

Intramolecular Electron Transfer within a Covalent, Fixed-Distance Donor–Acceptor Molecule in an Ionic Liquid

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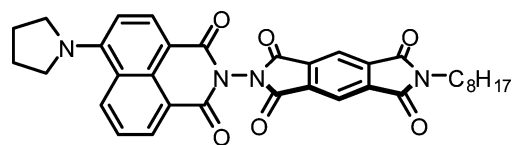
Intramolecular photoinduced charge separation and recombination within the donor–acceptor molecule 4-(*N*-pyrrolidino)naphthalene-1,8-imide-pyromellitimide, 5ANI–PI, are studied using ultrafast transient absorption spectroscopy in the room-temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [EMIM][Tf₂N]. The rate constants of both photoinduced charge separation and charge recombination for 5ANI–PI in [EMIM][Tf₂N] are comparable to those observed in pyridine, which has a static dielectric constant similar to that of [EMIM][Tf₂N] but a viscosity that is nearly 2 orders of magnitude lower than that of [EMIM][Tf₂N]. The electron-transfer dynamics of 5ANI–PI in [EMIM][Tf₂N] are compared to those in pyridine as a function of temperature and are discussed in the context of recently reported ionic liquid solvation studies.

Incorporating conventional organic solvents in potential molecular electronics and solar-energy-harvesting devices is difficult and in most cases impractical because of their high volatility. Ionic liquids (ILs) and in particular room-temperature ionic liquids (RTILs) represent an attractive alternative to traditional solvents for these applications because of their extremely low vapor pressure, high thermal and chemical stability, high ionic conductivity, and wide electrochemical window.^{1–3} For example, the incorporation of IL electrolytes into dye-sensitized solar cells has been reported with efficiencies comparable to those employing conventional solvents.^{4,5} To rationally integrate ILs into this and other types of devices, a comprehensive understanding of the influence of ILs on charge separation and transport is crucial. Thus far, experimental investigations of electron transfer in ILs have been confined to heterogeneous and intermolecular electron-transfer systems.^{6–10} These investigations have linked the significantly slower rates of diffusion-controlled intermolecular electron transfer in ILs to the effects of higher IL solvent viscosities compared to conventional (Debye) solvents. Recently, molecular dynamics simulations have examined the role of IL solvation effects on unimolecular electron-transfer dynamics.¹¹

In this work *intramolecular* electron transfer within a covalently linked donor–acceptor molecule having a strongly restricted donor–acceptor distance and orientation is studied in an IL. Because the rates of intramolecular electron transfer of the directly linked donor–acceptor pair presented here are not diffusion-limited, the measured electron-transfer kinetics will directly reflect the effects of IL solvent dynamics on the electron transfer. The hydrophobic RTIL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [EMIM][Tf₂N], was chosen for this study because of its relatively low viscosity (34 cP at 293K²), transparency in the visible spectral region,¹² and its

solvating ability for organic donor–acceptor molecules. [EMIM][Tf₂N] was synthesized by a one-step ion exchange reaction from the 1-methyl-3-ethylimidazolium bromide salt following a procedure published previously.²

The donor–acceptor molecule chosen for this study is 4-(*N*-pyrrolidino)naphthalene-1,8-imide-pyromellitimide, 5ANI–PI.¹³ Photoinduced charge separation to the radical ion pair state, 5ANI^{+•}–PI^{•–} and subsequent charge recombination have been investigated previously in a variety of media including conventional and liquid-crystal solvents using transient absorption spectroscopy.^{13–15}



5ANI-PI

Transient absorption studies were performed using a Ti:sapphire laser system that selectively excites the 5ANI donor with 414 nm, 120 fs pulses.¹⁶ The instrument response function for these experiments was 180 fs, and the radical ion pair state population was monitored using the PI^{•–} absorption band at 700 nm.¹³ Transient absorption kinetics of 5ANI^{+•}–PI^{•–} in different solvents at room temperature are shown in Figure 1. The charge-separation and -recombination rate constants are summarized in Table 1 along with the static dielectric constant and room-temperature viscosity of each solvent. The electron-transfer kinetics of 5ANI–PI in [EMIM][Tf₂N] at 293 K are surprisingly similar to those of 5ANI–PI in pyridine, despite the different solvation dynamics inherent in both solvents and the nearly 2 orders of magnitude difference in their viscosities at room temperature.

