Journal of Photochemistry and Photobiology A: Chemistry 321 (2016) 55–62

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Influence of imidazolium ionic liquids on fluorescence of push-pull diphenylbutadienes

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ARTICLE INFO

Article history:
Received 7 October 2015
Received in revised form 1 January 2016
Accepted 13 January 2016
Available online 19 January 2016

Keywords:
Solvatochromism
Red-edge excitation
Intramolecular charge transfer
Diphenylpolyenes

ABSTRACT

A series of donor–acceptor substituted diphenylbutadienes have been synthesized and their fluorescence properties in organic solvents and imidazolium ionic liquid media were investigated. Substituted diphenylbutadienes show remarkable solvatochromic emission in polar solvents and in ionic liquids due to intramolecular charge transfer. Interestingly, diphenylbutadiene containing methoxy donor and nitro acceptor exhibits excitation dependent emission behaviour in ethanol. Excitation dependent emission studies of fluorophores in ionic liquids show distinct emission signals due to the locally excited and the charge transfer states revealing the existence of two species. Time resolved experiments show single exponential decay in organic solvents and bi-exponential decay in ionic liquids media,an indication of interaction of fluorophores with different microenvironments.

1. Introduction

Ionic liquids (ILs) are molten salts consisting exclusively of anions or cations with high melting points [1]. Owing to their unique properties such as negligible vapour pressure, non-flammability, stability, modulation of anions and cations, ionic liquids have been extensively used in organic synthesis [2], catalysis[3], materials [4,5], electrochemistry [6,7], biological applications [8–11], other analytical application [12] and as a viable green alternative to conventional organic solvents [13]. ILs contains a charged hydrophilic head group and a hydrophobic alkyl tail region that result in selective interactions with the solute molecules. Subsequently interaction of several dipolar solutes or excited state charge-separated species with ILs was widely investigated [14]. Spectroscopic investigations with fluorophores such as coumarin 153 [15], prodan [16], fluorescein [17], dimethylamino cyanostilbene [18], 2-amino-7-nitrofluorene [19], julolidine derivatives [20] and charged or uncharged solutes [21] or other organic solutes [16,22–26] reveal that the interaction is dependent both on the local chemical environment of the ionic liquid and the nature of the solute. Investigations reveal information about polarity, importance of solvation, relaxation dynamics and internal motion of the solutes [20,27–30]. In this work, we examined the influence of imidazolium ionic liquids [1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF_4] and (1-buytl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4]) on the fluorescence properties of diphenylbutadiene systems bearing push-pull substituents. With suitable donor and/or acceptor substituents, the π-conjugated systems garner wide applicability as photoresponsive materials for optical and biological use [31]. In particular, diphenylbutadienes substituted with nitro group have shown remarkable solvent polarity dependent emission properties attributed to the formation of intramolecular charge transfer (ICT) [32,33]. In strongly polar solvents, nitro dienes show emission wavelength closer to or greater than 600 nm. Taking advantage of this red-shifted emission, we investigated the absorption and fluorescence properties of dienes (**1**–**5**) using imidazolium ionic liquids (Fig. 1) as solvent media and compared with the results obtained in conventional solvents. It is envisaged that the red-emission of these dienes negates interfering emission of the ILs. The results reveal interesting observations in the fluorescence properties of the dienes and are described below.

2. Experimental

2.1. Materials

Reagents required for the synthesis of imidazolium ionic liquids and diphenylbutadiene derivatives were obtained from Acros, Aldrich, Alfa Aeser and SD Fine chemicals Ltd. All the synthesized samples were characterized using NMR (Bruker AvanceIII-500 MHz)

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http://dx.doi.org/10.1016/j.jphotochem.2016.01.015
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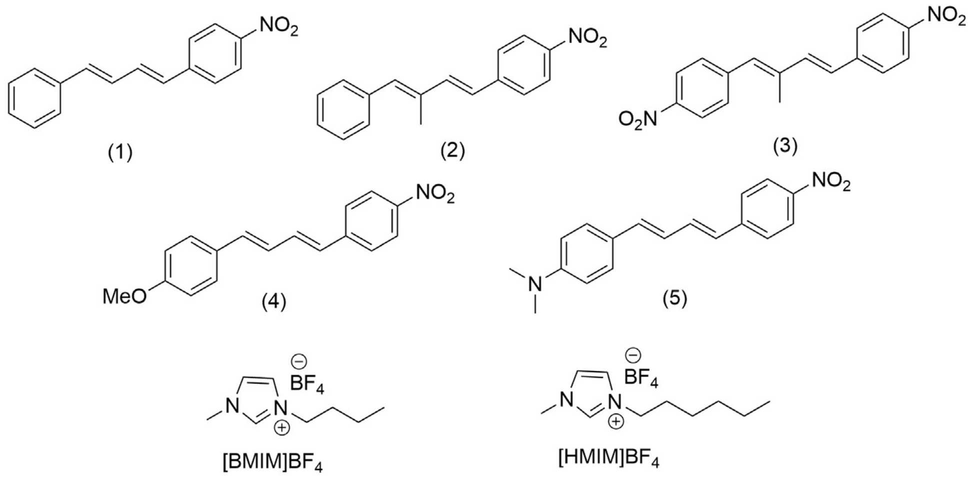


Fig. 1. Structures of diphenylbutadiene derivatives and imidazolium ionic liquids used.

