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Influence of Chiral Ionic Liquids on Stereoselective Fluorescence Quenching by Photoinduced Electron Transfer in a Naproxen Dyad

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Abstract

In a previous study of a naproxen dyad in a pair of *N*-methylimidazoliummethyl menthylether–NTf2 chiral ionic liquids (*J. Phys. Chem. B* **2008**, *112*, 7555), we observed that though intramolecular electron transfer was impeded, a consistent small stereodifferentiation in the fluorescence lifetime of the dyad was obtained. We proposed that this discrimination was purely electronic in nature and did not arise from geometrical effects, which can influence nonradiative rate processes, such as intramolecular electron transfer. In our present work, we have studied the interaction of the same chiral naproxen dyad molecule in both the previously studied menthyl-based NTf2 ionic liquids and also in bis(tertrabutylphosphonium) (TBP) d-,l-tartrate ionic liquids. Unlike in the menthyl-based IL pair, the amount of quenching is different in the bis(TBP) tartrate enantiomeric liquids and the tartrate enantiomers have a different temperature dependence on the nonradiative rate of the dyad. This chiral discrimination most likely arises from the steric effects of the different conformations of the chiral molecules. We have shown that the viscosity and polarity of the solvents can influence the rate of electron transfer. On the other hand, no such electron transfer quenching is observed in the menthyl-based NTf2 IL solvents. To our knowledge, this is the first example of *chiral* ionic liquids inducing a stereoselective fluorescence quenching by photoinduced, intramolecular electron transfer.

Disciplines

Chemistry | Organic Chemistry | Other Chemistry | Polymer Chemistry

Comments

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In a previous study of a naproxen dyad in a pair of *N*-methylimidazoliummethyl menthylether−NTf_2 chiral ionic liquids (*J. Phys. Chem. B* **2008**, *112*, 7555), we observed that though intramolecular electron transfer was impeded, a consistent small stereodifferentiation in the fluorescence lifetime of the dyad was obtained. We proposed that this discrimination was purely electronic in nature and did not arise from geometrical effects, which can influence nonradiative rate processes, such as intramolecular electron transfer. In our present work, we have studied the interaction of the same chiral naproxen dyad molecule in both the previously studied menthyl-based NTf_2 ionic liquids and also in bis(tertrabutylphosphonium) (TBP) D-,L-tartrate ionic liquids. Unlike in the menthyl-based IL pair, the amount of quenching is different in the bis(TBP) tartrate enantiomeric liquids and the tartrate enantiomers have a different temperature dependence on the nonradiative rate of the dyad. This chiral discrimination most likely arises from the steric effects of the different conformations of the chiral molecules. We have shown that the viscosity and polarity of the solvents can influence the rate of electron transfer. On the other hand, no such electron transfer quenching is observed in the menthyl-based NTf_2 IL solvents. To our knowledge, this is the first example of *chiral* ionic liquids inducing a stereoselective fluorescence quenching by photoinduced, intramolecular electron transfer.

