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Spectroscopic Study on Imidazolium-Based Ionic Liquids: Effect of Alkyl Chain Length and Anion

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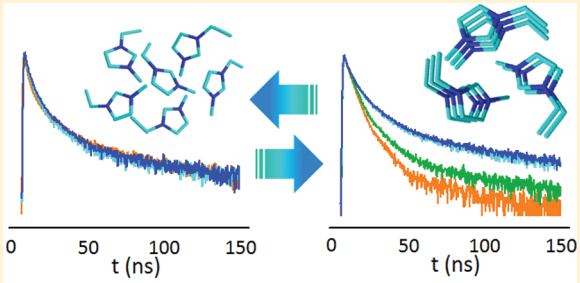
Supporting Information

ABSTRACT: Room temperature ionic liquids are currently used as functional materials in several application and their optical investigation can provide a better understanding of their physical and chemical behavior. Absorption and emission properties of imidazolium-based ILs have been attributed to the imidazolium moiety and related to the presence of energetically different aggregates. Here, time-integrated and time-resolved investigation has been carried out on 1-alkyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ionic liquids with different chain lengths in order to probe the occurrence of energy transfer processes, and hence to disclose the presence of various states with different energy. Such a study contributes to provide relevant insight on the effect of alkyl chain and anion type on the emission characteristics, and, hence, on the presence of associated structures.



Influence of Ionic Liquid association on photoluminescence decays

INTRODUCTION

In the last few years, a great effort has been devoted to the study of room temperature ionic liquids (RTILs or ILs) due to their peculiar chemical-physical properties and, hence, to their promising role as innovative materials for a wide number of applications. RTILs are compounds based on bare ions, weakly coordinated each others, thus resulting in liquid systems. Among their most important properties, it is worthwhile to mention their permanence in liquid state in a wide range of temperature, a very low vapor pressure, a wide electrochemical active window (up to 5.8 V) and high ionic conductivity (up to 100 mS cm^{-1}).[1] The most investigated ILs are made of organic cations, such as imidazolium, and inorganic anions, such as halides or fluorinated ions, since they have low melting point and viscosity, simplicity of synthesis, and good stability to oxidative and reductive conditions.[2] The IL properties arise from the specific combination of both the ions. As an example, the combination of 1-butyl-3-methylimidazolium (bmim) with tetrafluoroborate (BF_4) ion results in a hydrophilic IL, whereas the association of the same cation with hexafluorophosphate (PF_6) ion produces a strongly hydrophobic compound, and, in general the hydrophobicity of the cation increases with the length of the alkyl chain.[3] As a result, some IL thermodynamic properties, such as melting point, dielectric constant, viscosity, conductivity, density, thermal and chemical stability, are strictly dependent on the ion structures, which can be chemically tuned to tailor the IL properties for specific applications.[4,5] At present, RTILs are widely used to replace volatile solvents, such as organic compounds in chemical synthesis,[6] nanomaterial preparation[7] as well as in separation[8] or catalytic processes.[9] Among the several actual and future applications of ILs, certainly it is worth to notice their role in energy-related fields. Thanks to their favorable environmental and physical−chemical properties, namely the wide electrochemical window and the high thermal stability, ILs are indeed exploited as electrolytes for capacitors, batteries, and sensitized solar cells.[10]

New frontiers in advanced materials emerge from the weak ion coordination in the liquid state, which can promote the formation of architectures with a high structural order. ILs can organize themselves in polar and apolar domains, having distinct and well-defined properties, such as solvation dynamics and transport, that can be exploited in several technological applications. The manifestation of micro- and nanoheterogeneities in ILs come out from several experimental and theoretical investigations.[11−13] For instance, monodimensional and 3-dimensional ionic conductors have been prepared by self-organization of properly engineered ILs.[14,15] Furthermore, highly innovative hybrid materials can be achieved by dispersing nanosized-fillers in ILs, whose properties can be suitably designed for specific applications.[16]

IL self-organization is mainly guided by electrostatic interactions, van der Waals forces and hydrogen-bonds

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formation and is dependent on ion affinity, alkyl chain segregation and cation−anion coordination and interaction.[13,17] As a consequence, the overall IL organization is a function of several parameters. For instance, the alkyl chain segregation, due to weak van der Waals forces, promotes the formation of polar and apolar domains in absence of interactions among cations, while long alkyl chains have been found to favor the cation dissociation when strong cation−cation interactions are expected.[13,18,19] The structural organization of ILs is the base for the comprehension of their physical and chemical properties.[20] Computational studies, performed on imidazolium-based ILs, have demonstrated the formation of hydrogen bonds first in 1-ethyl-3-methylimidazolium chloride (emimCl), between chloride and one of the hydrogen atoms of the imidazolium cation, and later the bond formation with fluorine atoms in $bmimPF_6$.[21] In spite of the difficulty in defining general rules for the hydrogen-bonds formation, as a function of specific anion or cation, experimental measurements of thermodynamic properties, such as melting point,[22] have been finally found in a good agreement with the computational results. Indeed, 1,3-dialkylimidazolium ILs tend to form a hydrogen-bond network in which each anion is connected to a number of cations that depends not only on its coordination number (i.e., 3 for halides, 4 for BF_4, and 6 for PF_6) but also on the steric hindrance of substituents. Additionally, spectroscopic studies carried out on imidazolium-based ILs have shown the formation of associated forms of imidazolium cations directed by the $\pi-\pi$ interactions.[23] Several studies have been performed to elucidate solvation dynamics by monitoring the time-dependent fluorescence Stokes shift of a dipolar solute in a IL.[24] Similar studies have investigated fluorescence of organic probes in ILs, ultimately evidencing the shift of the emission spectrum to longer wavelengths, also called red-edge effect, thus confirming the existence of heterogeneities in ILs. Despite unremitting progresses in studying of ILs, by both theoretical and experimental works, some of their fundamental physical-chemical properties still remain to be fully elucidated. In particular, considerable efforts can be addressed to the exploration of the spectroscopic behavior of such systems, in view of their application in energy conversion related devices. Even though, at present, imidazolium-based are the most used ILs, their segregation dynamics are not yet well understood.[17] The optical characterization of some imidazolium-based ILs has been previously reported,[24−27] nevertheless the dependence of spectroscopic behavior on the chemical nature and the formation of associated forms are issues that still need to be investigated.

