6-10-2008

Influence of Chiral Ionic Liquids on the Excited-State Properties of Naproxen Analogs

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Abstract

The synthesis and decolorization of chiral room-temperature ionic liquids based upon 1-methyl imidazole and chloromethyl menthyl ether is reported. The excellent optical quality of these solvents permits the investigation of the effects of the two enantiomers on the excited-state photophysics of (*S*)-*N*-methyl-2-pyrrolidinemethyl 2(*S*)-(6-methoxy-2-naphthyl)propionate [(*S*,*S*)-NPX-PYR]. Whereas in conventional bulk polar solvents such as acetonitrile, (*S*,*S*)-NPX-PYR is known to execute excited-state intramolecular electron transfer and to form exciplexes, in these chiral solvents these nonradiative processes are absent. The chiral solvents do, however, induce a small but reproducible (~10%) stereodifferentiation in the fluorescence lifetime of (*S*,*S*)-NPX-PYR as well as in the parent compound, (*S*)-naproxen. To our knowledge, this is the first example of chiral ionic liquids inducing such an effect on photophysical properties.

Disciplines

Chemistry | Organic Chemistry | Other Chemistry | Polymer Chemistry

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Received: December 6, 2007; Revised Manuscript Received: March 28, 2008

The synthesis and decolorization of chiral room-temperature ionic liquids based upon 1-methyl imidazole and chloromethyl menthyl ether is reported. The excellent optical quality of these solvents permits the investigation of the effects of the two enantiomers on the excited-state photophysics of (*S*)-*N*-methyl-2-pyrrolidinemethyl 2(*S*)-(6-methoxy-2-naphthyl)propionate [(*S*,*S*)-NPX-PYR]. Whereas in conventional bulk polar solvents such as acetonitrile, (*S*,*S*)-NPX-PYR is known to execute excited-state intramolecular electron transfer and to form exciplexes, in these chiral solvents these nonradiative processes are absent. The chiral solvents do, however, induce a small but reproducible (∼10%) stereodifferentiation in the fluorescence lifetime of (*S*,*S*)-NPX-PYR as well as in the parent compound, (*S*)-naproxen. To our knowledge, this is the first example of chiral ionic liquids inducing such an effect on photophysical properties.

Introduction

Although the number of publications on room temperature ionic liquids (ILs) is continually increasing, only a few examples of chiral ILs have been reported so far. Howarth and co-workers described the use of chiral imidazolium cation in Diels−Alder reactions.[1] However, the synthesis of these systems required an expensive chiral alkylating agent. The use of ILs with chiral anions is somehow more obvious since some of these are readily available as sodium salts. For example, Seddon and co-workers investigated Diels−Alder reactions in lactate ILs.[2] More recently, Wasserscheid and co-workers synthesized three different groups of chiral ILs.[3] They observed the positive diasteriomeric interactions between racemic substrates and chiral IL by NMR spectroscopy. Bao et al. reported the first synthesis of chiral imidazolium ILs derived from natural amino acids.[4]

Armstrong and co-workers have provided the first application of chiral ILs as stationary phases in chromatography using chiral ILs stationary phases in gas chromatography. Several compounds have been separated using these IL-based chiral selectors. A large number of compounds, including alcohols, amines, sulfoxides, and epoxides were injected into the chiral ILs columns. These experiments demonstrate the first successful application of chiral ILs as stationary phases in gas chromatography.[5]

Chiral discrimination in excited-state processes has been studied by several groups in the past few years. The groups of Miranda[6–17] and Tolbert[18] have made considerable advances in this domain, and they cite a rather copious literature.

In this work we investigate the behavior of (*S*)-N-methyl-2-pyrrolidinemethyl 2(*S*)-(6-methoxy-2-naphthyl)propionate [(*S*,*S*)-NPX-PYR] (Figure 1) in two enantiomeric chiral ILs based upon chloromethyl menthyl ether. The choice of (*S*,*S*)-NPX-PYR as the chromophore was inspired by the work of Miranda and co-workers who have shown that its diastereomers exhibit different behavior with regard to electron transfer or exciplex formation.

