

Fluorescence of fullerene C₇₀ in ionic liquids

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ABSTRACT

It is shown that pristine fullerene C₇₀ can be solubilised in imidazolium, ammonium and phosphonium based ionic liquids (ILs) bearing long alkyl chains (C₈ or higher). The absorption and fluorescence properties are similar to those displayed in conventional polar solvents except in ILs containing chloride as the counter ion, which completely quenches the fluorescence of C₇₀. Fluorescence decay analysis using a sum of Becquerel functions to account for the complex decay of background emission allows the successful recovery of the solute's lifetime.

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1. Introduction

Room temperature ionic liquids (ILs) have been intensively studied in the last decade, and applied in organic synthesis [1], solar cells [2], fuel cells [3], analytical chemistry [4] and in chemical separations [5]. Their synthesis is relatively simple and the diversity of cations and anions available made the preparation of ILs a true 'a la carte' process to obtain compounds with the desired properties. The ILs have unique chemical and physical properties such as negligible vapor pressure, good thermal stability, high ionic conductivity and the ability to dissolve a wide range of compounds (organic, inorganic, polymers) [6].

The photochemistry and photophysics both of ILs and in ILs have been also studied [7,8]. The possibility to use ILs as new medium for photochemical reactions such as energy transfer, hydrogen transfer and electron transfer was evaluated by Garcia and co-workers [8]. These open the door to a new field of applications for ILs. Recently, several works have confirmed their versatility for photochemical and photophysical studies: photocatalysis using a ruthenium complex [9], OLEDs applications with an aromatic hydrocarbon [10], and steady state and time-resolved fluorescence measurement with dipolar dyes [11].

Fullerenes have also attracted considerable interest, with applications in energy, electronics, optics, biology, etc. [12]. Recently, fullerene C₇₀ was used as an outstanding fluorescence optical sensor for oxygen [13,14] and temperature [15,16]. Pristine fullerenes (C₆₀, C₇₀, C₇₆, and higher fullerenes) are sparingly soluble in most non-chlorinated solvents, e.g., aliphatic and aromatic hydrocarbons [17]. This issue is a major drawback in several possible applications of pristine fullerenes.

There are only a few studies of fullerenes dissolved in ILs, and exclusively for pristine C₆₀: application in stationary phases for gas chromatography [18], the electrochemical behavior in ILs mixtures [19], along with the infrared spectrum [20] and absorption spectrum [21]. As far as we know, pristine C₇₀ was never used in studies with ILs and there are no reports on the fluorescence properties of fullerenes in ILs.

In this work, we report the solubility and fluorescence properties of pristine fullerene C₇₀ in imidazolium, ammonium and phosphonium based ILs. Solubility, absorption and fluorescence emission spectra, fluorescence quantum yield and fluorescence lifetime are obtained for each family of ILs with different counter ions, and correlated with the ILs structure.

2. Experimental

C₇₀ (>99%) was obtained from SES Research. Dichloromethane (technical and spectroscopic grade), toluene (spectroscopic grade), activated charcoal, silica and Celite were purchased from Aldrich. The ILs were obtained from Solchemar. The ionic liquids used were: 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄]; 1-butyl-2,3-dimethyl imidazolium bis(trifluoromethylsulfonyl)imide, [BDMIM][Tf₂N]; 1-methyl-3-octylimidazolium tetrafluoroborate, [MOIM][BF₄]; 1-methyl-3-octylimidazolium hexafluorophosphate, [MOIM][PF₆]; 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide, [MOIM][Tf₂N]; 1-decyl-3-methylimidazolium tetrafluoroborate, [DMIM][BF₄]; methyl trioctylammonium chloride, [MTOA][Cl]; methyl trioctylammonium bis(trifluoromethylsulfonyl)imide, [MTOA][Tf₂N]; trihexyltetradecylphosphonium chloride, [THTDP][Cl]; trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide, [THTDP][Tf₂N]. Prior to use, the ILs were rigorously purified and decolorized. The ILs were dissolved in dichloromethane and the mixture was stirred for 2 days with activated charcoal. The resulting mixtures were filtered

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through a column comprised of Celite, silica and activated charcoal, and the solvent was removed under reduced pressure. All measurements were performed at room temperature. Fluorescence quantum yields (Φ_F) were determined using C_{70} in toluene as standard. The dissolution of C_{70} in the ionic liquids was performed in a 10 mm optical path length quartz cell, adding aliquots of C_{70} in dichloromethane (35 μM) to the ionic liquids (1.5 mL) at room temperature with continuous stirring for 5 min. After that, the solvent was slowly removed under reduced pressure for 1 h. The solubility is the maximum amount of C_{70} that can be added to the ILs without forming a suspension. To determine the solubility, aliquots of C_{70} in dichloromethane were added until a dark suspension was seen to appear. The maximum amount added just before suspension formation was taken to be the solubility. The photophysical experiments were carried out with concentrations at or slightly below the solubility value, always without suspension formation.