Some authors ascribe the absorption of imidazolium-based ILs to the presence of some unknown impurities, coming out from the synthetic procedure or from some decomposition.[28,29] Such absorption in the visible region, seems to disappear after a procedure of purification of the IL.[28] On the other hand, in several works it has been established that the imidazolium ionic liquids have non-negligible absorption beyond 300 nm, and their fluorescence behavior is ascribable to the presence of energetically different various associated forms of the imidazolium ions.[26,30] Here, the ILs have been purified by using standard techniques and a spectroscopic study of their optical behavior has been carried out. Namely, 1,3-dialkylimidazolium-based ILs with different alkyl chain lengths in the substituent at the cation ring, and anion chemical structure have been studied. The result of the spectroscopic analysis have been explained and, finally, correlated to the formation of IL associated forms. In particular, both time-integreted and time-resolved spectroscopic measurements have been performed on 1-alkyl-3-methyl imidazolium ILs, differing in the anion nature, namely tetrafluoroborate (BF_4) and hexafluorophosphate (PF_6), and with increasing length of the side alkyl chain, namely ethyl (emim), butyl (bmim), hexyl (hmim), and decyl (dmim). Two solvents with strongly different polarity, namely acetonitrile (ACN) and chloroform ($CHCl_3$), have been added to perturb the extent of association in the investigated ILs, hence to explore the optical properties by promoting the cation−cation association or dissociation. All the investigated ILs have been found partially or fully soluble in both less polar ($CHCl_3$) and polar (ACN) solvents. As polar solvents are able to dissolve the polar domains, and apolar solvents can only disperse the alkyl chains, the solubility in $CHCl_3$ increases as the alkyl chain length increases. The obtained results have been discussed in terms of the intrinsic emission characteristics of imidazolium-based ILs, consistently with what recently reported in Santhosh et al.[31] The present study aims at elucidating the dependence of the existence of associated forms on the ion molecular structures by exploiting time-resolved spectroscopy, which offers a powerful tool to shed light on the interaction dynamics involving excited states, including energy or charge transfer.

■ MATERIALS AND METHODS

All the investigated ILs, reported in Table 1, were synthesized and purified by using standard purification and decolourization procedures, including treatment onto active charcoal by Solvionic. Chloroform (99.8%) was purchased from Panreac, acetonitrile (>99.9%) was purchased from Sigma-Aldrich. Spectroscopic characterization was performed by using a reduced-volume quartz cuvette with an optical pathway of 1 cm. UV−vis absorption spectra were recorded by using a Varian Cary 5000 spectrophotometer. Time integrated and time-resolved UV−vis photoluminescence experiments were performed by using a HORIBA JOBIN-YVON FLOROLOG 3 spectrofluorimeter equipped with both a continuous wave Xe-lamp (450 W) and a ∼80 ps pulsed laser source (NanoLED 375 L), emitting at 375 nm with a repetition rate of 1 MHz, and interfaced with a time-correlated single photon counting (TCSPC) system. All acquired decay profiles were fitted by a triexponential decay function, as previously reported in Samanta et al.,[26]and average excited-state lifetime were calculated with the weighted mean formula

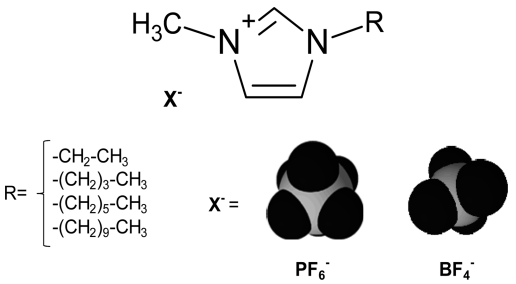
Table 1. Abbreviation and Main Physical Properties (Molecular Weight, Density, and Melting Temperature, Respectively) of the Investigated ILs

	M_w (g/mol)	d (g/mL)	T_m (°C)
$emimBF_4$	197.97	1.24	11
$bmimBF_4$	226.02	1.17	−75
$hmimBF_4$	254.08	1.15	−82
$dmimBF_4$	366.30	n.a.	n.a.
$bmimPF_6$	284.22	1.37	6−10
$hmimPF_6$	312.24	1.3	−73
$dmimPF_6$	424.46	solid	34

■ RESULTS AND DISCUSSION

The UV−vis time-integrated absorption and photoluminescence (PL) of imidazolium-based RTILs were investigated to

Scheme 1. Chemical Structure of the Investigated ILs



correlate their optical properties with the chemical ion structure.