and mass spectrometry (Waters Synapt G2S). Solvents used for absorption and fluorescence investigations were dried and distilled prior to use. To remove any nascent impurities that show absorption/fluorescence, particularly in the desired sample range, the synthesized ionic liquids are purified by dissolving them in dry acetonitrile (or acetone), treated with charcoal for 48 h and filtered by passing through a celite plug. These liquids were further transferred into reagent bottles and kept under vacuum at 60–65 °C for removal of any remnant organic impurities and water. Nitrogen was flushed through purified ionic liquids. UV-visible absorption spectra were recorded using Analytik Jena Specord plus 210 spectrophotometer and steady state fluorescence studies were carried out using Fluorolog-3spectrofluorimeter. Fluorescence life-times were determined by Edinburgh Lifespec II instrument using a 375 nm laser source excited at the emission maxima observed for the dienes in the given solvents. The percent error associated with the lifetime studies is 1.95–4%.

2.2. Preparation of samples for fluorescence measurements

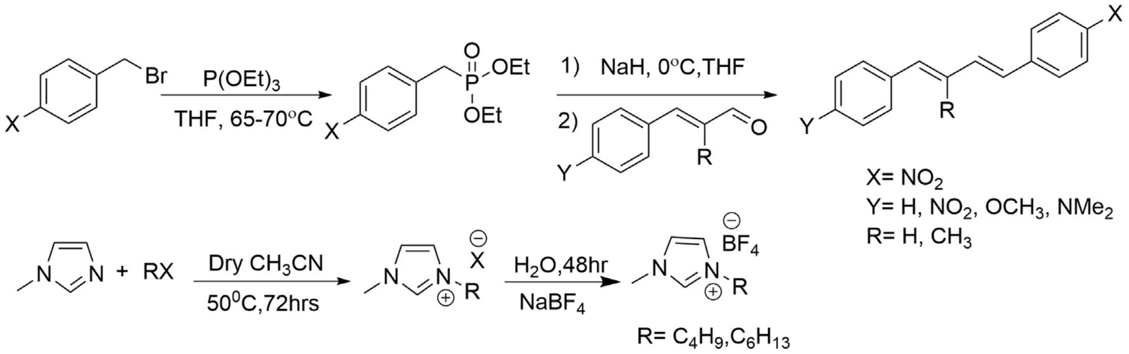
For the optical studies, a stock solution of dienes (**1**–**5**) in the respective solvent (10^{-3} M) was prepared. For ensuring solubility in ionic liquids, the solutions were sonicated for two minutes. 5 or 10 μL volumes of the stock solution were added to 1 mL of the solvent media (e.g. [Bmim]BF_4), the samples were shaken and allowed to equilibrate for at least five minutes at ambient temperature before recording the absorption or emission spectra. Typically the excitation wavelengths were set at the absorption maxima (λa) of the compounds under investigation. All the fluorescence spectra were recorded in 10 mm path length quartz cuvette with a slit width of 1–2 nm. Emission of ILs at the same excitation wavelength of the desired compound was recorded and was used as a blank and the emission was subtracted from sample +IL emission.

2.3. Synthesis

The butadiene derivatives were synthesized using previously reported procedures [34,35] by a reaction of the desired cinnamaldehyde with corresponding phosphonate esters. Ionic liquids with cationic component of 1-butyl-3-methylimidazolium (Bmim) and 1-hexyl-3-methylimidazolium (Hmim) and BF_4 as anionic counterpart were synthesized based on established literature [36] [Scheme 1]. The relevant experimental procedures and the characterization data are given in the supporting information

3. Results and discussion

A series of nitro substituted diphenylbutadienes bearing donor and acceptor substituents were synthesized and are shown in Fig. 1. Diene (**1**) contains an electron withdrawing nitro group at the *p*-position of the aromatic ring. Diene (**2**) differs from diene (**1**) in having a methyl group on the double bond. Diene (**3**) has two electron withdrawing nitro groups at *p,p′* positions of the aromatic ring and a methyl group on the double bond. Dienes (**4**) and (**5**) are



Scheme 1. Synthesis of diphenylbutadiene derivatives (**1**–**5**) and ionic liquids utilized in this study.

Table 1
Absorption and emission of dienes in ionic liquids, dioxane, ethanol and acetonitrile.

—	$[Bmim]BF_4$		$[Hmim]BF_4$		EtOH*		Dioxane		Acetonitrile	
	λ_a (nm)	λ_f (nm)	λ_a (nm)	λ_f (nm)	λ_a (nm)	λ_f (nm)	λ_a (nm)	λ_f (nm)	λ_a (nm)	λ_f (nm)
1	387	590	387	588	376	592	377	496	376	565
2	381	594	380	578	365	588	367	504	370	577
3	392	546	390	541	375	551	377	465	380	530
4	408	629	406	616	395	565	395	537	394	628
5	462	677	458	671	445	619	444	632	446	~610

* The reported emission is of long-wavelength CT band.

substituted with methoxy or dimethylamino donors and nitro acceptor.

