

Hydroxyl Ionic Liquids: The Differentiating Effect of Hydroxyl on Polarity due to Ionic Hydrogen Bonds between Hydroxyl and Anions

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The polarity of a series of ionic liquids (ILs) based on hydroxyethyl-imidazolium moiety with various anions ([PF₆], [NTf₂], [ClO₄], [DCA], [NO₃], [AC], and [Cl]) and their corresponding nonhydroxyl ILs was investigated by solvatochromic dyes and fluorescence probe molecules. Most of the nonhydroxyl ILs exhibit anion-independent polarity with similar $E_T(30)$ in the narrow range of 50.7–52.6 kcal/mol, except [EMIm][AC] (49.7 kcal/mol). However, the polarity of the hydroxyl ILs covers a rather wide range ($E_T(30) = 51.2$ –61.7 kcal/mol) and is strongly anion-dependent. According to their $E_T(30)$ or $E_T(33)$ values, the hydroxyl ILs can be further classified into the following three groups: (I) acetate-based hydroxyl ILs [HOEMIm][AC] exhibit polarity scale ($E_T(30) = 51.2$ kcal/mol) similar to short chain alcohol and fall in the range of the nonhydroxyl ILs; (II) Hydroxyl ILs containing anions [NO₃], [DCA], and [Cl] exhibit comparable polarity ($E_T(30) = 55.5$ –56.9 kcal/mol), moderately higher than those of their nonhydroxyl ILs; (III) Hydroxyl ILs containing anions [PF₆], [NTf₂], and [ClO₄] possess unusual “hyperpolarity” ($E_T(30) = 60.3$ –61.7 kcal/mol) close to protic ILs and water. Kamlet–Taft parameters and density functional theory calculations indicated that the greatly expanded range of polarity of hydroxyl ILs is correlated to an intramolecular synergistic solvent effect of the ionic hydrogen-bonded HBD/HBA complexes generated by intrasolvent HBD/HBA association between the anions and the hydroxyl group on cations, wherein hydroxyl group exhibits a significant differentiating effect on the strength of H-bonding and thus the polarity. Spiropyran-merocyanine equilibrium acted as a model polarity-sensitive reaction indeed shows obviously polarity-dependent solvatochromism, photochromism, and thermal reversion in hydroxyl ILs.

1. Introduction

Ionic liquids (ILs) have received increasing interest as alternative solvents and suitable soft materials in various applications because of their attractive properties, such as intrinsic ionic conductivity, low-vapor pressure, liquid in wide temperature range, and so forth.¹ Among the physicochemical properties investigated, polarity and hydrogen-bonding ability, varying according to their ionic structures, are of great importance for salivation and chemical reaction² in particular for designing ILs as solvents for cellulose.³

One of the attractive attributes of ILs is the potential to generate a wide range of types of ILs with fine-tuned physicochemical properties by the combination of various cations with anions, and rational functionalization of ions or the substitute.⁴ ILs with –OH functionalized cation (hereafter as hydroxyl ILs), which was first reported by Branco et al.,⁵ endows classical ILs with useful polarity/solvation properties, and could replace traditional alcohols in certain applications. Hydroxyl ILs was found to play an important role on the reaction. For example, addition of less than 1% hydroxyl ILs was sufficient to enhance the enzyme activity by a factor of up to 4 and also to increase the enantioselectivity of the reaction.⁶ Diels–Alder reactions sensitive to polarity processed in [HOEMIm][NTf₂] produced a much higher endo/exo ratio as compared to others.⁷ Hydroxyl

ILs were also suggested as excellent stabilizer for the synthesis of nanostructure material.⁸ For example, Rh nanoparticles can be readily synthesized and stabilized in hydroxyl ILs as compared to non functionalized ILs, providing an effective and highly stable catalytic system for biphasic hydrogenation reactions. More recently, hydroxyl ILs were successfully used as both solvent and template to synthesize LiFePO₄ powders with controlled size and morphology by low-temperature solvothermal-hydrothermal methods.^{8b} Hydroxyl ILs-based chloro-Ni(II) complexes were found to show effective thermochromic behavior with wider temperatures and more stable repeated-operations, wherein the hydroxyl group in ILs is more effective than those in water and alcohols to coordinate with the metal ion in the octahedral configuration.⁹ However, despite their extensive application of hydroxyl ILs and the large number of studies published in the past few years, some of their unique properties remain poorly understood, and little has been conducted to explore the relationship between ILs structure and solvent polarity.^{7,10} Hydroxyl ILs with variable anions was indeed found to highly influence their physicochemical properties and the corresponding solvent–solute interaction in these ILs. For example, spiropyran exhibited negative photochromism in [HOEMIm][NTf₂] and [HOEMIm][PF₆] of high polarity,¹¹ unlike positive photochromism found in general nonhydroxyl ILs and other hydroxyl ILs such as [HOEMIm][NO₃].

In the present work, we revealed an interesting and unusual polarity behavior of hydroxyl ILs based on imidazolium moiety with various anions ([PF₆], [NTf₂], [ClO₄], [DCA], [NO₃], [AC],

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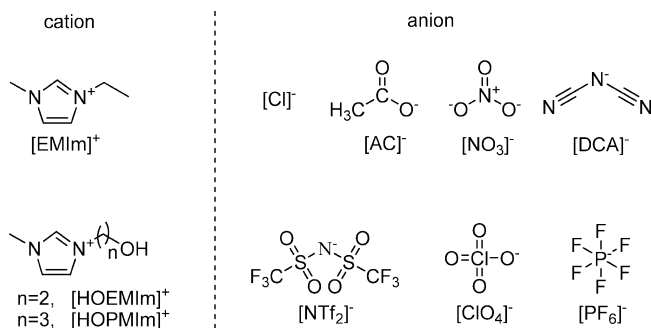


Figure 1. Structures and abbreviations of the cations and anions of ILs used in this study.

and [Cl]), wherein the hydroxyl groups exhibit a significant differentiating effect on their polarities. As compared to the nonhydroxyl ILs, the hydroxyl ILs exhibit a greatly expanded and strongly anion-dependent polarity. Kamlet–Taft solvent parameters (π^* , α , β), and computational analysis were further conducted to determine the correlation between the structures of ILs and their polarity.

2. Experimental Methods

2.1. Chemicals. All chemicals were commercially available and used as received. 2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's dye 30), 2,6-dichloro-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's dye 33), and dansylamide were purchased from Aldrich. 4-Nitroaniline (98%) and *N,N*-dimethyl-4-nitroaniline (>98%) was purchased from Alfa Aesar. 6-Nitro-BIPS was purchased from Tokyo Chemical Industry.

