref 11; g) ref 12; h) all values at 20 °C, ref 13; i) ref 14.

Apart from a wide variety of reactions that have already been carried out in ionic liquids,⁵ a large majority of the recent studies involving the ionic liquids are directed towards the characterization of their various properties. The increasing usage of these ionic liquids as media for organic synthesis,⁵ liquid-liquid extraction,¹⁶ electrochemical studies,¹⁷ mass spectrometry,¹⁸ solar cells,¹⁹ synthesis of nanoparticles,²⁰ gas sensors,²¹ and other applications is also evident from the literature. The number of papers on ionic liquids has increased almost exponentially in recent years.

SPECTROSCOPIC AND PHOTOPHYSICAL STUDIES

Several photophysical and spectroscopic studies have been carried out in ionic liquids during the past few years. NMR spectroscopy (nuclear Overhauser enhancements) has been used to obtain direct evidence of cation-cation, cation-water and cation-anion interactions in [bmim][BF₄].²² Wide angle X-ray scattering and Raman spectroscopic studies have confirmed the existence of two crystalline forms of [bmim]Cl.²³ IR spectroscopic studies on probe molecules have thrown light on the Lewis acidity of the ionic liquids.²⁴ A number of pulse radiolysis studies have also been made in ionic liquids.²⁵ Low frequency vibrational motions in ionic liquids have been studied by femtosecond optical Kerr effect.²⁶

A large number of photophysical studies in imidazo-

lium ionic liquids are aimed at quantifying the polarity of these media.^{9,13,14,27-29} Probe molecules whose absorption or fluorescence properties are sensitive to the surrounding medium (such as the dipolar molecules) have been exploited for this purpose. Among the solvatochromic probes, Reichardt's dye, nitroaniline and Nile Red are the most common ones. The fluorescent probes include coumarin-153, 4-aminophthalimide and 6-propionyl-2-dimethylaminonaphthalene (PRODAN). The vibronic band intensities in the fluorescence spectrum of pyrene or its derivatives have also been used to determine the polarity of neat ionic liquid.^{13,29} All these studies have indicated that most of the imidazolium ionic liquids are more polar than acetonitrile, but less polar than methanol. In fact, the polarity experienced by the probe molecules in commonly exploited ionic liquids is found very similar and comparable to that of the short-chain alcohols. The effect of polar additives such as water, alcohol or surfactants on the ionic liquid has also been examined using various probe molecules.²⁹ The effect of carbon dioxide on different fluorescent probe molecules dissolved in ionic liquids has also been examined.³⁰ Photoisomerisation process³¹ and rotation of solute molecules³²⁻³⁴ have also been investigated in ionic liquids. We have investigated intramolecular excimer formation process in these media.³⁵

While the steady state fluorescence spectra of the electron donor-acceptor molecules did not provide much information other than the polarity of the media, the time-resolved fluorescence behavior of these systems has been found to be much more informative.^{9,14,32-34,36-39} Since the ionic liquids are sufficiently polar, the time-dependent fluorescence behavior of dipolar solutes in these media is expected to provide information on the reorganization of the constituent ions around the photoexcited solute subsequent to instantaneous separation of charge.^{9,14,32-34,36-39} In this context it should be that the study of the dynamics of solvation is an active area of interest from a theoretical as well as from the experimental point of view. Solvation dynamics has been studied in a wide variety of polar solvents employing fluorescent probe molecules in which the charge separation reaction is much faster than the motion of the solvents. Though water and alcohols are the most commonly used media for this purpose, the organized assemblies have been investigated in recent years.

We have studied the picosecond time-resolved fluorescence behavior of several dipolar molecules such as coumarin 153 (C153), 4-aminophthalimide, PRODAN,

whose fluorescence behavior is well-known in conventional media, with a view to determining the time constant and mechanism of solvation in these ionic liquids.⁹ Following this initiation, we and several other groups subsequently examined solvation dynamics in ionic liquids.^{14,32-34,36-39} The signature of slow solvation in ionic liquids is apparent from the dependence of the fluorescence decay profiles on the monitoring wavelength. A typical behavior of this type is illustrated in Fig. 1. The decay profiles consist of a monotonous decrease of the fluorescence intensity with time when monitored at the short wavelength region of the fluorescence spectra. On the other hand, for a long monitoring wavelength, an initial rise followed by decay of the fluorescence intensity was observed. These studies have revealed that the dynamics of solvation in these media is much slower than in common organic solvents such as acetonitrile or alcohols and is non-exponential in nature. In many respects, the solvation process in the room temperature ionic liquids is similar to that observed in molten ammonium salts studied by Huppert and coworkers.⁴⁰ Almost 50% of the total solvation in imidazolium ionic liquids has been found to be ultrafast and could not be resolved in most of the studies.^{33,38} There is however disagreement among different groups on how fast this ultrafast component is.^{33,38} As far as the physical origin of the various components of the solvation dynamics is concerned, there also exists a difference of opinion.^{37,41-43} A number of theoretical, mostly computer simulation studies,⁴¹⁻⁴³ have been carried out with a view to examining the dynamics of solvent fluctuations in these