The absorption spectra were recorded with a Shimadzu UV-3101PC UV-Vis-NIR spectrophotometer and the fluorescence measurements were obtained with a Spex Fluorolog F112A fluorimeter. Time-resolved picosecond fluorescence intensity decays were obtained by the single-photon timing method with laser excitation at 590 nm and emission at 700 nm. The set up consists of a diode-pumped solid state Nd:YVO₄ laser (Millennia Xs, Spectra Physics) that can synchronously pump a mode-locked Ti:Sapphire laser (Tsunami, Spectra Physics, with tuning range 700–1000 nm, output pulses of 100 fs, and 80 MHz repetition rate that can be reduced down to 4 MHz by a pulse picker) or a cavity-dumped dye laser (701-2, Coherent, delivering 3–4 ps pulses of ca. 40 nJ pulse⁻¹ at 3.4 MHz) working with rhodamine 6G. Intensity decay measurements were made by alternated collection of impulse and decays with the emission polarizer set at the magic angle position. Impulses were recorded slightly away from the excitation wavelength with a scattering suspension. For the decays, a cut-off filter was used to effectively remove excitation light. Emission light was passed through a depolarizer before reaching the monochromator (Jobin-Yvon HR320 with a 100 lines/mm grating) and detected using a Hamamatsu 2809U-01 microchannel plate photomultiplier. No less than 10 000 counts were accumulated at the maximum channel. Decay data analysis with sums of exponentials and sums of compressed hyperbolae (Becquerel functions) was achieved by means of a Microsoft Excel spreadsheet specially designed for lifetime and anisotropy analysis (Berberan-Santos, unpublished).

3. Results and discussion

The chemical structures of the ILs used in this study are depicted in Fig. 1. The different families of ILs (imidazolium, ammonium and phosphonium) were combined with several counter ions, namely: tetrafluoroborate [BF₄], bis(trifluoromethylsulfonyl)imide [Tf₂N⁻], hexafluorophosphate [PF₆], and chloride [Cl⁻].

The ILs present a yellow colouration, due to impurities from the synthesis [22]. This colouration can be removed by a purification process using Celite, silica and activated charcoal. Although the purification process eliminates most of the colouration, some impurities still remain that are responsible for a moderate UV-Vis absorption and a weak but non-negligible emission, as shown in Fig. 2 for [DMIM][BF₄].

This is a problem when photophysical studies are carried out in ILs, and an adequate choice of fluorophores and excitation wavelengths must be done. In our particular case, the absorption and fluorescence emission spectra of ILs overlap part of C_{70} spectra (Fig. 2), and a solvent correction must be applied in order to compare spectra from different ILs.

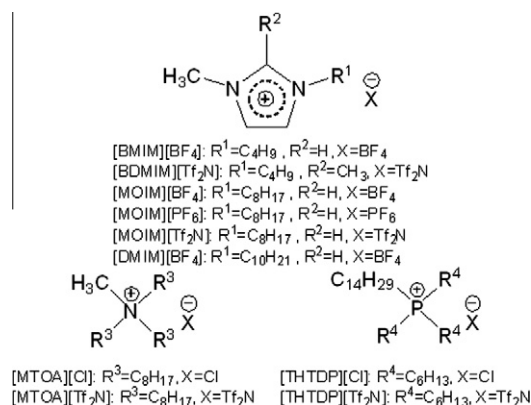


Fig. 1. Chemical structures of imidazolium, ammonium and phosphonium based ILs used in this study.

The solubility of pristine fullerenes (C_{60} , C_{70} , and higher fullerenes) is low in most solvents and they are only moderately soluble in aliphatic and aromatic hydrocarbons [17]. Table 1 presents the solubility of C_{70} in the ILs under study. C_{70} was dissolved in the ILs through consecutive additions of a dichloromethane solution, which was evaporated after homogenization of the mixture. The solubility was determined as the concentration before which solid C_{70} starts to precipitate.