Introduction

Chiral recognition is a very important phenomenon in biochemical systems as well as in technological applications, enabling specific design of pharmaceuticals, chiral sensors, and molecular devices.[1] In asymmetric organic photochemistry, chiral recognition in the excited state is vital to achieve enantioselectivity during photosensitization and quenching processes. As a result, investigation of stereoselective photochemical processes have become an attractive area in recent years,[2,3] and chiral ionic liquids provide a fascinating medium to study stereoselective processes. Only a few examples of chiral ionic liquids have been reported so far. Howarth and co-workers described the use of the chiral imidazolium cation in Diels−Alder reactions.[4] However, the syntheses of these systems required an expensive chiral alkylating agent and elaborate synthetic schemes. The synthesis of ionic liquids employing chiral anions can be more practical owing to the ready availability of many such anions as sodium salts. For example, Seddon and co-workers investigated Diels−Alder reactions in lactate ionic liquids.[5] More recently, Wasserscheid and co-workers synthesized three different groups of chiral ionic liquids.[6] They observed a positive diasteriomeric interaction between racemic substrates of sodium salt of chiral mosher's acid and chiral ionic liquids by NMR spectroscopy. Bao et al. reported the first synthesis of chiral imidazolium ionic liquids derived from natural amino acids.[7] Very recently Warner and co-workers have synthesized amino acid based chiral ionic liquids via anion metathesis reaction between commercially available D- and L-alanine *tert*-butyl ester chloride using a variety of counterions by employing lithium bis(trifluoromethanesulfonimide), silver nitrate, silver lactate, and silver tetrafluoroborate. In addition to NMR, they have used steady-state fluorescence to evaluate chiral recognition and enantioselectivity of the chiral ionic liquids on 2,2,2-trifluoroanthrylethanol, warfarin, and naproxen as chiral fluorophores.[8] Yu et al. have used chiral borate anions and immidazolium cations to synthesize varieties of ionic liquids which consist of both chiral cations and chiral anions.[9]

Armstrong and co-workers have used a variety of methods to synthesize chiral ionic liquids either from chiral starting materials or using asymmetric synthesis.[10] They have provided the first application of chiral ionic liquids as stationary phases in chromatography using chiral ionic liquids as stationary phases in gas chromatography. Several compounds have been separated using these ionic-liquid-based chiral selectors. A large number of compounds, including alcohols, amines, sulfoxides, and epoxides were injected into the chiral-ionic-liquid-based columns. These experiments demonstrate the first successful application of chiral ionic liquids as stationary phases in gas chromatography.[11] Ding et al. have been the first to report the use of chiral ionic liquids inducing irreversible, unimolecular photoisomerization of dibenzobicyclo[2.2.2]octatrienes to chiral products.[12]

Chiral discrimination in excited-state processes has been studied by several groups in the past few years. The groups of Miranda[13−24] and Tolbert[25] have made considerable advances in this domain. In our recent work on *N*-methylimidazoliummethyl menthylether−NTf_2 chiral ionic liquids,[26] we observed a 10% stereodifferentiation in the fluorescence lifetimes of the (*S*)-*N*-methyl-2-pyrrolidinemethyl 2(*S*)-(6-methoxy-2-naphthyl) propionate [(*S*,*S*)-NPX−PYR] dyad as well as in the parent compound, (*S*)-naproxen (*S*-NPX) (Figure 1). This differentiation was shown not to be due to any difference in physical

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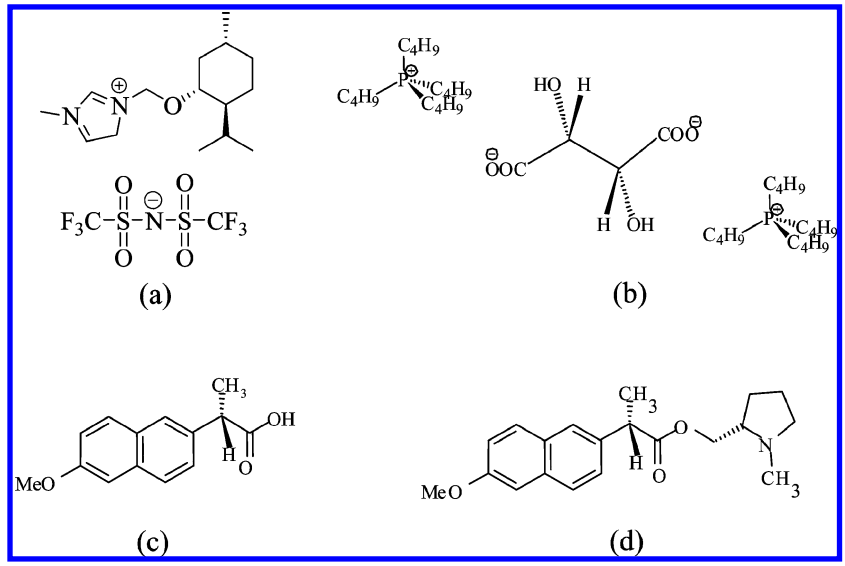
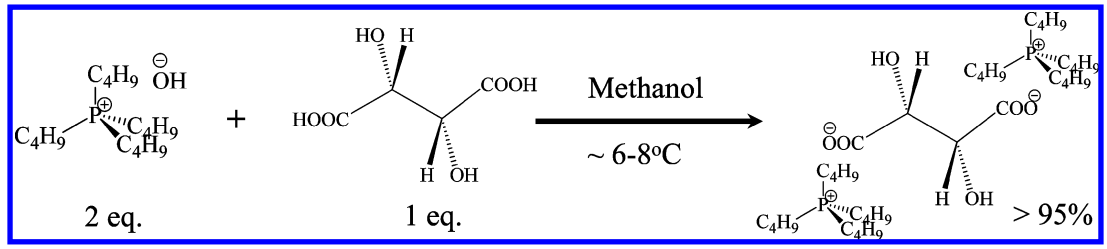