media. Shim et al. have assigned the fast component of the dynamics to the translation of the anion and the slow component to the collective motion of the anion and cation.⁴¹ However, according to Kobrak and Znamenskiy, the fast component arises from the collective cation-anion motion.⁴² The probe dependence of the solvation dynamics has also been examined recently.³³ Solvation dynamics in mixed solvents comprising ionic liquid and one conventional polar solvent as the components has also become a topic of recent interest.³⁹

During the course of our studies on the probe molecules, we have observed an excitation wavelength dependent shift of the fluorescence spectra of some dipolar molecules in room temperature ionic liquids.⁴⁴ This excitation wavelength dependence is attributed to two factors: first, the existence of a distribution of ground state molecules differing in their interaction energies with the room temperature ionic liquids, which results in inhomogeneous broadening of the absorption band; second, slow excited state relaxation processes such as solvation and/or energy transfer. While the ground state heterogeneity, which allows photoselection of the molecules, is present even in conventional fluid media, it is for the slow rate of the excited state processes, the excitation wavelength dependence is observable in ionic liquids. Since the fluorescence maximum of the dipolar systems are frequently used for the estimation of the polarity of the ionic liquids, the observation that these values can be excitation wavelength dependent suggests that utmost care is needed while selecting the probe molecules for these measurements.⁴⁴

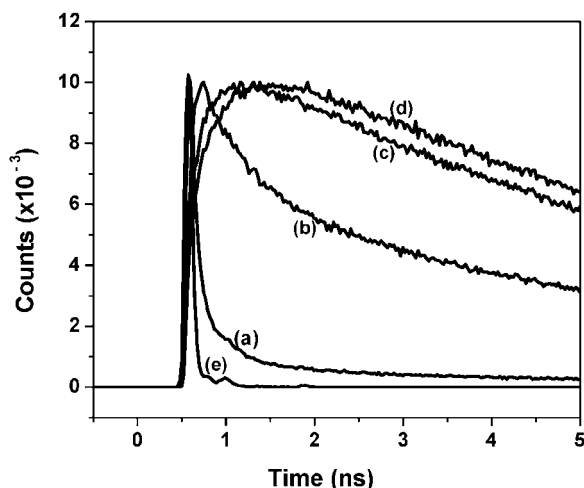


Fig. 1. Wavelength dependence of the fluorescence decay profiles of C153 in [bmim][Tf₂N]: (a) 450 nm, (b) 500 nm, (c) 550 nm and (d) 630 nm. $\lambda_{\text{exc}} = 375$ nm. The lamp profile is shown in (e).

OPTICAL PROPERTIES OF THE IMIDAZOLIUM IONIC LIQUIDS

The imidazolium ionic liquids are usually regarded as transparent substances having no absorption in the UV (above 250 nm) and visible region.^{13,45} Perhaps this explains how several studies, some of which are discussed above, could be made in these media. However, during the course of our studies we discovered that the imidazolium ionic liquids are not really optically transparent.⁴⁶ Even though the absorbance values in this region are not large, these cannot be ignored. We noted that the absorption is far from negligible at 300 nm and a long absorption tail extends even beyond 350 nm. Though the molar extinction coefficient values in this wavelength region are fairly low,

the OD value observed even at 350 nm is around 0.1 (in 1 cm path length cuvette) suggesting that nearly 20% of the incident light is absorbed at this wavelength.⁴⁶ For quite some time we thought that this absorption could be due to the presence of some impurity in the ionic liquids. However, we could finally establish that the absorption in this region is inherent to the ionic liquids. That this absorption is primarily due to the constituent imidazolium ion and its various associated structures is proved by controlled experiments in which imidazolium ion was generated from imidazole following addition of protons.⁴⁶