3.1. Absorption and emission of dienes in organic solvents and ionic liquids

Table 1 gives the details of absorption and emission of dienes (**1**–**5**) in organic solvents and ionic liquids. Diene (**1**) shows absorption maxima (λ_a) of 377 nm in dioxane. Diene (**2**) absorbs lower (367 nm) than diene (**1**). This lower absorption is caused by loss of planarity and consequent decrease in delocalization. Introduction of an electron acceptor (in **3**) or donor groups (in **4** & **5**) results in bathochromic absorption shifts. Among the dienes investigated, [5] containing dimethylamino donor and the nitro acceptor has the largest absorption maxima (~445 nm) [Fig 2a]. The absorption variations can be related to changes in electron delocalization owing to the presence of donor or acceptor groups. In contrast to the substituent dependent absorption shifts, variation in solvent polarity (from dioxane to acetonitrile) shows a weak influence on the absorption maxima. But, moderate absorption shifts (up to +18 nm shift) were found in imidazolium ionic liquids [Fig 2b]. This bathochromic shift in absorption of dienes in ionic liquids could be related to the viscosity effects [37]. Similar bathochromic absorption shifts were noted in polyethylene glycol and DMSO confirming the viscosity effect on absorption [Fig. S1]. It is pertinent to note that ILs $[Bmim][BF_4]$ and $[Hmim][BF_4]$, themselves have strong absorption in the range of 250–300 nm with the tail extending beyond 380 nm [Fig. S1]. This absorption is attributed to the presence of various energetically associated ionic species [38].

In non-polar dioxane, depending on the nature of substituent, dienes emits in the range of 496–632 nm.With increase in polarity, remarkable emission shifts (up to +96 nm) were observed. In polar solvents such as ethanol, diene (**1**) shows a weak shoulder band at ~600 nm and structured emission bands at 409, 435 and 458 nm [Fig. 3a]. Similarly, Dienes (**2**) and (**3**), show emission bands in the range of ~550–590 nm along with shorter wavelength bands [Fig. S2a–b]. Diene (**4**) has emission at ~570 nm and structured peaks at ~409, 435 and 458 nm [Fig. 3b]. In polar aprotic acetonitrile, the dienes have emission in between 565 nm and 628 nm [Fig. S2d]. No shorter wavelength structured emission peaks were seen. Such strong red-shifted emission bands in polar solvents are attributed to solvent reorganization and to intramolecular charge transfer [33,39]. Taking into account these observations, it is assumed that the long-wavelength band of dienes (**1**–**4**) in ethanol is due to the charge transfer (CT) band and the shorter wavelength band is due to the locally excited (LE) state species. The decreased emission intensity of the CT band in ethanol is due to strong solute-solvent H-bonding [33]. Interestingly we observed two emissive bands only in ethanol but not in other solvents. The observed structured emission peaks are at a lower energy to that noted in non-polar dioxane. If this emission is caused by LE state, the energies should be comparable or at a higher energy than that of dioxane. This may be just an anomaly. To test this, we recorded the emission of diene (**4**) in heptane. Heptane has a dielectric constant (1.92) that is lower than that of dioxane (2.24) [40]. In heptane, diene (**4**) exhibits structured emission bands with maxima at 455 nm and shoulder peaks at 430 nm and 479 nm [Fig. S3]. Despite having a small difference in dielectric constant, [4] exhibit broad bathochromic emission at 537 nm in dioxane. Such behaviour where emission in dioxane exceeds predictions based on the dielectric constant could be attributed to 'dioxane anomaly' [41]. Interactions such as H-bonding, conformational polarity and quadrupolar interactions allow dioxane to act like a polar solvent [41]. However, structured emission bands seen in heptane have comparable energies with

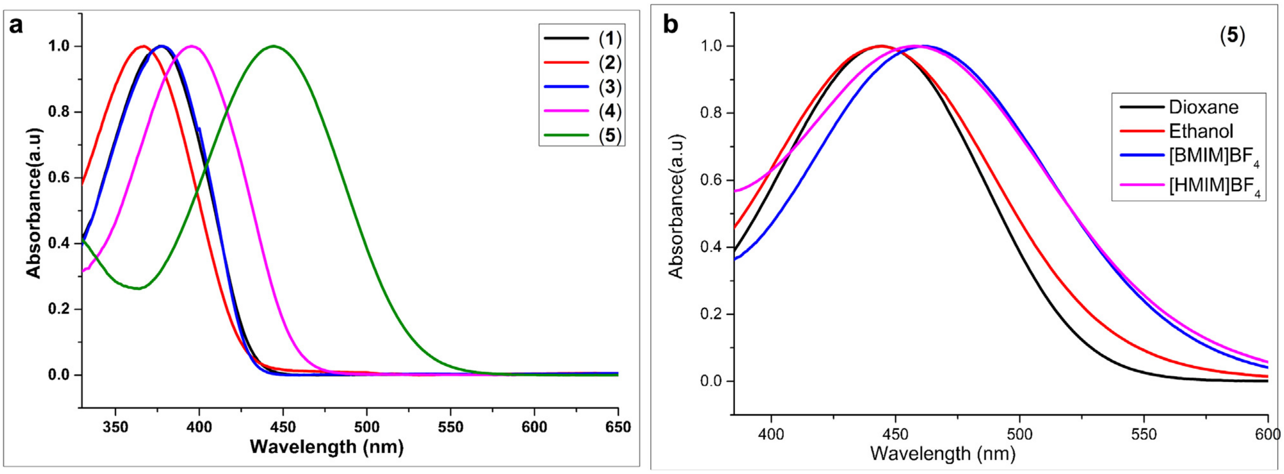


Fig. 2. a) Absorption of dienes (**1**–**5**) in $[Bmim]BF_4$; b) absorption of diene (**5**) in different solvents. Absorption spectra of other dienes in organic solvent and ionic liquid media are given in supporting information [Fig. S1].