Figure 1. Structures of (a) the chiral *N*-methylimidazoliummethyl menthylether bis(trifluoromethylsulfonyl)imide ionic liquid. (b) L-Dianionic tartrate ionic liquids with TBP (tetrabutylphosphonium) counter cations. (c) (*S*)-(+)-6-Methoxy-2-naphthylpropionic acid [*S*-naproxen, (*S*)-NPX]. (d) (*S*)-*N*-Methyl-2-pyrrolidinemethyl 2(*S*)-(6-methoxy-2-naphthyl) propionate [(*S*,*S*)-NPX−PYR].

SCHEME 1



properties of the ionic liquids (such as viscosity or polarity) or the presence of impurities. The choice of (*S*,*S*)-NPX−PYR as the chromophore was inspired by the work of Miranda and coworkers,[24] who have shown that its diastereomers exhibit different behavior with regard to electron transfer or exciplex formation in polar solvents. We proposed, consequently, that (*S*,*S*)-NPX−PYR would also provide a promising entrée into the study of chiral ionic liquids. But electron transfer, however, was frustrated in the *N*-methylimidazoliummethyl menthylether−NTf_2 chiral ionic liquids (Figure 1a), which we studied at room temperature. In the present work, we perform similar studies in a different pair of optically pure, chiral, enantiomeric ionic liquids, bis(tetrabutylphosphonium) (TBP) D-,L-tartrates (Figure 1b) to investigate further the effects of chiral ionic liquids on excited-state electron transfer. In addition, the temperature dependence of the photophysics of the dyad in both the menthyl-based NTf_2 and bis(TBP) tartrate solvents was investigated. Although photoinduced electron transfer has been studied in ionic liquids, to our knowledge, this would be the first example of *chiral* ionic liquids inducing a stereoselective fluorescence quenching by photoinduced intramolecular electron transfer.

Experimental Section

Materials. Tetrabutylphosphonium (TBP) hydroxide (40 wt % solution in water) and D-,L-tartaric acid were purchased from Aldrich. All HPLC grade organic solvents were obtained from Fisher. For the decolorization of ionic liquids, decolorizing charcoal was purchased from Acros Organics; silica gel for flash chromatography was from Fluorochem; and Celite and alumina were from Aldrich. (*S*)- and (*R*)-(+)-6-Methoxy-α-methyl-2-naphthaleneacetic acid (naproxen, NPX) were purchased from Sigma Aldrich and were used without any further purification. Coumarin 153 (C153) (Exciton Inc., Dayton, OH) was used as received. Acetonitrile (HPLC grade), methanol, acetone, and 99% (*R*)- and (*S*)-2-butanol were purchased from Aldrich and were used as received.

