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

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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.

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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][BF₄] and (1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄]) 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 Aesar and SD Fine chemicals Ltd. All the synthesized samples were characterized using NMR (Bruker AvanceIII-500 MHz)

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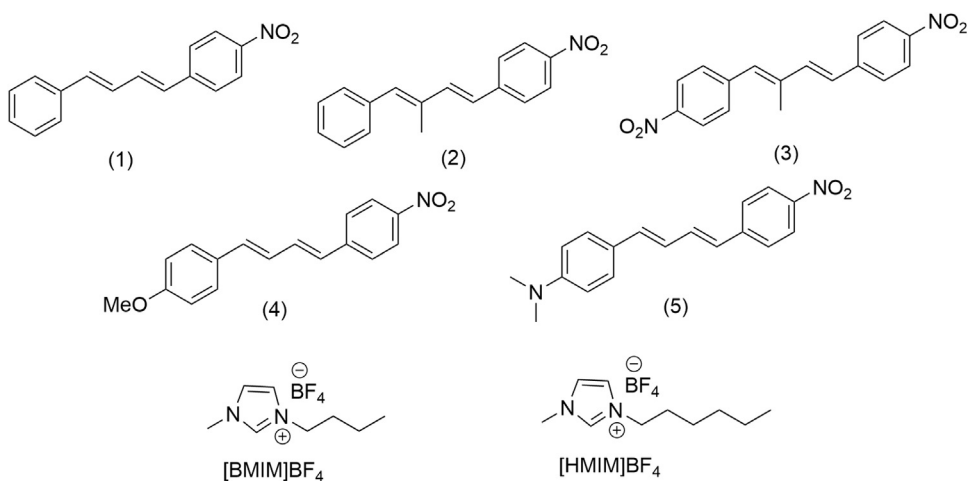


Fig. 1. Structures of diphenylbutadiene derivatives and imidazolium ionic liquids used.

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-3 spectrofluorimeter. 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 μ L volumes of the stock solution were added to 1 mL of the solvent media (e.g. [Bmim]BF₄), 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

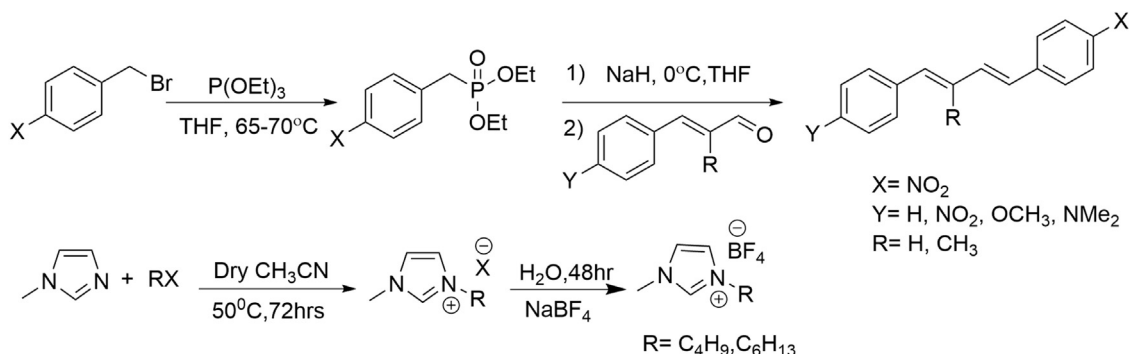
maxima (λ_a) of the compounds under investigation. All the fluorescence spectra were recorded in 10 mm path length quartz cuvette with a slit width of 1–2 nm. Emission of ILs at the same excitation wavelength of the desired compound was recorded and was used as a blank and the emission was subtracted 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 BF₄ 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.

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