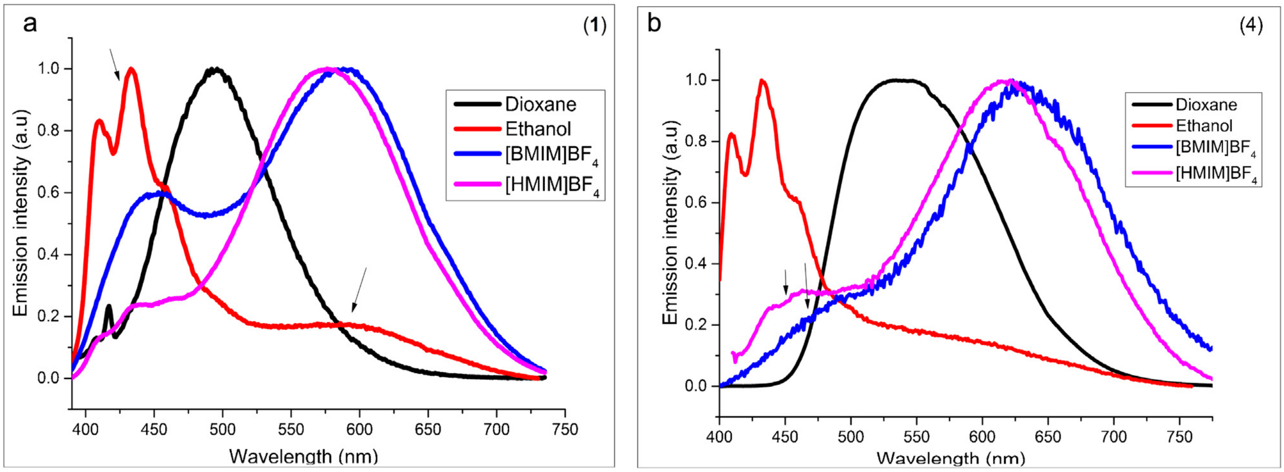


Fig. 3. Emission spectra of dienes a) (**1**) in dioxane, ethanol (λ_{ex} = 380 nm) and ionic liquid media (λ_{ex} = 390 nm) b) (**2**) in dioxane, ethanol, [Bmim] BF$_4$ (λ_{ex} = 400 nm) and in [Hmim] BF$_4$ (λ_{ex} = 410 nm). (For interpretation of the references to colour in the text the reader is referred to the web version of this article.)

shorter wavelength emission bands noted in ethanol. On the other hand, diene (**5**) shows only one emission band at $\sim$619 nm in ethanol as a result of intramolecular charge transfer [42] [Fig. S2c and d].

From these observations, it is evident that solvent plays a key role in affecting the emission properties of these dienes. To further understand the solvent effect, we examined emission of dienes in imidazolium ionic liquids [Bmim][BF$_4$] and [Hmim][BF$_4$]. The emission observed is same as the emission obtained in polar solvents [Table 1]. Unlike absorption, emission of dienes in [Hmim][BF$_4$] is slightly blue shifted in comparison to the emission seen in [Bmim][BF$_4$]. Even though H-bonding is seen in ILs, restricted intramolecular rotation due to stronger viscosity results in enhanced emission bands for these dienes. Importantly, the emission of these dienes shows weak shoulder bands at shorter emission wavelengths that may correspond to the locally excited (LE) state species. Here, it is important to note that ILs themselves possess characteristic emission which is dependent on the excitation wavelength (λ_{ex}) [43] [Fig. S4a–b]. At excitation of 380 nm or at 400 nm, [Bmim][BF$_4$] shows three emission bands, a maximum at 435 nm, a peak at 410 nm and a shoulder at 458 nm. Changing the λ_{ex} to 420 nm or 440 nm, a different but unstructured emission band at $\sim$508 nm was observed. This is a reproducible experiment to the earlier literature reported by Anunay Samanta's group [43] and is attributed to microheterogeneity of the ILs. Similar results were obtained with [Hmim][BF$_4$] [Fig. S4b]. Unlike conventional solvents, ILs possesses two microenvironments: polar and nonpolar. Depending on the solute-IL interaction, the fluorophores may prefer to be in different domains. Interaction with polar environment will result in a bathochromic shift and interaction with non-polar side chain will lead to emission corresponding to the non-polar solvents. In [Bmim][BF$_4$], dienes [**1**–**3**] shows emission at 590 nm (**1**), 594 nm (**2**) and 546 nm (**3**) that is comparable to the emission in ethanol. Therefore, we can presume that the dienes (**1–3**) have a clear preference to the polar environment. The observed shorter wavelength bands may be originating from the LE state or the ILs itself. In [Hmim][BF$_4$], diene (**4**) shows emission at $\sim$629 nm (λ_{ex}: 400 nm) with shorter wavelength bands near 440–450 nm and diene (**5**) shows strong emission band at $\sim$515 nm (λ_{ex}:445 nm) with very weak shoulder bands at $\sim$675 nm [Fig. 3 and Fig. S2c]. Like in dienes (**1**–**3**) these shorter wavelength bands could be due to LE states of these chromophores.