2.2. Synthesis of Ionic Liquids. All ILs with different cation and anion structures (Figure 1), namely, 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIm][PF₆]), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([EMIm][NTf₂]), 1-ethyl-3-methylimidazolium perchlorate ([EMIm][ClO₄]), 1-ethyl-3-methylimidazolium dicyanamide ([EMIm][DCA]), 1-ethyl-3-methylimidazolium nitrate ([EMIm][NO₃]), 1-ethyl-3-methylimidazolium acetate ([EMIm][AC]), and their corresponding hydroxyl ILs, that is, 1-hydroxyethyl-3-methylimidazolium hexafluorophosphate ([HOEMIm][PF₆]), 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([HOEMIm][NTf₂]), 1-hydroxyethyl-3-methylimidazolium perchlorate ([HOEMIm][ClO₄]), 1-hydroxyethyl-3-methylimidazolium dicyanamide ([HOEMIm][DCA]), 1-hydroxyethyl-3-methylimidazolium nitrate ([HOEMIm][NO₃]), 1-hydroxyethyl-3-methylimidazolium acetate ([HOEMIm][AC]), and 1-hydroxyethyl-3-methylimidazolium chloride ([HOEMIm][Cl]), were prepared according to the well-established procedure,⁵ and confirmed by ¹H NMR, electrospray ionization mass spectrometry (ESI-MS). All ILs were dried under vacuo at 80 °C for 10 h prior to water content determination and spectral analysis. The details of the synthesis and characterization of ILs are available in Supporting Information.

2.3. Instrumentation. 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. The steady-state fluorescence spectra were recorded with a Hitachi F-7000 FL spectrophotometer by using a 2.5 nm for both excitation and emission band-pass. The emission spectra were collected at 90° to the excitation. Fourier transform infrared (FTIR) data were acquired from 4000 to 400 cm⁻¹ on a Thermo-Nicolet 5700

FTIR spectrometer. ¹H NMR spectra were conducted on a Bruker AMX FT 400-MHz NMR spectrometer and chemical shifts were reported downfield in parts per million (ppm, δ) from a tetramethylsilane reference. The water content in the ILs was determined by a coulometric Karl Fischer analysis (Metrohm KF coulometer).

2.4. Methods. All absorbance and fluorescence probe stock solutions were prepared in absolute methanol, except for that of spiropyran, which was prepared in acetone as we mentioned early,^{11b} UV irradiation (365 nm, 10 mW/cm²) of spiropyran/ILs solution was performed to achieve the photostationary state (PSS) for equilibrium and kinetic measurements. To prepare a given probe/ILs solution, an aliquot of probe of known amount in methanol (0.1 mL) was micropipetd into a 1.0 cm quartz cuvette charged with 1 mL ILs. After removing the residual solvent in vacuum, the solution was subjected to spectra analysis. The concentration of probe molecule in ILs is 1×10^{-4} M for Reichardt's dye, 5×10^{-5} M for both *N,N*-diethyl-4-nitroaniline and 4-nitroaniline, 1×10^{-5} M for both dansylamide and pyrene, and 1×10^{-4} M for spiropyran in general hydroxyl ILs while 1×10^{-5} M in [HOEMIm][AC] and [EMIm][AC] due to its high extinction coefficient in the two hydroxyl ILs.

2.5. Determination of $E_T(30)$ and Kamlet–Taft Parameters. Reichardt's dye 30 was chosen to estimate the polarity of ILs, due to its well-established empirical solvent polarity scales based on molecular liquids, which exhibited one of the largest solvatochromic effects of any known organic molecule (from $\lambda_{\max} = 810$ nm in diphenyl ether to $\lambda_{\max} = 453$ nm in water).¹² The polarity scale, $E_T(30)$, is defined as

$$E_T(30) (\text{kcal mol}^{-1}) = 28\,591/\lambda_{\max} (\text{nm}) \quad (1)$$

where λ_{\max} is the wavelength maximum of the lowest energy band, intramolecular charge-transfer (CT) π – π^* absorption band of the zwitterionic phenolate molecule.

The solvent dipolarity/polarizability, π^* , which was initially defined by Kamlet, Abboud, and Taft, is normalized by taking dimethyl sulfoxide ($\pi^* = 1.00$) and cyclohexane ($\pi^* = 0.00$) as references, and can be correlated to the wavelength maximum of the lowest energy band of *N,N*-dimethyl-*p*-nitroaniline (DMPNA), a non-hydrogen bond donor solute¹³

$$\pi^* = (28.18 - 10^4/\lambda_{\text{DMPNA}} (\text{nm}))/352 \quad (2)$$

The hydrogen bond donating acidity (HBD), α , is calculated using the $E_T(30)$ and π^* values

$$\alpha = (E_T(30) (\text{kcal mol}^{-1}) - 31.2 - 11.5\pi^*)/15.2 \quad (3)$$

Finally, the hydrogen bond accepting basicity (HBA), β , for solvents can be determined by using the enhanced solvatochromic shift ($-\Delta\Delta\nu(1-2)$) of 4-nitroaniline (**3**) relative to the homomorphic *N,N*-dimethyl-4-nitroaniline (**5**) and using the expression, with hexamethylphosphoramide (HMPA) as the reference

$$\beta = \Delta\Delta\nu_s(\mathbf{3-5})/\Delta\Delta\nu_{\text{HMPA}}(\mathbf{3-5}) = [\nu(\mathbf{5})0.9841 + 3.49 - \nu(\mathbf{3})]/2.759 \quad (4)$$

TABLE 1: $E_T(30)$ and $E_T(33)$ Scales,^a and Kamlet-Taft Parameters of ILs^b

	ILs	$E_T(30)$	$E_T(30)^c$	$E_T(33)$ (λ_{\max}^d)	E_T^N	π^*	α	β
1	[EMIm][PF ₆]	52.6	52.4	61.8 (463)	0.676	0.99	0.66	0.20
2	[EMIm][NTf ₂]	52.0	52.4	61.8 (463)	0.657	0.90	0.76	0.28
3	[EMIm][ClO ₄]	52.4	52.4	61.8 (463)	0.670	1.11	0.56	0.41
4	[EMIm][DCA]	51.7	51.7	61.1 (468)	0.648	1.08	0.53	0.35
5	[EMIm][NO ₃]	51.5	52.5	61.9 (462)	0.642	1.13	0.48	0.66
6	[EMIm][AC]	49.8	49.1	58.7 (487)	0.590	1.09	0.40	0.95
7	[HOEMIm][PF ₆]	61.7 ^e	60.8	69.4 (412)	0.957	1.11	1.17	0.15
8	[HOEMIm][NTf ₂]	60.8	62.1	70.6 (405)	0.929	1.03	1.17	0.34
9	[HOEMIm][ClO ₄]	60.3	59.3	68.1 (420)	0.914	1.13	1.06	0.16
10	[HOEMIm][DCA]		56.1	65.1 (439)	0.784	1.11	0.80	0.51
11	[HOEMIm][NO ₃]		55.6	64.7 (442)	0.769	1.11	0.77	0.65
12	[HOEMIm][Cl]		55.6	64.7 (442)	0.769	1.16	0.73	0.68
13	[HOEMIm][AC]	51.2	51.3	60.8 (470)	0.633	1.04	0.53	0.90
	[HOPMIm][NTf ₂]	56.8			0.806	1.06 ^j	0.90 ⁱ	0.24 ⁱ
	[HOPMIm][AC]	51.1			0.630	1.08 ⁱ	0.51 ⁱ	0.99 ⁱ
	[EtNH ₃][NO ₃] ^f	61.6			0.954	1.12 ⁱ	1.10 ⁱ	0.46 ⁱ
	[MOEMPy][OTf] ^g	60.2			0.910			
	[P ₂₁ (OH)][NTf ₂] ^h	60.8			0.929			
	Water ⁱ	63.1			1.000	1.09 ^j	1.17 ^j	0.47 ^j

^a kcal/mol. ^b For [EMIm][NO₃], [EMIm][PF₆], and [HOEMIm][Cl], the parameters were determined at a supercooled state. ^c $E_T(30)$ derived from the $E_T(33)$ according to the eq 6. ^d nm. ^e Data from ref 11b. ^f Data from ref 20. ^g 1-Methyl-1-(2-methoxyethyl)-pyrrolidinium trifluoromethylsulfonate in ref 21. ^h Estimated by E_{NR} from ref 10. ⁱ Data from ref 13a. ^j Data derived from *N,N*-diethyl-4-nitroaniline and 4-nitroaniline.