The solubility of C_{70} in the ILs under study depends mainly on the length of the aliphatic carbon chains of the cation. This is clear from the trend observed for the imidazolium ILs family: C_{70} is insoluble in the butyl derivative ([BMIM]), slightly soluble in the 1-butyl-2-methyl derivative ([BDMIM]), and more soluble in the octyl ([MOIM]) and decyl ([DMIM]) derivatives. The solubilities in phosphonium ([THTDP]) and ammonium ([MTOA]) ILs are comparable to the values obtained for [DMIM].

The counter ions do not affect the C_{70} solubility in the ILs (Table 1 – check the solubilities in [MOIM][BF₄], [MOIM][PF₆] and [MOIM][Tf₂N]), except when chloride is used as counter ion (Table 1 – compare [MTOA][Cl] vs. [MTOA][Tf₂N], and [THTDP][Cl] vs. [THTDP][Tf₂N]). In these cases, the C_{70} solubility is slightly lower when compared to the same cation with another counter ion.

The dissolution of C_{70} in the ILs can be followed by the electronic absorption spectrum of the resulting solution. Fig. 3 shows the absorption spectra of C_{70} in [DMIM][BF₄] at different concentrations. The spectra were corrected for [DMIM][BF₄] absorption.

The absorption spectrum obtained for C_{70} in [DMIM][BF₄] is similar to that in dichloromethane (Fig. 2). The same was observed for all the other ILs studied.

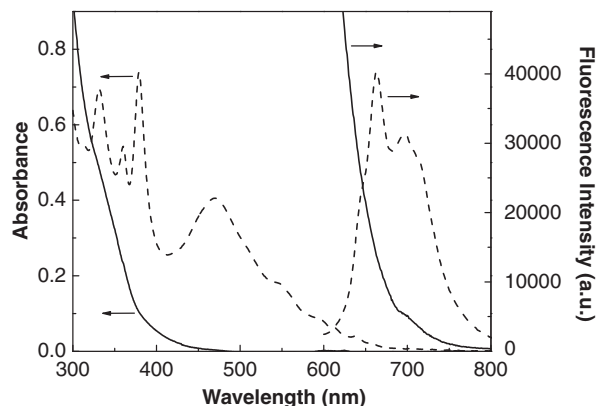


Fig. 2. Absorption (1 cm pathlength) and fluorescence ($\lambda_{exc} = 500$ nm) spectra of neat [DMIM][BF₄] (solid line) and of C_{70} in dichloromethane (48 μM , dashed line).

Table 1

Solubility and selected fluorescence quantum yields and fluorescence lifetimes (excitation at 590 nm and fluorescence recorded at 700 nm) of fullerene C_{70} in different ionic liquids and some conventional solvents.

Ionic liquid	Solubility ($\mu\text{g/mL}$)	$\Phi_F/10^{-4}$	τ_F (ns)
[BMIM][BF ₄]	0	–	–
[BDMIM][Tf ₂ N]	20	–	–
[MOIM][BF ₄]	40	6	–
[MOIM][PF ₆]	40	2	–
[MOIM][Tf ₂ N]	40	3	0.7
[DMIM][BF ₄]	60	5	0.6
[MTOA][Cl]	50	–	–
[MTOA][Tf ₂ N]	80	2	–
[THTDP][Cl]	40	–	–
[THTDP][Tf ₂ N]	60	9	0.8
Methylcyclohexane	380 ^a	6 ^b	0.65 ^b
Toluene	1406 ^c	5.7 ^b	0.65 ^b

^a Estimated from C_{60} in Ref. [1].

^b Ref. [23].

^c Ref. [17].

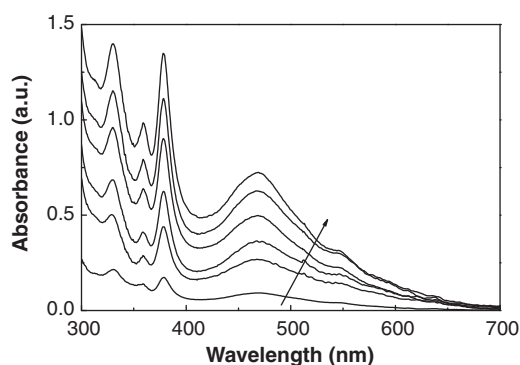


Fig. 3. Absorption spectra of C_{70} in [DMIM][BF₄] at different concentrations (between 0.9 and 7.1 μM) and corrected for the [DMIM][BF₄] absorption.

