Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Deviation of Polarity from Linearity in Liquid Mixtures Containing an Ionic Liquid

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1. Sources, purification methods and final purities of substances used in the study:

1-Methylimidazole with 99 % purity, *n*-butylbromide with 99% purity, sodium dicyanamide with 98 % purity and 2,6-diphenyl-4-(2,4,6-triphenyl-pyridinium-1-yl)phenolate (≥90%) were purchased from M/s Sigma Aldrich. 1-Methylimidazole and *n*-butylbromide were distilled prior to their use. Sodium tetrafluoroborate (98%) is used as obtained from Merck. Methanol with 99.7% purity, formamide with 99.5% purity and DMSO with 99.5% purity were used as purchased from Merck. Milli-Q water with the specific conductance of 5.5×10^{-6} Sm^{-1} was used throughout the experiments.

Table S1: Source of compounds, the purification methods applied and final purities of the compounds used in the study.

Compound	**Source**	**Purification Methods**	**Final Purity**
1-methylimidazole	M/s Sigma Aldrich	Distillation	>99.7%
n-butylbromide	M/s Sigma Aldrich	Distillation	>99.7%
Reichardt's $E_T(30)$ dye	M/s Sigma Aldrich	Used as is	>90%
Sodium tetrafluoroborate	M/s Merck Ltd.	Used as is	>98%
Sodium dicyanamide	M/s Sigma Aldrich	Used as is	>98%
Methanol	M/s Merck Ltd.	Used as is	>99.7%
DMSO	M/s Merck Ltd.	Used as is	>99.5%
Formamide	M/s Merck Ltd.	Used as is	>99.5%
Water		Milli-Q water	With specific conductance of 5.5×10^{-6} Sm^{-1}
$[C_4C_1im][BF_4]$	Synthesised in the laboratory	Excess salts were removed by filtration through Buckner funnel with celite powder. Water and DCM was removed by high vacuum 50-70°C.	Purity >99% Halide contents < 25 ppm, water content < 50 ppm
$[C_4C_1im][N(CN)_2]$	Synthesised in the laboratory	Excess salts were removed by filtration through Buckner funnel with celite powder. Water and DCM was removed by high vacuum 50-70°C.	Purity >99% Halide contents < 30 ppm, water content < 50 ppm