Here, $\nu(3)$ and $\nu(5)$ are the wavenumbers (10^{-3} cm^{-1}) of the observed absorbance maxima for 4-nitroaniline and *N,N*-diethyl-4-nitroaniline, respectively.¹⁴

3. Results and Discussion

3.1. Polarity of Hydroxyl ILs. Since the data on the purity of ILs are critical to the assessment of their physicochemical properties and the polarity of ILs was reported to be water-sensitive,¹⁵ before every test of probe behavior the purity of ILs was first determined. To ensure that the water and other volatile solvents in ILs was reduced as low as possible, each IL was kept in a vacuum (pressure 10^{-2} – 10^{-3} mbar) at 80 °C for 10 h prior to water content determination and spectral analysis. The purity of each IL was first verified by NMR spectroscopy to check for residues of unreacted reactants or residual solvents. The effect of water content of ILs on the polarity ($E_T(33)$ scale) was carefully checked. As can be seen from Supporting Information, Table S1, generally, the “wet” ILs was much more polar than “dry” ILs studied in this work. The water effect on polarity, however, could not account for the greatly expanded range of polarity of hydroxyl ILs, which could be really induced by the OH functionalization.

Reichardt's dye 30 ($pK_a = 8.6$) are not directly available for some hydroxyl ILs ([HOEMIm][DCA], [HOEMIm][NO₃], and [HOEMIm][Cl]) because in such solvents the long-wavelength CT absorption band disappeared,¹⁶ currently interpreted as the protonation of phenolate oxygen atom arising from the acidity of these hydroxyl ILs.¹⁷ The problematic protonation of the Reichardt's dye 30 probe in hydroxylic ILs is also reported by Jin et al.¹⁰ Herein the $E_T(30)$ data for the three ILs were derived from $E_T(33)$, polarity scale of a less basic probe, 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate ($pK_a = 4.78$),¹⁸ or derived from E_{SP} (as discussed below). However, Nile Red, a probe insensitive to acidity and usually used for probing polarity of ILs, is not employed due to the nonlinear relationship between E_{NR} and $E_T(30)$.¹⁹

$E_T(33)$ and $E_T(30)$ values of six nonhydroxyl ILs and four hydroxyl ILs were involved to establish the linear relationship between $E_T(33)$ and $E_T(30)$ in these ILs, as described in eq

6 (data were shown in Supporting Information, Table S2 and Figure S2)

$$E_T(30) = 1.09396(\pm 0.06589)E_T(33) - 15.15814(\pm 4.19764) \quad (6)$$

$r = 0.9858$, standard error of estimate = 0.81665.

Then the resulted equation was used to estimate the $E_T(30)$ for hydroxyl ILs, in particular for the three acidic ones.

Meanwhile, $E_T(30)$ values of these ILs derived from the relationship established by Sarkar et al. were also given for comparison (Supporting Information, Table S2) but had shown obviously higher deviation.²² This is not unexpected since the latter originated from linear regression analysis of nearly all molecular solvents but one IL, while in this work the correlation was derived from all ILs. This indicated that ILs exhibit different solvation behavior of probe molecule as compared to molecular solvents, which was more obvious in the case of E_{SP} as discussed below.

$E_T(30)$ and $E_T(30)$ derived from $E_T(33)$ in hydroxyl ILs and nonhydroxyl ILs were listed in Table 1, together with the values of water and several polar ILs for comparison. Note that the $E_T(30)$ values of the acidic hydroxyl ILs for the following discussion is derived from $E_T(33)$, while for other ILs $E_T(30)$ values are the experimental results. Although it is well-known that anions present in ILs play a significant role in the property of ILs, such as melting points, thermal stability, and decomposition temperature,² it is clear that all of the nonhydroxyl ILs containing variable anions show comparable $E_T(30)$ scales in the range of 49.8–52.6 kcal/mol, irrespective of the nature of anion. This protocol still holds true when the alkyl substituent was changed from ethyl to butyl, ($E_T(30)$ values range from 50.5 kcal/mol for [BMIm][AC] to 52.9 kcal/mol for [BMIm][ClO₄], in Supporting Information, Table S3). Interestingly, it is not the same case for the corresponding hydroxyl ILs, which covered a rather wide range of $E_T(30)$ (51.2–61.7 kcal/mol), depending strongly on the nature of the anion. A plot of $E_T(33)$ values of the hydroxyl-ILs is shown in Figure 2. Clearly from Table 1 and Figure 2, three groups or clusters of hydroxyl-ILs

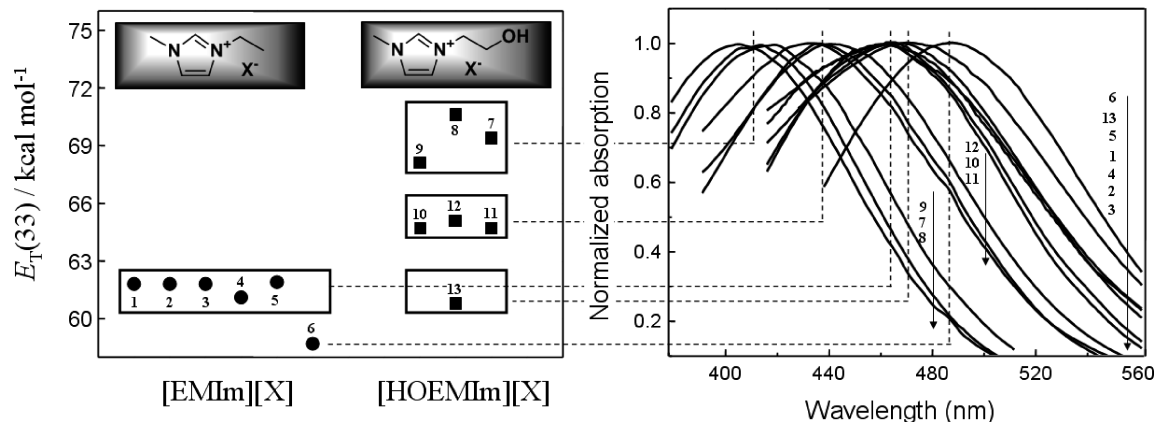


Figure 2. (Left) Plot illustrating the grouping of the seven tested hydroxyl ILs based upon their $E_T(33)$ scales, together with the six nonhydroxyl ILs. (Right) Normalized absorption spectra of Reichardt's dye 33 in these ILs.