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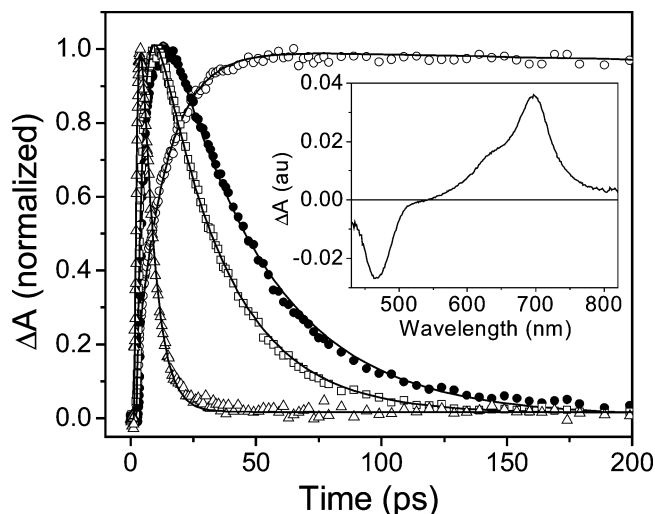


Figure 1. Transient absorption kinetics for 5ANI-PI in acetonitrile (Δ), pyridine (\square), toluene (\circ), and [EMIM][Tf₂N] (\bullet) at 293 K monitored at 700 nm. The inset shows the transient spectrum of 5ANI⁺-PI⁻ in [EMIM][NTf₂] 9 ps after excitation.

TABLE 1: Electron-Transfer Rate Constants of 5ANI-PI at 293 K in Solvents of Dielectric Constant (ϵ_s) and Viscosity (η)

solvent	$k_{CS} (\times 10^{11} \text{ s}^{-1})$	$k_{CR} (\times 10^{10} \text{ s}^{-1})$	ϵ_s	η , (cP)
pyridine	3.6 ± 0.1	3.7 ± 0.1	12.5^{39}	$0.88^{a,39}$
[EMIM][Tf ₂ N]	2.3 ± 0.1	2.6 ± 0.1	12.3^{30}	$34^{b,2}$
acetonitrile	7.7 ± 0.1	20 ± 1	36.6^{39}	$0.37^{a,39}$
toluene	0.84 ± 0.05	0.0075 ± 0.0002	2.38^{39}	$0.56^{a,39}$

^a 298 K. ^b 293 K.

The electron-transfer kinetics of 5ANI-PI were also measured by transient absorption spectroscopy as a function of temperature from 256 to 308 K in [EMIM][Tf₂N] and from 258 to 308 K in pyridine. The temperature dependence of the electron-transfer rate constants for both charge separation and recombination in these two solvents is illustrated in Figure 2 and detailed in Tables S1 and S2 (Supporting Information). As these plots reveal, the charge separation and recombination rate constants for 5ANI-PI in pyridine do not depend significantly on temperature within the range measured, which is consistent with results reported previously.¹⁵ In contrast, over a similar temperature range, while the charge separation rate constant for 5ANI-PI in [EMIM][Tf₂N] remains temperature independent, the charge-recombination rate constant displays a significant temperature dependence.

Solvent effects on electron-transfer reactions are usually categorized as static or dynamic. Static solvent effects are usually described by a structureless dielectric bath, for example, the Born dielectric continuum model, and are incorporated into theoretical electron-transfer models via the static dielectric constant of the medium. The Marcus expression for the rate of a nonadiabatic electron-transfer reaction is given by^{17,18}

$$k_{ET} = \frac{2\pi V_{DA}^2 \exp(-\Delta G^*/k_B T)}{\hbar \sqrt{4\pi \lambda k_B T}} \quad (1)$$

where V_{DA} is the electronic coupling matrix element, $\Delta G^* = (\Delta G + \lambda)^2/4\lambda$ is the activation energy for electron transfer, ΔG is the free energy of reaction, and λ is the total reorganization energy. The total reorganization energy is the sum of two components: the internal reorganization energy of the donor and acceptor, λ_i , and the solvent reorganization energy, λ_s . Using

