

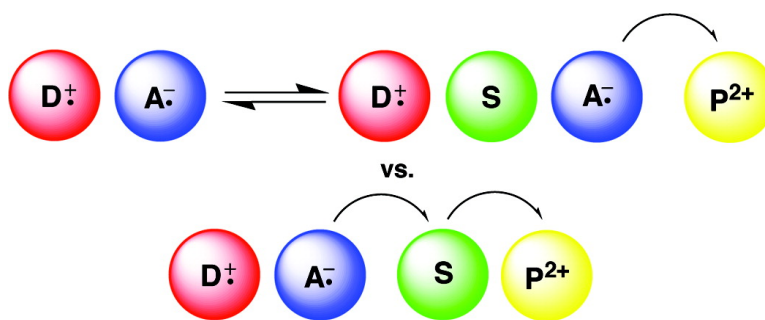
Communication

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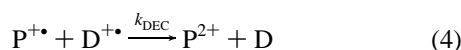
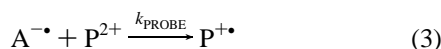
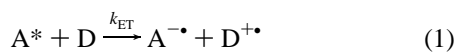
Solvent-Mediated Photoinduced Electron Transfer in a Pyridinium Ionic Liquid

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Photoinduced electron transfer (PET) is a fundamental process that is central to a variety of applications including solar energy conversion,¹ photolithography,² molecular photonics,³ phototriggering,⁴ and the synthesis of complex molecules.⁵ Equation 1 depicts a simple example of this wherein an excited-state electron acceptor, A, abstracts an electron from a ground-state donor, generating two radical species, A^{-•} and D^{+•}. Usually, the net efficiency of PET reactions is determined by the rate of energy-wasting back electron transfer reactions (eq 2) relative to the completing chemical reactions or charge separation process (eq 3).

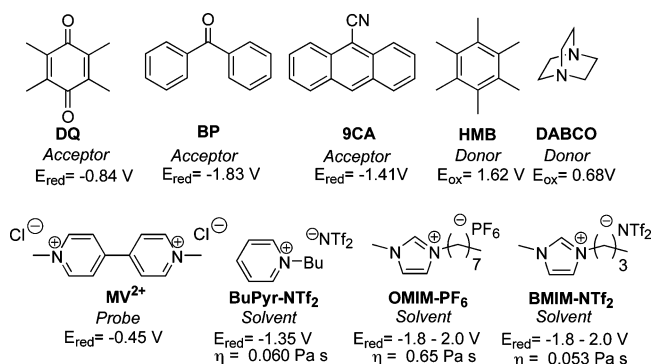


Following the pioneering theoretical insights of Marcus,⁶ experimentalists have sought to optimize the efficiency of PET reactions. Thus there have been extensive studies on the effects of the driving force, electronic coupling, and the solvent medium on the rates of these reactions.^{6–10}

Room temperature ionic liquids (ILs) have found many intriguing applications in synthetic chemistry,¹¹ electrochemistry,¹² and separation science.¹³ Their ionic nature implies that they might be able effect efficient charge separation in PET processes via specific ion-pairing interactions. On the other hand, typical ILs have high viscosities which tend to slow diffusion rates and reduce the rate for cage escape. A recent study of PET rate constants in an imidazolium-based IL showed that the reorganization energies are not qualitatively different from what is observed in solvents of moderate polarity.¹⁴ This observation is consistent with solvatochromic, simulation, and ET studies which indicate that imidazolium-based ionic liquids have polarities comparable to those of acetonitrile or ethanol.^{15–22}

A pulse radiolysis study by Behar et al. suggested to us that pyridinium ionic liquids could facilitate rapid intermolecular electron transfer reactions.^{23,24} Presumably, the favorable reduction potential of the pyridinium cation permits electron migration to occur via a secondary reduction of one or more solvent cations. The experiments described herein were aimed at determining whether such a solvent-mediated pathway can be exploited as a means of segregating charges generated in PET reactions and what, if any, rate acceleration could be realized relative to comparable processes that rely on the diffusion of photogenerated radical ions. It is shown that in cases where the redox potentials are favorable (BP/DABCO in BuPyr-NTf₂) the solvent actively facilitates the PET process. It is further demonstrated that this solvent-mediated pathway increases the rates and efficiencies of PET reactions.