3.2. Effect of concentration on emission of fluorophores

To understand the origin of the high energy emission peak in ILs we studied dependence of concentration on emission. For this experiment, the desired diene was dissolved in IL and small aliquots (5–10 μL amounts) were added to 1 mL of ionic liquid.

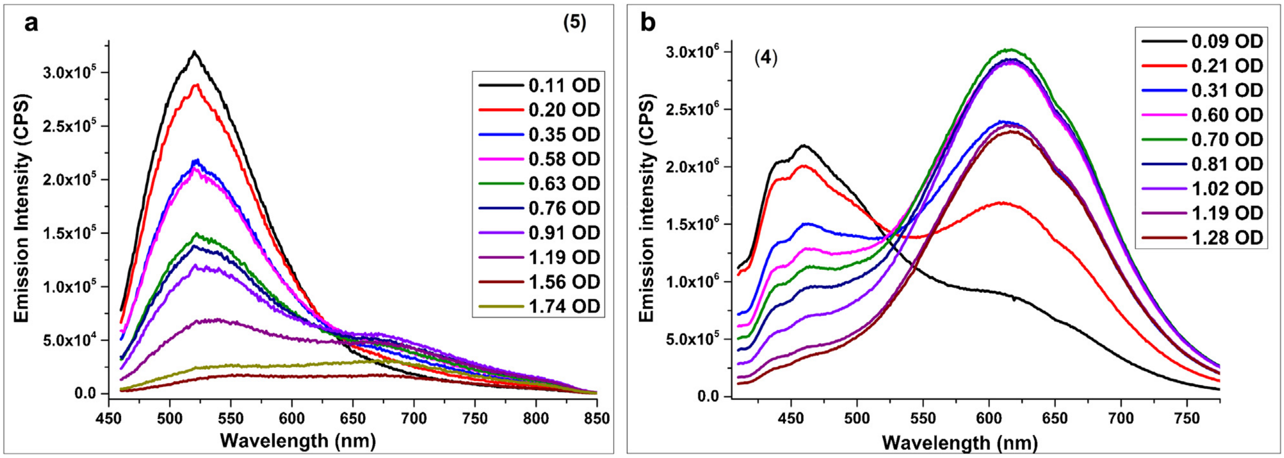


Fig. 4. Emission of dienes with increasing concentration of the fluorophore in [Hmim]BF$_4$ for a): Diene (**5**) at λ_{ex} = 450 nm and b): diene (**4**) at λ_{ex} = 400 nm. The spectra of other dienes are shown in in ESI Fig. S5.

Upon an increase in concentration of the fluorophore, an initial increase in intensity of the long wavelength band followed by intensity drop was observed as a result of concentration quenching. In the case of diene (**5**), at very high optical density (0.91 or 1.74) two clear emission bands one at 513 nm and another at ~670 nm are seen) [Fig. 4a]. If the emission is due to IL alone, a drop in fluorescence intensity was not anticipated. Therefore we attribute the short wavelength band due to the LE state and the long wavelength band due to the CT state: characteristic dual fluorescence behaviour. Other dienes also show comparable concentration quenching behaviour. In all the cases, there is not any appearance of a new emission band [Fig S5]. The emission at ~515 nm, for (**5**), closely correlates with the emission measured in non-polar solvents such as heptane or methylcyclohexane [33]. Taking into account this emission data, one can hypothesize that the fluorophore has preferential hydrophobic interaction with the IL environment bearing predominantly hydrophobic alkyl side chains. The longer wavelength band at ~675 nm corresponds to the interaction of the fluorophore with the polar environment [Fig. 4a] of ionic liquids. In the case of diene (**4**), we can also notice two emission bands at optical densities of 0.31 to 0.81 which upon further increase in concentration results in the more dominant CT band [Fig. 4b]. Therefore based on these observations it is likely that fluorophores experience differential interaction with diverse microenvironments of ionic liquids and contribute to dual emission characteristics. This behaviour is also observed in organic solvents such as ethanol but not seen in dioxane. At certain concentrations dual emission behaviour, is also clearly noted [Fig. 5] even in ethanol. It should be noted that solubility of dienes in ionic liquids is not as quick as in organic solvents (dioxane, ethanol or acetonitrile). Though the samples were sonicated prior to the measurement, small contribution from the emission due to aggregates may also occur.

Preferential H-bonding interaction with strongly basic amino group in (**5**) could explain the observed weak CT emission band. No such interactions are possible for other dienes due to lack of such strong basic groups and therefore the long wavelength band emission is preserved in ionic liquid media.

