



# Studies on intramolecular electron transfer reaction in donor–spacer–acceptor systems in room-temperature ionic liquids



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## ABSTRACT

The role of ionic liquids on intramolecular photoinduced electron transfer (PET) kinetics has been investigated by employing two nitrobenzoxadiazole-based flexible donor–spacer–acceptor (DSA) derivatives in two room-temperature ionic liquids. In the DSA systems dimethyl amino group acts as the donor, alkyl group acts as the spacer unit and nitrobenzoxadiazole as the acceptor unit. The results are also compared in a conventional organic solvent acetonitrile. Two different flexible DSA systems are purposefully chosen so as to eliminate the effect of transport phenomenon on electron transfer process. The electron transfer process has been studied by steady state and time-resolved fluorescence measurements. The reaction kinetics have been followed via time-resolved fluorescence measurements and analyzed by using a two-state model. It has been observed that dynamics of solvation of the concerned media plays important role in governing the rate of PET process. The results show that PET rates are hindered in the RTILs compared to that in acetonitrile. Slow solvation rate in RTILs is believed to be responsible for slow rate of PET process in ionic liquids.

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## 1. Introduction

Ionic liquids (ILs) are one of the actively pursued topics in the recent past because of their interesting physicochemical properties such as low vapor pressure, high thermal and chemical stability, shear viscosity, surface tension, wide electrochemical window, and high conductivity [1–8]. They represent an excellent alternative for conventional organic solvents in various electrochemical applications [9–11]. To employ ILs to their full potential in such devices it is pertinent to understand the effects of ILs on electron transfer process. Reports have shown that the rate of photoinduced intermolecular electron transfer in room temperature ionic liquids (RTILs) is slower than that in conventional solvents [12–21] which is attributed to the high viscosities of RTILs which lead to slower rate of self-diffusion of the reactants. Studies on intramolecular photoinduced electron transfer (PET) provide a comprehensive comparison between conventional solvents and ILs by eliminating the differences which arise due to transport phenomenon. Studies on intramolecular PET in conventional solvents have been carried out by various research groups [22–28]. The first example of the photoinduced intramolecular electron transfer in ionic liquid was described by Wasielewski and coworkers [29]. The authors have shown that the rate constants of both photoinduced charge separation and charge recombination in RTILs are comparable to those observed in common organic solvent pyridine. It may be noted that pyridine has static dielectric constant comparable to that of RTILs but its viscosity is nearly 2 orders of

magnitude lower than that of RTILs. Because of these observations they have pointed out that the fast translational processes in RTILs contribute predominantly to the electron transfer process [29]. In a recent investigation, Sahu et al. [30] have investigated a photoinduced electron transfer reaction that is coupled to an intramolecular isomerization in auramine O, using a novel two-dimensional multiple population-period transient spectroscopy. For ionic liquid solvents, heterogeneous distribution of overall reaction rate has been observed because of the heterogeneous distribution of reaction barrier heights. Another work by Wu et al. [31] revealed that intramolecular reaction rates are hindered in RTILs for various perylene tetracarboxylic diimide (PDI) compounds. They propose a two-conformation mechanism for PET for two of the PDI compounds. Due to the solvation in RTILs the energy difference between the two conformations is enhanced and hence population of the conformer which could easily undergo PET, is decreased. Furthermore, the conformation change from one state to other has been blocked because of the large viscosity of the RTILs due to which PET is hindered. In a recent report Lee et al. [32] have studied the intramolecular electron transfer kinetics of a donor–spacer–acceptor (DSA) system in various RTILs and compared the same with conventional solvents. Their investigation revealed a broad and distributed reaction rate in RTILs compared to that in conventional solvents. Studies on excited state intramolecular PET by Maroncelli and group [33] by employing 9-(4-biphenyl)-10-methylacridinium (BPAC<sup>+</sup>), crystal violet lactone (CVL), and bianthryl in a variety of ionic liquid have shown that PET is solvent controlled. An interesting example of effect of chiral IL on PET in naproxen dyads has been shown by Bose et al. [34]. The authors have shown that the chiral IL bis(terbutylphosphonium) (TBP) D-,L-

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tartrate can induce stereoselective fluorescence quenching by photo induced intramolecular electron transfer. They have observed that chiral discrimination by ionic liquids on both radiative and nonradiative processes. Another study on PET in zinc-porphyrin (ZnP)n-viologen(V) linked compounds with various methylene groups ( $n = 4,6,8$ ) in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) has been carried out by Yamada and coworkers [35] through fluorescence and transient absorption spectroscopy. Their results indicate that a biradical is generated in the IL. The authors have observed unique effects of temperature and methylene chain length on electron-transfer and magnetic field effects in the IL, probably due to the unique properties of the viscous IL. Very recently intramolecular PET from an N,N-dimethyl-p-phenylenediamine donor to a coumarin 343 acceptor bridged by a diproline spacer was studied by Castner and coworkers [36] using time-resolved fluorescence measurements in three ionic liquids and in acetonitrile. The authors have shown that the conformational variation induced by the two proline bridge results in significant variation in the donor-acceptor electronic coupling. They have observed that the electron transfer dynamics include both adiabatic and nonadiabatic contributions because of variation in the donor-acceptor electronic coupling. The intramolecular PET was found to be in the Marcus inverted regime similar to that has been observed by Lee et al. [32] for the DSA system containing single proline bridge with same donor and acceptor moieties.

