Photochromism of Spiropyran in Ionic Liquids: Enhanced Fluorescence and Delayed Thermal Reversion

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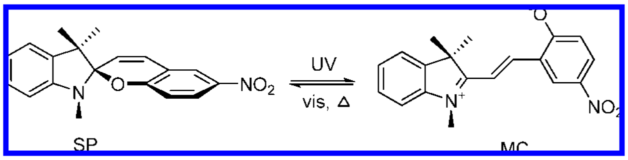
Received: January 15, 2009; Revised Manuscript Received: March 2, 2009

Photochromism of spiropyran and thermal reversion of MC in a series of imidazolium-based ionic liquids (ILs) were investigated via fluorescence and UV−vis absorption spectra. The fluorescence emission maxima (λ_{em}) of the colored merocyanine (MC) form is polarity dependent in all ILs and fluorescence intensity enhancement was first observed in ILs with respect to that observed in organic solvents (e.g., in [HOMIm][PF_6], nearly 32-fold enhancement than ethanol). Moreover, the thermal decay of MC in all ILs is uniformly first order, and in comparison with polar solvents possessing comparable polarity (such as ethanol and acetonitrile), a significant retardation of the decay rate and increase of half-lifetime of MC form was observed, in particular at elevated temperature (e.g., at 313 K, MC decay with k of 5.19×10^{-4} and 34.7×10^{-4} s^{-1} in [BMMIm][BF_4] and ethanol, respectively). Abnormal thermodynamics of the thermal decay of MC in ILs were observed, activation energies in less polar ILs (88−97 kJ mol^{-1}) have a larger value than in polar ILs (70−82 kJ mol^{-1}), opposite that in organic solvents (70−80 kJ mol^{-1} in nonpolar solvents and around 100 kJ mol^{-1} in polar solvents), and all ILs exclusively exhibit minus activation entropies (−85.4 to −24.5 J K^{-1} mol^{-1}), similar to that of nonpolar solvents. Desolvation due to the conformational change during the thermal reversion between MC and the transition state may be the key to interpret this experimental result.

1. Introduction

Photochromism of molecules has recently been the subject of much attention due to its potential applications in the development of optical waveguides, light modulators, optical storage media, and other optical solid-state devices.[1] Of particular interest is a class of photochromic compounds known as spiropyrans, which have been extensively studied due to their excellent characteristics such as high fatigue resistance and good quantum yields.[2] Generally, spiropyran exists in the dark as closed colorless form (SP) that absorbs light predominantly in the ultraviolet region due to less polar and conjugated structure with reciprocally orthogonal fragments. The transition from the thermodynamics more stable closed form to the open colored form can be induced by irradiation with UV light. It has been confirmed by experiment and quantum-chemical calculations that the open form exists as neutral quinoid in nonpolar solvents whereas the zwitterionic merocyanine (MC) form is predominant in polar solvents. The latter has a dipolar planar structure with delocalized π-electrons, which exhibit long-wavelength absorption and can thermally or photochemically (>400 nm) convert back to SP. Thus, spiropyrans are able to undergo reversible structural transformation between SP and MC (Scheme 1), with significant changes in their photochemical and photophysical properties. However, the application of spiropyran is inevitably limited by the fact that MC is thermally unstable. General approaches to stabilize the MC include inhibiting the thermal reversion through proton,[3] polar solvents such as fluoroalcohols,[4] metal ion to complex with the phenolate,[5] or incorporating SP into rigid matrixes such as polymers and sol gels.[6] Moreover, it was reported that fluorescence of spiropyran (exclusively stem from the emission of MC) is enhanced with addition of metal ions to chelate with the induced phenolate.[5b] Photodynamic

SCHEME 1: Photochromism of Spiropyran between the Closed (SP) and Open (MC) Forms



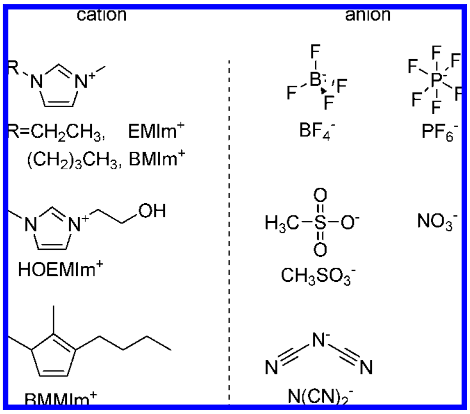


Figure 1. ILs used in this study and their structures.

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10.1021/jp9004218 CCC: $40.75

TABLE 1: Photophysical Constants of MC in ILs and Organic Solvents at 298 K

substance	λ_{max} (nm)	E_{SP} (kcal mol^{-1})	λ_{em} (nm)
hexane	620[a]	46.1	
toluene	596[b]	48.0	655[b]
1,4-dioxane	590[a]	48.5	
THF	584	49.0	654[b]
acetone	565[a]	50.6	634
DMF	560[a]	51.1	
acetonitrile	555[a]	51.5	634
ethanol	537	53.2	622
[BMIm][BF_4]	542	52.8	601
[BMMIm][BF_4]	552	51.8	600
[EMIm][BF_4]	533	53.6	609
[EMIm][$N(CN)_2$]	551	51.9	622
[BMIm][PF_6]	541	52.8	605
[HOEMIm][PF_6]	506	56.5	585
[HOEMIm][NO_3]	541	52.8	605
[BMMIm][$N(CN)_2$]	554	51.6	613
[EMIm][CH_3SO_3]	549	52.1	607
[BMIm][NO_3][b]	551	51.9	611

[a] Data from ref 36. [b] Data from ref 8.

sensing material using spiropyran was first reported by Winkler et al. that spiropyrandinolines function as sensors for metal ions in the parts per billion range, where fluorescence emission spectra was enhanced 14-fold after complexed with metal ions,[7] and also the fluorescence of spiropyran was used as polarity indicator for the microenvironment around this probe molecule.[8] However, the fluorescence application of MC is inevitably hampered by its intrinsic weak intensity (fluorescence quantum yield of MC in ethanol was as low as 0.012[9]).