Synthesis of Chiral Dianionic Tartrate ILs with Tetrabutylphosphonium (TBP) Counter Cations. Nonracemic, dianionic, low-melting, colorless organic salts from L-tartaric acid, were prepared by reacting tetrabutylphosphonium hydroxide (2 equiv) with L-tartaric acid (1 equiv) in cold methanol (Scheme 1). L-Tartaric acid (10.000 g, 6.67×10^{-2} mol) was dissolved in methanol (~150 mL) in a round-bottomed flask (500 mL) and kept in an ice water bath (~20 min) in order to lower the solution temperature to ~6−8 °C. Precooled (~5−7 °C) tetrabutylphosphonium hydroxide (40 wt % solution in water: 46.512 mL, 3.33×10^{-2} mol) was gradually added while stirring the cold methanolic tartaric acid solution. Keeping the reaction mixture in an ice−water bath was necessary in order to obtain colorless low melting salts as final products. Otherwise, a pale-yellow color results. Complete removal of the solvent was achieved by first evaporating it in a rotary-evaporator at room temperature to obtain a dense liquid and then keeping the resulting content in a vacuum oven (−30 in. Hg) at room temperature for 3 days. All salts resulted in good yield (>95%) as colorless liquids. Characterizations of the salts are provided in the Supporting Information. The other enantiomer was also synthesized and characterized using identical methods described above for L-tartrate salts.

The syntheses of (*S*,*S*)-NPX−PYR and the *N*-methylimidazoliummethyl menthylether−NTf_2 ionic liquids are described in detail elsewhere.[26] For the methylmenthyl ether based ILs,

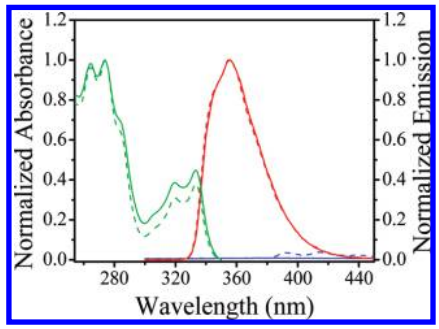


Figure 2. Normalized absorption (green) and emission spectra (red) of the (*S*,*S*)-NPX−PYR dyad in the D- (—) and L- (- - -) tartrate ionic liquid. The fluorescence maximum of the dyad in both of the ILs is ~355 nm. The fluorescence spectra of the ILs (blue) are plotted on the same scale, but their intensity is negligible compared to that of the naproxen derivatives. The fluorescence spectra were obtained by exciting the sample at 266 nm with a 2-nm bandpass.

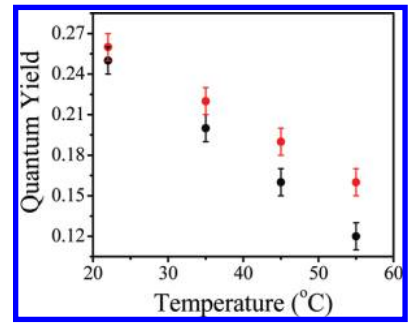


Figure 3. Plot of singlet quantum yields against temperature of the (*S*,*S*)-NPX−PYR dyad in D- (black dots) and L- (red dots) tartrate ionic liquids, obtained from the steady-state emission spectra, taking tryptophan in buffer (pH 7.0) as the standard ($\Phi_{trp} = 0.18$).[34−36] The error bars are based on the average of three measurements. The fluorescence quantum yields are almost same at 22 °C, but they increasingly differ with temperature.