3.3. Effect of excitation wavelength in ethanol and ionic liquids

Ideally, the emission peak is independent of the excitation wavelength because of the time scale of the processes involved. But as shown in Fig. S4, one of the key observations of ionic liquid emission is its Red-edge excitation (REE) phenomena, where depending on the excitation wavelength, shifts in emission wavelength were observed [43,44]. The interaction of ILs with some dipolar molecules also leads to such excitation dependent emission wavelength [23]. We therefore examined the excitation wavelength (λ_{ex}) dependence for dienes (**1–5**) in organic solvents and IL media. As shown in Fig. S7 ESI, at λ_{ex} of 350 nm, diene (**1**), show two emission regions, one a structured emission band with a maximum at ~435 nm and another long wavelength band at ~592 nm in ethanol. As the excitation wavelength is increased [λ_{ex}(420 nm)], the structured emission peaks decrease in intensity and a stronger emission band appears at ~592 nm. Dienes (**2**) and (**3**) also have analogous observations and the spectral details are given in ESI [Fig S7]. On the other hand, diene (**4**) containing a methoxy donor and a nitro acceptor group show a different excitation dependent emission pattern [Fig. 6a]. Upon excitation at the blue end of the absorption spectrum (λ_{ex}: 360 nm), structured emission at ~409, 435 and 458 nm was noted along with a broad drooping shoulder. With increasing λ_{ex}(380 nm, 400 nm, 420 nm) a small but gradual shift in the emission in the range of ~545–565 nm was seen. Excitation at red-end (λ_{ex}:440 nm) of the absorption spectrum results in emission at ~572 nm. Further excitation at the extreme red end of the absorption spectrum (λ_{ex}:480 nm) results in a strongly red-shifted emission at ~615 nm. This is a surprising observation. Although one can ascribe this to characteristic Red-Edge excitation (REE) phenomena, REE is most often observed with membrane bound probes or in viscous media [45,46]. Therefore observance in ethanol suggests that this large red-shifted emission may be due to the solvent relaxation involving the charge transfer state. This excitation dependence was not observed in non-polar solvent such as a dioxane. In more viscous IL media, such excitation dependent study reveals two distinct emission regions one at ~458 nm and another at ~618 nm corresponding to the LE and CT states respectively [Fig. 6b and Fig. S8] for dienes (**1**–**4**). With increase in excitation wavelength only the CT band is prominent in both organic and ionic liquid media (Fig. 6).

3.4. Excitation Spectra

As showed in Fig. 6, diene (**4**) in ethanol shows interesting REE behaviour. To understand whether this is due to the presence of different excited state species, we monitored excitation spectra for ethanol solution of diene (**4**) at different emission wavelengths (λ_{em}). The excitation spectra are shown in Fig. 7. The excitation maxima, 395 nm obtained at λ_{em} of 610 nm (wavelength

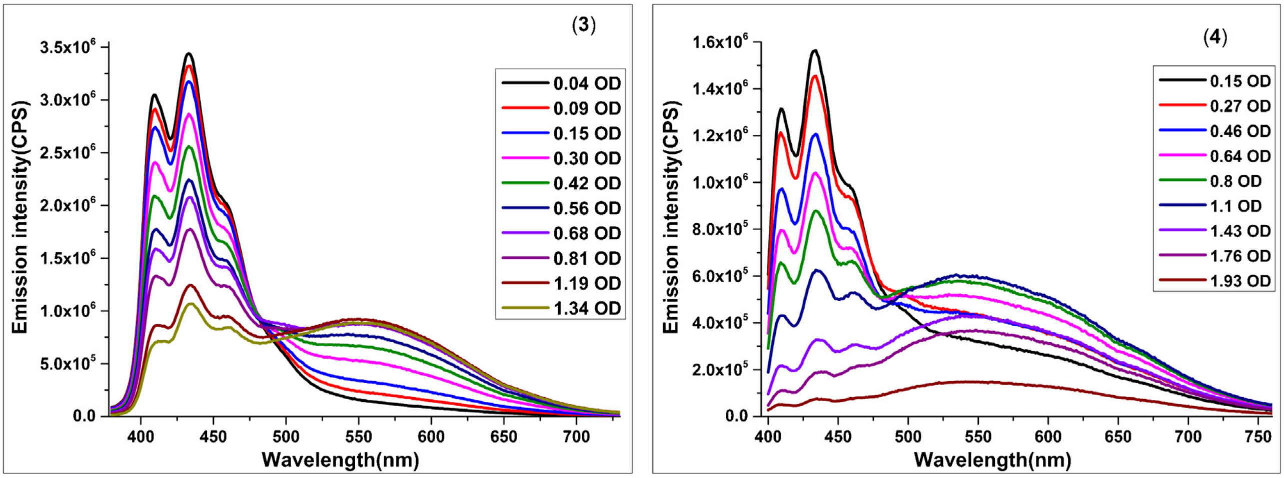


Fig. 5. Concentration dependent emission of dienes (**3**) at λ_{ex} = 370 nm and (**4**) at λ_{ex} = 390 nm in ethanol. The spectra of other dienes are shown in in ESI (Fig. S6).