with similar $E_T(33)$ or $E_T(30)$ values are observed, (I) hydroxyl ILs containing strong basic anion [AC] exhibit polarity scale ($E_T(30) = 51.2$ kcal/mol) similar to short chain alcohol, only slightly higher than the value of its nonhydroxyl ILs [EMIm]-[AC]. By and large, the $E_T(30)$ scale of [HOEMIm][AC] fall in the range of the six nonhydroxyl ILs. (II) Hydroxyl ILs containing anions [NO₃], [DCA], and [Cl] exhibit comparable polarity ($E_T(30) = 55.6$ – 56.1 kcal/mol), moderately higher than those of their nonhydroxyl ILs. (III) Hydroxyl ILs containing anions [PF₆], [NTf₂], and [ClO₄] showed “hyperpolarity” ($E_T(30) = 60.3$ – 61.7 kcal/mol). In particular for [HOEMIm][PF₆], its $E_T(30)$ scale is as high as 61.7 kcal/mol, comparable to that of protic ILs [EtNH₃][NO₃] and only slightly less than that of water. Results using empirical solvent polarity scales indicated that most ILs have similar polarities. For example, polarity of 1,3-dialkylimidazolium-based ILs correspond to that of short-chain primary and secondary alcohols and secondary amides such as *N*-methylformamide.²³ Only few ILs of high polarity were reported, as shown in Table 1. First is the protic ILs, such as primary, secondary, and tertiary alkylammonium salt, and protic imidazolium-based ILs.²⁴ Second is the 1-methyl-1-(2-methoxyethyl)-pyrrolidinium trifluoromethylsulfonate ([MOEMPy][CF₃SO₃]), as reported by Kaar and co-workers.²¹ To the best of our knowledge, [HOEMIm][PF₆] should be the most polar nonacidic ILs reported to date. Moreover, lengthening the methylene spacer between hydroxyl group and imidazolium ring induced distinct decrease in $E_T(30)$ scales ([HOEMIm][AC] and [HOEMIm][NTf₂] compared to [HOPMIm][AC] [HOPMIm][NTf₂], respectively, as shown in Table 1). The decrease is similar, but of large magnitude than the case of nonhydroxyl ILs, in particular for hydroxyl ILs with “hyperpolarity”.

To explore the unusual polarity behavior of hydroxyl ILs, their empirical Kamlet–Taft parameters (dipolarity/polarizability, π^* ; HBD acidity, α ; HBA basicity, β) were determined (Table 1). All hydroxyl ILs have higher π^* values (1.03–1.16) than molecular solvents, and in most cases slightly higher than nonhydroxyl ILs. However, little variation between hydroxyl ILs themselves was observed, indicating the strong and comparable ability of the solvent dipolarity/polarizability of these hydroxyl ILs. The HBD ability, α value, was said to be largely determined by the availability of hydrogen bond donor sites on the cation. For example, values for the imidazolium salts (0.3–0.8) are slightly lower than those for the monoalkylammonium salts (0.8–0.9).^{1a} However, it appears that more basic anions give much lower α value with a common cation in the hydroxyl ILs. Values range from 1.06–1.17 for the group III

TABLE 2: Solvatochromic Probe (Reichardt's 30) Responses in Binary ILs + Ethanol Solutions (molar ratio = 1/1) under Ambient Conditions

ILs	ethanol mole fraction (λ_{\max} (nm))			$\Delta\lambda$ (nm)	
	0	0.5	1	$\lambda_0 - \lambda_{0.5}$	$\lambda_1 - \lambda_{0.5}$
[EMIm][PF ₆]	544	518	547	26	29
[BMIm][PF ₆]	547	518 ^a	547	29	29
[EMIm][NTf ₂]	550	525	547	25	22
[EMIm][ClO ₄]	541	523	547	18	24
[BMIm][NO ₃]	549	538	547	11	9
[EMIm][NO ₃]	555	534	547	21	13
[BMIm][DCA]	556	543	547	13	4
[EMIm][DCA]	553	539	547	14	8
[BMIm][Cl] ^b	565 ^c	548	547	17	−1
[EMIm][AC]	574	549	547	25	−2

^a Ethanol mole fraction equal to 0.40 and data from ref 25.

^b [BMIm][Cl] was given to be instead of [EMIm][Cl]. ^c Indirect λ_{\max} value recalculated from $E_T(30)$ according to ref 23.

ILs and are significantly lower for group II (0.73–0.80) and group I (0.53). The former is comparable to the case of high polar liquid [EtNH₃][NO₃] and water, while the latter corresponds to nonhydroxyl ILs. On the other hand, the HBA parameter β , which is said to be controlled solely by the anions,^{1a} increase in the order similar to the nonhydroxyl ILs, but of large magnitude. Combined with the above results, one can think that the difference in polarity for hydroxyl ILs could be mainly ascribed to the expanded HBD ability generated by the hydrogen bond donor (OH) on the cation, while less influenced by the dipolarity/polarizability and HBA basicity. Further, the different HBD ability induced by the hydroxyl group could be indicative of the interaction between the anion and the hydrogen bond donor (OH). It can be concluded that the ability of anions of hydrogen bonds in these hydroxyl ILs is the following: [PF₆] \approx [NTf₂] \approx [ClO₄] < [DCA] \approx [NO₃] \approx [Cl] < [AC].

The hydroxyl group is indispensable for the enhanced and expanded polarity, since the $E_T(30)$ scales for the 1/1 (molar ratio) binary mixtures of ethanol and the nonhydroxyl ILs were exclusively decreased as compared to each of the component (Table 2), and the magnitude of decrease for group III anions is somewhat higher than for group II and I anions, as shown in Figure 3. The case is similar to the work reported by Pandey et al., who first found that ethanolic solutions of [BMIm][PF₆] possess unexpectedly larger polarity than each of the component,²⁵ and further found that the binary mixture of [BMIm][PF₆] and tetraethylene glycol exhibit larger polarity than each component in the full composition range. They called it

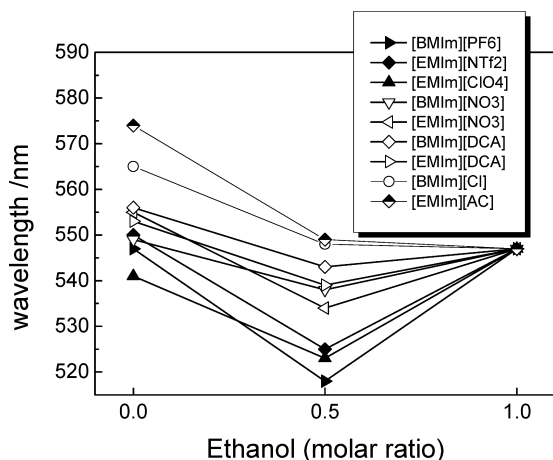
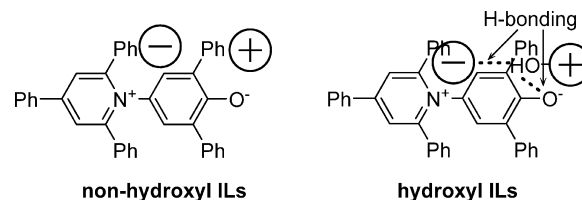


Figure 3. Solvatochromic probe responses in binary ILs + ethanol solutions (molar ratio = 1/1) under ambient conditions.

“hyperpolarity” and attributed it to the synergistic solvent effect of the hydrogen-bonded HBD/HBA complexes generated by intersolvent HBD/HBA association between the acidic C(2)-H on [BMIm]⁺ and the ether oxygens of tetraethylene glycol.