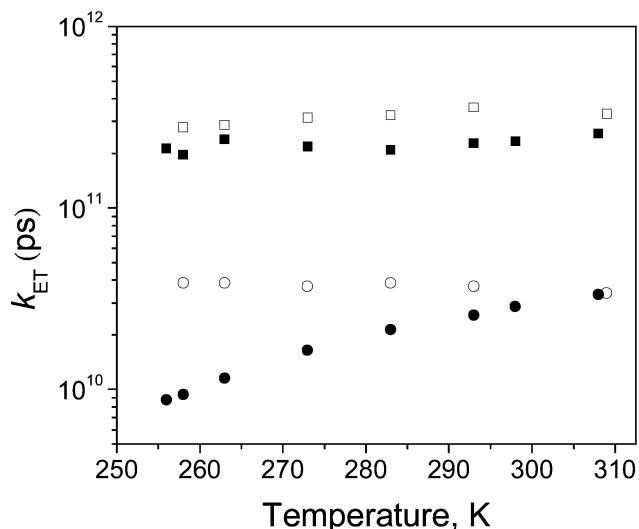


Figure 2. Temperature dependence of charge separation (squares) and recombination (circles) rate constants for 5ANI-PI in [EMIM][Tf₂N] (filled) and pyridine (unfilled). Data in pyridine at 309 K are taken from ref 15.

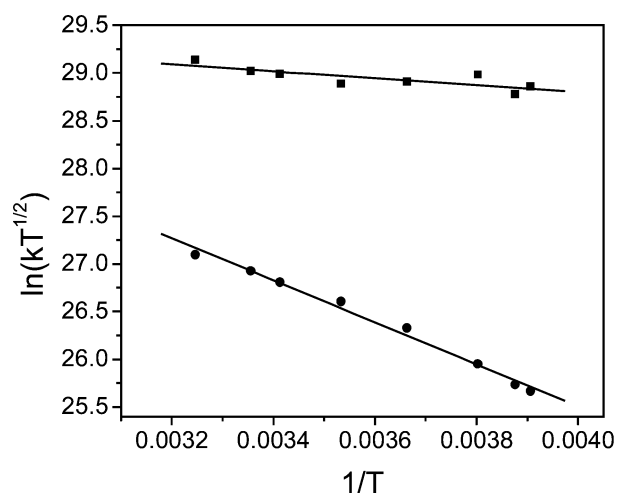


Figure 3. Plot of $\ln(kT^{1/2})$ vs $(1/T)$ for charge separation (\blacksquare) and recombination (\bullet) within 5ANI-PI in [EMIM][Tf₂N].

the dielectric continuum model, Marcus has shown that λ_s can be estimated using^{17,18}

$$\lambda_s = e^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{2r_{12}} \right) \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_s} \right) \quad (2)$$

where r_1 and r_2 are the ionic radii, r_{12} is the ion pair distance, e is the charge of the electron, ϵ_s is the static dielectric constant of the solvent, and ϵ_0 is the high-frequency dielectric constant of the solvent.

Equation 1 assumes that the electron transfer is nonadiabatic, implying that solvent motions are fast compared to the electron-transfer rate. If this assumption holds, then $\ln(k_{ET}T^{1/2})$ should vary linearly with $(1/T)$ with a slope of $-\Delta G^*/k_B$. Temperature-dependence studies of 5ANI-PI in pyridine have shown that both charge separation and recombination are nonadiabatic.^{14,15} The plots of $\ln(k_{ET}T^{1/2})$ versus $(1/T)$ in Figure 3 show a linear relationship for both charge separation and recombination within 5ANI-PI in [EMIM][Tf₂N] with $\Delta G^* = 0.005$ eV and 0.032 eV, and $V = 46$ cm⁻¹ and 350 cm⁻¹, for charge separation and recombination, respectively. These results suggest that both electron-transfer reactions of 5ANI-PI in [EMIM][Tf₂N] are also nonadiabatic. Even for the charge-recombination

reaction, the value of V is less than twice kT . This is a somewhat surprising result because ILs solvate dipolar species by fundamentally different processes than do polar Debye solvents.¹⁹ For D–A molecules such as 5ANI–PI studied in Debye solvents, reorientation of the dipolar solvent is faster than the formation or decay of 5ANI⁺–PI[–]. Consequently, only static solvent effects on the electron-transfer reactions need be considered, and the dielectric continuum model has been found to adequately characterize the solvent effects on electron-transfer reactions of 5ANI–PI.¹⁵