A second observation that points to further limitation of the imidazolium ionic liquids in optical studies is that when excited in the UV or early part of the visible region, these liquids exhibit fluorescence that covers a large part of the visible region and show dramatic excitation wavelength dependence.⁴⁶ A typical fluorescence behavior of the imidazolium ionic liquid is shown in Fig. 2. What appears quite interesting is that unlike the conventional fluorescence, here the emission maximum shifts towards the longer wavelength as the excitation wavelength is increased. The excitation wavelength dependent fluorescence behavior, which is quite dramatic in the present case, though uncommon, is not unprecedented. In viscous media or in organized assemblies, a similar excitation wavelength dependent shift of the fluorescence maximum of dipolar systems has been observed previously and is known as Red-Edge

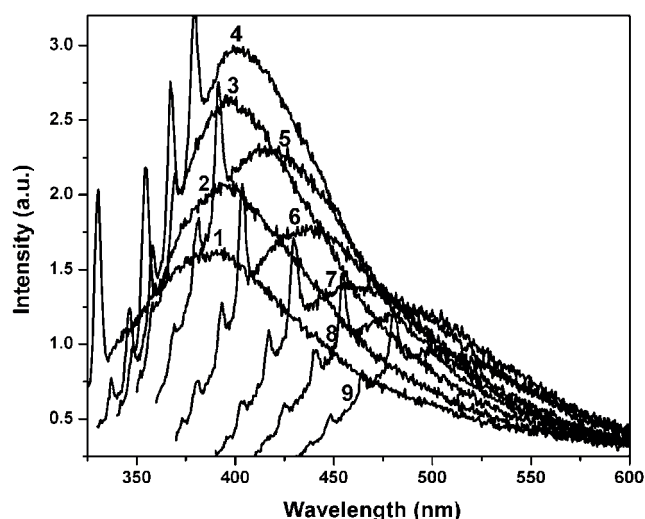


Fig. 2. Emission spectra of [bmim][BF₄] in acetonitrile (0.13 M). Excitation wavelengths are: (1) 300 (2) 320 (3) 330 (4) 340 (5) 350 (6) 360 (7) 380 (8) 400 (9) 420 nm. The sharp peaks on the broad emission envelope are Raman bands.

Effect, which is commonly abbreviated as REE.⁴⁷ According to the literature,⁴⁷ two essential conditions must be met to observe excitation wavelength dependent emission behavior of the kind shown here. First, there must be a distribution of energetically different species in the ground state. Second, the rate of the excited state relaxation between these energetically different species must be slower than the fluorescence lifetime of these species. The first condition ensures that selective excitation of energetically different species is possible and the second one ensures that it is possible to observe emission from each species excited. Taking into consideration the two factors, it is not difficult to understand why imidazolium ionic liquids exhibit REE. First, the long absorption tail due to imidazolium ionic liquids has been attributed to various associated structures that are energetically different.⁴⁶ It has also been established that the broad fluorescence band originates from these associated species. That the energy transfer between these species is not efficient is understandable when taking into consideration the sub-nanosecond fluorescence lifetime of these species.⁴⁶

CONCLUDING REMARKS

That the imidazolium ionic liquids are not only suitable media for chemical reactions but also promising media for photophysical studies is already evident from the literature presented above. Notwithstanding the recent findings on the absorption and fluorescence behavior of the imidazolium ionic liquids, which point to some of the shortcomings of these substances in optical studies, we believe that the number of photophysical studies in ionic liquids will continue to grow in the coming years as the absorption due to the ionic liquids, particularly in the longer UV and visible region, is small and the fluorescence quantum yield is low. Due precaution is however needed in these studies, particularly when dealing with systems that absorb in the UV region or that are weakly emitting. Relatively less explored ionic liquids, particularly those based on the pyrrolidinium cation, could also be media of photophysical studies in the future. In the coming years, as our understanding of the various properties of the ionic liquids develops, it may then be possible to regulate the photophysical behavior of the substances with the help of these designer solvents. However, we may have to wait for some time for this to happen.

ACKNOWLEDGEMENT

This work has been supported by the Council of Scientific and Industrial Research (CSIR), Department of Science and Technology (DST), Government of India, and UPE Program of University Grants Commission (UGC). PKM and AP thank CSIR for Fellowships.

Received May 4, 2005.