2. Structures of the ionic liquids and solvatochromic dyes used in the study

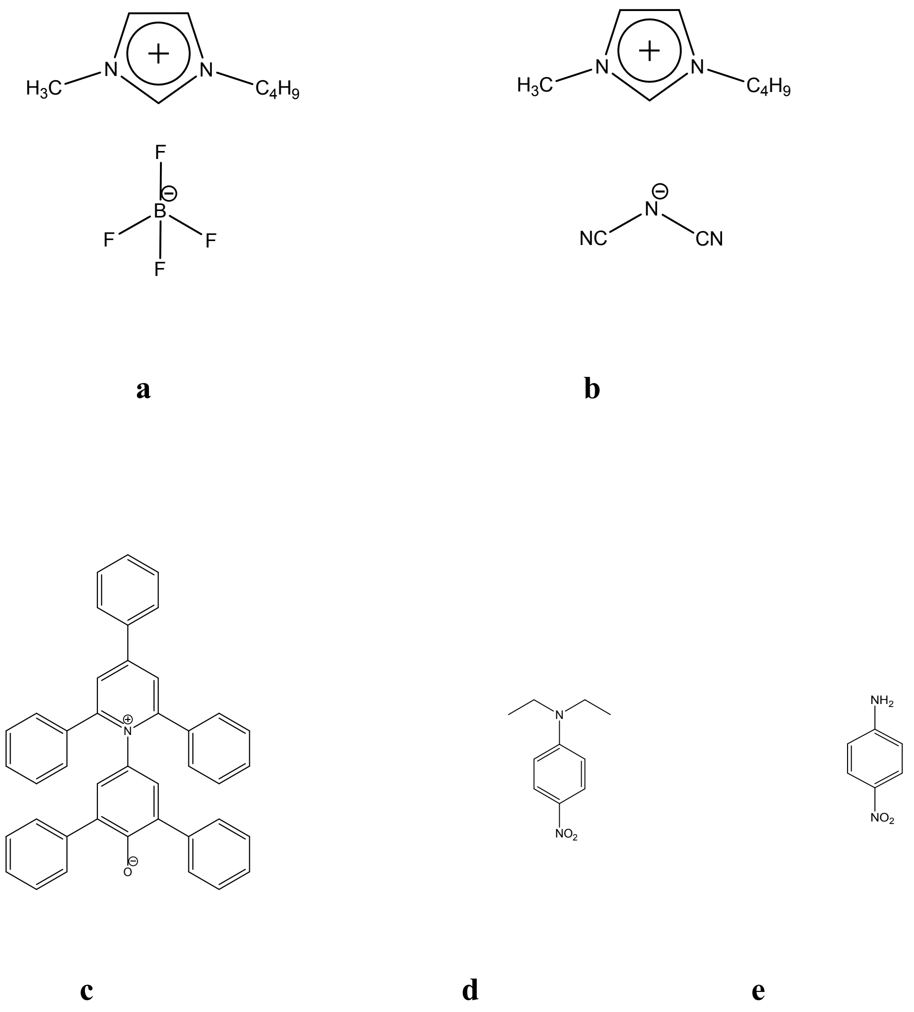


Figure S1. Structures of (**a**) [C_4C_1im][BF_4], (**b**) [C_4C_1im][N(CN)$_2$], (**c**) Reichardt's $E_T(30)$ dye, (**d**) Diethylnitroaniline dye and (**e**) Nitroaniline dye.

3. Synthesis and purification of ionic liquids

Synthesis of ionic liquid was carried out according to the standard procedures described in the literature. First [C_4C_1im]Br ionic liquid was synthesized by the quarternization reaction of 1-methylimidazole and *n*-butyl bromide.[1,2] For this 1-methylimidazole and n-butyl bromide were mixed in 1:1.2 molar ratio and heated under reflux condenser for 15 h at 60°C, in inert atmosphere under nitrogen gas. Excess of *n*-butyl bromide was removed by the extraction process using ethyl acetate. The ionic liquid was then dried thoroughly under high vacuum for 6 h at 70°C.

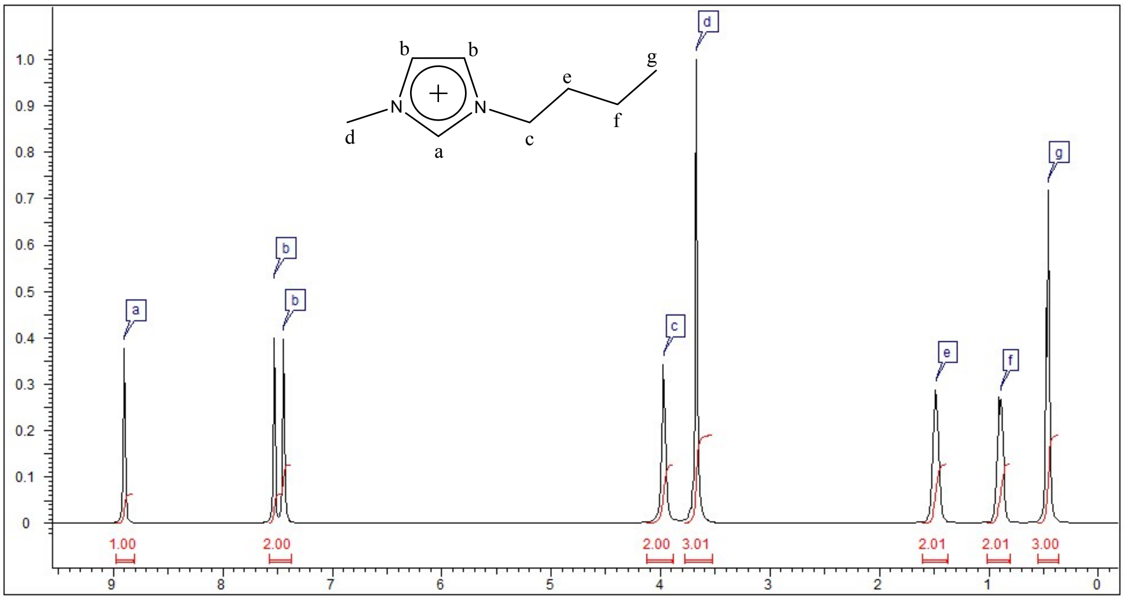
Synthesis of [C_4C_1im][BF_4] and [C_4C_1im][$N(CN)_2$] were carried out by the anion exchange reaction of [C_4C_1im]Br.[3] [C_4C_1im]Br was dissolved in dichloromethane and then sodium salt containing the respective salt was mixed (1.2 molar ratio to that of [C_4C_1im]Br). The reaction mixture was allowed to stir for 24 h at room temperature in inert atmosphere under nitrogen gas. Excess of salts ware removed by multiple filtration using Buckner funnel, dichloromethane was used as the solvent and celite was used to capture the excess salts. The dichloromethane was removed by rota-vapour at 50°C. Thereafter, the ionic liquids were allowed to dry under high vacuum for 6-10 h at 70°C.