Gordon and co-workers suggested that $E_T(30)$ in general ILs is mainly influenced by the strength of H-bonding between the phenoxide group on Reichardt's dye and the hydrogen atoms on the imidazolium ring.²⁶ In hydroxyl ILs, it should be stressed that the strong polarity is independent of the imidazolium moiety as well as the C(2)-H on imidazolium, since some pyrrolidinium and alkylammonium-based hydroxyl ILs also given high polarity.¹⁰ $E_T(30)$ of Reichardt's dye in hydroxyl ILs could be mainly influenced by the hydroxyl group, which acted as hydrogen bonds donor modulated by the anion. Herein the greatly expanded polarity of hydroxyl ILs is proposed to be correlated to an intramolecular synergistic solvent effect of the hydrogen-bonded HBD/HBA complexes generated by intrasolvent HBD/HBA association between the anions and the hydroxyl group on cations,¹⁶ where the hydroxyl group exhibit a significant differentiating effect on the strength of H-bonding and thus the polarity. Considering that Reichardt's dye is particularly sensitive to HBD solvents and dipolarity/polarizability effect,^{15,27} it can be conjectured that in hydroxyl ILs the phenolate oxygen on Reichardt's dye as a strong electron-pair donor (EPD) or HBA center¹⁶ is suitable for ionic/charge–charge interactions with the anions of ILs and specific for hydrogen-bond interactions with HBD hydroxyl group on cations. Simultaneously, there could exist somewhat ionic/charge–charge interactions between the positive charge of the pyridinium moiety and the cations of ILs, although it was said that the pyridinium ring does not act as an electron-pair acceptor (EPA) due to its delocalized and shielded positive charge by the three 2,4,6-phenyl groups. All of these solute–solvent interactions facilitate stabilization of the ground state of ionic probe, leading to increased and expanded polarity of hydroxyl ILs. In hydroxyl ILs [HOEMIm][DCA], [HOEMIm][NO₃], [HOEMIm][Cl], and in particular [HOEMIm][AC], the hydrogen atom of the hydroxyl group is fixed by the strong H-bonding between hydroxyl group and the coordinative and nucleophilic anions, giving less freedom and acidity to interact with the phenolate part of the solvatochromic betaine dye. This was evidenced by their relatively low HBD ability (low α values as shown in Table 1). On the other hand, the formed strong hydrogen-bond in turn play as a bridge that bind the cation and anion (similar to the case reported by Wu et al.),^{11a} which enhance the rigidity of both the cation and anion, decreasing the magnitude of interac-

SCHEME 1: Cartoon Illustrating Plausible Interaction between Reichardt's Dye and ILs



tion with negatively charged phenolate oxygen and positively charged pyridinium moiety and leading to a lower polarity than other hydroxyl ILs. In contrast, for the hydroxyl ILs [HOEMIm][PF₆], [HOEMIm][NTf₂], and [HOEMIm][ClO₄] the weak H-bonding between cations and anions, as well as the resulting high HBD ability of hydroxyl group induces efficient electrostatic and hydrogen-bond interactions between ILs and zwitterionic dye, thus stabilizing the ground state of ionic probe and giving “hyperpolarity”. A cartoon representation with plausible interaction between Reichardt's dye and ILs is provided in Scheme 1. It can be further proposed that the differentiated effect of hydroxyl group in ILs is only quite effective to ionic solutes with strong HBA ability, while less effective for neutral solutes. This was further supported by the interaction between hydroxyl ILs and the zwitterionic merocyanine probe or neutral solutes (dansylamide and pyrene), as discussed below.

3.2. Computational Analysis (Density Functional Theory Calculations). The structural properties of ILs were obtained by density functional theory (DFT) calculations to find out which geometry is more favorable and to determine the strength of the cation–anion interaction, and finally, to know about the influence of hydrogen bonds between hydroxyl and anions on the polarity. All the calculations were performed with the Gaussian 03 programs using the B3LYP/6-31+G(d,p) method.²⁸ The presence of a minimum amount of energy was ensured by the lack of imaginary vibrational frequencies. The gas-phase energy of the ion-pair formation has been estimated using the equilibrium described in eq 5, according to Turner et al.²⁹

$$\Delta E_{\text{IL}} (\text{KJ/mol}) = 2625.5[E_{\text{AX}}(\text{au}) - (E_{\text{A}^+}(\text{au}) + E_{\text{X}^-}(\text{au}))] \quad (5)$$

where E_{AX} is the energy of the ionic system and E_{A^+} , E_{X^-} is the energy of the pure cation and anion, respectively.

For the sake of brevity, only three hydroxyl ILs ion pair ([HOEMIm][AC], [HOEMIm][Cl], and [HOEMIm][PF₆]) belonging to each type as representative examples were analyzed in the gas phase and were compared with their nonhydroxyl ILs. The optimized geometries as well as calculated structural parameters of the hydroxyl and nonhydroxyl ILs, including ΔE_{IL} , bond length and angle, asymmetric vibrational frequency (ν_a) and dipole moment (μ , Dybe), are given in Figure 4 and Table 3, respectively (atom coordinates shown in Supporting Information).

For nonhydroxyl ILs, the anion was located in front of the imidazolium ring, close to the C2–H2 group (Figure 4). Further, [PF₆] is above the imidazolium ring while [Cl] and [AC] were nearly located in the plane of the imidazolium ring and much more closed to the methyl group. This is in good agreement with previous theoretical reports at different levels.³⁰ From the bond distances of C2–H2 and H2...X as well as interaction energies (ΔE_{IL}), it can be clearly obtained the order of the intensity of H-bonding between anions and H2, as follows: [AC] > [Cl] > [PF₆], consistent with

