

Excited state dynamics of 9,9'-bianthryl in room temperature ionic liquids as revealed by picosecond time-resolved fluorescence study

DINESH CHANDRA KHARA, ANIRUDDHA PAUL, KOTNI SANTHOSH and ANUNAY SAMANTA*

School of Chemistry, University of Hyderabad, Hyderabad 500 046

e-mail: assc@uohyd.ernet.in

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Abstract. Picosecond time-resolved fluorescence measurements have been carried out on 9,9'-bianthryl in three imidazolium ionic liquids to probe the excited state dynamics. In the early time-scale, the fluorescence spectra of bianthryl have been found to consist of emission from both locally excited (LE) and charge transfer (CT) states. The LE → CT relaxation time, as estimated from the decay of the fluorescence intensity of the LE emission, is found to vary between 230 and 390 ps, while the average solvent relaxation time, as estimated from the analysis of time-dependent fluorescence Stokes shift, is found to vary between 620 ps and 1840 ps, depending on the viscosity of the ionic liquids. The results confirm that while in conventional less viscous solvents the CT formation kinetics of bianthryl occurs simultaneously with the solvation dynamics, in ionic liquids the two processes mostly occur in different time scales.

Keywords. Ionic liquids; bianthryl; time-resolved fluorescence; solvent relaxation dynamics; excited state relaxation dynamics.

1. Introduction

Room temperature ionic liquids (ILs) are increasingly being used as novel media for the study of various photophysical and photochemical processes.^{1–11} Among the photoprocesses investigated so far notable are the studies on dynamic Stokes shift and solvation dynamics of dipolar probes, intramolecular excimer formation, photo-induced electron and proton transfer reactions, photoisomerization reaction, etc.^{1–11} Very recently, Nagasawa *et al* have studied the excited state dynamics of 9,9'-bianthryl (BA, chart 1) in imidazolium ionic liquids using femtosecond time-resolved absorption and picosecond time-resolved fluorescence spectroscopic techniques.¹² BA is a well-known system whose excited state behaviour and dynamical processes have been studied extensively in a range of conventional solvents.^{13–21} The interest in BA is mainly due to the fact that this pre-twisted molecule with mutually perpendicular anthracene rings in the ground state undergoes symmetry breaking upon excitation and its fluorescence spectra show distinct charge transfer

(CT) character, especially in polar solvents.^{13–15} In nonpolar solvents the first excited state (S_1) is predominantly a locally excited (LE) state with very little or no CT character,^{14–16} whereas, in highly polar solvents a CT state, which is formed rapidly from the LE state, is the emitting state.^{17–19} The transient absorption study on BA in the picosecond and sub-picosecond regime has revealed the ultrafast time-scale (20–50 ps) of the formation of the CT state in conventional solvents of low viscosity.¹⁹ However, in more viscous media this time is much longer, indicating the effect of viscosity on the symmetry-breaking process.²⁰

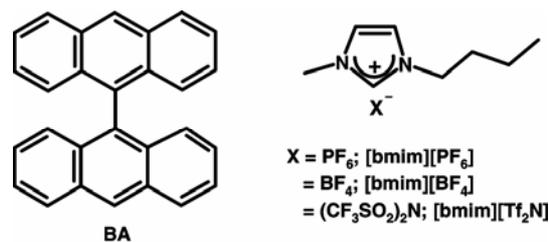


Chart 1. Structure/abbreviation of 9,9'-bianthryl and the ionic liquids employed in the present study.

*For correspondence

The recent femtosecond transient absorption measurements in ILs by Nagasawa *et al* suggest that charge transfer in BA is multi-exponential with the time scale ranging from sub-picosecond to several hundreds of picoseconds, the latter being dependent on the viscosity of the media.¹² On the other hand, the fluorescence study reveals dynamic Stokes shift of the CT emission in the nanosecond time domain, reflecting the stabilization of the CT state through solvent reorganization.¹²

However, one aspect of the relaxation dynamics of BA in ILs that is not clear from the results presented in this interesting study is the following. Since the LE and CT emission bands of BA overlap significantly in the 21000–25000 cm^{-1} , and the LE state, which is the precursor of the CT state, survives for several hundreds of picoseconds,¹² one expects its signature on the fluorescence spectra as well, particularly in the early time domain. However, this is surprisingly not the case. The lack of any signature of the LE state in the time-resolved fluorescence spectra, even in the early time domain, appears inconsistent and it implies that the LE state may be much short-lived than what is indicated by the time-resolved absorption measurements. In order to resolve this important issue concerning the excited state dynamics of BA in ILs we have taken up this work in which we have investigated the time-resolved fluorescence behaviour of BA in three different ILs (chart 1) based on 1-butyl-3-methylimidazolium cation.