Motivated by the aforementioned investigations, we have studied intramolecular PET process in two different electron donor-spacer-acceptor (DSA) systems namely 4-(N,N-dimethylethylenediamino)-7-nitrobenz-2-oxa-1,3-diazole (NBDEA) and 4-(N,N-dimethylpropylenediamino)-7-nitrobenz-2-oxa-1,3-diazole (NBDPA) in two RTILs, 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]) and 1-Hexyl-3-methylimidazolium tetrafluoroborate ([HMIM][BF<sub>4</sub>]), by steady state and time-resolved fluorescence measurements. These DSA systems differ from each other only by the length of spacer unit. We have purposefully chosen NBDEA and NBDPA as *through-space* intramolecular photoinduced electron transfer (PET) from dimethyleamino group (donor) to the nitrobenzoxadiazole (acceptor) moiety is well established [37–41]. For example many flexible nitrobenzoxadiazole-based systems has been used as fluorescent sensor for transition metal ions due the favorable PET occurring in them [39,40]. It may be mentioned in this context that a recent review article by Ramchandram has nicely demonstrated that efficient sensors for analyte of interest can be designed and developed with the proper tuning of PET communication between donor and acceptor moieties [42]. In the present case, electron transfer rates are determined by comparing the fluorescence lifetimes of the DSA molecule with their parent molecule 4-aminonitrobenzoxadiazole (NBDH). We have compared the electron transfer kinetics in RTILs with closely

polar conventional solvent acetonitrile (ACN). The chemical structures of the fluorescent probes and the RTILs are shown in Chart 1.

## 2. Experimental section

### 2.1. Materials

Reagents for the synthesis of different NBD compounds were purchased from Sigma-Aldrich Chemicals and were used without any further purification. The RTILs [EMIM][BF<sub>4</sub>] and [HMIM][BF<sub>4</sub>] were obtained from Merck, Germany (>99% purity) and used as received. The water and halide contents of the ILs were <100 ppm.

### 2.2. Synthesis of NBDH

NBDH was prepared from 4-chloro-7-nitrobenz-2-oxa-1,3-diazole (NBD-Cl) by following a standard procedure (Scheme 1, Supplementary information). [30] The compound was characterized by <sup>1</sup>H NMR. Yield of NBDH ~50%.

<sup>1</sup>H NMR of NBDH (DMSO-d<sub>6</sub>, ppm): δ 8.89 (s, 2H), 8.52 (d, 1H), 6.42 (d, 1H).

### 2.3. Synthesis of NBDEA and NBDPA

Comp. A (NBD-Cl, 75 μl, 0.75 mmol) dissolved in 5 ml of ethyl acetate was added drop wise to a solution of B (N,N-dimethylethylenediamine or N,N-dimethylpropylenediamine, ~50 mg, 0.5 mmol) in ethyl acetate (5 ml) under ice cold condition with stirring for 4 h to yield the desired compound. The completion of reaction was ensured by thin layer chromatography. Pure compound was obtained by column chromatography in neutral alumina (EtOAc/hexane = 50%). The scheme of the reaction is given in Scheme 2 (Supplementary information). Yield of NBDEA ~48%. Yield of NBDPA ~43%. The compounds were characterized by <sup>1</sup>H NMR.

<sup>1</sup>H NMR of NBDPA (DMSO-d<sub>6</sub>, ppm): δ 8.53 (d, 1H), 6.42 (d, 1H), 3.51 (t, 2H), 2.36 (t, 2H), 2.18 (s, 6H), 1.82 (m, 2H).

<sup>1</sup>H NMR of NBDEA (DMSO-d<sub>6</sub>, ppm): δ 8.51 (d, 1H), 6.44 (d, 1H), 3.56 (t, 2H), 2.58 (t, 2H), 2.21 (s, 6H).

### 2.4. Instrumentation

The absorption and fluorescence spectra were measured using a Perkin Elmer (Lambda-750) spectrophotometer and Perkin Elmer, LS55 spectrofluorimeter respectively. The fluorescence spectra were corrected for the spectral sensitivity of the instrument. Emission spectra of the probes were recorded with background correction for the emission from ionic liquids. Time-resolved fluorescence measurements were carried out using a time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh, OB920). The samples were excited at 405 nm using a picosecond laser diode (EPL). For lifetime measurements the signals were collected at magic angle (54.7°) using a Hamamatsu microchannel plate photomultiplier tube (R3809U-50). The lamp profile was recorded by a scatterer (dilute ludox solution in water) in place of the sample. The instrument response functions (FWHM) of our setup was ~95 ps for 405 nm picosecond diode laser. Decay curves were analyzed by nonlinear least-squares iteration procedure using F900 decay analysis software. The qualities of the fit were judged by the chi square ( $\chi^2$ ) values and weighted deviations were obtained by fitting. The temperature was maintained by circulating water through the cell holder using a Quantum, North West (TC 125) temperature controller. The viscosities of the RTIL were measured by LVDV-III Ultra Brookfield Cone and Plate viscometer (1% accuracy and 0.2% repeatability).

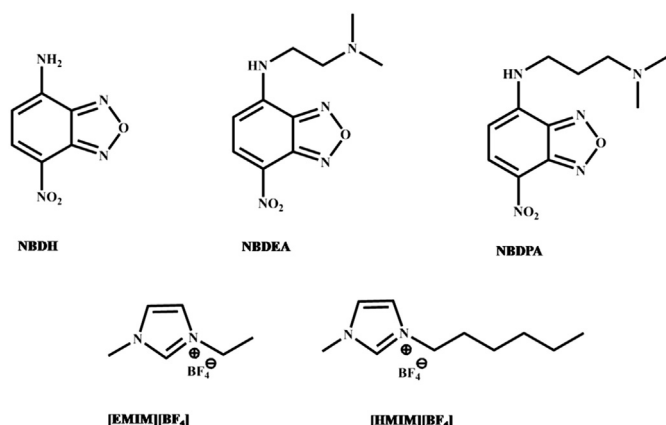


Chart 1. Molecular diagrams of the RTILs and the fluorescent probes.

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