Figure 1 reports the comparison of absorption (A) and the PL emission (B) spectra among some representative pure ILs.

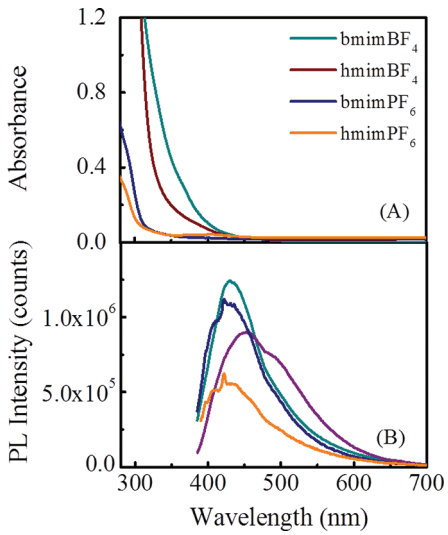


Figure 1. Pure imidazolium-based ILs absorption (A) and PL (B) spectra (excitation wavelength = 375 nm).

They all absorb in the UV region, and exhibit an extended absorption tail at longer wavelength. The intense signal below 250 nm in the absorption spectra can be ascribed to $\pi-\pi^*$ transitions of isolated imidazolium ion moiety. The long tail of the absorption spectra could be reasonably ascribed to the presence of various associated structures of imidazolium rings that are energetically different.[26] The fact that the long tail of the absorption spectra is inherently due to the imidazolium moiety of the ionic liquid and not due to the impurities was clearly established from the control experiments of Samanta and co-workers.[25,26,32] However, some of the current literature on ILs seems to indicate that the imidazolium salts present no absorption in UV−vis region (above 300−350 nm) and that any absorption beyond this wavelength could be ascribed to the presence of impurities.[29]

On the other hand, it has been extensively demonstrated, also by means of control experiments, that, in spite of the rigorous purification procedures, ILs exhibit a residual absorption, inherent to the IL itself and not due to possible impurities, and a weak fluorescence.[24−26,32] In our case, the ILs have been carefully purified, therefore the resulting absorption and emission characteristics can be reasonably ascribed to the intrinsic nature of the investigated ILs. In addition the change in the emission spectra after dilution with solvents, as discussed in the next section, strongly supports our findings.

The spectral behavior of such compounds has been generally ascribed to the imidazolium cation, aromatic in nature and having a sextet of π-electrons.[33] HOMO and LUMO levels of an aromatic structure depend on both the ring structure and the presence of electron donor/acceptor substituents. In addition, the overlap of π-orbitals can extend the electron delocalization, causing a decrease in HOMO/LUMO distance, hence a red-shift of the optical features. Such a phenomenon is common in imidazolium-based ILs, in which the cation−cation interactions induce the formation of imidazolium aggregated forms. As a consequence, spectroscopic properties of imidazolium-based ILs can be deeply affected by their association, which could be, on the other hand, also influenced by alkyl chain length and anion nature. Many primary spectroscopic features of these compounds have been previously studied by Samanta and co-workers.[24,26,32] They found that the PL spectrum of imidazolium ILs consists of two components, the first ascribable to the isolated imidazolium cation moiety, and the second, at lower energy, due to imidazolium associated forms, whose intensity and position vary with the excitation wavelength.

Even though the IL optical features are reported in literature as related mainly to the imidazolium moiety[24,26,32] the recorded absorption spectra seems to be affected by the anion chemical nature as well as by the length of the alkyl chain. In particular, in the investigated range, BF_4-based ILs exhibit a red-shifted and more intense absorption than the PF_6-based counterparts, while a decrease in absorbance has been detected by increasing the length of the alkyl chain. Such a phenomenon can be reasonably related to the different associated structures, whose extent could be limited in presence of longer alkyl chains and larger anions. Indeed, in our case, i.e. in the presence of aromatic cation, imidazolium, the formation of associated forms can be thought to be mainly directed by $\pi-\pi$ interactions, thus resulting "hindered" by long chains.

Remarkably, this issue goes in the opposite direction with respect to what has been reported for ILs formed of aliphatic cations, in which longer chains promote domain aggregation due to the predominance of apolar chains segregation.[34]

The PL spectra of the investigated ILs are typically found to be dependent on both the anion and the alkyl chain length, when the samples are excited at 375 nm (Figure 1B). Generally the PL emission of the isolated imidazolium ring has not been detected in the investigated spectral range, since it is positioned below 375 nm, as it is also demonstrated by exciting at shorter wavelength (∼300 nm). Indeed, Figure 2 reports the PL spectra of $bmimPF_6$ recorded by varying the excitation wavelength from 280 to 420 nm. At short excitation wavelength, the ILs emission spectra can be attributed to the presence of both isolated and associated imidazolium-based structures. The emission band at longer wavelengths is compatible with a radiative recombination of associated structures. Interestingly, such a band moves toward lower energy by increasing the excitation wavelength,[26] for all investigated ILs, both in presence and in absence of solvents (data not reported).[26] The dependence of the position of the peak on the excitation wavelength can be related to the red-edge effect (REE), which has been demonstrated to occur in luminescent systems able to emit from different energy levels having a fluorescence decay rate faster than or comparable to energy transfer.[35] Such a phenomenon has been reported in literature for luminescent