REFERENCES

- Seddon, K. R. *J. Chem. Tech. Biotechnol.* **1997**, *68*, 351.
- Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.
- (a) Baiker, A. *Chem. Rev.* **1999**, *99*, 453. (b) Jessop, P. J.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475. (c) Darr, J. A.; Poliakov, M. *Chem. Rev.* **1999**, *99*, 495.
- (a) Seddon, K. R. *Nature (Materials)* **2003**, *2*, 363. (b) Seddon, K. R.; Stark, A.; Torres, M. J. In *Clean Solvents: Alternative Media for Chemical Reactions and Processing*; Abraham, M. M. L., Ed.; ACS Symposium Series 819: Washington DC, 2002. (c) *Ionic Liquids, Industrial Applications for Green Chemistry*; Rodgers, R.; Seddon, K. R., Ed.; ACS Symposium Series 818: Washington DC, 2002. (d) Brennecke, J. F.; Maginn, E. J. *AIChE J.* **2001**, *47*, 2384.
- (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667. (c) *Ionic Liquids in Synthesis*; Welton, T.; Wasserscheid, P., Ed.; VCH-Wiley: Weinheim, 2002. (d) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3772. (e) Sheldon, R. *Chem. Commun.* **2001**, 2399.
- (a) Gordon, J. E.; Subba Rao, G. N. *J. Am. Chem. Soc.* **1978**, *100*, 7445. (b) Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195. (c) Sun, J.; Forsyth, M.; MacFarlane, D. R. *J. Phys. Chem. B* **1998**, *102*, 8858. (d) Chen, H.; Kwait, D. C.; Gonen, Z. S.; Weslowski, B. T.; Abdallah, D. J.; Weiss, R. G. *Chem. Mater.* **2002**, *14*, 4063. (e) Lind, J. E.; Abdel-Rehim, H. A. A.; Rudich, S. W. *J. Phys. Chem.* **1966**, *70*, 3610.
- Wilkes, J. S.; Zaworotko, M. *J. Chem. Commun.* **1992**, 965.
- Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *Chem. Phys. Chem.* **2004**, *5*, 1106.
- (a) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 4447. (b) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 6670.
- Law, G.; Watson, P. R. *Langmuir* **2001**, *17*, 6138.
- Fuller, J.; Carlin, R. T.; De Long, H. C.; Haworth, D. *Chem. Commun.* **1994**, 299.
- Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *J. Chem. Soc., Perkin Trans. 2* **2001**, 433.
- Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, *35*, 1168.
- Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2003**, *107*, 7340.
- (a) Huddleston, J. G.; Willauer, H. D.; Swatlowksi, R. P.; Visser, A. E.; Rodgers, R. D. *Chem. Commun.* **1998**, 1765. (b) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; De Souza, R. F.; Dupont, J. *Polyhedron* **1996**, *15*, 1217.
- Huddleston, J. G.; Rogers, R. D. *Chem. Commun.* **1998**, 1765.
- (a) Dickinson, V. E.; Williams, M. E.; Hendrickson, S. M.; Masui, H.; Murray, R. W. *J. Am. Chem. Soc.* **1999**, *121*, 613. (b) Ding, J.; Zhou, D.; Spinks, G.; Wallace, G.; Forsyth, S.; Forsyth, M.; MacFarlane, D. *Chem. Mater.* **2003**, *15*, 2392. (c) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *Chem. Phys. Chem.* **2004**, *5*, 1106.
- Armstrong, D. W.; Zhang, L. K.; He, L.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679.
- Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Gratzel, M. *J. Phys. Chem. B* **2003**, *107*, 13280.
- Itoh, H.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3026.
- Buzzeo, M. C.; Hardacre, C.; Compton, R. G. *Anal. Chem.* **2004**, *76*, 4583.
- Mele, A.; Tran, C. D.; Lacerda, S. H. D. P. *Angew. Chem. Int. Ed.* **2003**, *42*, 4364.
- Katayanagi, H.; Hayashi, S.; Hamaguchi, H.; Nishikawa, K. *Chem. Phys. Lett.* **2004**, *392*, 460.
- Yang, Y.; Kou, Y. *Chem. Commun.* **2004**, 226.
- (a) Behar, D.; Neta, P.; Schultheisz, C. *J. Phys. Chem. A* **2002**, *106*, 3139. (b) Skrzypczak, A.; Neta, P. *J. Phys. Chem. A* **2003**, *107*, 7800. (c) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 5468.
- Hyun, B.-R.; Dzyuba, S. V.; Bartsch, R. A.; Quitevis, E. L. *J. Phys. Chem. A* **2002**, *106*, 7579.
- Aki, S. N. V. K.; Brennecke, J. F.; Samanta, A. *Chem. Commun.* **2001**, 413.
- (a) Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2790. (b) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591. (c) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591. (d) Crowhurst, L.; Lancaster, N. L.; Arlandis, J. M. P.; Welton, T. *J. Am. Chem. Soc.* **2004**, *126*, 11549.
- (a) Fletcher, K. A.; Pandey, S. *J. Phys. Chem. B* **2003**, *107*, 13532. (b) Fletcher, K. A.; Pandey, S. *Langmuir*, **2004**, *20*, 33.
- (a) Baker, S. N.; Baker, G. A.; Kane, M. A.; Bright, F. V. *J. Phys. Chem. B* **2001**, *105*, 9663. (b) Lu, J.; Liotta, C. L.; Eckert, C. A. *J. Phys. Chem. A* **2003**, *107*, 3995.
- Chakrabarty, D.; Chakraborty, A.; Hazra, P.; Seth, D.; Sarkar, N. *Chem. Phys. Lett.* **2004**, *397*, 216.
- (a) Ingram, J. A.; Moog, R. S.; Ito, N.; Biswas, R.; Maroncelli, M. *J. Phys. Chem. B* **2003**, *107*, 5926. (b) Ito, N.; Arzhantsev, S.; Heitz, M.; Maroncelli, M. *J. Phys. Chem. B* **2004**, *108*,