2. Experimental

2.1 Materials

9,9'-bianthryl (BA) was synthesized by dimerization of anthraquinone following the reported procedure of Magnus *et al*.²² The compound was characterized by spectroscopic techniques (¹H-NMR, ¹³C-NMR and IR) and the purity was checked by chromatography. The electronic absorption and fluorescence spectra of the prepared BA were found consistent with the literature. The three ionic liquids, [bmim][PF₆] [bmim][BF₄] and [bmim][Tf₂N], were procured from Kanto Chemicals and were kept under vacuum overnight prior to use. The water and halide content of the ILs were similar to those used in the study of Nagasawa *et al*.¹² The viscosities of [bmim][PF₆] [bmim][BF₄] and [bmim][Tf₂N] were estimated to be 260, 98 and 50 cP, respectively at 25°C.

2.2 Instrumentation

The viscosity of the ionic liquid was measured by a LVDV-III Ultra Brookfield Cone and Plate viscometer (1% accuracy and 0.2% repeatability). The absorption and steady-state fluorescence spectra were recorded on a UV-Visible spectrophotometer (Cary 100, Varian) and a spectrofluorimeter (FluoroLog-3, Jobin Yvon), respectively. The fluorescence spectra were corrected for the instrumental response. Time-resolved fluorescence measurements were carried out using a time-correlated single-photon counting (TCSPC) spectrometer (5000, IBH), using a diode laser ($\lambda_{\text{exc}} = 374 \text{ nm}$) as the excitation source and an MCP photomultiplier (Hamamatsu R3809U-50) as the detector (response time 40 ps). The width of the instrument function, which was limited by the FWHM of the exciting laser pulse, was 65 ps. The decay curves were analysed by an iterative reconvolution program, which made the effective time-resolution of the set-up around 50 ps. Further details on the instrumental set-up and data analysis procedure can be found from one of our recent publications.⁴ All experiments were performed at 25°C.

3. Results and discussion

3.1 Steady-state behaviour

Representative steady-state absorption and fluorescence spectra of BA in [bmim][PF₆] are shown in figure 1. Very little difference in the spectral behaviour of BA can be observed in different ILs. The 0-0 transition is estimated to be around 25400 cm^{-1} from the structured absorption spectrum, which is not very different from that observed in polar conventional solvents such as acetonitrile (25650 cm^{-1}).¹⁶ The steady-state fluorescence spectra of BA in ILs are characterized by a broad emission, which is indicative of the charge transfer nature of the band, as is the case with the ordinary polar solvents.^{13–15} One can also observe some structure near the onset of the broad emission ($\sim 410 \text{ nm}$), where the LE emission (as evident from the emission spectrum of BA in hexane, shown in figure 1) is expected. We note in this context that the fluorescence spectral behaviour of BA in ILs, including even the structured portion of the emission, is very similar to that observed by Nagasawa *et al*.¹² The emission maxima ($\lambda_{\text{max}}^{\text{fluo}}$) of BA in ILs are found centered around 480 nm, which is nearly 10 nm red-shifted compared to acetonitrile

($\lambda_{\text{max}}^{\text{fluo}} = 470.6 \text{ nm}$).¹⁵ This observation is consistent with the measured polarity parameters of ILs, which suggest that the ILs are more polar than acetone-trile.⁷

3.2 Time-resolved fluorescence

In each IL, we have measured the emission decay profiles of BA at 5/10 nm interval across the entire steady-state emission spectra by selecting the wavelength using a monochromator with a bandpass of 2 nm. The total number of measurements was around 26–28 in each IL. Wavelength-dependent decay profiles, which are a typical signature of slow solvation dynamics, have been observed. One representative wavelength dependent decay behaviour is illustrated in figure 2. When monitored at the shorter wavelength region, only monotonous decay is observed, and at the longer wavelengths, the time profiles consist of a slow rise followed by the decay.