The apparent nonadiabatic behavior of the charge separation and recombination reactions for 5ANI–PI measured in [EMIM][Tf₂N] suggests that the dielectric continuum model may also be appropriate to describe the solvent effects of ILs on fast electron-transfer reactions. Although several recent studies have also employed dielectric continuum models to describe the solvation dynamics of ILs,^{12,20–24} recent reports by Maroncelli et al. suggest that these models may not be appropriate.^{25,26} For example, there are significant discrepancies among the reported polarities of ILs, which may be attributed, in part, to the dependence of the polarity scales on the experimental method of measurement. The effective polarities of imidazolium-based ILs, determined by the spectral shifts of solvatochromatic probe molecules, are reported to be higher than that of acetonitrile.^{3,27,28}

Static dielectric constants are an important indicator of solvent polarity, but the high electrical conductivity of ILs precludes the use of traditional techniques for measuring ϵ_s . The static dielectric constants for several ILs have been experimentally determined recently, however, using microwave dielectric relaxation spectroscopy.²⁹ On the basis of this measurement, $\epsilon_s = 12.3$ for [EMIM][Tf₂N],³⁰ which is similar to $\epsilon_s = 12.5$ for the polar Debye solvent pyridine. However, the relationship between static dielectric constants and solvation energies of dipolar solutes in conventional dipolar solvents may not hold for ILs.^{25,26} Other studies have shown the inadequacies of comparing IL solvent effects to those of conventional solvents with similar dielectric constants. Notably, Samanta's recent study of intermolecular electron transfer between pyrene and *N,N*-dimethylaniline in a series of ILs showed that contrary to expectations based on behavior in pyridine (similar dielectric constant), there was no evidence for exciplex formation in the ILs.⁹ In our study, the electron-transfer rate constants for 5ANI–PI were measured in two organic solvents that match the extremes of the reported polarity estimates for [EMIM][Tf₂N]: pyridine ($\epsilon_s = 12.5$) and acetonitrile ($\epsilon_s = 36$). As mentioned above, the rate constants measured in pyridine and [EMIM][Tf₂N] are similar, whereas those measured in acetonitrile are substantially faster than those in pyridine and [EMIM][Tf₂N], which is consistent with the increased polarity of acetonitrile. In contrast, both of the rate constants measured in the lower-polarity solvent toluene ($\epsilon_s = 2.4$) decrease significantly relative to those measured in pyridine and [EMIM][Tf₂N].

The lack of consensus in recent literature on how to model IL solvent relaxation dynamics speaks to the significantly more complicated nature of solvation in ILs versus conventional solvents. Most solvation studies of imidazolium-based ILs identify two dynamic regimes of solvent relaxation.^{19,31–34} Theoretical and experimental studies have revealed both a fast initial relaxation process, which has been linked to the small-amplitude translational motion of either the anion³⁴ or cation³² depending on the charge distribution of the solute, and a much slower relaxation event corresponding to collective motion of the anion and cation.¹⁹ Reports of the shorter solvation component lifetime vary wildly, ranging from subpicosecond³³

to hundreds of picoseconds.¹⁹ Most experimental solvation studies are based on fluorescence decay behavior of probe molecules in ILs. The large distribution of reported lifetimes for a given IL can in part be attributed to the effect of different charge distributions of the probe molecule used in these studies.³¹ Also, studies using time-correlated single photon counting with time resolutions on the order of 50 ps often yield lifetimes that are instrument-response-limited. Recent work employing time-resolved emission techniques with higher time resolution revealed that a significant part of IL solvent relaxation occurs on the ultrafast (sub-ps) time scale,^{25,33} which is consistent with theoretical predictions of fast solvation behavior of imidazolium-based ILs.^{34–36} These reports also suggest that a more accurate description of IL solvation is that it occurs with a broad distribution of relaxation times extending to the subpicosecond time scale. Recent molecular dynamics simulations have shown that partial ordering within ILs may also take place if the alkyl chains attached to the imidazolium ions are sufficiently long.^{37,38} This effect may contribute to the distribution of observed solvation time scales as well. Despite the varying accounts of IL solvation dynamics, many reports emphasize that a significant percentage of the relaxation occurs on the ultrafast time scale.