The fluorescence emission of C_{70} in the ILs increases linearly with the amount of fullerene in solution. The fluorescence spectrum of C_{70} in [THTDP][Tf₂N], corrected for [THTDP][Tf₂N] emission, is presented in Fig. 4 along with the fluorescence spectrum in methylcyclohexane.

The spectra of Fig. 4 show two prominent bands, typical of C_{70} emission, the low energy band showing a noticeable shoulder. When going from methylcyclohexane to an IL, the first band, located at 652 nm in methylcyclohexane, red shifts and is intensified with respect to the second band, located at 696 nm in methylcyclohexane. It is known [23] that the first band is associated with

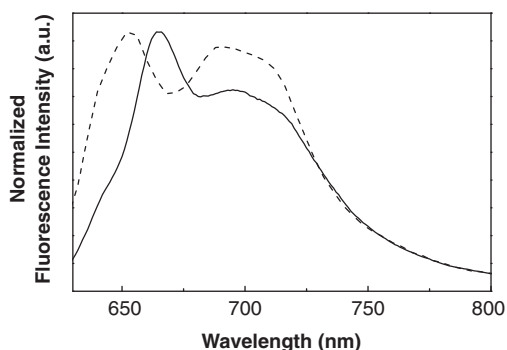


Fig. 4. Normalized fluorescence spectra ($\lambda_{\text{exc}} = 500 \text{ nm}$) of C_{70} in [THTDP][Tf₂N] (7.1 μM , solid line) and in methylcyclohexane (12.3 μM , dashed line).

the weakly allowed $S_2 \leftarrow S_0$ transition, while a nearby shoulder, located at 660 nm in methylcyclohexane (not apparent in Fig. 4 owing to the wide emission band passes used), corresponds to the nearly forbidden $S_1 \leftarrow S_0$ transition. An increased interaction with the solvent has thus the expected effect of preferential enhancement of the 660 nm transition, along with some red shift (664 nm in THTDP, 664 nm in dichloromethane, see Fig. 2) [23].

Essentially identical emission spectra are observed for the rest of the ILs under study, except for the ILs with chloride as counter ion. In these cases ([MTOA][Cl] and [THTDP][Cl]), no fluorescence emission was detected. The highly concentrated chloride anions (ca. 2 M) completely quench the C_{70} fluorescence, probably by means of an electron transfer mechanism.

The fluorescence quantum yield (Φ_F) obtained for C_{70} in the ILs (Table 1) is of the same order of magnitude of the values reported in the literature for other solvents [23]. It should be remarked that even selecting the longest excitation wavelengths and with concentrations of C_{70} nearing the solubility limit, the IL background contribution to the total steady-state emission varied between 23% and 60%, depending on the IL. This results from the low solubilities in ILs and from the low fluorescence quantum yield of C_{70} .

The impurities present in the neat ILs are responsible for complex fluorescence decays observed even in the absence of C_{70} . The decays of the neat ILs were satisfactorily fitted only with a sum of four exponentials, with components ranging from less than a picosecond (accounting for light scattering) to a few nanoseconds (average decay time around 2 ns). The decay of solutions of C_{70} in ILs is again fitted by a sum of four exponentials, in some cases imperfectly. As a consequence, any C_{70} lifetime determination by this method is unreliable, as no component can be assigned with confidence to the solute, and indeed none fell in the expected range of values in most cases. A different approach [24,25], already applied to complex decays with success [26], was attempted. The method is based on the analysis with a sum of compressed hyperbolae, or Becquerel functions [24,27]. The method is now briefly described.

The Becquerel decay function is

$$I(t) = \frac{1}{(1 + ct/\tau_0)^{1/c}} \quad (1)$$

where $0 < c < 1$. The parameter τ_0 has dimensions of time. Note that when $c \rightarrow 0$ the Becquerel function reduces to an exponential.