The time-resolved emission spectra (TRES) have been constructed by fitting the individual decay curves to a multiexponential function followed by normalization of the decay traces by steady-state spectra, a procedure described earlier.⁴ The TRES for BA in [bmim][PF₆] is shown in figure 3 for a wide range of time-scale (in ps–ns regime). It can be seen clearly that in the short time-scale (0–150 ps), the TRES are a combination of two distinct bands; a structured high energy band with peak at around 23800 cm⁻¹ and a broad band extending over several

thousands of wavenumbers in the low energy region. A closer look at this figure reveals that while the sharp structure on the broad emission envelope decays rather rapidly (with no shift in its position) and vanishes almost completely in about 200 ps, the broad band displays a time-dependent Stokes shift of the maximum that continues for a much longer time (up to several nanoseconds). A similar observation has been made in [bmim][BF₄] and [bmim][Tf₂N].

It is thus evident that the time-dependent emission behaviour of BA reveals two relaxation processes, not just one, as found recently by Nagasawa *et al.*¹² In the short time scale, the decay of the sharp peak at around 23800 cm⁻¹ is the most prominent feature of relaxation and at longer time, when the sharp peak has decayed completely, the relaxation process consists of dynamic Stokes shift of the CT emission maxima. As the sharp peak position matches closely with the peak position of the LE state as observed in nonpolar solvents like hexane or cyclohexane,^{14,15} it is evident that the decay of the LE state is what is observed in the early time scale. On the other hand, monotonic red shift of the CT band is the typical signature of the solvent relaxation dynamics.

Since evolution of the CT state from the LE state is commonly an ultrafast process, we can expect to miss a large part of this dynamics due to limited time-resolution ($\sim 50 \text{ ps}$) of our set-up. What we have captured in our measurements is essentially the slow component of this dynamics. A quantitative estimate of the slow component of the dynamics is obtained from the decay of the emission intensity at 23800 cm⁻¹

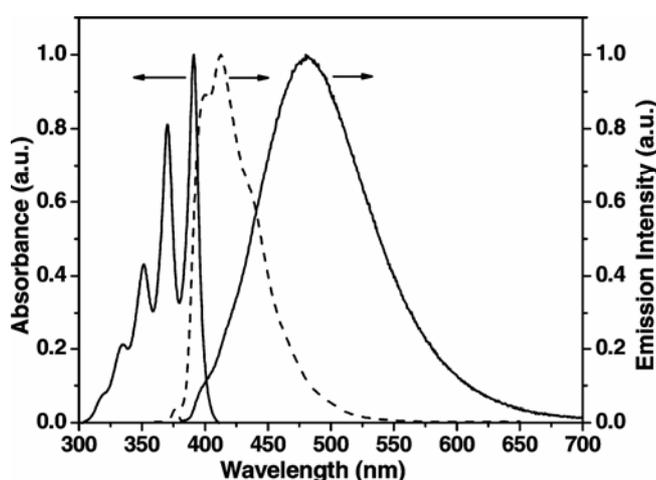


Figure 1. Steady-state absorption and emission spectra of BA in [bmim][PF₆] (—): excitation wavelength for emission ($\lambda_{\text{exc}} = 374 \text{ nm}$) and emission spectra of BA in *n*-hexane (---). All spectra are normalized at the corresponding peak maximum.

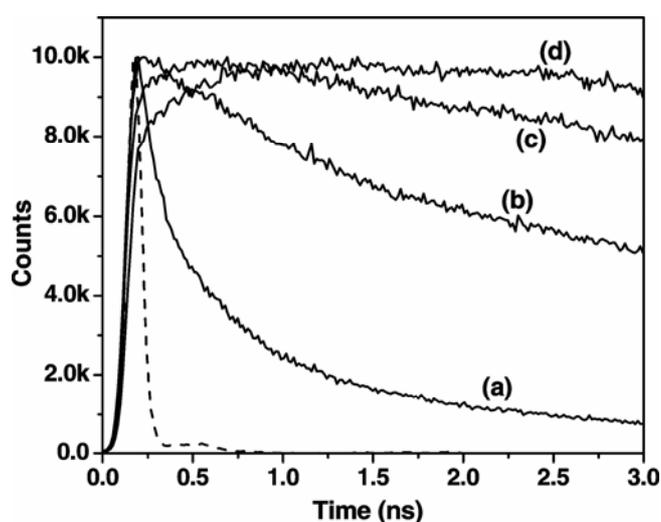


Figure 2. Wavelength-dependent decay profiles of BA in [bmim][PF₆]. (a) 410 nm, (b) 480 nm, (c) 520 nm, (d) 580 nm. The lamp profile is shown as dashed line.