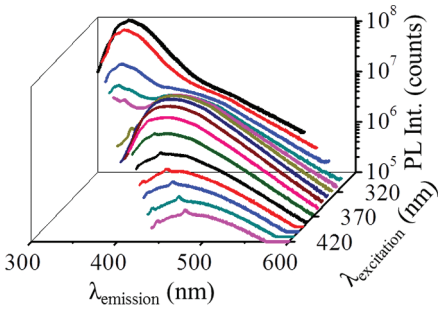


Figure 2. PL spectra of $bmimPF_6$ as a function of the exciting wavelength, from 280 to 420 nm. The spectra have been normalized to the lamp excitation intensity at the different wavelengths.

probe dispersed in ILs[26] as well as in neat ILs, as a consequence of their microheterogenities,[36] which can be thought to act in energy transfer process. In the investigated imidazolium-based ILs, the REE occurrence can be reasonably explained by the presence of distinct imidazolium associated forms in the IL, and emitting from distinct energy states.[24,32]

Therefore, when IL are excited at 375 nm the resulting PL bands can be safely considered as a convolution of distinct emission bands due to the associated structures.

The different emission intensity (Figure 1B) of the bands recorded for the different ILs can be ascribed not only to the specific extinction coefficient, but also to the different degree of association of the ILs. Indeed the presence of apolar and polar microheterogeneities, arising from the alkyl chain and polar moieties, respectively, can affect to different extent IL association.

Moreover, the PL spectra show the occurrence of sharp and well-defined peaks, at fixed shifts from the excitation wavelength (about 3000 cm^{-1}), due to the Raman-scattering of C–H bonds.[37]

Effect of Alkyl Chain Length. Spectroscopic investigation has been carried out in order to elucidate the effect of alkyl chain length on the occurrence of associated forms in the ILs. In Figure 2 is reported the PL spectrum of ILs, where two distinct components, at higher and at lower energy, can be ascribed, respectively, to isolated and associated imidazolium ions.[26] To clarify such an issue, ILs have been dispersed in solvents with different polarity to promote possible dissociation or association. The IL solubility has been found complete in ACN, while the ILs are only partially soluble in $CHCl_3$, as the latter has a limited ability in dispersing the polar fraction. This result has also been supported by dynamic light scattering measurements (see Supporting Information).

The solubility in both solvents confirms the coexistence of polar and apolar domains, more or less segregated, formed by ions and alkyl chains, respectively. IL polarity decreases by increasing the alkyl chain length, thus corresponding to an increase of the solubility in $CHCl_3$.

Parts A and B of Figure 3 report the normalized PL spectra of $dmimBF_4$ and $emimBF_4$, respectively, pure and in $CHCl_3$ and ACN solution (100 mg/mL), acquired by exciting the samples at 300 nm. Pure $dmimBF_4$ PL spectrum shows an emission line-shape which is the convolution of an intense component at about 370 nm, ascribable to isolated imidazolium ion, with a weak contribution at longer wavelength, likely due to imidazolium associated structures. Conversely, pure $emimBF_4$ PL spectrum exhibits only the band ascribable to the radiative recombination of imidazolium in associated

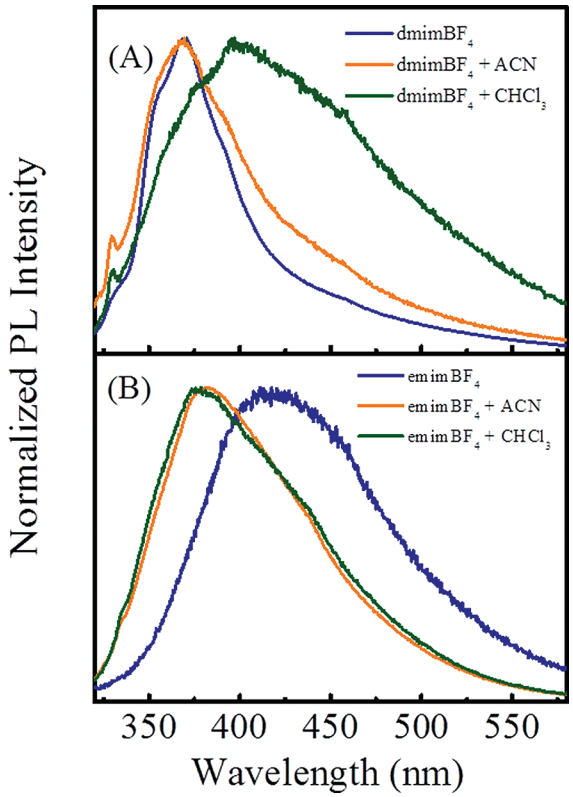


Figure 3. Comparison between the normalized steady-state PL spectra of $dmimBF_4$ (A) and $emimBF_4$ (B), pure (blue line), 100 mg/mL in $CHCl_3$ (green line), and 100 mg/mL in ACN (orange line), respectively (excitation wavelength = 300 nm).