- 5771.
33. Ito, N.; Arzhantsev, S.; Maroncelli, M. *Chem. Phys. Lett.* **2004**, *396*, 83.
34. Chakrabarty, D.; Hazra, P.; Chakraborty, A.; Seth, D.; Sarkar, N. *Chem. Phys. Lett.* **2003**, *381*, 697.
35. Karmakar, R.; Samanta, A. *Chem. Phys. Lett.* **2003**, *376*, 638.
36. Saha, S.; Mandal, P. K.; Samanta, A. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3106.
37. Arzhantsev, S.; Ito, N.; Heitz, M.; Maroncelli, M. *Chem. Phys. Lett.* **2003**, *381*, 278.
38. Chowdhury, P. K.; Halder, M.; Sanders, L.; Calhoun, T.; Anderson, J. L.; Armstrong, D. W.; Song, X.; Petrich, J. W. *J. Phys. Chem. B* **2004**, *108*, 10245.
39. (a) Baker, S. N.; Baker, G. A.; Munson, C. A.; Chen, F.; Bukowski, E. J.; Cartwright, A. N.; Bright, F. V. *Ind. Eng. Chem. Res.* **2003**, *42*, 6457. (b) Chakrabarty, D.; Chakraborty, A.; Seth, D.; Hazra, P.; Sarkar, N. *Chem. Phys. Lett.* **2004**, *397*, 469. (c) Chakrabarty, D.; Chakraborty, A.; Seth, D.; Sarkar, N. *J. Phys. Chem. A* **2005**, *109*, 1764.
40. (a) Bart, E.; Melstin, A.; Huppert, D. *J. Phys. Chem.* **1994**, *98*, 3295. (b) Bart, E.; Melstin, A.; Huppert, D. *J. Phys. Chem.* **1994**, *98*, 10819.
41. Shim, Y.; Duan, J. S.; Choi, M. Y.; Kim, H. J. *J. Chem. Phys.* **2003**, *119*, 6411.
42. Kobrak, M. N.; Znamenskiy, V. *Chem. Phys. Lett.* **2004**, *395*, 127.
43. (a) Margulis, C. J.; Stern, H. A.; Berne, B. J. *J. Phys. Chem. B* **2002**, *106*, 12017. (b) Del Popolo, M. G.; Lynden-Bell, R. M.; Kohanoff, J. *J. Phys. Chem. B* **2005**, *109*, 5895. (c) Lynden-Bell, R. M.; Kohanoff, J.; Del Popolo, M. G. *Faraday Discuss.* **2005**, *129*, 57.
44. Mandal, P. K.; Sarkar, M.; Samanta, A. *J. Phys. Chem. A* **2004**, *108*, 9048.
45. (a) Billard, I.; Moutiers, G.; Labet, A.; El Azzi, A.; Gaillard, C.; Mariet, C.; Lutzenkirchen, K. *Inorg. Chem.* **2003**, *42*, 1726. (b) Muldoon, M. J.; Mc Lean, A. J.; Gordon, C. M.; Dunkin, I. R. *Chem. Commun.* **2001**, 2364. (c) Lancaster, N. L.; Salter, P. A.; Welton, T.; Young, G. B. *J. Org. Chem.* **2002**, *67*, 8855.
46. (a) Paul, A.; Mandal, P. K.; Samanta, A. *Chem. Phys. Lett.* **2005**, *402*, 375. (b) Paul, A.; Mandal, P. K.; Samanta, A. *J. Phys. Chem. B* **2005**, *109*, 9148.
47. Demchenko, A. P. *Luminescence* **2002**, *17*, 19.