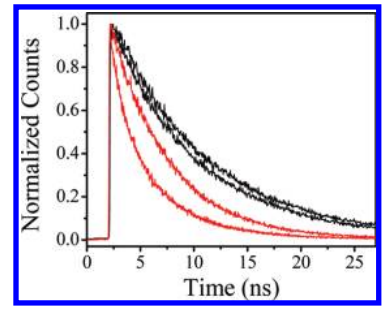


Figure 4. Fluorescence decay traces ($\lambda_{ex} = 266$ nm, $\lambda_{em} \geq 300$ nm) of (*S*,*S*)-NPX−PYR in D-,L-tartrate ionic liquids at room temperature (black) and at 55 °C (red). Traces for all the temperatures are not shown for clarity of presentation. There is an ~10% decrease in the lifetime of (*S*,*S*)-NPX−PYR in D-tartrate compared to that in L-tartrate at room temperature, whereas the difference of lifetime increased with temperature. The lifetimes of (*S*,*S*)-NPX−PYR in the chiral ILs are given in Table 1.

our previously published (vide infra) purification method was used. For the (TBP)−titrate ILs, no decoration method was necessary as they were synthesized with no color by a new procedure reported herein. Viscosity measurements were made with ViscoLab 4000 piston style viscometer from Cambridge Applied system at temperatures 22, 35, 45, and 55 °C.

Steady-State Measurements. Steady-state absorption spectra were obtained on a Hewlett-Packard 8453 UV−visible spectrophotometer with 1-nm resolution. The optical density was ≤0.8 at 266 nm. Steady-state fluorescence spectra were obtained on a Spex Fluoromax-2 with a 2-nm bandpass and corrected for lamp spectral intensity and detector response. For both fluorescence and absorption measurements, a 3-mm path-length quartz cuvette was used. Naproxen and dyad samples were excited at 266 nm, and coumarin 153, at 420 nm.

Fluorescence Lifetime Measurements. Lifetime measurements were acquired using the time-correlated single-photon counting (TCSPC) apparatus described elsewhere.[27,28] The data were acquired in 1024 channels. Usually the time window was chosen to be ≥4 times that of the fluorescence lifetime measured. The instrument response function had a full width at half-maximum (fwhm) of ~50 ps. A 3-mm path length quartz cuvette was used for all the time-resolved measurements. Fluorescence decays were collected at the magic angle (polarization of 54.7°) with respect to the vertical excitation light at 266 nm, with ~30 000 counts in the peak channel.

Results and Discussion

Our chiral ionic liquids are transparent from 380 to 800 nm. Contrary to the report by Samanta and co-workers,[29] who proposed that ionic liquids can be intrinsically colored, we find that their preparation can produce small amounts of strongly absorbing and emitting species, which can present problems in performing and analyzing spectroscopic studies,[30] and that, in fact, these impurities can alter physical properties such as the viscosity. We have used either the protocol cited above to purify these solvents or have taken precautions to make them in colorless form. All the measurements were performed at low temperatures (<70 °C). To ensure that the ionic liquids did not deteriorate on heating, absorbance and fluorescence spectra at all temperatures were monitored and found to be unperturbed.

Representative steady-state absorption and emission spectra of the (*S*,*S*)-NPX−PYR dyad in the two enantiomeric bis(TBP) tartrate ionic liquids, along with the intrinsic fluorescence of the ionic liquids excited at 266 nm, are given in Figure 2. The fluorescence intensity of the ionic liquids is negligible in comparison to that of the solute, verifying the solvents' high level of purity. The chiral dyad molecule showed identical emission spectrum in the bis(TBP) D-,L-tartrate solvents, with peak maxima at 355 nm. In the menthyl-based NTf_2 ionic liquids, the peak maxima are identical, but slightly blue-shifted to 352 nm.

Steady-state spectra were also obtained as a function of temperature. The fluorescence intensity decreased differently for the two tartrate liquids, without any shift in the peak maxima. Steady-state quenching was observed to be higher in the case of the D-isomer. The fluorescence quantum yield (Φ) was calculated using tryptophan in buffer (pH 7.0) as a standard. A clear difference in the extent of quenching of the dyad was observed in the bis(TBP) D-,L-tartrate solvents (Figure 3).