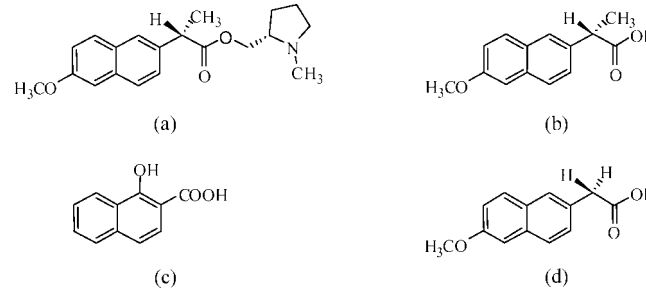

Figure 1. Structures of (a) (*S*,*S*)-NPX-PYR, (b) (*S*)-(+)-6-methoxy-2-naphthylpropionic acid [naproxen, NPX], (c) 1-hydroxy 2-naphthoic acid, and (d) 6-methoxy-2-naphthalene acetic acid.

It was felt, consequently, that (*S*,*S*)-NPX-PYR would also provide a promising entrée into the study of chiral ILs. Although these effects are small, they are larger than those predicted by Craig and Mellor[19] and by Dissado[20] for chiral discrimination of *purely electronic* phenomena.

Experimental Section

Materials. 1-Methylimidazole, (+)/(−)-chloromethyl menthyl ether, and bis(trifluoromethane)-sulfonimide lithium ($LiNTf_2$) salt were purchased from Aldrich. All high-performance liquid chromatography grade organic solvents were obtained from Fisher. For the decolorization of ILs, decolorizing charcoal was purchased from Acros Organics, silica gel for flash chromatography from Fluorochem, and celite and alumina from Aldrich. (*S*)- and (*R*)-NPX (98% purity) and 1-hydroxy-2-naphthoic acid (≥99% purity) were purchased from Aldrich and used as received. 6-Methoxy-2-naphthalene acetic acid (≥99% purity) was purchased from Cayman Chemicals and was used as received. C153 was purchased from Exciton Inc. (Dayton, OH) and used without further purification.

Synthesis of (*S*,*S*)-NPX-PYR. The procedure described elsewhere was followed.[17] To a stirred solution of (*S*)-(+)-6-methoxy-2-naphthylpropionic acid (0.50 g, 2.17 mmol) in dichloromethane (CH_2Cl_2) (20 mL) thionyl chloride (1.21 mL, 16.6 mmol) was added. The resulting mixture was then boiled for 2 h before

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10.1021/jp711508b CCC: $40.75
Published on Web 06/10/2008

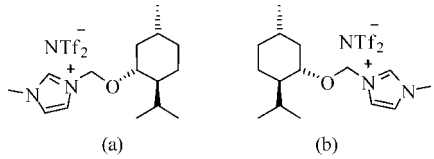
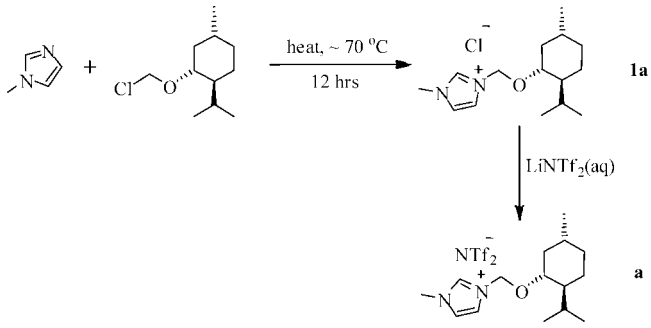


Figure 2. Structures of (a) (−)- and (b) (+)-room temperature ILs (RTILs), which were synthesized from (−)- and (+)-chloromethyl menthyl ether, respectively.

SCHEME 1



cooling to room temperature. The solution was then concentrated in vacuo, and the residue was directly used for the next step. To a stirred solution of (*S*)-*N*-methyl-2-pyrrolidinemethanol (0.27 mL, 2.28 mmol) in CH_2Cl_2 (5 mL) at 0 °C triethyl amine (0.48 mL, 3.47 mmol) was added. The mixture was stirred at 0 °C for 5 min whereupon a solution of the material prepared above (unpurified acid chloride) was added. The resulting solution was stirred at 0 °C for 30 min and then for 1 h at room temperature. The reaction was quenched by the addition of saturated ammonium chloride solution and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were then dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified via flash chromatography (100% ethyl acetate) to provide the desired compound. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.42−1.52 (1H, m), 1.59 (3H, d, J = 6.8 Hz), 1.62−1.85 (3H, m), 2.13−2.21 (1H, m), 2.30 (3H, s), 2.35−2.43 (1H, m), 2.96−3.03 (1H, m), 3.89 (1H, q, J = 6.8 Hz), 3.90 (3H, s), 4.02−4.12 (2H, m), 7.10−7.16 (2H, m), 7.42 (1H, dd, J = 8.4, 1.6 Hz), 7.66−7.72 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 18.6, 23.1, 28.5, 41.6, 45.6, 55.5, 57.9, 63.9, 67.3, 105.7, 119.1, 126.2, 126.5, 127.3, 129.1, 129.5, 133.9, 135.9, 157.8, 174.9.