For completely monotonic decays, the fluorescence intensity $I(t)$ is given by the integral:

$$I(t) = \int_0^\infty f(\tau) \exp(-t/\tau) d\tau \quad (2)$$

where $f(\tau)$ is the probability density function (pdf) of lifetimes. For the Becquerel decay function, this function is the inverse-gamma pdf, given by

$$f(\tau) = \frac{1}{\alpha \Gamma(1/c)} \left(\frac{\alpha}{\tau}\right)^{1/c+1} \exp\left(-\frac{\alpha}{\tau}\right) \quad (3)$$

with $\alpha = \tau_0/c$. For small c the coefficient of variation (the ratio of the standard deviation to the mean) of the pdf is $c^{1/2}$. Eq. (3) is a flexible distribution function because it can closely approximate the actual distribution in many situations ranging from a narrow one ($c \approx 0$), where the decay is essentially exponential, to a very broad ($c \approx 1$) distribution, where the decay is close to hyperbolic, with a power law dependence on time (for sufficiently long times). The distribution function Eq. (3) is asymmetric for any $c > 0$ and its maximum occurs at $\tau_0/(1+c)$, whereas the ensemble average decay time is $\langle \tau \rangle = \int_0^\infty \tau f(\tau) d\tau = \int_0^\infty I(t) dt = \frac{\tau_0}{1-c}$.

A more general approach is to write a complex decay as a sum of Becquerel (compressed hyperbola) functions [24–26],

$$I(t) = \sum_i \frac{a_i}{(1 + c_i t / \tau_i)^{1/c_i}} \quad (4)$$

with $\sum_i a_i = 1$. We assume here that all a_i are positive. The distribution of lifetimes corresponding to Eq. (4) is a weighted sum of inverse-gamma pdfs,

$$f(\tau) = \sum_i a_i f_i(\tau) = \sum_i \frac{a_i}{\alpha_i \Gamma(1/c_i)} \left(\frac{\alpha_i}{\tau}\right)^{\frac{1}{c_i}+1} \exp\left(-\frac{\alpha_i}{\tau}\right) \quad (5)$$

and the ensemble average decay time is thus

$$\langle \tau \rangle = \sum_i \frac{a_i \tau_i}{1 - c_i} \quad (6)$$

It is observed that it is usually possible to describe complex fluorescence decays with a few Becquerel components, in general less than the number of components required when fitting with sums of exponentials [26]. Eq. (4) can also be used for this conventional type of analysis (sums of exponentials) by setting all c_i parameters to a value close to zero such as 0.001 (corresponding to a coefficient of variation of 3%), see Table 2.

The fluorescence lifetimes of C_{70} in some ILs are given in Table 1. Results for [DMIM][BF₄], chosen as a representative example, are now discussed in detail. Results for neat [DMIM][BF₄] and for C_{70} dissolved in [DMIM][BF₄] are collected in Table 2. An extra exponential term with near zero lifetime (not included in Table 2) accounting for scattered light was consistently recovered in all cases. Apart from this extrinsic term, the fluorescence decay of the neat IL is complex, and can be fitted equally well with a sum of three exponentials (first row of Table 2) and with a sum of two Becquerel functions (second row of Table 2). The chi-squared is slightly above 1 but the residuals are nearly random. As the intrinsic decay of C_{70} is expected to be single exponential, and the decay of C_{70} dissolved in [DMIM][BF₄] contains the background contribution from the IL fluorescent impurities, a constrained fit was carried out, the decay function used being the sum of the two Becquerel components previously determined for the neat IL with a single exponential term with floating lifetime (third row of Table 2). The chi-squared obtained is somewhat unsatisfactory and the residuals are not random, but the lifetime recovered, 0.5 ns, is not far from that of C_{70} in conventional organic solvents, 0.65 ns. The recovered parameters do not change appreciably when fitting all Becquerel parameters (fourth row of Table 2). Most change only slightly, including the lifetime of the exponential term that now approaches 0.6 ns. Furthermore, the chi-squared is satisfactory and the residuals random. The corresponding distributions of lifetimes are depicted in Fig. 5. Similar results were obtained for

Table 2

Data analysis of the fluorescence decays of neat [DMIM][BF₄] and of C_{70} (7.1 μ M) in [DMIM][BF₄]. Excitation wavelength: 590 nm. The model is a sum of compressed hyperbolae according to Eq. (4). x_i are the fractional intensities defined as $x_i = \frac{a_i \tau_i / (1 - c_i)}{\sum_j a_j \tau_j / (1 - c_j)}$.