structures. The PL line-shape changes significantly when both $emimBF_4$ and $dmimBF_4$ are diluted with solvents, as the contribution of each emitting form to the overall emission changes. When $emimBF_4$ is diluted, with $CHCl_3$ or ACN, the contribution of the component ascribable to isolated ions increases in the spectra, causing a blue-shift of the overall emission (Figure 3B). On the other hand, $CHCl_3$ and ACN seem to have opposite effects on the PL spectrum of $dmimBF_4$. In fact when diluted with ACN the $dmimBF_4$ PL spectrum is dominated by the contribution, at higher energy, of imidazolium isolated ions, while such a contribution completely disappears when $dmimBF_4$ is diluted with $CHCl_3$ and its PL spectrum shows only the emission band at lower energy, typical of associated forms.

Therefore, the dilution of $emimBF_4$ with either $CHCl_3$ or ACN causes the partial dissociation of the associated imidazolium rings as a consequence of the dilution effect, while for $dmimBF_4$ $CHCl_3$ promotes the formation of associated structures. This evidence could be explained by considering the different length of the side alkyl chain on the imidazolium ion. Indeed, the degree of aggregation of imidazolium-based ILs decreases with an increase in the side chain length,[13] resulting in two different PL spectra of neat ILs.[13] Namely, in presence of $CHCl_3$, dmim tends to form associated structures, due to the occurrence of weak van der Waals interactions among the longer alkyl chains, which lead the formation of polar and apolar domains. Conversely, the emim, strongly aggregated when pure, shows a lower degree of association in both solvents, which can be explained in term of dilution.[25] Such a behavior could be ascribed to the affinity of

the $CHCl_3$ to the apolar portion of the IL, favoring the associated structures in the case of longer alkyl chain IL. Therefore, $CHCl_3$ can be though to ultimately perturb the degree of interactions of the single IL units to a significant extent, higher than in case of the polar ACN.

The effect of association on the optical properties has been then investigated by means of PL time-resolved (TR) spectroscopy.

TR measurements have been carried out on all the investigated ILs, exciting at 375 nm and revealing the emission in correspondence of the main PL component (at around 430 and 490 nm), in order to evaluate solvent influence on the radiative recombination dynamics of distinct aggregated forms. The time decay profiles of $emimBF_4$ and $dmimBF_4$, pure, in $CHCl_3$ and in ACN solution (100 mg/mL), have been compared in Figure 4, parts A and B. The presence of a solvent, in both cases, causes a decrease of the decay rate only for the emission at low energy (~490 nm) of the $emimBF_4$, while no significant change is observed in the emission at high energy (~430 nm). The calculated average lifetime at 430 nm of $emimBF_4$ is 9 ns, for pure IL and for their $CHCl_3$ and ACN solution, while at 490 nm it changes from 17 to 13 ns, passing from pure to $CHCl_3$ or ACN solution. Conversely, the recombination dynamics of $dmimBF_4$ result unchanged when diluted in any solvent, and the average lifetime is approximately 11 ns for both peaks (three exponential fitting parameters are reported in Supporting Information). From the steady-state PL spectra (Figure 3A,B), the formation of imidazolium aggregates appears favored when the alkyl chain is short, and it is also affected by the presence of the solvents. In addition, $\pi-\pi$ interactions among imidazolium ions in associated structures, whose emission wavelength depends on their size: the longer the emission wavelength, the larger the associated structures. In the case of $emimBF_4$ the decay rate of emitters at 430 nm is always faster than that observed at 490 nm, and the highest difference in decay rate is detected in pure IL, although the same trend is followed, to different extent, by $CHCl_3$ or ACN IL solutions. This behavior can be explained assuming that, the aggregation degree is high, particularly in short alkyl chain pure ILs, and the distance among differently sized imidazolium aggregates is compatible with the occurrence of Förster resonant energy transfer (FRET) from the aggregates emitting at lower wavelength to those emitting at higher one. Conversely, in the case of $dmimBF_4$, all the recorded decay profiles result basically overlapping and no significant variation in the average lifetime is observed, thus suggesting that the solvent presence does not affect the recombination dynamics, at both 430 and 490 nm emitting wavelengths. When the alkyl chain is longer, the average distance between emitting species increases, since alkyl chains act as spacers, and the FRET efficiency is reduced. $CHCl_3$ is able to disperse alkyl chains, but has no affinity to the polar moiety, thus ultimately favoring imidazolium aggregation, as can be inferred from the steady-state PL emission spectrum (Figure 3B), which shows the predominance of the lower energy component. Nonetheless, the occurrence of aggregates seems not to affect the PL time evolution, as the decay rates measured in $CHCl_3$ are similar to those measured in pure IL and in ACN solution.