Chart 1. Structures and Redox Properties of Donors, Acceptor, Probe Molecule, and IL Solvents



PET reactions using the donors and acceptors shown in Chart 1 were examined. The primary acceptors, BP and DQ, react from their triplet excited states. Thus, abstraction of an electron from the donor, DABCO, generates triplet ion radical pairs. The 9CA/HMB system, in contrast, is known to produce a singlet radical ion pair, which has a low barrier to back electron transfer and normally produces ion radicals with low efficiency.⁹

Five different solvents were employed. It was expected that BuPyr-NTf₂, being more easily reduced than the primary acceptors, BP and 9CA, would mediate electron transfer to the probe. The remaining solvents, having more negative reduction potentials, would be incapable of mediating PET. Thus reduction of the probe would only occur via diffusion of the photoreduced acceptor. Benzene and MeCN were chosen as conventional nonpolar and polar molecular solvents. The ILs, OMIM-PF₆ and BMIM-NTf₂, have, respectively, high viscosity and a viscosity similar to that of BuPyr-NTf₂.

Both the triplet and singlet PET reactions were characterized using laser flash photolysis (LFP), wherein a photoexcited acceptor (A = DQ^{3*}, BP^{3*}, 9CA^{1*}) abstracts an electron from a ground-state donor (D = DABCO, HMB). The rates and efficiencies for charge separation and intermolecular electron transfer are monitored by a subsequent reaction of A^{-•} with a probe ion (P = MV²⁺), whose reduced form is conveniently detected via its strong absorbance at 610 nm.

In CH₃CN, LFP provides transient spectra typical for such systems in conventional polar solvents. For example, LFP of BP with DABCO generates the transient spectra of the BP^{-•} (545 nm) and the DABCO^{+•} (460 nm). Addition of the MV²⁺ quenches the BP^{-•} and gives rise to MV^{+•}. Similarly, LFP of DQ/DABCO and 9CA/HMB provide the corresponding ion radical transients, and the inclusion of MV²⁺ quenches the anion radicals and generates the probe ion radical, MV^{+•}. Similar spectroscopic behavior is seen in BMIM-NTf₂ and OMIM-PF₆.

Contrasting behavior is seen in BuPyr-NTf₂. With BP/DABCO, no signal for BP^{-•} is observed, even in the absence of MV²⁺. This is consistent with the expected secondary electron transfer to the

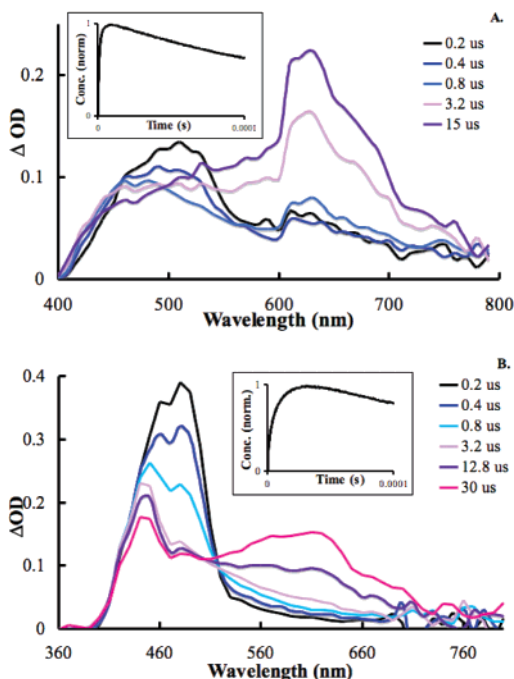


Figure 1. (A) Transient absorption spectra of BP/DABCO/MV²⁺ in BuPyr-NTf₂ with inset of waveform at 610 nm, and (B) transient absorption spectra of DQ/DABCO/MV²⁺ in BuPyr-NTf₂ with inset of waveform at 610 nm.