On the other hand, ionic liquids (ILs) have attracted much attention in various areas due to their unique physicochemical properties such as extremely low volatility, excellent solvating characteristics, and high ionic conductivity.[10] ILs have been described as the "designer solvents" owing to their ability to influence various physicochemical properties by alteration of the cation or anion. Publications to date have revealed the solvation interactions in ILs.[11] It was shown that replacement of organic solvents by ILs can lead to remarkable improvements in the well-known reaction (such as Beckmann rearrangement[12] and Diels−Alder reaction[13]) and can also exhibit unusual chemical reactivity.[14] One of the possible reasons for the unusual effect of ILs is probably due to its inherent nature (liquid ionic media), as it is known that ILs, in a broad sense, consist mainly of cation−anion pairs and larger charged and neutral ion clusters confirmed by the experimental evidence.[15] In solution of ILs, the solvation shell around the solute molecule supplied by the ionic solvent brings about unique effect on chemical reaction.

It was reported that Coulombic interaction contributes to the stability of zwitterionic merocycanine isomers[16] and electrostatic interaction between MC and zwitterionic amino acid was investigated and used to transport amino acid.[17] It is interesting to note that MC possessing a counter cationic and an anion center behaves like a zwitterionic ionic liquid; thus, special electrostatic interaction between counterionic moiety of ILs and the zwitterionic forms maybe exists. Meanwhile, photochromism of spiropyran and thermal reversion of MC could be affected by the unique inherent nature of ILs. Indeed, photochromism of spiropyran in ILs has been recently reported by Wu et al. and found that spiropyran in ILs containing anions from carboxylic acids exhibit (positive or negative) photochromism or not.[18] Byrne et al. studied the photo-, thermo-, and solvatochromic properties of the SP in a series of [NTf_2]-based ILs and SP-MC equilibrium was found to be sensitive to the nature of the cations.[19] However, the particular effect of ILs on the solute and thus on this ionic reaction (especially the thermal reversion), and the interaction between ILs and zwitterionic MC, is still far from a complete understanding. In this work, we studied the fluorescence of MC and the thermal reversion of MC to SP in a series of imidazolium-based ILs. It was found that the fluorescence intensity is greatly enhanced in ILs as compared to those of organic solvents, although the emission maxima are only slightly dependent on polarity. The thermal reversion is retarded as compared to those of organic solvents such as ethanol, in particular at elevated temperature (e.g., at 313 K, MC decay with k of 5.19×10^{-4} and 34.7×10^{-4} s^{-1} in [BMMIm][BF_4] and ethanol, respectively). In addition, the activation energy in less polar ILs (88−97 kJ mol^{-1}) is larger than in polar ILs (70−82 kJ mol^{-1}), in contrast to what is observed in organic solvents.

2. Experimental Methods

2.1. Chemicals and Synthesis of ILs. 6-Nitro-BIPS (Tokyo Chemical Industry) and the solvatochromic Reichardt's dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate hydrate (Aldrich) were used as received. A series of ILs with different cation and anion structures (as shown in Figure 1), i.e., 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF_4]), 1-ethyl-3-methylimidazolium mesylate ([EMIm][CH_3SO_3]), 1-ethyl-3-methylimidazolium dicyanamide ([EMIm][$N(CN)_2$]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF_6]), 1-butyl-3-methylimidazolium nitrate ([BMIm][NO_3]), 1-hydroxyethyl-3-methylimidazolium hexafluorophosphate ([HOEMIm][PF_6]), 1-butyl-3-methylimidazolium nitrate ([HOEMIm][NO_3]), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMIm][BF_4]) and 1-butyl-2,3-dimethylimidazolium dicy-

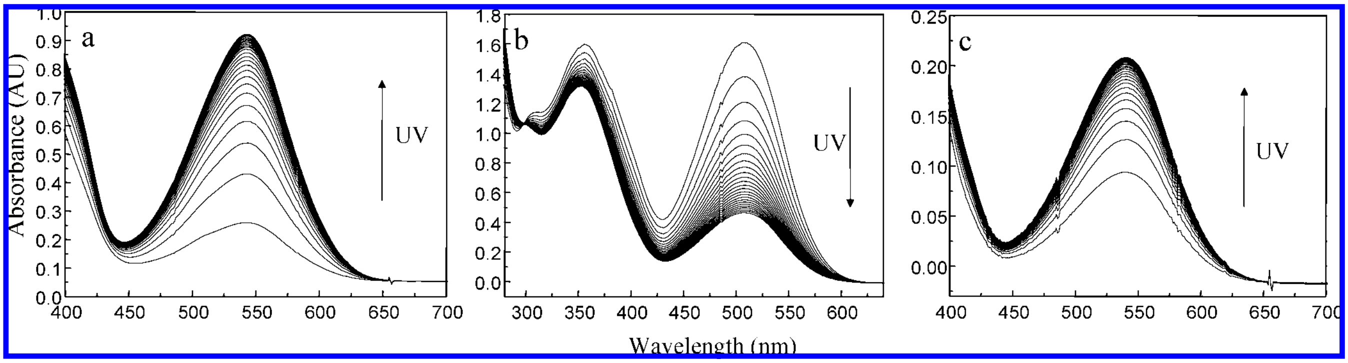


Figure 2. Overlay UV−vis absorption spectra of SP in (a) [BMIm][PF_6], (b) [HOEMIm][PF_6], and (c) [HOEMIm][NO_3] upon consecutive UV irradiation (1×10^4 M, at 298 K, time interval = 60 s).