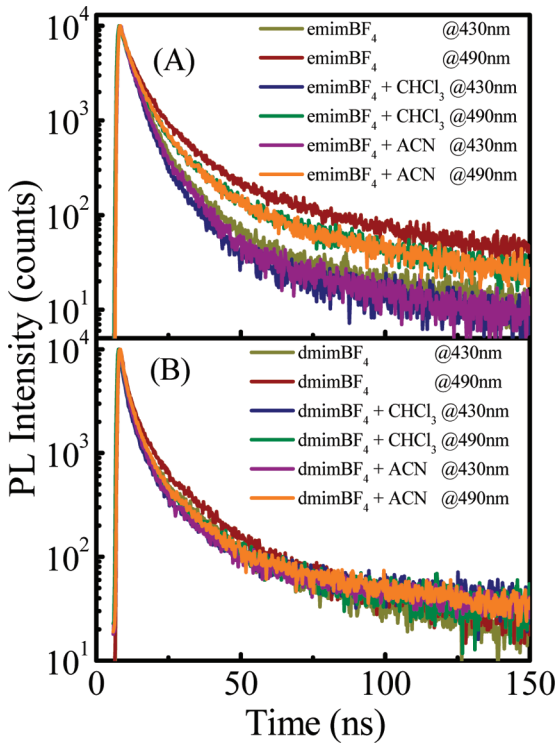


Figure 4. Comparison between the decays of $emimBF_4$ and $dmimBF_4$, as pure and in $CHCl_3$ or ACN solution (100 mg/mL), recorded at 430 and 490 nm (excitation wavelength = 375 nm).

In order to elucidate this aspect, Figure 5 reports the recorded decay profiles of all investigated BF_4-based ILs. Each panel shows data measured at different emission wavelengths of a single IL, respectively, (A) $emimBF_4$, (B) $bmimBF_4$, (C) $hmimBF_4$, and (D) $dmimBF_4$. Insets illustrate the steady-state PL emission of each IL excited at 375 nm, and display the distinct emission wavelengths where the TR measurements have been performed. Figure 5A reports the PL decay of $emimBF_4$ measured at four spaced emission wavelengths. The data point out that the average recombination time passes from 6 to 18 ns, increasing with the sampled emission wavelength, hence with the reduction of the emitted energy. This effect drastically reduces when the alkyl chain length increases (Figure 5B,C) and vanishes for $dmimBF_4$ (Figure 5D) with an average lifetime of 11 ns at all the investigated emission wavelengths. PF_6-based ILs show the same trends, although less evident (data not reported). These results further support the occurrence of FRET among different-sized associated structures, and the measured decay profiles clearly indicate that the FRET efficiency is higher for short-chain ILs, while it is limited by longer alkyl chains on the imidazolium ring, acting as spacers between emitting associated structures.

Effect of the Anion. The possible effect of the anion on the recombination dynamics of imidazolium associated structures has been also investigated. Figure 6 reports the comparison between the fluorescence decay profiles, measured on the PL emission peak, for BF_4- and PF_6-based ILs characterized by different chain lengths, bmim (A), hmim (B), and dmim (C), respectively. In general, PL intensity of BF_4-based ILs decays faster than PF_6-based ones, and the difference in the average lifetime decreases moving from shorter (bmim, Figure 6A) to longer alkyl chain length (hmim and dmim, Figure 6, parts B and C, respectively). The decays reported in panels B and C are completely overlapped for the first 10 ns, while gradually diverging for a longer time scale. Passing from PF_6 to BF_4 anion, the average mean lifetime decreases from 20 to 7 ns for bmim, from 13 to 7 ns for hmim, and from 13 to 11 ns for