Synthesis and Decoloration of Nonracemic Low-Melting Organic Salts. Room-temperature nonracemic ILs (**a**) and (**b**) (Figure 2) were prepared according to a previously published procedure.[21−23] Briefly (Scheme 1), (−)-chloromethyl menthyl ether (10.00 mL, 4.85 × 10^{-2} mol) was stirred for 12 h with a slight excess of 1-methylimidazole (4.260 mL, 5.34 × 10^{-2} mol) while heating at ~70 °C in a round-bottomed flask (50 mL) attached to a refluxing condenser. The resulting salt (**1a**) was dissolved in deionized water (~5 mL). To purify the chloride salt from any unreacted 1-methylimidazole present in the aqueous solution, simple liquid−liquid extractions were carried out five times with five portions (10 mL) of ethyl acetate using a separatory-funnel (250 mL). The aqueous layer containing the chloride salt was separated, and an aqueous solution (10 mL) containing $LiNTf_2$ (16.48 g, 5.74 × 10^{-2} mol) was added to carry out the metathesis process. Room-temperature chiral IL (**a**) was separated as a hydrophobic layer and extracted using CH_2Cl_2 (3 × 5 mL portions). The CH_2Cl_2 containing the IL was washed with water (6 × 20 mL) and dried with anhydrous sodium sulfate (20 g), which was removed by filtration. The filtrate was heated in vacuo at 40 °C to remove the excess solvent. The product was obtained as a pale-yellow liquid (23.40 g, 4.402 × 10^{-2} mol, > 90% yield). The same technique was carried out to synthesize (**b**).

TABLE 1: Characteristics of Chiral ILs

RTIL[a]	viscosity (cP)	weight % H_20	τ_R (ns)[b]
(+)	940 ± 5.0	0.07	22.0 ± 0.5
(−)	920 ± 5.0	0.06	21.0 ± 0.5

[a] Both the ILs show an ~1.5 ns average fluorescence lifetime (λ_{ex} = 266 nm, $\lambda_{em} \geq$ 300 nm). Their fluorescence spectra are presented in Figure 3. [b] Rotational diffusion time of coumarin 153 in each of the ILs. Fluorescence anisotropy decays were single exponential.

Both synthesized ILs were decolorized according to a procedure described previously.[24] Briefly, a column was prepared as follows. A conventional column used for flash chromatography was packed with the following compounds: celite on the bottom to trap charcoal particles; flash chromatographic silica gel and alumina in the middle for decolorizing/removal of polar and inorganic impurities; charcoal on the top for decolorizing.[24] The column was treated with CH_2Cl_2 (3 × 200 mL). The ILs were dissolved in CH_2Cl_2 (200 mL) and passed through the column. Dichloromethane (200 mL) was passed through the column to elute the remainder of the IL. To purge the IL through the column, N_2 gas was passed over the column. The eluted solution was then concentrated under reduced pressure and finally by heating at 60 °C in vacuo overnight. The structures were validated using ^{1}H NMR and ESI-MS.

Viscosity measurements were made with a ViscoLab 4000 piston style Viscometer from Cambridge Applied system at 22.3 ± 0.1 °C. The viscosities of the ILs did not change over chromophore concentrations providing absorbances of 0.1−0.8 (at 266 nm in a 3-mm path length cuvette, the conditions over which our optical measurements were made, see below). The relative viscosity of the two enantiomeric ILs was also assessed by measuring the rotational diffusion time, τ_R, of the fluorescent probe, coumarin 153. Within experimental error, τ_R, was same in both solvents (Table 1). Water content was assessed with a coulometric Karl Fischer Titration (Mettler Toledo DL 39).

Sample Preparation. A small amount of chromophore was added to chiral ILs and kept overnight at room temperature to ensure complete solubilization as the ILs were viscous. These solutions were used for steady-state and time-resolved measurements. The absorbance at 266 nm was maintained between 0.1−0.8 to avoid the inner filter effect. Results were found to be identical for a given sample throughout the absorbance range mentioned above. For all measurements, a 3-mm path-length quartz cuvette was used. All experiments were done at room temperature.