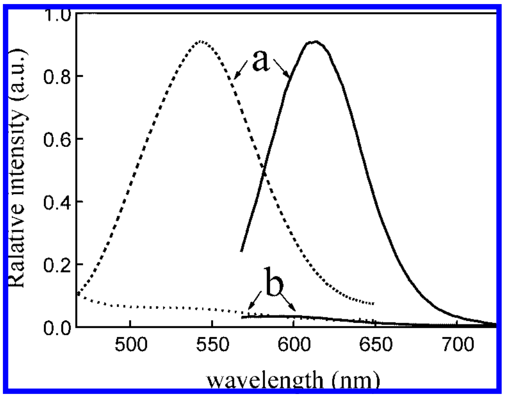


Figure 3. Absorption spectra (---) and emission spectra (—) of spiropyran in [BMIm][PF$_6$] (1×10^{-4} M) after (a) UV and (b) vis irradiation ($\lambda_{ex} = 540$ nm).

anamide ([BMMIm][N(CN)$_2$]), were synthesized in our laboratory according to the literature methods and purified following standard procedures.[20]

2.2. Sample Preparation. Spiropyran is nearly insoluble in these ILs due to the nonpolarity of the closed SP form. To prepare a given SP/ILs solution, individual 1 mM stock solutions of SP were prepared in acetone and then an appropriate amount of the stock solution was micropipeted into a clean dry quartz cuvette. An appropriate volume of ILs was then transferred to the cuvette equipped with a stir bar. Residual acetone was then evaporated in vacuum and then the sample was mixed for at least 24 h in the dark to achieve equilibrium prior to measurements. For all results reported here, the fluorophore concentration in ILs was 1×10^{-4} M.

2.3. Polarity and Viscosities of the ILs. The polarity of the ILs using Reichardt's dye was measured at 298 K according to a literature method.[21] The viscosity of each IL was measured on a Brookfield DV-III+ viscometer.

2.4. Absorption Spectra and Fluorescence. The UV−visible spectra were recorded on an Agilent 8453 diode array spectrophotometer. Standard 1 cm cells were housed and the temperature was controlled (±0.1 K) by circulation of water. UV irradiation about 6−12 min for all studied ILs was conducted to achieve the photostationary state (PSS) for equilibrium and kinetic measurements. Visible irradiation to accelerate the reversion of MC to SP is generally less than 7 min. The steady-state fluorescence spectra were recorded with a Hitachi F-7000 FL spectrophotometer by using 2.5 nm for both excitation and emission band-pass. The emission spectra were collected at 90° to the excitation. Only the spectra obtained after UV irradiation were used to calculate the absorption and emission peaks for the solvatochromic and fluorescence analysis. The UV light source was performed with a high-pressure mercury lamp through a filter (365 nm, 10 mW/cm^2).

2.5. Fluorescence Quantum Yields. Fluorescence quantum yields (Φ) of MC were determined using cresyl violet acetate in methanol as reference (the Φ of cresyl violet acetate was taken to be 0.55 with excitation equal to 546 nm),[22] which are obtained by eq 1 through stepped decrease of the concentration of MC after UV irradiation and than getting the gradient from the plot of integrated fluorescence intensity vs absorbance. Correction for the refractive index was applied according to the established protocols.

$$\Phi_X = \Phi_R \frac{I}{I_R} \frac{A_R}{A} \frac{n_X^2}{n_R^2} = \Phi_R \frac{\mathrm{Grad}_X}{\mathrm{Grad}_R} \frac{n_X^2}{n_R^2} \qquad (1)$$

where the subscripts R and X denote reference and test, respectively, Φ is the fluorescence quantum yield, Grad is the gradient, and n is the refractive index of the solvent.

2.6. Measurements of Kinetic Rate Constants of the Thermal Reversion. The decay rate constants for the thermal reversion of MC in ILs were obtained by monitoring absorption changes intermittently for a MC-rich solution kept in the dark at constant temperatures (T) using the following equation:

$$\ln(A_t - A_e) = -kt + \ln(A_t - A_0) \qquad (2)$$

where A_0, A_t, A_e are the absorbance of MC at time 0, t and at equilibrium, respectively, and k is the thermal decay rate constant. The Arrhenius activation energy (E_a) and frequency factor (A) were evaluated from the Arrhenius plot using the following equation:

$$\ln k = \ln A - E_a/RT \qquad (3)$$

The half-lifetime ($t_{1/2}$) of MC is obtained by the following equation:

$$t_{1/2} = \ln 2/k \qquad (4)$$

The values of the activation entropy (ΔS^*) was obtained through the following equation:

$$\Delta S^* = [\ln A - 1 - \ln(k_B T/h)]R \qquad (5)$$

where A is the frequency factor and k_B and h are Boltzmann's and Planck's constants, respectively.