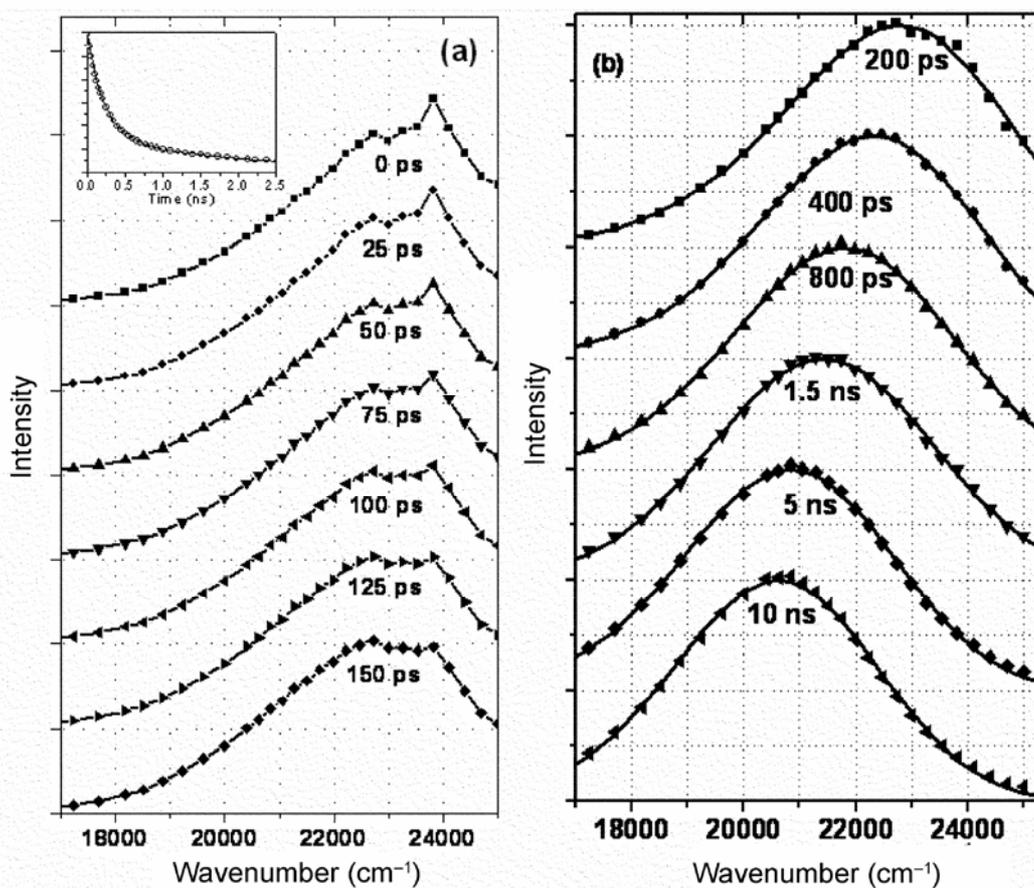


Figure 3. (a) Time-resolved emission spectra (TRES) of BA in [bmim][PF₆] at the early stage of dynamics. The inset shows the decay of the emission intensity at 23800 cm⁻¹, which corresponds to the peak position of the LE emission. The maximum of the CT bands are normalized in each case. (b) TRES for BA in [bmim][PF₆] in the long time-scale. All spectra are normalized at the corresponding peak maximum. ($\lambda_{\text{exc}} = 374$ nm). The spectral data points are fitted to log normal function.