Steady-State and Time-Resolved Measurements. UV−visible absorption spectra were obtained on Hewlett-Packard 8453 UV−visible spectrophotometer with 1-nm resolution. Fluorescence spectra were obtained on a Spex Fluoromax-2 with a 2-nm bandpass and corrected for lamp spectral intensity and detector response. The apparatus for time correlated single photon counting is described elsewhere.[25] Briefly, the fundamental from the homemade mode-locked Ti−sapphire oscillator was modulated by a Pockels cell (Model 350−160, Conoptics Inc.) to reduce the repetition rate to 8.8 MHz. The excitation source (266 nm) was generated by sum frequency generation of the fundamental red light (~800 nm) and the second harmonic blue light (~400 nm) using an U-Oplaz Technologies frequency tripler (Model TP-2000B). Fluorescence decay traces were

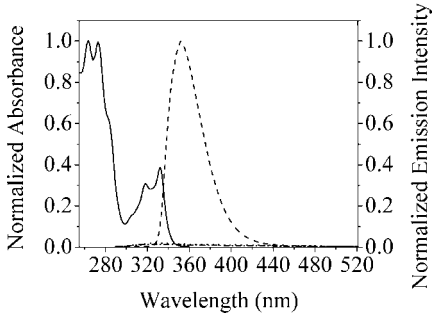


Figure 3. Normalized absorption (solid line) and fluorescence emission (dashed line) spectra of (*S*,*S*)-NPX-PYR in (+)-RTIL. The fluorescence maximum is at 352 nm. Dotted and dash−dotted lines represent emission from the (+)- and (−)-RTIL. The fluorescence spectra of the chiral solvents are plotted on the same scale, and 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.

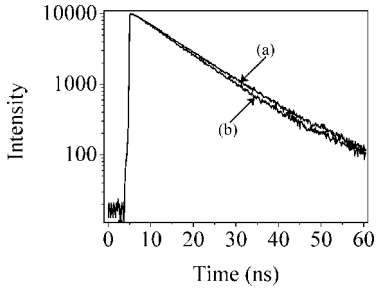


Figure 4. Fluorescence decay traces (λ_{ex} = 266 nm, $\lambda_{em} \geq$ 300 nm) of (*S*,*S*)-NPX-PYR in (a) (−)- and (b) (+)-RTIL. There is an ∼10% decrease in lifetime of (*S*,*S*)-NPX-PYR in (+)-RTIL compared to that of in (−)-RTIL. The lifetime of (*S*,*S*)-NPX-PYR in acetonitrile is ∼3.1 ns in acetonitrile due to intramolecular electron transfer. In the chrial RTILs, the lifetime is significantly increased and there is a difference in lifetime in the two solvents (Table 2).

recorded by exciting the sample at 266 nm and collecting the emission at ≥300 nm by using a microscope slide to filter out the exciting source. Fluorescence decays were collected at the magic angle (polarization of 54.7°) with respect to the vertical. To obtain the rotational dynamics of coumarin 153, samples were excited at 407 nm, and emission was collected parallel and perpendicular to the polarization of the excitation light. For fluorescence lifetime measurements, typically ∼10000 counts were collected at the peak channel, except for 6-methoxy-2-naphthalene acetic acid in chiral IL where ∼ 5000 counts were collected at the peak channel.

Results and Discussion

Our chiral ILs are transparent from 390 to 800 nm. Contrary to the report by Samanta and co-workers[26] who proposed that ILs can be intrinsically colored, we find that their preparation can introduce small amounts of strongly absorbing and emitting species, which can present problems in performing and analyzing spectroscopic studies,[27] and that, in fact, these colored impurities can alter physical properties such as the viscosity. We have used the protocol cited above to purify these solvents.