3. Results and Discussion

3.1. Solvatochromism. MC was known to have negative solvatochromism, meaning that their absorption undergoes hypsochromic (blue) shift in solvents of increasing polarity, caused by intermolecular interactions between the solute and solvent that modify the energy gap between the ground and excited states (the dipole moments of ground state and the first excited singlet state are about 20 and 12 D,[23] respectively).[24] This phenomenon has been studied primarily for its potential use as an empirical indicator of the solvent polarity. Wu et al. employed polarity scale E_{SP} (E_{SP} (kcal·mol^{-1}) = 28 591/λ_{max} (nm)), instead of $E_T(30)$, as direct polarity indicator for ILs and a good linearity between E_{SP} and $E_T(30)$ was obtained. Using the established method, the polarity of ILs studied here can be evaluated by E_{SP}. The data presented in Table 1 suggest that [BMIm][BF$_4$], [BMIm][PF$_6$], and [HOEMIm][NO$_3$] provide comparable polar microenvironments. A decrease of E_{SP} and blue shift of λ_{max}(MC) with increasing length of the substituted alkyl chain on the imidazlium is observed ([EMIm][BF$_4$] vs [BMIm][BF$_4$]). As the C2−H on imidazolium is substituted with CH$_3$, the λ_{max} is red shifted and E_{sp} decreases, consistent with the significant decrease of $E_T(30)$ ($E_T(30)$ of [BMIm][BF$_4$] and [BMMIm][BF$_4$] is 52.5 and 49.4 kcal mol^{-1}, respectively). Among all of the ILs studied, [HOEMIm][PF$_6$] exhibits the highest E_{sp} and hence the highest polarity.

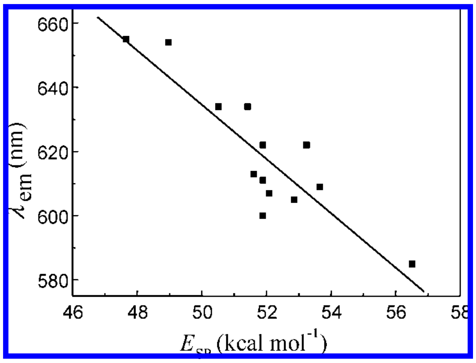


Figure 4. Correlation of the polarity scale (E_{SP}) and fluorescence emission maxima (λ_{em}) of SP in ILs and organic solvents.

Upon UV irradiation, the absorption spectra in the visible range ascribed to MC are greatly enhanced and always show a single structureless and symmetric band in all ILs (typical case is shown in Figure 2), indicating the presence of a unique MC isomer in ILs at thermal equilibrium,[25−27] which was further confirmed by the fluorescence excitation spectra method reported by Wohl et al. that the maximum of the excitation spectrum of MC in ILs does not obviously shift (less than 10 nm with variable fluorescence emission from 600 to 700 nm) in the wavelength at which fluorescence emission is measured.[28] It was found that SP in most of the ILs exhibit positive photochromism that the absorption of MC increased under UV irradiation, except that of [HOEMIm][PF$_6$], and in which SP exclusively exhibits negative photochromism; i.e., it gives a deep color in the dark with a blue shift absorption at 506 nm, close to the reported value of *trans*-MC-M^{2+} complex.[5a] The color is bleached by irradiation with either UV or visible light with an isosbestic point of 298 nm (Figure 2b). When the irradiation is ceased, the color reappears thermally. Indeed, similar phenomena have also been found in SP/[HOEMIm]-based IL while containing [NTf$_2$] as anion.[18] Though the real reason for this negative photochromism is still not clear at this stage, we can conclude that the unexpected negative photochromic behavior cannot be explained simply by the interaction of hydroxy-based cation with MC, since negative photochromism is not found in ILs with corresponding cation such as [HOEMIm][NO$_3$] (Figure 2c), which must be correlated to their higher E_{SP} or $E_T(30)$ (e.g., E_{SP} = 56.5 kcal mol^{-1} and $E_T(30)$ = 61.7 kcal mol^{-1} for [HOEMIm][PF$_6$]) and MC in these ILs is much more stable than SP.[29] The photochromic behaviors of SP in all the mentioned ILs were in accordance with the conclusion draw by Wu et al. that the spiropyrans contain less polar alkyl groups show positive photochromism with the E_{SP} scales less than about 53.9, while negative ones with the E_{SP} scales larger than 53.9.[18]

3.2. Fluorescence. Fluorescence is considered to be one of the most attractive signal outputs owing to its high sensitivity, easy detection and low-cost procedure.[30] It is well-known that the MC form of spiropyran is fluorescent while the closed form SP not.[17b,31] The fluorescence properties of MC in various ILs was studied, to understand the effect of the structure and physicochemical properties of ILs on the fluorescence efficiency of MC form.

Emission spectra of spiropyran after UV and visible light irradiation were recorded, together with the absorption spectra. The case of [BMIm][PF$_6$] is shown as a typical set in Figure 3. No obvious fluorescence as well as visible absorption after visible light irradiation is observed. Upon UV irradiation, however, a greatly enhanced fluorescence emission at 605 nm attributed to MC is observed (the weak fluorescence of blank ILs can be neglected), and in all ILs we observed only a featureless and broad spectrum. Note that the red fluorescence of the SP solution was photoreversible.