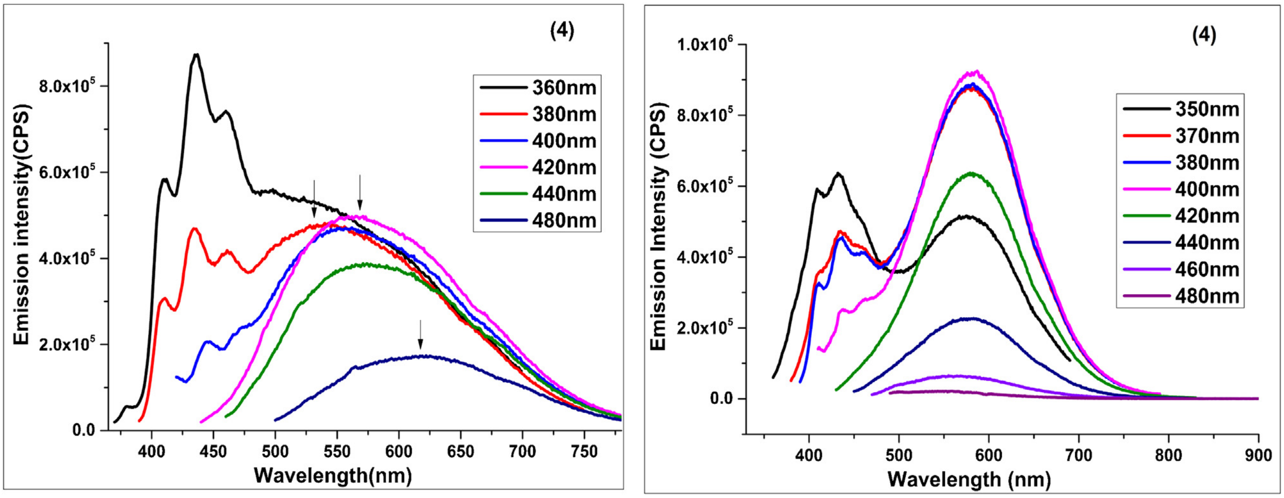


Fig. 6. Emission of diene (**4**) at different excitation wavelengths in ethanol and [Hmim]BF_4].

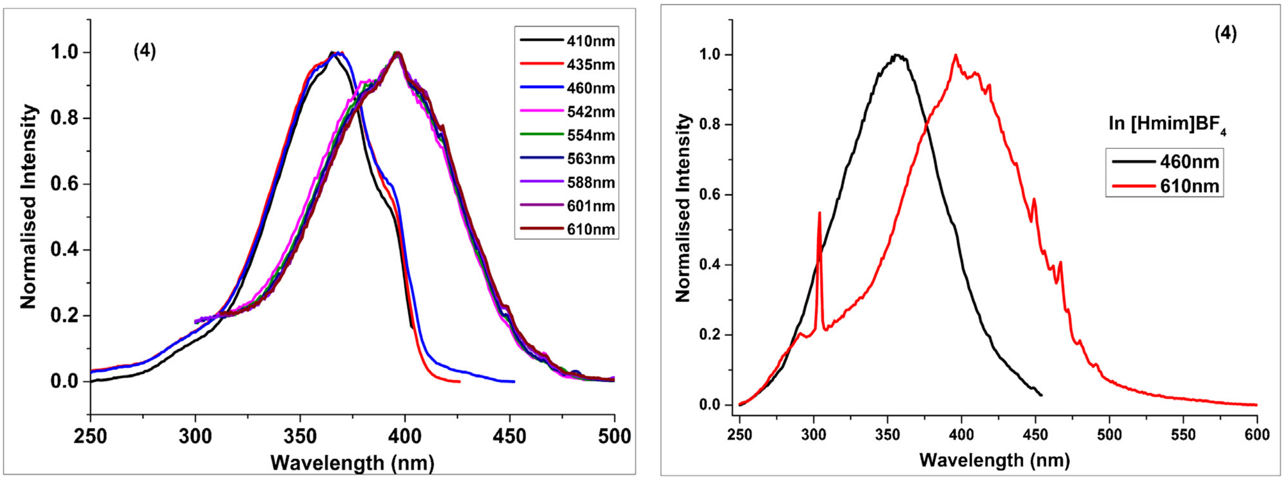


Fig. 7. Excitation spectra of diene (**4**) in ethanol and in [Hmim][BF4] obtained at different emission wavelengths. (For interpretation of the references to colour in the text the reader is referred to the web version of this article.)

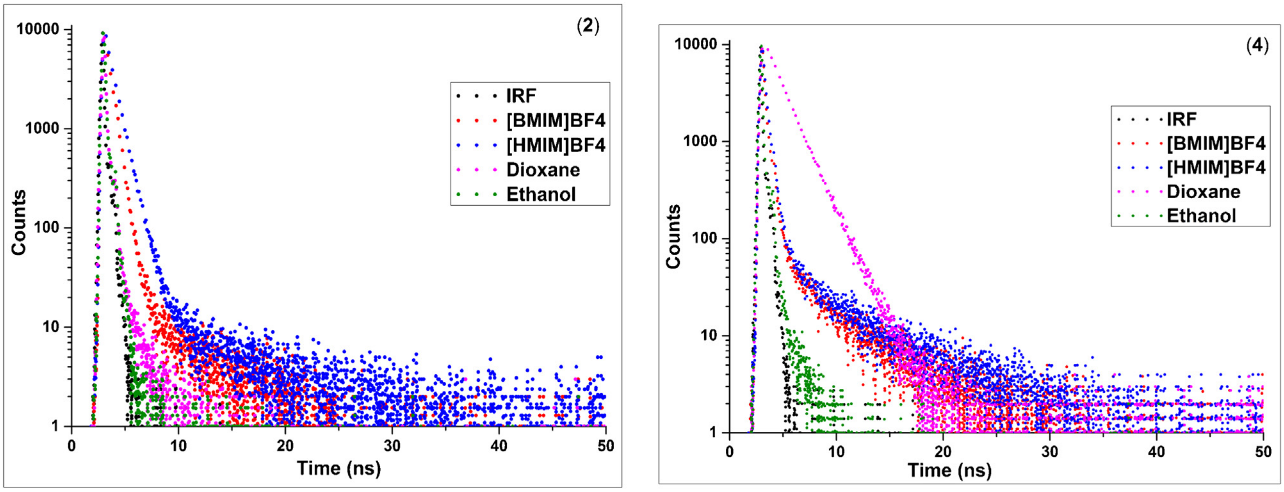


Fig. 8. Lifetime decay profiles of dienes (**2**) and (**4**) in different solvents. λ_{ex} for (**2**): 590 nm [Bmim]BF_4; 587 nm [Hmim]BF_4; 602 nm EtOH; 476 nm dioxane; λ_{ex} for (**4**): 692 nm [Bmim].12 BF_4; 619 nm [Hmim]BF_4; 541 nm EtOH and 537 nm for dioxane.