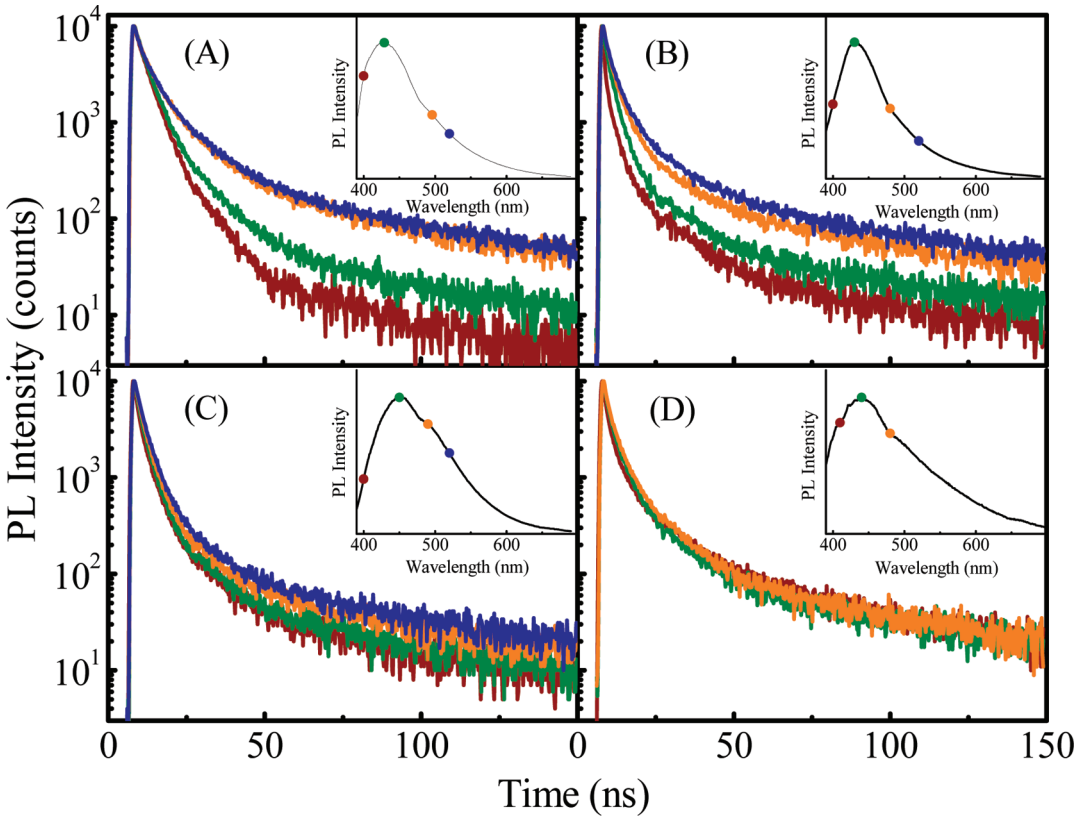


Figure 5. Time-resolved fluorescence decays of (A) emimBF_4, (B) bmimBF_4, (C) hmimBF_4, and (D) dmimBF_4. Insets report the steady-state luminescence spectra of the corresponding IL, and each colored dot indicates to the sampled wavelength for the time-resolved decay plotted with the corresponding color (excitation wavelength = 375 nm).

dmim. It is worthwhile to note that the only difference in each pair of ILs in the panels of Figure 6 is in the anion size and geometry, being PF_6 octahedral and larger than the tetrahedral BF_4. These anions are well-known for their tendency to form hydrogen-bonds with imidazolium hydrogen atoms, producing an organized network.[22] As a result, for a fixed cationic alkyl chain length, the distance between emitting species can be reasonably controlled by the anion steric hindrance and coordination. The difference in recombination dynamics can be ascribed to the presence of a FRET mechanism, more efficient in BF_4-based ILs than in PF_6-based ones, due to the different distances among associated structures, smaller in BF_4-based ILs than in PF_6-based ones. Finally, the influence of the anion on the imidazolium recombination dynamic decreased with longer alkyl chain, which limits hydrogen-bond and associated structures formation.

■ CONCLUSION

In summary, the effect of the alkyl chain length and of the anion nature on the optical properties of dialkyl substituted imidazolium ILs have been studied. In particular their optical properties have been investigated by: i. changing the alkyl substituent from ethyl to decyl, ii. considering two distinct anions, namely BF_4 and PF_6. Two distinct solvents have been used to probe the organization of imidazolium ILs.

The spectroscopic properties of such compounds have been found strongly sensitive to the presence of imidazolium associated structures, able to absorb and emit at longer wavelengths than those typical of isolated imidazolium ion. Thus, the overall emission spectra is the result of the convolution of two different contributions, ascribable to isolated imidazolium ion and associated forms, respectively. The PL emission line-shape has resulted directly dependent on the chemical ion structure. In addition, the extent of formation of associated structures has been seen limited for longer alkyl chain ILs. The equilibrium between isolated/associated imidazolium rings has been probed by diluting the ILs with solvents having different polarity, which have been demonstrated able to influence the association phenomena. However, less polar solvents such as $CHCl_3$ exhibit an elevated affinity with alkyl chains, thus promoting the formation of imidazolium aggregates in the case of longer alkyl chains.

PL TR investigation, allowing to measure the excited-states average lifetime of associated forms, emitting at distinct wavelength, has pointed out the occurrence of FRET among distinct aggregated species. The measured decay profiles, suggesting a higher FRET efficiency for short-alkyl chain ILs, indicates that alkyl chain can act as a spacer between emitting associated structures.

Finally, for a fixed cationic alkyl chain length, the distance between emitting species is influenced by the anion steric hindrance and coordination. These results, elucidating the peculiar spectroscopic behavior of the investigated ILs, have allowed to extend the fundamental understanding of such emerging class of compounds, offering also useful insight for their applications in innovative optical devices.

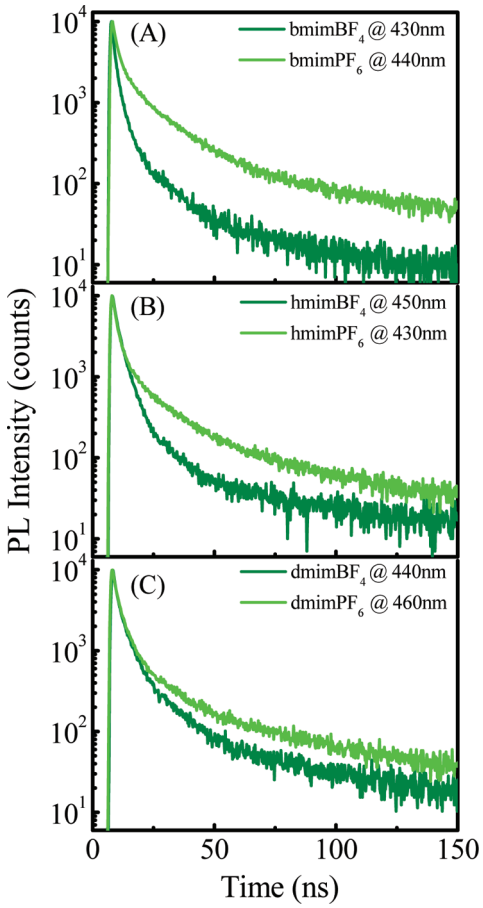


Figure 6. Comparison of PL intensity decays between BF_4- and PF_6-based (A) bmim, (B) hmim, and (C) dmim in $CHCl_3$ solution (100 mg/mL), measured in correspondence of the maximum PL emission.