Time-resolved experiments were also performed on the (*S*,*S*)-NPX−PYR dyad in the D-,L-tartrate ionic liquids. A 10% difference in lifetime (~8.9 and ~8.1 ns) is observed in the two chiral solvents at room temperature (Figure 4), which is consistent with our previous results in the menthyl-based ionic liquids.[26] As a control, similar experiments were also done with (*S*)-naproxen, which is the parent compound of the dyad, and the stereodifferentiation in the lifetimes is also observed at room temperature (Figure 5). To ensure that this discrimination is not due to impurities in the ionic liquids, (*S*)- and (*R*)-naproxen were also studied in the same ionic liquids, and a ~10% difference in fluorescence lifetimes was observed for the two naproxen isomers (Table 1). As a further control, lifetimes of the dyad molecule were also determined in (*R*)- and (*S*)-2-

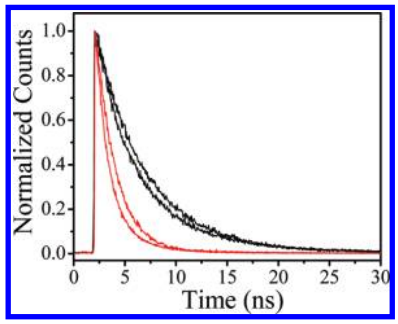


Figure 5. Fluorescence decay traces (λ_{ex} = 266 nm, $\lambda_{em} \geq$ 300 nm) of (*S*)-NPX in D-,L-ionic liquids at room temperature (black) and at 55 °C (red) There is a consistent ~10% decrease in lifetime of (*S*)-NPX in L- compared to that of in D- at room temperature, and this difference of lifetime is conserved with increasing temperature.

TABLE 1: Fluorescence Lifetimes and Steady-State Quantum Yields of (*S*,*S*)-NPX−PYR and (*S*)-NPX in Different Solvents

solute	solvent[a]	temp (°C)	lifetime[b,c] (ns)	Φ[b]
(*S*,*S*)-NPX−PYR	D-IL	22	8.1 ± 0.2	0.25 ± 0.01
	L-IL		8.9 ± 0.2	0.26 ± 0.01
	D-IL	35	6.1 ± 0.2	0.20 ± 0.01
	L-IL		7.1 ± 0.2	0.22 ± 0.01
	D-IL	45	4.3 ± 0.2	0.16 ± 0.01
	L-IL		6.1 ± 0.2	0.19 ± 0.01
	D-IL	55	3.3 ± 0.2	0.12 ± 0.01
	L-IL		5.3 ± 0.2	0.16 ± 0.01
	(*R*)-2-butanol	22	8.6 ± 0.3	
	(*S*)-2-butanol		7.5 ± 0.3	
	acetonitrile		3.2 ± 0.3	
(*S*)-NPX	D-IL	22	5.0 ± 0.2	
	L-IL		4.2 ± 0.2	
	D-IL	55	2.0 ± 0.1	
	L-IL		1.6 ± 0.1	
	acetonitrile	22	7.2 ± 0.2	
(*R*)-NPX	D-IL		4.5 ± 0.2	
	L-IL		3.6 ± 0.2	

[a] IL: Bis(tetrabutylphophonium) (TBP) tartrate ionic liquids. [b] Error bars are based on the average of three measurements. [c] All of the fluorescence lifetimes reported are single exponential, except for that of the D-tartrate at 45 and 55 °C, where they are fit to a sum of two exponentials and an average lifetime is reported.