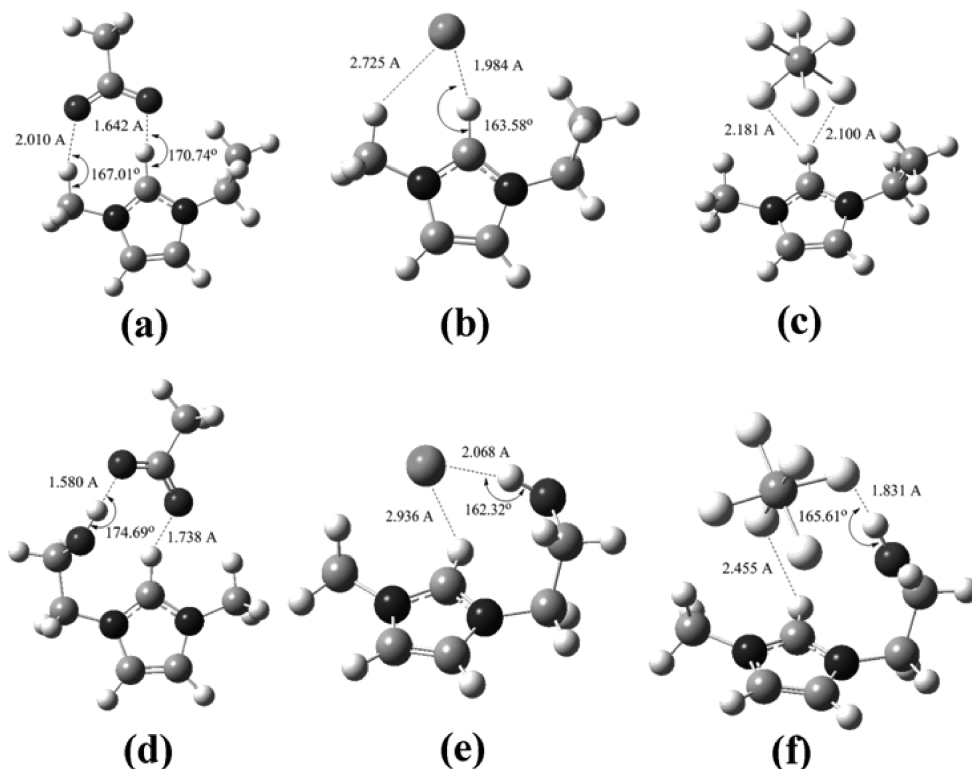


Figure 4. The optimized geometries of six ILs from B3LYP/6-31+g(d,p). (a) [EMIm][AC], (b) [EMIm][Cl], (c) [EMIm][PF₆], (d) [HOEMIm][AC], (e) [HOEMIm][Cl], and (f) [HOEMIm][PF₆] (H-bond is indicated as dashed line).

TABLE 3: The Calculated Parameters of Six ILs in the Gas Phase at B3LYP/6-31+G(d, p) Level

ILs	ΔE_{IL} (KJ/mol)	C2—H2 (Å)	H2...X (Å)	O—H (Å)	H...X (Å)	ν_a (C2—H2) (cm ⁻¹) ^a	ν_a (O—H) (cm ⁻¹) ^a	μ (D)
[EMIm][PF ₆]	-323.1	1.080	2.100			3289		14.8
[EMIm][Cl]	-378.1	1.123	1.984			2620		12.6
[EMIm][AC]	-416.8	1.136	1.642			2455		9.9
[HOEMIm][PF ₆]	-330.4	1.078	2.455	0.975	1.831	3325	3670	13.3
[HOEMIm][Cl]	-397.1	1.076	2.936	0.996	2.068	3335	3252	10.3
[HOEMIm][AC]	-437.9	1.111	1.738	1.015	1.580	2795	2902	10.5

^a Calculated by eq 6.

the results obtained from HBD/HBA. However, the difference in intensity of hydrogen bonds for the various anion-based nonhydroxyl ILs is not enough to differentiate their polarities, since the (C2)H2 is less acidic and free to interact with the phenolate oxygen of Reichardt's dye, as indicated by the comparable hydrogen bond donating ability of the nonhydroxyl ILs (α values in Table 1). As for hydroxyl ILs, calculated ion-pair formation energies are noticeably lowered as compared to the nonhydroxyl ILs, suggesting that ionic-pair structures are stabilized by the appended OH. Coherently, the locations of the anion are obviously changed, moving closed to the hydroxyl group and the O—H...X are nearly a line (angles are shown in Figure 4). The weak shortening of C2—H2 bonds and the noticeable increasing of H2...X distances, as well as the (O)H...X distances much shorter than the van der Waals distance of X...H (Cl...H = 2.95 Å, O...H = 2.72 Å, F...H = 2.67 Å³¹), imply that there are strong H-bonding of the anions with the hydroxyl group ((O)H...X), instead of the initially formed H-bonding (C2)H2...X in nonhydroxyl ILs. Although frequency analysis shown some difference from the experiment results, the computed C2—H2 and O—H stretching modes are in good agreement with the previous theoretical result.³² The results of the asymmetric vibration of the hydroxyl group (ν_a (O—H)) indicated that there existed strong hydrogen bonding between the anion and the hydrogen atom of hydroxyl in [HOEMIm][AC] while relatively weak hydrogen bonding in [HOEMIm][PF₆]. This strong

interaction effectively weaken the O—H bond, resulting in a decrease of ν_a (O—H) in [HOEMIm][AC]. Further consideration of the different charge densities of the anions [AC], [Cl], and [PF₆], as indicated by Hunt et al.,³³ and in combination of the change of O—H distances, we are convinced that the introduction of hydroxyl on cation inevitably differentiate the H-bonding intensity for the various anions, which is responsible for their expanded polarity scale.

3.3. Solvatochromic, Photochromism, and Thermal Reversion of Spiropyran in Hydroxyl ILs. Merocyanine (MC), zwitterionic isomer of photochromic spiropyran, was known to have negative solvatochromism, meaning that its 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.³⁴ The negative solvatochromism of MC has been used as an empirical indicator of the polarity of organic solvents, surface, and ionic solvents.^{11a,35} Recently, Wu et al. employed polarity scale E_{SP} (E_{SP} (kcal/mol) = 28 591/ λ_{max} (nm)) of four spiropyran compounds with different substituents, instead of $E_{\text{T}}(30)$, as direct polarity indicator for ILs.^{11a} On the basis of our previous work on photochromism of spiropyran in ILs,^{11b} we further investigated the solvatochromism, photochromism, and thermal reversion of MC (6-NO₂ spiropyran, Supporting Information, Figure S1) in the

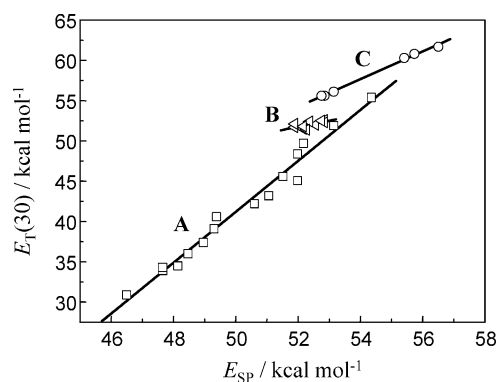


Figure 5. Plot of the $E_T(30)$ scales versus the E_{SP} scales of 16 molecular solvents (A), 10 imidazolium-based nonhydroxyl ILs (B), and 6 hydroxyl ILs (C) (for data of molecular solvents and nonhydroxyl ILs, see Table S4 in Supporting Information). The results of correlation analysis for the 6-NO₂ spiropyran dye is the following: molecular solvents, $E_T(30) = 3.15689E_{SP} - 116.64031$ ($r = 0.98929$, $s = 1.08431$); nonhydroxyl ILs, $E_T(30) = 0.76774E_{SP} + 11.81871$ ($r = 0.66113$, $s = 0.33564$); hydroxyl ILs, $E_T(30) = 1.71679E_{SP} - 35.0399$ ($r = 0.998$, $s = 0.20293$). Note that acetate-based ILs of strong hydrogen-bond basicity were not involved due to its invalidity in determining the polarity scales of the ILs.

hydroxyl ILs to gain insight into the polarity of hydroxyl ILs and the interaction between ionic solute with ILs. Here MC was used for a number of reasons. The first arise from the similarity in structure between MC and Reichardt's dye. Both of them are zwitterion, thus useful information derived from MC can be compared to Reichardt's dye. Second, the relatively lower basicity of MC makes it more appropriate than Reichardt's dye for the acidic hydroxyl ILs. Third, $E_T(30)$ data for acidic