■ ASSOCIATED CONTENT

Supporting Information

DLS measurements and three-exponential fitting parameters of PL decays. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Torimoto, T.; Tsuda, T.; Okazaki, K.; Kuwabata, S. *Adv. Mater.* **2010**, *22*, 1196.
(2) Handy, S. T. *Curr. Org. Chem.* **2005**, *9*, 959.
(3) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.
(4) Dzyuba, S. V.; Bartsch, R. A. *ChemPhysChem* **2002**, *3*, 161.
(5) Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 7264.
(6) Haumann, M.; Riisager, A. *Chem. Rev.* **2008**, *108*, 1474.
(7) Biswas, K.; Rao, C. N. R. *Chem.—Eur. J.* **2007**, *13*, 6123.
(8) Han, X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, *40*, 1079.
(9) Conrad Zhang, Z.; Bruce, C. G.; Helmut, K. Catalysis in Ionic Liquids. *Adv. Catal.* **2006**, *49*, 153.
(10) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8*, 621.
(11) Triolo, A.; Russina, O.; Bleif, H.-J.; Di Cola, E. *J. Phys. Chem. B* **2007**, *111*, 4641.
(12) Pierola, I. F.; Pacios, I. E. *J. Fluoresc.* **2012**, *22*, 145.
(13) Canongia Lopes, J. N. A.; Pádua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 3330.
(14) Ichikawa, T.; Yoshio, M.; Hamasaki, A.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2007**, *129*, 10662.
(15) Luczak, J.; Hupka, J.; Thoming, J.; Jungnickel, C. *Colloids Surf., A* **2008**, *329*, 125.
(16) Nakashima, T.; Nonoguchi, Y.; Kawai, T. *Polym. Adv. Technol.* **2008**, *19*, 1401.
(17) Mele, A.; Tran, C. D.; De Paoli Lacerda, S. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4364.
(18) Fu, H.; Zhu, G.; Wu, G.; Sha, M.; Dou, Q. *Chem. Res. Chin. Univ.* **2011**, *27*, 688.
(19) Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Farrar, D. H.; Lough, A. J.; Loh, W.; da Silva, L. H. M.; Dupont, J. *J. Phys. Chem. B* **2005**, *109*, 4341.
(20) Castner, E. W.; Margulis, C. J.; Maroncelli, M.; Wishart, J. F. *Annu. Rev. Phys. Chem.* **2011**, *62*, 85.
(21) Huang, J.-F.; Chen, P.-Y.; Sun, I. W.; Wang, S. P. *Inorg. Chim. Acta* **2001**, *320*, 7.
(22) Dong, K.; Zhang, S.; Wang, D.; Yao, X. *J. Phys. Chem. A* **2006**, *110*, 9775.
(23) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247.
(24) Samanta, A. *J. Phys. Chem. B* **2006**, *110*, 13704.
(25) Paul, A.; Mandal, P. K.; Samanta, A. *J. Phys. Chem. B* **2005**, *109*, 9148.
(26) Paul, A.; Mandal, P. K.; Samanta, A. *Chem. Phys. Lett.* **2005**, *402*, 375.
(27) Paul, A.; Samanta, A. *J. Chem. Sci.* **2006**, *118*, 335.
(28) Tang, F.; Wu, K.; Ding, L.; Yuan, J.; Liu, Q.; Nie, L.; Yao, S. *Sep. Purif. Technol.* **2008**, *60*, 245.
(29) Burrell, A. K.; Sesto, R. E. D.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. *Green Chem.* **2007**, *9*, 449.
(30) Samanta, A. *J. Phys. Chem. Lett.* **2010**, *1*, 1557.
(31) Santhosh, K.; Banerjee, S.; Rangaraj, N.; Samanta, A. *J. Phys. Chem. B* **2010**, *114*, 1967.
(32) Mandal, P. K.; Paul, A.; Samanta, A. *J. Photochem. Photobiol., A* **2006**, *182*, 113.
(33) Krygowski, T.; Oziminski, W.; Ramsden, C. *J. Mol. Model.* **2011**, *17*, 1427.
(34) Guo, J.; Baker, G. A.; Hillesheim, P. C.; Dai, S.; Shaw, R. W.; Mahurin, S. M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12395.
(35) Demchenko, A. P. *Luminescence* **2002**, *17*, 19.
(36) Hu, Z.; Margulis, C. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 831.
(37) Elaiwi, A.; Hitchcock, P. B.; Seddon, K. R.; Srinivasan, N.; Tan, Y.-M.; Welton, T.; Zora, J. A. *J. Chem. Soc., Dalton Trans.* **1995**, 3467.