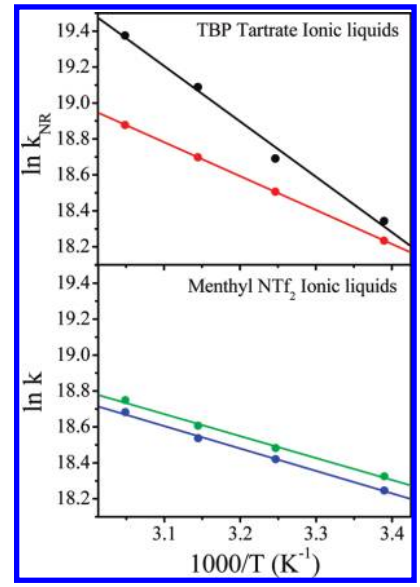


Figure 6. Arrhenius plots obtained from fluorescence lifetimes of the (*S*,*S*)-NPX−PYR dyad in the D- (black dots) and L- (red dots), tartrate ionic liquids (upper panel), and in (+)-(green dots) and (−)-(blue dots) menthyl-based ionic liquids (lower panel). The activation energy, E_a, for the menthyl-based IL pair is almost the same, 2.48 and 2.43 kcal mol^{-1}, but for the tartrates it is 6.2 and 3.7 kcal mol^{-1}, for the D- and L-isomers, respectively, suggesting that electron transfer quenching is occurring in the tartrate ionic liquids, but not in the menthyl-based pair. The frequency factors, *A*, are 3.0 × 10^{12} and 4.9 × 10^{10} s^{-1} for the D- and L-tartrates and 5.8 × 10^{9} and 5.7 × 10^{9} s^{-1} for the (+)- and (−)-menthyls, respectively.

TABLE 2: Viscosity, η (cP), Data for Chiral Ionic Liquids

	η, TBP tartrate		η, menthyl NTf_2	
temp (°C)	D	L	(+)	(−)
22	123 ± 3	125 ± 3	940 ± 10	930 ± 10
35	46 ± 2	46 ± 2	265 ± 5	270 ± 5
45	30 ± 2	31 ± 2	120 ± 3	118 ± 3
55	24 ± 2	23 ± 2	60 ± 2	61 ± 2

The viscosity activation energy ($E_{a,\eta}$) was calculated from the slope of the plot of ln($1/\eta$) versus $1/T$. $E_{a,\eta}$ was larger in the menthyl-based pair than in the tartrate pair: 15.8 and 9.2 kcal/mol, respectively.

butanol. In all cases, the chiral differentiation of lifetimes is consistent (Table 1). This unambiguously indicates that the observed difference in lifetimes is not due to fortuitous impurity quenching, but to solute−solvent interactions.

Lifetime quenching was monitored as a function of temperature, and Arrhenius plots were constructed from the nonradiative rates (assumed to be from intramolecular electron transfer) extracted from the lifetime data. The activation energies are different for the tartrates: 6.2 and 3.7 kcal/mol for the D- and L-forms, respectively. In the case of the menthyl-based pair, they are equal within experimental error: 2.45 kcal/mol (Figure 6). This suggests that the chiral donor−acceptor dyad interacts differently in the two chiral tartrate ionic liquids.

The pyrrolidine moiety in the dyad is a potential electron donor, and the naphthalene ring acts as an acceptor. The interaction of the donor−acceptor moiety (in the excited state) with the two chiral solvents must be sufficiently different to produce different excited-state kinetics. The viscosity and solvent motion play an important role by influencing twisting motion of single bond and chain conformation linking the donor and acceptor moieties. The dependence of viscosity of the ionic liquids on temperature is shown in Table 2. The bis(TBP) tartrate ionic liquids are less viscous than the menthyl-based ionic liquids and most likely favor the attainment of preferred geometries for electron transfer to occur, which is also consistent with the lower viscosity activation energy of the former (Table 2). In our case, the less viscous tartrate ionic liquids, probably allows the pyrrole nitrogen to come into closer proximity with the naphthyl ring by undergoing a conformational change of the donor−acceptor linking chain at higher temperatures, resulting in the electron transfer, which is not seen in highly viscous menthyl-based ionic liquids.