ILs can be derived from E_{SP} , since good linearity between $E_T(30)$ and E_{SP} for a series of molecular and ionic solvents was reported.^{11a,35a} However, direct fitting $E_T(30)$ to E_{SP} for both molecular solvents and ILs similar to the previous method inevitably lead to relatively large error and poor linear relationship.¹¹ Thus a plot of the $E_T(30)$ scales versus the E_{SP} scales is fitted individually for 16 molecular solvents, 11 imidazolium-based nonhydroxyl ILs, and 7 hydroxyl ILs, respectively (Figure 5). It is evident that the $E_T(30)$ scales monotonic increased with E_{SP} scales in the full polarity range for all molecular and ionic solvents, due to negative solvatochromism of both probes. In addition, good linearities were obtained for the three series, especially for hydroxyl ILs. Using the evaluated linear relationship given in Figure 5, the $E_T(30)$ value of the hydroxyl ILs were quantitatively estimated (shown in Table 5), which was close to the experimental result and is indicative of the comparability between Reichardt's dye and MC in ILs. In comparison with molecular solvents, however, MC seems to be more insensitive to the solvent polarity in ILs, as indicated by the slope of fitted line. This suggested that the interaction between ILs and MC is much stronger than the case of ILs and Reichardt's dye, probably due to the free and adaptive zwitterionic structure.

In previous work, we and Wu et al. also found that the photochromic behavior of spiropyran in ILs is directly related to its microenvironment. Whether a spiropyran displayed positive (in general ILs) or negative photochromism (e.g., in [HOEMIm][PF₆], the absorption of MC decreased by irradiation with either UV or visible light) or not is strongly dependent on the $E_T(30)$ scales (or E_{SP} scales) and the structure of the surrounding ILs. Figure 6 presents the normalized absorption spectra of MC in hydroxyl ILs. As can be seen from Figure 6

TABLE 4: Solvatochromism, Photochromism, and Thermal Reversion of Spiropyran in ILs

ILs	λ_{\max} (nm)	E_{sp} (kcal/mol)	$E_T(30)$ (kcal/mol) ^a	$10^3 k$ (s ⁻¹)	$t_{1/2}$ (min)	photochromism ^b
[EMIm][PF ₆]	541	52.8	52.4(52.6)	<i>c</i>	<i>c</i>	<i>c</i>
[EMIm][NTf ₂]	544	52.6	52.2(52.0)	0.378	30.56	P
[EMIm][ClO ₄]	546	52.4	52.0(52.4)	0.686	16.84	P
[EMIm][DCA]	551	51.9	51.6(51.7)	0.382	30.24	P
[EMIm][NO ₃]	548	52.2	51.9(51.5)	0.813 ^d	14.21 ^d	P
[EMIm][AC]	433	66.0	<i>e</i>	<i>e</i>	<i>e</i>	none
[HOEMIm][PF ₆]	506 ^g	56.5 ^g	62.0(61.7)	0.0237 ^f	487.45 ^f	N
[HOEMIm][NTf ₂]	513	55.7	60.6(60.8)	0.0489	236.25	N
[HOEMIm][ClO ₄]	516	55.4	60.1(60.3)	0.0297	388.97	N
[HOEMIm][DCA]	538	53.1	56.2(56.1)	0.655	17.64	P
[HOEMIm][NO ₃]	541	52.8	55.7(55.6)	0.407 ^f	28.38	P
[HOEMIm][Cl]	542	52.8	55.5(55.6)	<i>c</i>	<i>c</i>	<i>c</i>
[HOEMIm][AC]	422	67.1	<i>e</i>	<i>e</i>	<i>e</i>	none

^a Estimated from E_{sp} and the experiment value of $E_T(30)$ was given in parentheses for comparison (note: $E_T(30)$ for acidic hydroxyl ILs was derived from $E_T(33)$). ^b P, positive photochromism; N, negative photochromism; none, no evident photochromism. ^c No data can be given since the metastable supercooled state is liable to freeze. ^d Measured at a supercooled state. ^e No data can be given since acetate-based ILs of strong hydrogen-bond basicity were not involved due to its invalidity in determining the polarity scales of the ILs. ^f Data from ref 11b.

TABLE 5: λ_{em} of Dansylamide and Pyrene I_1/I_3 Value in ILs and Other Solvents under Ambient Conditions

solvent	λ_{em} ^a (nm)	pyrene ^b I_1/I_3	solvent	λ_{em} (nm)	pyrene I_1/I_3
[EMIm][PF ₆] ^c	516	1.62	[HOEMIm][PF ₆]	527	1.72
[EMIm][NTf ₂]	515	1.62	[HOEMIm][NTf ₂]	515	1.51
[EMIm][ClO ₄]	514	1.70	[HOEMIm][ClO ₄]	527	1.69
[EMIm][DCA]	506	1.61	[HOEMIm][DCA]	518	1.58
[EMIm][NO ₃] ^c	512	1.61	[HOEMIm][NO ₃]	507	1.59
[EMIm][AC]	482	1.33	[HOEMIm][Cl] ^c	503	1.57
dichloromethane	497	1.19	[HOEMIm][AC]	480	1.38
ethanol	502	1.12	acetonitrile	509	1.50
methanol	503	1.24	water	549	1.46 ^d

^a Excited at 351 nm. ^b Excited at 337 nm. ^c Measured at a supercooled state. ^d Pyrene concentration in water was ~0.1 mM.

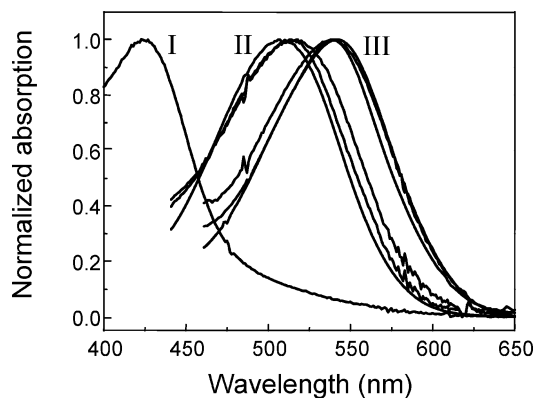


Figure 6. Normalized absorption spectra of MC in hydroxyl ILs. From left to right: [HOEMIm][AC] (I), [HOEMIm][PF₆], [HOEMIm][NTf₂], and [HOEMIm][ClO₄] (II), and [HOEMIm][DCA], [HOEMIm][NO₃], and [HOEMIm][Cl] (III).

and Table 5, all hydroxyl ILs can be classified into three groups according to their absorption positions and photochromic behavior of MC, similar to the case of Reichardt's dye. (I) MC in less polar hydroxyl ILs with anions [NO₃], [DCA], and [Cl] exhibited absorption band centered at $\lambda_{\text{max}} = 540$ nm and indeed shown positive photochromism, similar to the case in nonhydroxyl ILs and general organic solvents; (II) Negative photochromism were observed in polar hydroxyl ILs, [HOEMIm][PF₆], [HOEMIm][NTf₂] and [HOEMIm][ClO₄], together with a hypsochromic (blue)-shift band around $\lambda_{\text{max}} = 510$ nm, suggested that MC is much more stable than SP in high polar hydroxyl ILs. This is in accordance with the conclusion drawn by Wu et al. that the spiropyrans containing less polar alkyl groups show positive photochromism with the E_{SP} scales less than about 53.9 kcal/mol, while negative ones with the E_{SP} scales larger than 53.9 kcal/mol;^{11a} (III) However, for acetate-based hydroxyl ILs, the spiropyran appeared as pale yellow with a corresponding strong absorption band at 422 nm, much lower than as expected from its $E_{\text{T}}(30)$ scales. Meanwhile, no evident photochromism is observed in these ILs. The results indicated that spiropyran may not present as fully trans-MC forms in this ionic liquid, but stable *cis*-merocyanine complexes.^{11a} In fact, no matter whether a hydroxyl is appended, the specific photochromism in acetate-based ILs always hold true.