in the early time scale, say 0–4 ns. The best fit is found to be bi-exponential with the short time component contributing to nearly 80–90% of the decay. This time is ascribed to the time constant (τ_{CT}) of the formation of the CT state. The τ_{CT} values obtained in different ILs are collected in table 1. In this context we note that for reasons not clear to us Nagasawa *et al* did not observe any sign of the decaying LE state in their TRES even though their time resolution (30 ps) was better than ours.¹² It is possible that they have missed the 23800 cm⁻¹ sharp peak as the decay curves were sampled at intervals of 5–10 ns. In their transient absorption measurements, Nagasawa *et al*¹² found the formation of the CT state to be multi-exponential with an appreciable contribution (almost 1/3rd) from a substantially long time-component of 140–330 ps, the exact magnitude of

which is dependent on the viscosity of the media, whereas the associated sub-picosecond component (typically 0.5 ps) was found to be independent of viscosity.¹² These values are also collected in table 1. As can be seen, these values are very similar to those obtained by us. The viscosity dependence of the lifetime of the LE state, as indicated in the two studies, is also quite similar. Therefore, we can conclude that LE \rightarrow CT relaxation dynamics, at least the latter stage of it, is possible to observe in picosecond time-resolved fluorescence study.

The time constant of the solvent relaxation of the CT state can be calculated from the time dependence of the spectral shift correlation function, $C(t)$, which is defined in terms of the peak frequencies at various times as, $C(t) = [\bar{\nu}(t) - \bar{\nu}(\infty)] / [\bar{\nu}(0) - \bar{\nu}(\infty)]$.

Table 1. Relaxation parameters of the dynamical processes of BA in the three ILs of different viscosity.

ILs	η^a (cP)	Short component of the decay at 23800 cm^{-1} ($\tau_{\text{CT}}/\text{ns}$) ^b	Decay parameters of the spectral shift correlation function ^c		Average solvation time τ_{av}^d (ns)	Literature value of longest time-constant (in ns) for CT formation ^e	Observed shift ($\Delta\bar{\nu}/\text{cm}^{-1}$)
			τ_1/ns (a_1)	τ_2/ns (a_2)			
[bmim][PF ₆]	260	0.22 (0.75)	0.39 (0.6)	4.0 (0.4)	1.84	0.33 (0.3)	2940
[bmim][BF ₄]	98	0.14 (0.8)	0.25 (0.6)	2.67 (0.4)	1.22	0.22 (0.3)	2820
[bmim][Tf ₂ N]	50	0.12 (0.9)	0.23 (0.8)	2.17 (0.2)	0.62	0.14 (0.36)	3020

^aMeasured at 25°C. ^bShort component of the bi-exponential fit in a short time-scale (0–4 ns), the numbers in the parenthesis indicate the weighted amplitude. ^cObtained from the bi-exponential fit to the data. ^dAverage solvation time $\tau_{\text{av}} = a_1 \tau_1 + a_2 \tau_2$, where $a_1 + a_2 = 1$, experimental error is $\pm 5\%$. ^eFrom ref 12. The numbers in the parenthesis indicate the weighted amplitude

The determination of the peak frequencies (in cm^{-1}) of the measured spectra at zero time $\bar{\nu}(0)$ and at early times is found to be not so straightforward in the present case because of considerable overlap of the LE and CT emission. We considered an average of the peak wavenumbers of the two components of emission as a fair approximation of the value of $\bar{\nu}(0)$ and $\bar{\nu}(t)$ values at the early stage of the dynamics. This was achieved by fitting the TRES to the log-normal function, just like it is done for the later stages dynamics, when CT emission is the only component observed (figure 3b). Following this procedure, the total time dependent shifts of the emission, $\Delta\bar{\nu} = \bar{\nu}(0) - \bar{\nu}(\infty)$, are found to be 2940, 2820 and 3020 cm^{-1} in [bmim][PF₆], [bmim][BF₄] and [bmim][Tf₂N], respectively (table 1).