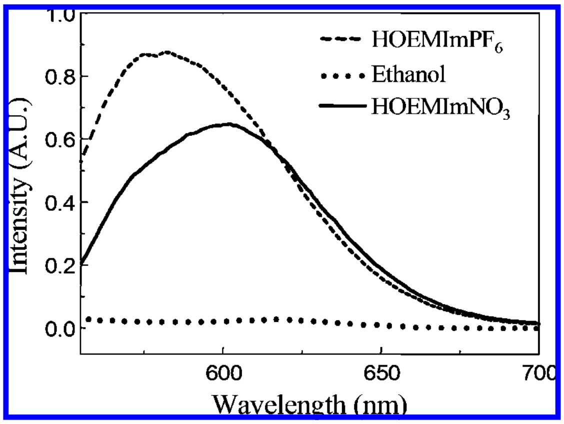


Figure 5. Normalized fluorescence spectra of MC in ethanol, [HOEMIm][NO$_3$] and [HOEMIm][PF$_6$] (with the same absorption of 0.11 and at respective excitation maxima).

TABLE 2: Fluorescence Quantum Yields of MC in ILs and Organic Solvents at 298 K

ILs	λ_{ex}	λ_{em}	η	Φ
acetonitrile	555	634	0.344	0.005
ethanol	535	622	1.074	0.016[a]
[EMIm][BF$_4$]	530	609	37.2	0.118
[BMIm][BF$_4$]	540	601	105.0	0.199
[BMIm][PF$_6$]	539	605	260.0	0.289
[BMIm][NO$_3$]	551	611	266.0	0.323
[HOEMIm][NO$_3$]	540	605	360.9	0.417
[BMMIm][BF$_4$]	551	600	630.0	0.500
[HOEMIm][PF$_6$]	510	585	424.9	0.510

[a] The fluorescence quantum yield in ethanol is higher than the reported value in ref 9 (0.12).

The emission properties of MC are strongly dependent upon the nature of their environment, which exhibit a large blue shift on going from a nonpolar to a polar environment and could be used as polarity indicator.[8] Using emission as polarity indicator could make the concentration of the probe much lower than that required for an absorption probe and thus minimizes the possibility of any probe-probe interactions that may usually occur during absorption probe studies. Herein, we use emission properties of MC as indicator to probe the microenvironment polarity of the surrounded ILs with E_{SP} as polarity reference directly. It can be seen from Figure 4 that the emission maxima (λ_{max}) of the MC is basically linear (correlation factor R^2 = 0.776) with E_{SP} in ILs and organic solvents. As to the enlarged views of the region of ILs themselves, however, the emission maxima change very little as a function of E_{SP} and no obvious linear relationship is observed. Using λ_{ex} = 530−555 nm, MC form showed red emission in most ILs with maxima around 600−613 nm (except [HOEMIm][PF$_6$], which emit fluorescence at 585 nm with λ_{ex} = 510 nm), obviously blue shift as compared to that in the corresponding polar solvents. The case is unlike their absorption spectra, for which the absorption maxima (λ_{max}) in ILs fall in the range of polar solvents (between ethanol and acetonitrile). This disagreement could be related to the high viscosity of ILs, which elongate the solvent relaxation of the excited state of MC, and consequently the emission is mainly resulted from the excited state close to Franck−Condon state.[30] The longest emission of MC in [EMIm][N(CN)$_2$] due to its lowest viscosity support this.

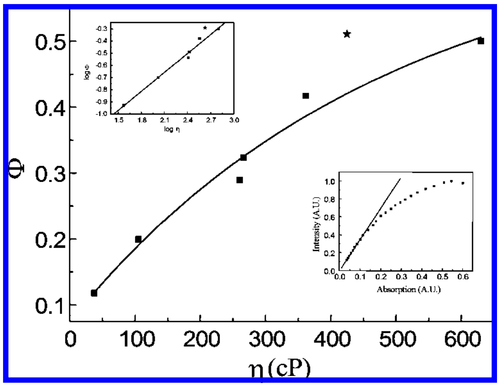


Figure 6. Dependence of quantum yields (Φ) of MC on the viscosity of ILs at 298 K ([HOEMIm][PF$_6$] denoted as star is not included when fitting). Left inset shows the plot of log Φ vs log η in ILs and right inset shows the normalized fluorescence intensity of MC in [BMIm]-[NO$_3$] with increasing absorption (absorptions lower than 0.12 were used to calculate quantum yield).

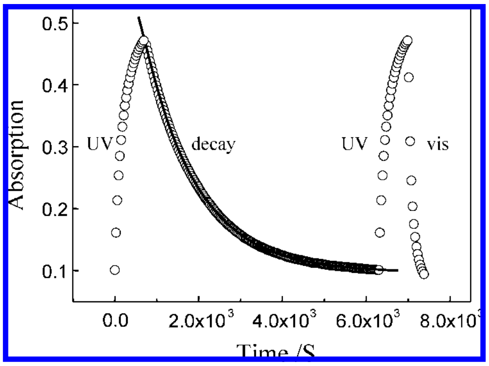


Figure 7. Time evolutions of the UV−vis absorption spectra (λ_{max} = 541 nm) of MC in [BMIm][PF$_6$] upon UV irradiation, consequent thermal reversion, and upon visible irradiation (T = 298 K, time interval = 30 s, the line is the best-fit curve with monoexponential function).