Viscosity is not the sole criterion determining the possibility of electron transfer. The dielectric constant of the solvent or, more appropriately, the micropolarity is equally important because it also influences the radiative and nonradiative rate constants.[31] A detailed study of electron transfer from *N*,*N*-dimethyl aniline (DMA) to pyrene in ionic liquids was undertaken by Paul and Samanta,[32] who made several observations. First, the rate of electron transfer in the ionic liquid is smaller than that in conventional organic solvents, which was attributed to the higher bulk viscosity of the ionic liquids. Second, the rate constant for electron transfer in the ionic liquids

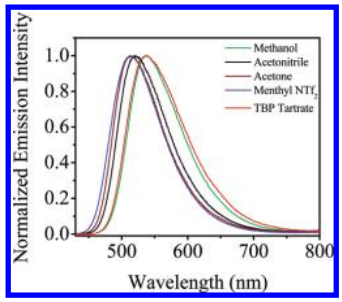


Figure 7. Normalized steady-state emission spectra of C153 in different solvents. The fluorescence spectra were obtained by exciting the sample at 420 nm with a 2-nm bandpass. From the peak maxima, the order of polarity of the solvents is: menthyl ILs < acetone < acetonitrile < tartrate ILs ≈ methanol. The $E_T(30)$ values of the menthyl ionic liquids are 41.1 and 41.3, and those of tartrate ionic liquids are 53.3 and 53.5.

is in general 2−4 times larger than the diffusion controlled values. This was attributed to the difference between microviscosity and bulk viscosity in ionic liquids, which was originally suggested by Skrzypczak and Neta.[33] Third, as in our case, no exciplex emission was observed in any of the ionic liquids studied, which is striking given that the DMA−pyrene system is well-known for exciplex formation in conventional bulk solvents. The lack of exciplex formation led the authors to conclude that it is the microscopic and not the bulk polarity that could be related to the $E_T(30)$ scale that determines the formation of exciplex in ionic liquids.

In order to determine the relative polarity of the ionic liquids studied here, steady-state emission spectra of coumarin 153 have been obtained in a series of solvents. Coumarin 153 (C153) is an extremely well-studied solvatochromic probe, whose emission is highly sensitive to solvent polarity. From Figure 7, it can be seen that the emission of C153 in the bis(TBP) tartrate ionic liquids is red-shifted compared to that in the menthyl-based NTf_2 ionic liquids. Thus the former being more polar, solvates the charge transferred polar excited state of the dyad, imparting more stability and in turn facilitates electron transfer, which is absent in the menthyl-based ionic liquids.

Conclusion

In our previous work,[26] we observed that, although electron transfer was frustrated in the menthyl-based NTf_2 ionic liquids, still a consistent small stereodifferentiation in the fluorescence lifetime of (*S*,*S*)-NPX−PYR and (*S*)-naproxen was obtained. We proposed that this discrimination was purely electronic in nature and did not arise from geometrical effects, which can influence nonradiative rate processes, such as intramolecular electron transfer. In our present work, we have studied the interaction of the same chiral naproxen dyad molecule in both the previously studied menthyl-based NTf_2 ionic liquids and also in bis(tertrabutylphosphonium) tartrate ionic liquids. Unlike in the menthyl pair, the amount of quenching is different in the bis(TBP) tartrate isomeric liquids; and the tartrate enantiomers have a different temperature dependence on the nonradiative rate of the dyad. This chiral discrimination most likely arises from the steric effects of the different conformations of the chiral molecules. We have shown that viscosity and polarity of the solvents can influence the rate of electron transfer. On the other hand, no such electron transfer quenching is observed in the menthyl-based NTf_2 solvents. To our knowledge, this is the first example of *chiral* ionic liquids inducing a stereoselective fluorescence quenching by photoinduced, intramolecular electron transfer. It is noteworthy that we have observed chiral discrimination by ionic liquids on both radiative and nonradiative processes.

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Supporting Information Available: Structural characterization of the bis(TBP) tartrate ionic liquids. This material is available free of charge via the Internet at http://pubs.acs.org.

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