Table 1. Rate Constants and Quantum Yields for PET Reactions

entry	solvent	acceptor	k_{BET}^a	k_{PROBE}^a	k_{DEC}^a	Φ_{SEP}
1	CH ₃ CN	DQ	15.3	38.4	1.74	0.50
2	CH ₃ CN	BP	47.4	14.2	5.18	0.70
3	CH ₃ CN	9CA	<i>b</i>	<i>b</i>	<i>b</i>	0.25
4	benzene	9CA	<i>b</i>	<i>b</i>	<i>b</i>	0.05
5	BuPyr-NTf ₂	DQ	0.45	0.15	0.59	0.90
6	BuPyr-NTf ₂	BP	1.03	1.00	0.12	0.89
7	BuPyr-NTf ₂	9CA	3.64	0.49	0.05	0.65 ^c
8	BMIM-NTf ₂	BP	0.10	0.21	0.15	0.85
9	BMIM-NTf ₂	9CA	<i>b</i>	<i>b</i>	<i>b</i>	0.03
10	OMIM-PF ₆	BP	1.80	0.15	N/A ^d	N/A ^d
11	OMIM-PF ₆	9CA	<i>b</i>	<i>b</i>	<i>b</i>	0.20

^a Rate constants are in units of M⁻¹ s⁻¹ and are $\times 10^9$. Measurements were made at 20 ± 1 °C. Values determined are within $\pm 10\%$ error. ^b Signal not sufficient enough to accurately determine rate. ^c Determined within $\pm 5\%$ error. ^d See Supporting Information for experimental detail.

solvent cations and is further confirmed by the observation of the growth of MV²⁺ when the probe is added (Figure 1a). In contrast, DQ⁻, which is not expected to be capable of solvent reduction, is detected in the DQ/DABCO LFP experiment (at 445 nm). Addition of the probe also results in formation of MV²⁺ but at a lower rate (Figure 1b).

Quantitative analysis of the LFP data shows that solvent mediation increases both rates and efficiencies for electron transfer. Rate constants k_{BET} , k_{PROBE} , and k_{DEC} were determined from numerical simulations of LFP transient absorption signals for MV²⁺, unless otherwise noted and assuming the mechanism in eqs 2–4. The reported values (Table 1) represent averages from at least five measurements on three different independently prepared solutions (≥ 15 total). In all cases, independent measurements provided values within 10% of the mean. Additionally, Φ_{SEP} was determined using the yield of MV²⁺ at saturating concentrations of MV²⁺ (see Supporting Information).

The 9CA/HMB system shows very low Φ_{SEP} in nonpolar solvents and in ILs incapable of mediating electron transfer (entries 4, 9, and 11). However, in BuPyr-NTf₂, we detect higher yields of MV²⁺ (entry 7). This is significant as 9CA/HMB gives a singlet radical ion pair with a very low barrier to back electron transfer. Nonetheless, this system provides efficient charge separation in BuPyr-NTf₂.

A comparison of entry 6 with 8 and 10 demonstrates that electron transfer from BP⁻ to MV²⁺ (k_{PROBE}) is an order of magnitude faster in BuPyr-NTf₂ than the other ILs, which supports the solvent-mediated ET pathway for BuPyr-NTf₂. A solely diffusive ET pathway is illustrated in entries 5, 8, and 10. Electron transfer from DQ⁻ to MV²⁺ is approximately 1×10^8 M⁻¹ s⁻¹ in these cases.

The LFP experiments described above show that BuPyr-NTf₂ can actively facilitate PET reactions by providing a solvent-mediated pathway for electron transfer. Further work will be necessary to fully elucidate the nature of this process. For example, the current experiments do not distinguish a solvent hopping pathway from a pathway in which a reduced solvent cation diffuses to the probe. In the former case, greater rates may be realized in more organized media such as ionic liquid crystals.²⁵ Results from the latter will be reported in due course.

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Supporting Information Available: Experimental procedures including preparation of ILs, viscosity measurements, and general procedures for LFP experiments, detailed procedure for kinetic simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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