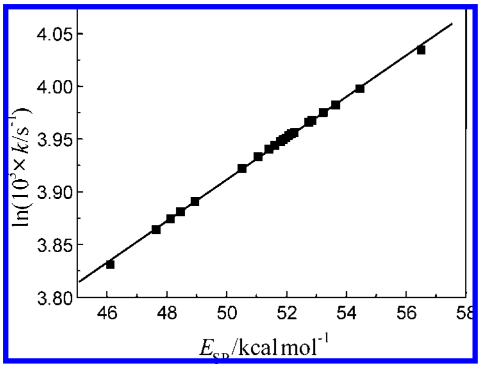
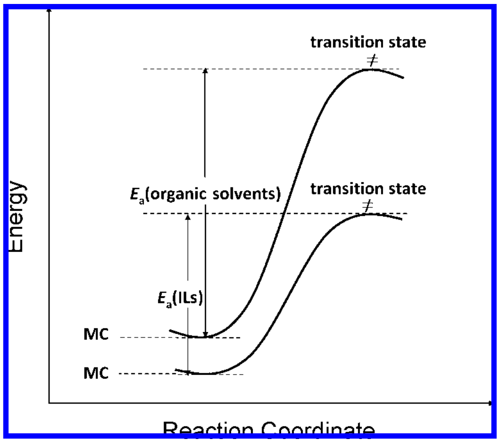


Figure 8. Plot of ln(10^3k/s^{-1}) vs E_{SP} for the thermal reversion of MC to SP in ILs and organic solvents (line is linear best fit to data, correlation factor R^2 = 0.999).

SCHEME 2: Energy Diagram for the Activation Process of Thermal Reversion of MC in General ILs and Polar Organic Solvents



One key feature should be noted is that, under the same conditions, the fluorescence intensity of MC is greatly enhanced as the solvent changed from organic solvents to ILs. With the same low absorption, the fluorescence intensity of MC in [HOEMIm][PF$_6$] is almost 32-fold larger that in ethanol (Figure 5). In view of the wide application of MC fluorescence as mentioned earlier, the strong fluorescence in ILs is very useful.

Fluorescence quantum yields (Φ) of MC in several ILs are listed in Table 2. The quantum yields of MC were found to be independent of the polarity (E_{sp}) of ILs, while increases almost monoexponentially with viscosity (η) (Figure 6; note that one abnormal sample that deviates from the fitting line is [HOEMIm][PF$_6$], which could be related to its negative photochromism), suggesting that viscosity and possibly hardness of the matrix play a dominant role in the fluorescence efficiency. Considering that the MC contains a methine bridge consisting of three conjugated C=C bonds like a molecular rotor and hence the internal molecular rotation relaxes its energy, the viscosity dependence of fluorescence is not unexpected. The rotation of MC is hindered by increasing viscosity, leading to a weaker coupling of the excited state with upper levels of the ground state, which results in a decrease in the energy dissipation rate of the excited state through internal radiationless channels to the ground states.[32−34] Consequently, the rate of population decay via radiative transitions (fluorescence intensity) increases. According to the Förster−Hoffmann equation,[35] the fluorescence quantum yields (Φ) of the molecular rotor probe should be related to its viscosity (η), as described by eq 6, in which C is a constant, and the fractional number x is a free volume parameter that depends on the structural properties of the rotor.

$$\log \Phi = C + x(\log \eta) \tag{6}$$

A plot of log Φ vs log η according to eq 6 is linear (left inset shown in Figure 6). The estimated slope (x = 0.52 ± 0.03) of the straight line is found much lower than the reported value for 9-(dicyanovinyl)julolidine (x = 0.58[36] or 0.6[33]), indicating the less free volume dependence of MC. To the best of our knowledge, it could be the first report of fluorescence enhancement of MC in solvents, especially in ILs. Such viscosity-dependent fluorescence intensity could be used to investigate the microviscosity around the probe[36] and hence an easy way to monitor online the progress of bulk polymerization, in order to prevent runaway reactions, is of great practical interest.[34] However, the fluorescence intensity of MC at high concentration in ILs is lower than as expected due to strong inner-filtering effect, although MC has high quantum yields (right inset in Figure 6).

3.3. Kinetic Rate and Activation Energy. When spiropyran is solvated in ILs (1 × 10^4 M^{-1} cm^{-1}) and located in the dark, we obtained light- to deep-red solution, indicating the presence of both SP and MC forms, further confirmed by the absorption around 350 nm and in the visible region. The equilibrium constants of SP-MC at 298 K in the dark, K_e, obtained with molar extinction coefficient in polar solvent, ε_{MC} = 3.5 × 10^4 M,

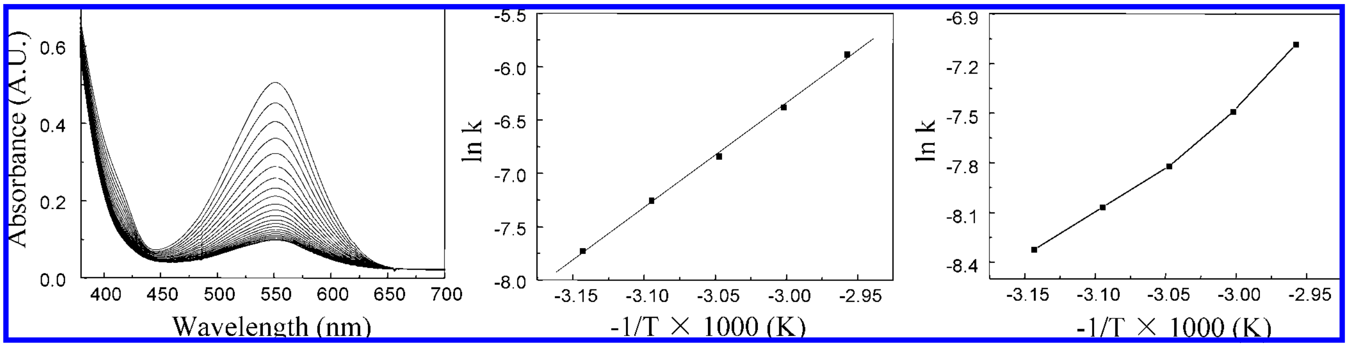


Figure 9. Overlay spectra of the first-order thermal decay of MC in [BMIm][NO$_3$] (left, 1×10^4 M, at 298 K, time interval = 300 s). Arrhenius plot for the thermal decay of MC in [BMMIm][N(CN)$_2$] (Middle, correlation factor $R^2 = 0.998$) and [HOEMIm][NO$_3$] (right).