	τ_i (ns)	c_i	a_i	x_i	χ_R^2
Neat IL	0.16	0.001 ^a	0.57	0.10	1.3
	0.92	0.001 ^a	0.28	0.28	
	3.89	0.001 ^a	0.15	0.62	
Neat IL	0.14	0.58	0.25	0.27	1.3
	1.79	0.34	0.75	0.73	
	0.14 ^a	0.58 ^a	0.31	0.10	
C_{70}	0.53	0.001 ^a	0.44	0.23	1.9
	1.79 ^a	0.34 ^a	0.25	0.67	
	0.35	0.19	0.53	0.22	
C_{70}	0.55	0.001 ^a	0.23	0.12	1.1
	2.20	0.23	0.24	0.66	

^a Fixed.

two other ILs, see Table 1. From the ensemble of analyses it can be concluded that: (i) the fluorescence decays of neat ILs are complex and usually well described by a sum of two Becquerel terms; (ii) the decay of C_{70} in the ILs is single exponential and with a lifetime close to that measured in conventional solvents. This approach can be generally applied to compare experiments using ILs from different sources, taking the care to always measure the decay of the pure IL.

Fullerene C_{70} is a molecule highly susceptible of nucleophilic and electrophilic attacks [12], and the chemical stability of C_{70} depends on the environment where it is dispersed/solubilised. The chemical stability of C_{70} in the ILs under study was evaluated by monitoring the absorption and emission spectra for several weeks. Three ILs were selected, one from each family under study, but all with bis(trifluoromethylsulfonyl)imide as the counter ion. The chemical stability is very different and decreases in the following order: phosphonium–imidazolium–ammonium. In the case of [THTDP][Tf₂N], the absorption and fluorescence spectra remain almost unchanged after 1 week. For [MTOA][Tf₂N] and [OMIM][Tf₂N], the absorption and emission spectra are suppressed after 2 and 5 days, respectively. The different stability of C_{70} in each IL can be explained by the nucleophilic behavior of the respective cation.

The solubility, permeability, and diffusion of gases in ILs have been studied recently [28–30]. Oxygen, together with nitrogen, presents the lowest values for the above parameters. These findings lead us to investigate the possible use of ILs as media for oxygen and temperature sensors based on the thermally activated delayed fluorescence (TADF) of C_{70} [31], as TADF is only detected in the presence of residual amounts of oxygen, owing to the efficient quenching of the triplet state by oxygen. A solution of C_{70} in [THTDP][Tf₂N] was degassed and sealed afterwards. No variation was detected in the fluorescence emission after degassing. Similar attempts using other ILs gave an identical result. Efficient deactiva-

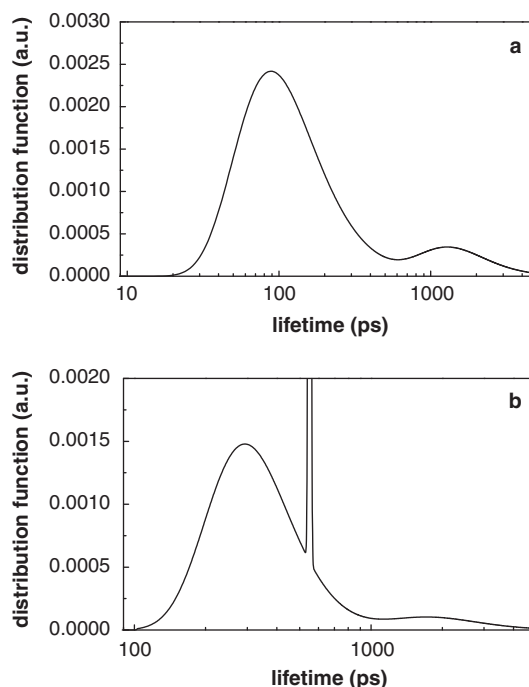


Fig. 5. Fluorescence lifetime distributions of [DMIM][BF₄] background emission (a) and of a 7.1 μ M solution of C_{70} in [DMIM][BF₄] (b). The narrow peak at 550 ps in (b) corresponds to the exponential decay of C_{70} . Excitation wavelength 590 nm, emission wavelength 700 nm.

tion of the triplet excited state, which is involved in the TADF mechanism, can account for this observation.

4. Conclusions

Fullerene C₇₀ dissolves in imidazolium, ammonium and phosphonium based ionic liquids bearing long alkyl chains (C₈ or higher). The fluorescence properties of C₇₀ in ILs are similar to those observed in conventional polar solvents, except when chloride is present as the counter ion, in which case a complete quenching of the fluorescence is observed. In spite of significant background fluorescence, decay analysis using a sum of Becquerel functions to account for the background emission allowed to successfully recover the solute's lifetime.

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