Representative normalized steady-state absorption and emission spectra of (*S*,*S*)-NPX-PYR in (+)-RTIL are shown in Figure 3, as well as the fluorescence spectra of the chiral solvents. Figure 4 presents the fluorescence lifetime decay of (*S*,*S*)-NPX-PYR in the (+)- and (−)-RTIL respectively, where a stereo differentiation of ∼10% was observed with lifetime value of ∼10.5 ns (Table 2). Earlier Miranda and co-workers reported

TABLE 2: Fluorescence Lifetime Parameters of (*S*,*S*)-NPX-PYR and Related Systems

System	τ (ns)[a]
(*S*,*S*)-NPX-PYR; (+)-RTIL	10.0 ± 0.3
(*S*,*S*)-NPX-PYR; (−)-RTIL	10.9 ± 0.2
(*S*)-NPX; (+)-RTIL	10.8 ± 0.3
(*S*)-NPX; (−)-RTIL	9.7 ± 0.3
(*S*)-NPX; acetonitrile	7.2 ± 0.2
(*S*,*S*)-NPX-PYR; acetonitrile	3.1 ± 0.5
1-hydroxy-2-naphthoic acid; (+)-RTIL	2.4 ± 0.2
1-hydroxy-2-naphthoic acid; (−)-RTIL	2.4 ± 0.2
6-methoxy-2-naphthalene acetic acid; (+)-RTIL	11.5 ± 0.2
6-methoxy-2-naphthalene acetic acid; (−)-RTIL	11.5 ± 0.2

[a] The error bars are based on the average of three measurements. Fluorescence lifetime decays were fit to a single-exponential model.

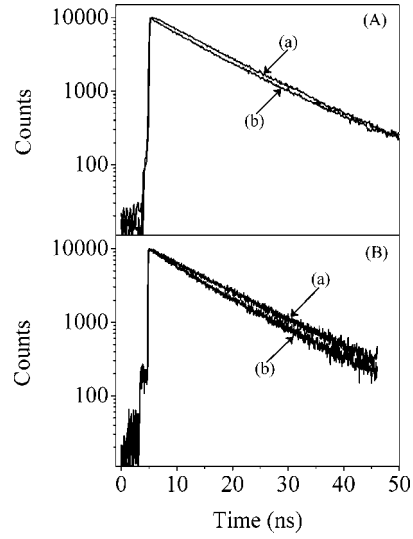


Figure 5. (A) Fluorescence decay traces (λ_{ex} = 266 nm, $\lambda_{em} \geq$ 300 nm) of (*S*)-NPX in (a) (+)- and (b) (−)-RTIL. (B) Fluorescence decay traces (λ_{ex} = 266 nm, $\lambda_{em} \geq$ 300 nm) of (a) (*R*)- and (b) (*S*)-NPX in (−)-RTIL. Both systems, (*S*)-NPX in (+)/(−)-RTIL and (*S*)-/(*R*)-NPX in (−)-RTIL, show an ∼10% difference in lifetime. The lifetime of (*S*)-NPX is comparable with (*S*,*S*)-NPX-PYR in these two ILs, which indicates no quenching by intramolecular electron transfer or exciplex formation.

fluorescence lifetimes of (*S*)-NPX, (*S*,*S*)-NPX-PYR, and (*R*,*S*)-NPX-PYR in acetonitrile as 7.4, 3.0, and 2.3 ns, respectively.[17] Thus, the presence of the longer lifetime of (*S*,*S*)-NPX-PYR in the chiral ILs studied was surprising and suggested that the two partners of the dyad were not participating in either electron transfer or exciplex formation, which was the observation of Miranda and co-workers in acetonitrile. As a control experiment, we studied the photophysics of the parent molecule, (*S*)-NPX, in the two chiral ILs and found similar lifetimes with a stereo differentiation of ∼10% as well, thus indicating that the PYR moiety is not interacting with NPX in the chiral ILs. Figure 5 presents the fluorescence decays of (*S*)-NPX in the (+)- and (−)-RTIL, respectively; the fluorescence decay of (*R*)-NPX in (−)-RTIL is also shown. Steady-state fluorescence measurements of (*S*,*S*)-NPX-PYR and (*S*)-NPX in the two chiral ILs did not provide any evidence of exciplex formation—i.e., an emission band to the red at ∼550 nm. On the basis of these results, we conclude that the stereodifferentiation observed in the dyad is not due to nonradiative processes between the two moieties because if this were the case we would not have seen similar lifetime values in (*S*)-NPX.