according to previously published procedures,[24b,27] is given in Table 1. Obviously, K_e in all ILs is comparable with those for polar solvents such as acetonitrile and ethanol, with the exception of [HOEMIm][PF$_6$], which have the highest K_e, nearly 4-fold larger than the average value of the others, probably due to the negative photochromism of SP in [HOEMIm][PF$_6$] that MC is more easily formed in the equilibrium. Although K_e for MC in ILs is comparable with those in organic solvents, the yield of MC in the PSS during UV irradiation is lower in ILs (note that the UV light wavelength is longer than the cutoff points of all ILs studied here,[37] thus efficient photochromism of SP to MC was warranted by the transparence of ILs around 365 nm). In [BMIm][PF$_6$], for example, MC was formed with a yield of 20% in the PSS (irradiating 6 min), which is lower than the 48% obtained in ethanol (irradiating 6 min).

The time evolutions of the UV−vis absorption spectra of SP at 542 nm in [BMIm][PF$_6$] upon UV irradiation, consequent thermal reversion, and upon visible irradiation are shown as a typical example in Figure 7. The thermal decay after UV irradiation is found to be slow while visible light irradiation considerably accelerates.

The thermal decay of MC to SP in all ILs studied could be very well described by a single exponential at any temperature (typical set is shown in Figure 7), indicating a homogeneous environment of the ILs. The thermal reversion involves an intramolecular charge recombination process and hence the decay rate of the MC is polarity dependent. As illustrated in Figure 8, ln(10^3k) scales linearly with the E_{SP} in ILs and organic solvents. The thermal decay of MC in ILs are much smaller than those in nonpolar solvents such as DMF, chloroform, and toluene, and are comparable to that observed in polar ethanol and corporated into biopolymers.[6a] Thus, we can conclude that MC is stabilized in ILs, which can be further evaluated by the case at elevated temperature. In [BMMIm][BF$_4$], for example, MC decay with k of 5.19×10^{-4} s^{-1} at 313 K, much slower than in ethanol (34.7×10^{-4} s^{-1}), although they have comparable k at 298 K. The corresponding half-lifetime ($t_{1/2}$) of MC in ILs is nearly 7-fold larger than that in ethanol at 313 K. Further, most of the imidazolium cation-based ILs was found to show lower k than those of the reported ILs with pyridinium cation and phosphonium cation,[19] probably due to formation a through-space orbital interaction with the MC isomer calculated from ab initio molecular orbital theory and density functional theory calculations. If the imidazolium is functionalized with OH, there is a moderate decrease of rate constant, due to the stabilization of polar MC through hydrogen bonding between phenolic oxygen and OH. The reaction became faster on decreasing the chain length on the imidazolium ring, reflecting a small increase of the polarity of the medium. However, for [BMIm][BF$_4$] and [BMIm][PF$_6$] with comparable polarity indicated by λ_{max} and $E_T(30)$, the rate for the latter is nearly twice as that of the former. Among all ILs investigated, [BMMIm][BF$_4$], though having relatively lower polarity, exhibits the lowest thermal reversion rate, which could be ascribed to its relatively high viscosity. It is probable that no aggregate of MC existed in ILs, because there was no change in k with increasing concentration of the spiropyran (0.5×10^{-4} M,

TABLE 3: Equilibrium Constant and Kinetic Parameters for the Thermal Decay of MC in ILs and Organic Solvents at 298 K

solvent	10^2K_e	10^3k/s^{-1}	$t_{1/2}$ (min)	E_a (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
hexane		47.7[a]	0.24	76.4[a]	−22.3[a]
benzene		66.2[a]	0.17	70.6[a]	−38.6[a]
1,4-dioxane		56.6[a]	0.11	77.4[a]	−17.6[a]
acetone		7.28	0.43	101[a]	43.3[a]
DMF		1.55[a]	7.45	96.2[a]	15.9[a]
acetonitrile	3.85[c]	2.92	3.96	102.4	50.4[a]
ethanol	4.57[c]	0.612	18.88	102.2	84.4
[BMIm][BF$_4$]	4.62	0.396	29.17	73.8	−71.9
[BMMIm][BF$_4$]	1.48	0.107	107.97	90.9	−24.5
[EMIm][BF$_4$]	3.76	0.232	49.80	70.9	−85.4
[EMIm][N(CN)$_2$]	6.78	0.382	30.24	96.1	−31.3
[BMIm][PF$_6$]	1.88	0.792	14.59	70.6	−76.2
[HOEMIm][PF$_6$][b]	15.24	0.0237	487.45	97.0	
[HOEMIm][NO$_3$]	4.69	0.407	28.38		
[BMMIm][N(CN)$_2$]	4.23	0.404	28.60	81.5	−61.3
[EMIm][CH$_3$SO$_3$]	3.64	0.336	34.36	75.9	−84.2
[BMIm][NO$_3$]	2.64	0.498	23.20	88.5	−43.4

[a] Data from ref 25. [b] Activation parameters of the negative thermal photochromism. [c] Data from ref 19.