Table 2
Lifetime data of dienes (**1**–**5**) in dioxane, ethanol and ionic liquids.

Diene	Solvent	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2
1	$[Bmim]BF_4$	0.16 (12.18%)	0.59 (87.82%)		1.004
	$[Hmim]BF_4$	0.31 (15.98%)	0.95 (82.94%)	4.51 (1.08%)	1.006
	Dioxane	0.14 (100%)			1.113
	Ethanol	0.11 (100%)			1.020
2	$[Bmim]BF_4$	0.14 (18.03%)	0.53 (80.53%)	4.63 (1.44%)	1.007
	$[Hmim]BF_4$	0.26 (22.81%)	0.85 (75.81%)	5.98 (1.39%)	1.007
	Dioxane	0.08 (100%)			1.168
	Ethanol	0.08 (100%)			1.032
3	$[Bmim]BF_4$	0.24 (52.76%)	0.56 (40.33%)	5.15 (6.91%)	1.005
	$[Hmim]BF_4$	0.72 (63.31%)	1.65 (23.92%)	11.10 (12.76%)	1.116
	Dioxane	0.05 (100%)			1.101
	Ethanol	0.13 (100%)			1.037
4	$[Bmim]BF_4$	0.15 (81.13%)	0.53 (15.07%)	4.36 (3.79%)	1.194
	$[Hmim]BF_4$	0.18 (69.74%)	0.52 (23.86%)	6.00 (6.40%)	1.071
	Dioxane	1.72 (100%)			0.844
	Ethanol	0.03 (100%)			1.007
5[*]	$[Bmim]BF_4$	0.31 (7.45%)	1.17 (30.45%)	4.01 (40.78%)	1.200
	$[Hmim]BF_4$	0.86 (19.45%)	3.46 (32.18%)	11.96 (48.37%)	1.090
	Dioxane	2.01 (100%)			1.127
	Ethanol	0.08 (100%)			1.068

[*] For (**5**) a fourth lifetime component (10.15 (21.32%) is also seen) in $[Bmim]BF_4$.

corresponding to the CT emission) is comparable to the λ_{abs} of diene (**4**). This excitation maximum remains constant with decrease of emission wavelength until 540 nm. However, excitation at ~460 nm (λ_{em}) results in a spectrum that is different and has a maximum at ~367 nm. This may be attributed to the presence of a discrete excited state species. Similar results were obtained for dienes in $[Hmim][BF_4]$. The excitation of dienes corresponding to the emission wavelength of long wavelength CT band results in excitation maxima that match approximately with the absorption maxima with minor variations. But, recording the excitation spectra at ~460 nm (λ_{em}), results in excitation maxima in the range of 350–360 nm. While it would be convenient to label this as the excitation due to the LE emissive state, the overlap of IL excitation makes its interpretation difficult.

To understand the interaction of the fluorophores with organic solvents and ILs, we measured fluorescence lifetimes for the dienes. The data is given in Table 2. A mono-exponential fit was observed for all the dienes in organic solvents (dioxane or ethanol). For dienes (**1–4**) in ionic liquids, the data could only be fitted in multi-exponential decay, indicating interaction of the fluorophore in different microenvironments corresponding to hydrophobic and hydrophilic regions [Fig. 8 and Fig. S9]. To understand the dual emission nature of fluorophores, the lifetime of diene (**4**) in ethanol at two different wavelengths was recorded. Excitation at 541 nm, corresponding to the emission of the CT band, a mono-exponential decay with a lifetime of 0.032 ns was observed and excitation at ~433 nm, a bi-exponential decay was noted [Fig. S10]. For diene (**5**), the decay pattern obtained is multi-exponential and this matches with the decay pattern of ILs [Fig. S11]. It is thus hard to predict preferential interaction of diene (**5**) in IL media. However, single exponential decay was found in organic solvents for diene (**5**).

4. Conclusions

In summary, nitro substituted diphenylbutadienes were synthesized and examined for their fluorescence properties in organic and imidazolium ionic liquid media. Even though cationic components of the ionic liquids have different alkyl chain lengths, we observed very little difference in emission maxima of the dienes. Interestingly, we observed excitation wavelength dependent emission in ethanol for *p*-methoxy *p*′-nitro diphenylbutadiene. With change in excitation wavelength, other dienes show distinct emission bands one corresponding to the locally excited state and the CT band. Such behaviour is also reported in ionic liquid media. The measured emission maxima values and the multi-exponential decay of the dienes reflect the propensity of their interaction with different microenvironment of ionic liquids.

Acknowledgements

Authors thank DST (SR/S1/PC-024/2010) and IIT Gandhinagar for financial support and the reviewers during the review process.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2016.01.015.

Synthetic procedures, characterization data and Figs. S1–11 are provided.

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