As illustrated in Figure 2, temperature has a much greater effect on the charge-recombination kinetics of 5ANI–PI in [EMIM][Tf₂N] than in pyridine. The rate of charge separation has a weak temperature dependence in both solvents. To understand these results, we need to address the effect of temperature on viscosity of the IL versus pyridine as well as the internal structural dynamics of 5ANI–PI that are coupled to electron transfer. Both conventional³⁹ and IL solvents experience increased viscosity with decreased temperature, but for ILs that change in viscosity is significantly more pronounced.² Compared to [EMIM][Tf₂N], the change in viscosity of pyridine is much smaller over the temperature range used to study the electron-transfer reactions in this work.³⁹ Using the semiempirical relationship between the average solvation time ($\langle \tau_{\text{solv}} \rangle$) and viscosity (η) developed by Maroncelli for ionic liquids,²⁶ and the Arrhenius relationship developed for η ,⁴⁰ we found that the approximate values of $\langle \tau_{\text{solv}} \rangle$ for [EMIM][Tf₂N] range from 2 ns at 256 K to 142 ps at 308 K, Table S1 (Supporting Information). Thus, the observed charge separation and recombination reactions for 5ANI–PI in [EMIM][Tf₂N] are substantially faster than $\langle \tau_{\text{solv}} \rangle$ at all temperatures measured. This result suggests that both charge separation and recombination within 5ANI–PI are more strongly influenced by the fast translational processes in [EMIM][Tf₂N] that contribute to the distribution of solvation times characterized by $\langle \tau_{\text{solv}} \rangle$ rather than the slower motions that are responsible for its bulk viscosity.

In addition to the influence of solvent motions, previous studies have investigated whether internal structural dynamics associated with charge separation and recombination in 5ANI–PI contribute to λ_1 .¹⁵ These studies suggest that, although not important to the charge-separation reaction, the rotation of the pyrrolidine ring about the C–N bond joining it to the naphthalene ring is coupled to the charge-recombination process. The large change in 5ANI–PI charge-recombination rate constant with temperature in [EMIM][Tf₂N] versus pyridine is consistent with the strong dependence of [EMIM][Tf₂N] viscosity on temperature over the range examined. Only the charge-recombination rate constant is affected because the recombination reaction involves a larger λ_1 than does charge separation. An electron-transfer reaction involving a greater structural

change in the donor and/or acceptor should be more dependent on solvent viscosity and therefore the change in viscosity with temperature.

The molecule chosen for this study, 5ANI-PI, represents a prototypical rigid donor-acceptor system for which the electron-transfer dynamics are well characterized in conventional solvents. Transient absorption measurements of this molecule in [EMIM][Tf₂N] reveal charge-separation and recombination-rate constants similar to those of 5ANI-PI in pyridine, which has a comparable static dielectric constant. Temperature-dependence studies show that the charge-recombination pathway is significantly temperature-dependent in the IL only. This result is attributed to a combination of the changes in IL viscosity over the temperature range measured and the larger internal reorganization that 5ANI-PI undergoes upon charge recombination compared to charge separation. This work represents the first experimental example of intramolecular photoinduced electron transfer in an IL. It shows that the unique properties of ILs may be used to control the rates of electron transfer in donor-acceptor systems in ways that are complementary to both conventional organic solvents and liquid crystals. We are currently exploring the scope of this control using a variety of donor-acceptor systems.

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Supporting Information Available: Temperature dependence of the electron-transfer rate constants for both charge separation and recombination and approximate values of $\langle \tau_{\text{solV}} \rangle$ for [EMIM][Tf₂N]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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