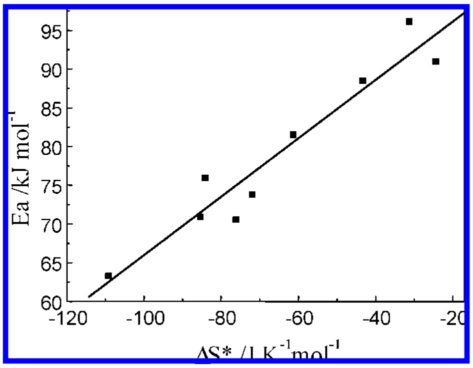


Figure 10. Correlation between E_a and ΔS^* of thermal reversion of MC in ILs (298 K, correlation factor $R^2 = 0.905$).

0.75×10^{-4} M, and 1×10^{-4} M in [EMIm][BF_4]),[38] which could be ascribed to the relatively high polarity of ILs.

For most ILs, the correlation between the ln k and $-1/T \times 1000$ is of good linearity (typical case is shown in Figure 9b), thus the first-order rate plots between 293 and 313 K (with increasing step of 5 K) can be used to calculate the activation energy (E_a) of the thermal reversion. It was demonstrated that E_a is significantly sensitive to the polarity of the microenvironment, typically 70−80 kJ mol^{-1} in nonpolar solvents and around 100 kJ mol^{-1} in polar media.[25] However, it is not the same case in ILs, which can be classified into three categories according to their E_a values (summarized in Table 3): (a) ILs with relatively low polarity, such as [EMIm][$N(CN)_2$] (96.14 kJ mol^{-1}), [BMMIm][BF_4] (90.9 kJ mol^{-1}), and [BMIm][NO_3] (88.51 kJ mol^{-1}), have higher E_a, comparable to those of polar solvents such as acetonitrile and ethanol. (b) But for the other polar ILs, E_a falls in the range of 70−82 kJ mol^{-1}, close to that observed in less polar organic solvents. E_a values for these ILs were found to be related to their polarity; e.g., [BMIm][BF_4] and [BMIm][PF_6] with comparable polarity exhibit the same magnitude of E_a (70.55 and 73.80 kJ mol^{-1}). A similar density dependency of the activation energy is observed for the thermal decay of MC in medium-density fluids CHF_3 that E_a tends to decrease with decreasing dielectric constant in liquid solutions, which was ascribed to desolvation due to the conformational change.[26] This argument may be applied to the present system. In the activation process, the conformational changes of the molecule lead to the rearrangement of the solvent molecules, which may result in a relatively larger desolvation effect during the reaction process in ILs. (c) Unexpectedly, for the hydroxyl-tethered cation-based ILs, [HOEMIm][NO_3], the linearity between rate constant and temperature is not effective and the first-order rate plots temperatures give a discernible curvature (Figure 9c), implying that either the pre-exponential factor (or frequency) A or activation energy E_a or both are temperature dependent.[39] Thus, any change in temperature is bound to alter both the H-bonding ability and the viscosity of ILs and the observed temperature effect may result from a change in both these parameters.

Considering that the thermal decay rate k is mainly dependent on the activation energy E_a and activation entropy ΔS^*, ($k = (k_BT/h)e^h(RT)^{n-1} \exp((\Delta_r S_m^*(c^\ominus))/R) \exp(E_a/(RT))$),[40] investigation of the ΔS^* is necessary. It was found that ΔS^* obtained in all ILs were negative (−85.4 to −24.5 J K^{-1} mol^{-1}), in contrast to positive values obtained for polar organic solvents, while similar to that of less polar organic solvents. From the negative values, it can be deduced that the degree of order of solvated MC increases by going to its transition state in ILs. Thus, the transition state may be more stabilized by ILs compared to organic solvents possessing corresponding polarity, lowering the activation energy (Scheme 2). This finding is in line with the lower E_a observed in ILs and further confirmed by the fact that E_a was compensated by ΔS^*. As illustrated in Figure 10, E_a show linear correlation with ΔS^* in all ILs. According to the previous reports, the transition state of the thermal reversion is suggested as either biradical form or cis-ionic transition sate,[36] and both results of E_a and ΔS^* obtained here indicated that the latter is more favorable.

4. Conclusions

In summary, the effect of composition and properties of ILs on the photochromism of spiropyran and the thermal reversion of MC was investigated via fluorescence and UV−vis absorption spectra. Spiropyrans are able to give reversible photochromism in most of the ILs studied. The thermal decay rates in ILs are lower than those in organic solvents and are comparable to those of incorporated into organic−inorganic hybrid matrixes[6a] and MC form show enhanced stability in ILs. Furthermore, the thermal reversion in ILs exhibits abnormal thermodynamics compared to molecular solvents (lower activation energy and minus activation entropy). This could be due to stabilization of the zwitterionic form by the counterionic parts of ILs. These results provide a design platform for selecting appropriate ILs, not the tedious synthesis of substituted spiropyran, for the purpose of fine tuning the thermal stabilities of their colored open forms.

Acknowledgment. The authors thank the National Natural Science Foundation of China (No. 20533080, 20225309, and 50421502) for financial support.

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JP9004218