In addition to the solvatochromic and photochromism behavior of spiropyran, we have further investigated the effect of polarities of hydroxyl ILs on the thermal reversion of spiropyran from MC to closed colorless form (SP). The decay rate constants (k) and half-lifetime ($t_{1/2}$) for the thermal reversion of MC in ILs were obtained according to the established methods.^{11b} Although the decay rates of the thermal reversion of MC involving an intramolecular charge recombination process is polarity dependent, group II hydroxyl ILs of high $E_{\text{T}}(30)$ scales such as [HOEMIm][DCA] and [HOEMIm][NO₃] exhibit comparable k and half-lifetime with those of both nonhydroxyl ILs and short chain alcohols,^{11b} probably due to their comparable E_{sp} scales. Further, the results are almost one magnitude higher than the thermal recovery of MC in group III hydroxyl ILs, which possess higher E_{sp} and $E_{\text{T}}(30)$ and exhibit negative photochromism. Note that acetate-based hydroxyl ILs exhibited no evident thermal decay.

3.4. Photophysical Neutral Probe Studies. Other than the zwitterionic probe, neutral fluorescence probe molecules such as dansylamide and pyrene also preferred as indicator for polarity, which can overcome the problems such as the large size and the charge on the Reichardt's dye pose, and also the

concentration of the fluorescent probes ($\leq 10^{-5}$ M) used can be much lower than that required for an absorption probe.³⁶ This minimizes the possibility of any probe–probe interaction(s) that may occur during absorption probe. Indeed, the two fluorescence solvatochromic probes have been extensively used to investigate the microenvironment and polarity of ILs.^{22,37}

3.4.1. Dansylamide. Dansylamide is widely used as fluorescence probe for polarity because its emission property is very sensitive to the nature of its local environment. Large bathochromic shift of the emission is observed on going from a nonpolar to a polar environment. Table 5 lists the corresponding emission maxima (λ_{em} nm) of dansylamide (5-*N,N*-dimethylamino-1-naphthalenesulfonamide in Supporting Information, Figure S1) in nonhydroxyl and hydroxyl ILs. Generally, λ_{em} values determined for the hydroxyl ILs increased with the polarity, while the corresponding nonhydroxyl ILs exhibit slight change. For example, the measured λ_{em} values within less polar hydroxyl ILs [HOEMIm][NO₃] and [HOEMIm][Cl] (except that of [HOEMIm][DCA]) are close to that observed in short chain alcohol and acetonitrile, suggesting a similar microenvironment sensed by dansylamide when dissolved in these hydroxyl ILs and the organic solvents. However, the λ_{em} values in the polar hydroxyl ILs are greatly enhanced but significantly lower than that of water.

3.4.2. Pyrene. The pyrene solvent polarity scale is defined by the I_1/I_3 emission intensity ratio, where I_1 corresponds to the $S_1(v=0) \rightarrow S_0(v=0)$ transition, and I_3 denotes the intensity of the $S_1(v=0) \rightarrow S_0(v=1)$ transition in pyrene.³⁸ The I_1/I_3 emission intensity ratio increases with increasing solvent polarity. The measured data in Table 5 are obviously lower than the result obtained by Fletcher et al.,^{37a} which is not unexpected as the pyrene I_1/I_3 values depend strongly on experimental conditions.³⁹ Herein we can compare the pyrene I_1/I_3 values in all the solvents under the similar experimental conditions. The I_1/I_3 value nearly constant for all of the nonhydroxyl ILs, with the exception of [EMIm][AC]. In contrast, the I_1/I_3 value for hydroxyl ILs increased roughly with the polarity, range from 1.38 for [HOEMIm][AC] to 1.72 for [HOEMIm][PF₆]. However, all ILs exhibit high I_1/I_3 value even beyond that of water, which is obviously different from the case sensed by dansylamide. From the above results, one can see that both the two probes exhibit polarity-responsive fluorescence for nonhydroxyl and hydroxyl ILs, which is consistent with the case of the zwitterionic molecule in these ILs but show apparent discrepancies in the polarity. This could be because the neutral solutes (dansylamide and pyrene) are less influenced by the ILs solvent, as compared to ionic solutes (Reichardt's dye and MC).

4. Conclusions

In summary, although the nonhydroxyl ILs based on imidazolium moiety possess polarity falling within the same narrow range of values ($E_{\text{T}}(30) = 49.8\text{--}52.6$ kcal/mol), a greatly expanded polarity ($E_{\text{T}}(30) = 51.2\text{--}61.7$ kcal/mol) of the corresponding hydroxyl ILs with various anions ([PF₆], [NTf₂], [ClO₄], [BF₄], [DCA], [NO₃], [AC], and [Cl]) were first observed and shown appreciable anion-dependence. Among all hydroxyl ILs, those based on anions [PF₆], [NTf₂], and [ClO₄] possess unexpected "hyperpolarity" ($E_{\text{T}}(30) = 60.3\text{--}61.7$ kcal/mol) close to protic ILs and water. The polarity of the hydroxyl ILs increased in the order [AC] < [Cl] \approx [DCA] \approx [NO₃] < [ClO₄] \approx [NTf₂] \approx [PF₆], rather similar to the trend of the HBA ability and can be classified into three groups. Further characterization by Kamlet–Taft parameters and computational analysis indicated that the greatly expanded range of polarity of hydroxyl

ILs is correlated to an intramolecular synergistic solvent effect of the hydrogen-bonded HBD/HBA complexes generated by intrasolvent HBD/HBA association between the anions and the hydroxyl group on cations. The appended hydroxyl group exhibits a profound differentiating effect on the strength of the formed H-bonding between hydroxyl and anions, which in turn induced difference in multiple solute–solvent interactions, involving the ionic/charge–charge interactions of ILs and the zwitterionic probe, and the hydrogen-bond interactions of the phenolate oxygen and HBD hydroxyl group on cations of ILs. The effect of structure and polarity of hydroxyl ILs on a model polarity-sensitive ionic reaction (thermal reversion of spiropyran) was indeed show a noticeably polarity-dependent solvatochromism, photochromism, and thermal reversion. Noteworthy is that the hydroxyl ILs of “hyperpolarity”, which behaved as single-component substance and not as a mixture, will certainly fill the polarity gap between water and general organic solvents and could be employed as high polar nonacidic and nonaqueous ionic media for synthesis and catalysis, especially for the polarity-promoted applications. Our work also confirmed the increased cation–anion interactions through introduction of a more active group and demonstrated the possibility of rational design and synthesis of polarity-specific ILs.

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Supporting Information Available: Experimental details of synthesis and characterizations of ILs (^1H NMR, ESI-MS, and water content), $E_{\text{T}}(30)$ and E_{SP} scales in ILs, as well as atom coordinates of ILs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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