To test whether the observed stereodifferentiation in the lifetimes is not due to the presence of impurities in the chiral RTILs, it was

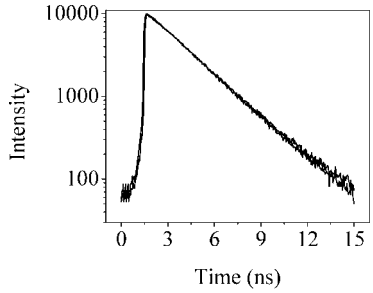


Figure 6. Fluorescence decay traces ($\lambda_{ex} = 266$ nm, $\lambda_{em} \geq 300$ nm) of 1-hydroxy-2-naphthoic acid in (+)- and (−)-RTIL. Its fluorescence lifetime in the two chiral ILs is identical, ~2.4 ns.

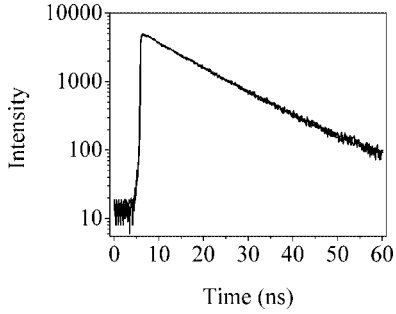


Figure 7. Fluorescence decay traces ($\lambda_{ex} = 266$ nm, $\lambda_{em} \geq 300$ nm) of 6-methoxy-2-naphthalene acetic acid in (+)- and (−)-RTIL, showing identical fluorescence lifetimes of ~11.5 ns.

TABLE 3: Comparison of (*S*)- and (*R*)-NPX

system	τ (ns)[a]	Φ_f[b]
(*S*)-NPX; (+)-RTIL	10.8 ± 0.3	0.38 ± 0.02
(*S*)-NPX; (−)-RTIL	9.7 ± 0.3	0.36 ± 0.02
(*R*)-NPX; (+)-RTIL	12.0 ± 0.2	–
(*R*)-NPX; (−)-RTIL	10.9 ± 0.2	–

[a] The error bars are based on the average of three measurements. Fluorescence lifetime decays were fit to a single-exponential model. [b] Fluorescence quantum yield. The quantum yield values of (*S*)-NPX in chiral RTILs were calculated taking tryptophan/buffer (pH = 7.0) as standard ($\Phi_f^{Trp} = 0.18$).[36–38]

necessary to study the fluorescence lifetime of some suitable achiral probe in them. A naphthalene-based achiral probe molecule that is soluble in them is 1-hydroxy-2-naphthoic acid, which yields identical lifetimes in the (+)- and (−)-ILs, is shown in Figure 6. Another test case is provided by 6-methoxy-2-naphthalene acetic acid, whose fluorescence lifetime decays in the (+)- and (−)-RTILs are presented in Figure 7 and which give identical time constants of 11.5 ns. These results strongly suggest that the difference in fluorescence lifetimes observed in either (*S*)-NPX and (*S*,*S*)-NPX-PYR are entirely due to the presence of the chiral centers in the naproxen analogs. Furthermore, to ensure that the difference in lifetime is not induced by slight differences in the physical properties of the chiral RTILs (Table 1), we have measured lifetimes of (*R*)- and (*S*)-NPX in (−)-RTIL. These enantiomers also reflect an ~10% difference in lifetime (Table 3). This unambiguously indicates that the differences observed here are entirely due to chiral solute−solvent interactions.

This is the first example of which we are aware where electron transfer is frustrated in an IL. Naively on the basis of the emission maximum of the probe molecule, coumarin 153, our ILs are slightly less polar than acetone on an $E_T(30)$ scale (Figure 8). The most likely conclusion to draw is that the local environment of the solute with respect to the solvent differs drastically from what is expected based upon a measurement

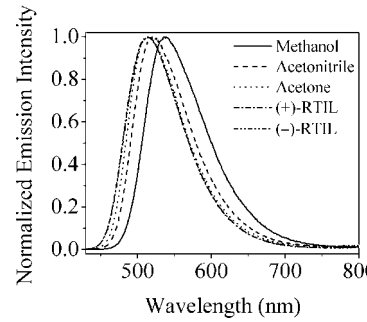


Figure 8. Normalized steady-state emission spectra of C153 in different solvents. The excitation wavelength is 420 nm. The $E_T(30)$ values were obtained from the peak maxima as determined from log-normal fits to the spectra. The $E_T(30)$ values were found to be 41.1 and 41.3 for the (+)- and (−)-RTIL, respectively, slightly less than the corresponding value in acetone, 42.2.