In the present situation, it is difficult to estimate the exact amount of ultrafast component of the dynamics that is missed in our measurements because of the ambiguity associated with the determination of the precise values of $\bar{\nu}(0)$ and also due to the involvement of more than one excited state in the emission process.²³ Nonetheless, an approximate estimate of the missed component of the dynamics can be calculated from the following consideration. The Stokes shift observed in the steady-state spectra in ILs is around 4700 cm^{-1} . The reported Stokes shift of the steady state fluorescence spectra of BA in nonpolar solvents like hexane, cyclohexane, perfluoro-*n*-hexane, etc varies between 900 and 1500 cm^{-1} .¹⁵ Since, in these solvents the emitting state is almost purely an LE state, whose solvent stabilization is negligible, we can assume that in ILs the total expected time-dependent shift due to solvation will amount to ~ 3200 – 3800 cm^{-1} , whereas the observed shift is 2800–3000 cm^{-1} depending on the IL. Hence, the extent of the missing component is in

the range of only 200–1000 cm^{-1} . This implies that the missing component is quite less and is not more than 25%. Considering the fact that charge transfer occurs mostly in an ultrafast time scale,¹² we can surmise that the formation of CT state is almost completed in the early stage of dynamic solvation and so at a longer time-scale (ps–ns regime), the excited-state dynamics entirely involves the solvation process.

Biexponential fits to the $C(t)$ vs t plots (figure 4) yielded the time constants for the solvation of the CT state of BA. The time constant of the short component of this dynamics is measured to be 390 ps, 250 ps and 230 ps for BA in [bmim][PF₆], [bmim][BF₄] and [bmim][Tf₂N], respectively and the corresponding long component is 4.0 ns, 2.67 ns and 2.17 ns. The average solvation time, τ_{av} , estimated in these three ILs is 1.84 ns, 1.22 ns and 0.62 ns, respectively (table 1). The average solvation time (τ_{av}) increases with increasing viscosity of the media. These values are in good agreement with those estimated by Nagasawa *et al*¹² and other studies.^{2,4,5} If we compare the τ_{CT} values (150–300 ps) with these τ_{av} values, we can see that even though the CT formation kinetics depends on the viscosity of the ILs (at least in part), the influence of viscosity is much more dominant on the solvation process. Therefore, while in ordinary polar solvents the CT formation kinetics occurs simultaneously with the solvation dynamics, the two processes are mostly occur in different time-scale in ILs.

4. Conclusion

The time-resolved fluorescence spectra of bianthryl in imidazolium ionic liquids reveal overlapping dual emission arising from the locally excited (LE) and

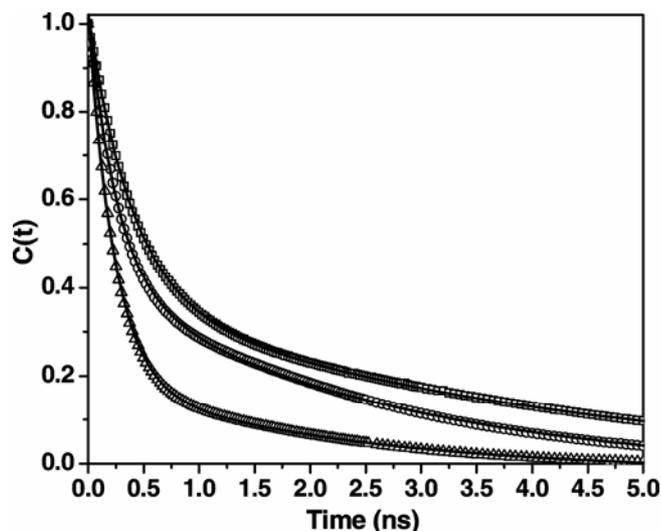


Figure 4. Decay of the spectral shift correlation function, $C(t)$, of BA in [bmim][PF₆] (□), [bmim][BF₄] (○) and [bmim][Tf₂N] (△). In each case the solid line denotes the bi-exponential fit to the data.

charge transfer (CT) states. This observation allowed us to capture the dynamics of both LE → CT relaxation and solvent relaxation from fluorescence measurements. The results show that the charge transfer dynamics, a part of which is viscosity dependent, is faster than the solvation dynamics in ionic liquids. As such these two relaxation processes occur in two different time scales and hence, in this respect the excited state dynamics of bianthryl in ionic liquids is different from that in conventional solvents, where both the dynamics occur in similar time scale.

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Supplementary material

Figures showing wavelength dependent decay profiles and time-resolved emission spectra of bianthryl in [bmim][BF₄] and [bmim][Tf₂N] are provided in the web version.

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