of the bulk properties. There is a growing body of literature that deals with electron transfer in ILs, and differences with respect to polar solvents have been generally noted. The majority of these studies deal with intermolecular quenching. Skrzypczak and Neta have studied electron transfer between pyridinyl and alkylpyridinyl radicals and duroquinone by pulse radiolysis.[28] They found that the rate constant of the reaction is significantly higher in ILs compared to the diffusion-controlled value, whereas in conventional solvents these corresponding rate constants are only slightly higher. This was explained by proposing voids between molecules of the ILs and the possibility of the diffusion of reacting species through the segment of ions while the bulk viscosity reflects overall movement of whole ions. Photoinduced electron transfer between dicyclopentadiene and 2,4,6-triphenylthiapyrylium in [$BMIM^+$][PF_6^-] was measured by Garcia and co-workers and compared to that in zeolite.[29] These authors also demonstrated that the rate of electron transfer in IL is slower compared to that of in conventional organic solvents which was attributed to the higher bulk viscosity in ILs.

A detailed study on electron transfer from *N*,*N*-dimethyl aniline (DMA) to pyrene in ILs was undertaken by Paul and Samanta,[30] who made several observations. First, the rate of electron transfer in the IL is smaller than that in conventional organic solvents, which was attributed to the higher bulk viscosity of the ILs. Second, the rate constant for electron transfer in the ILs is in general 2−4 times larger than the diffusion controlled values. This was attributed to the difference between microviscosity and bulk viscosity in ILs, which was originally suggested by Skrzypczak and Neta.[28] Third, no exciplex emission was observed in any of the ILs 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 which could be related to the $E_T(30)$ scale that determines the formation of exciplex in ILs.

The quenching of 9,10-dicyanoanthracene by a series of electron donors was investigated in two ILs, which differ in the length of the alkyl chains.[31] In this study the rate of the quenching reactions was also found to be larger than that predicted from the diffusion-controlled value. Moreover the solvent reorganization energies were found to be lower than that of conventional polar solvents. In the electron transfer reaction from metal complexes to oxygen in imidazolium ILs where a dramatic acceleration of reaction rate was observed which was attributed to the stabilization of the oxygen radical

anion through coordination with the acidic C2−H of imidazolium ILs.[32] Theoretical aspects of electron transfer in ILs were discussed by Kim and co-workers.[33,34]

The literature on the corresponding intramolecular quenching in ILs is rather sparse. Lockard and Wasielewski studied intramolecular charge separation and recombination within 4-(*N*-pyrrolidino)naphthalene-1,8-imide-pyromellitimide (5ANI-PI) in $[EMIM^+][NTf_2^-]$.[35] The authors found the rate constants for both photoinduced charge separation and recombination in ILs are comparable to those in pyridine, which has a static dielectric constant similar to that of the IL. The observed rate constants are intermediate between the corresponding values in acetonitrile and toluene, which was considered to represent relatively polar and nonpolar solvents. This suggests that the observed rate constants track the bulk polarity of the solvents, which is in contrast to Samanta's work on intermolecular electron transfer from DMA to pyrene.

Conclusions

While the effects we observe are in general smaller than those reported by, for example, the groups of Miranda and Tolbert, it should be noted that these workers monitored spectral and kinetic changes that were intimately coupled to steric factors. It seems that our results are purely electronic in nature, as there is evidence of neither electron transfer nor exciplex formation for (*S*,*S*)-NPX-PYR in the chiral ILs.

Earlier work[19,20] has provided an analysis and an estimate of the effect of chiral discrimination on optical spectra. The crucial term in the Hamiltonian giving rise to these effects is an electric-magnetic cross term in the total dispersion energy. Because of the relative size of magnetic and electric dipole couplings, chiral discrimination based upon these factors has been estimated to be ∼0.1%. The effects observed here are manifested in the radiative rate of the chromophores and are much larger than those predicted,[19,20] being ∼10%.

In conclusion, we report here the first example of photophysical stereodifferentiation induced by chiral ILs. This differentiation does not appear to result from geometrical effects influencing nonradiative rates such as intramolecular electron transfer or exciplex formation. It is remarkable that the ILs deactivate these nonradiative processes. Insofar as magnetic effects are believed to lie at the origin of such effects, it would be interesting to measure their magnitude as a function of magnetic field strength, and current work along those lines is being pursued in our laboratory.

Acknowledgment. D.W.A. thanks the Robert A. Welch Foundation (Y-0026) for its support. We thank Professor Xueyu Song for helpful discussions.

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JP711508B