4. Characterization and purity of ionic liquids

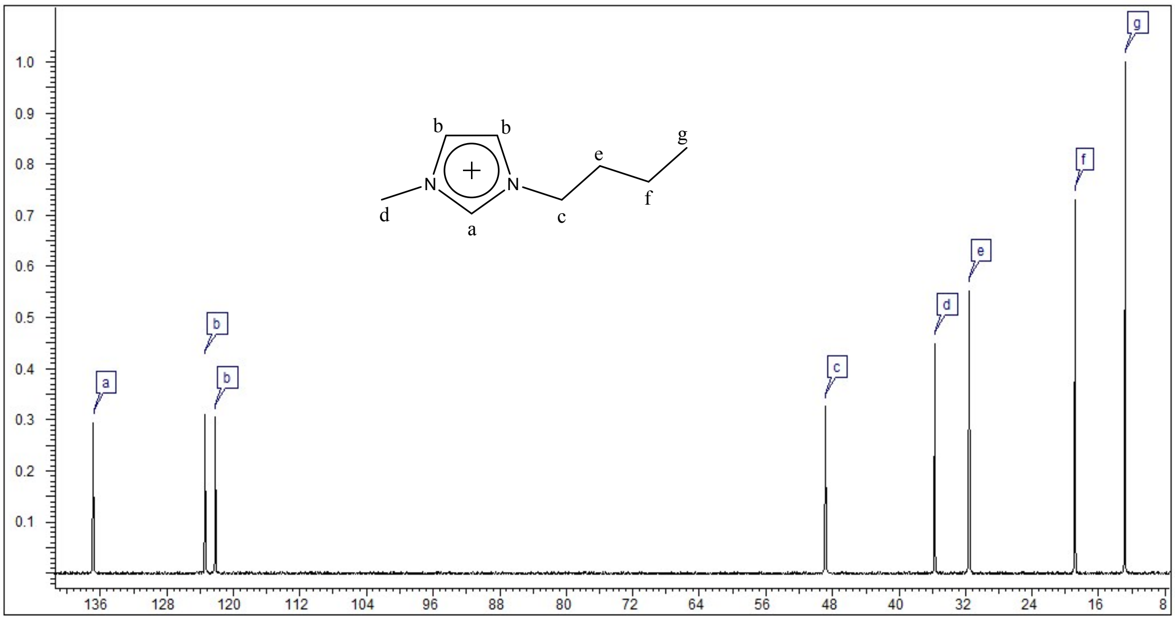
Characterization of ionic liquids was done using the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR techniques. In order to check the dissociation of ionic liquid in water mixtures the NMR spectra were also recorded of the mixture of [C_4C_1im][BF_4] with methanol and water. The spectra for ^{1}HNMR were recorded at 200 MHz NMR spectrometer from Bruker India Pvt. Ltd. whereas, the ^{13}C and ^{19}F NMR spectra were recorded at 500 MHz NMR spectrometer from Bruker India Pvt. Ltd. All the NMR spectra were taken in the neat state (no deuterated solvent was added to the samples), using $CDCl_3$ capillary as antilock. The NMR spectra obtained for the ionic liquids in its pure state and in the ternary mixture are given in **Figure S2**.

The water content of the ionic liquids was measured using coulometer and was found to be less than 50 ppm. The halide contents of ionic liquid were measured using the standard Volhard titration method and were found to be less than 25 ppm for [C_4C_1im][BF_4] and less that 30 ppm for [C_4C_1im][$N(CN)_2$].[4] As it can be assumed that the sodium metal will exist in the form of its salt with bromide ion, its expected amount present in the samples is less than 30 ppm.

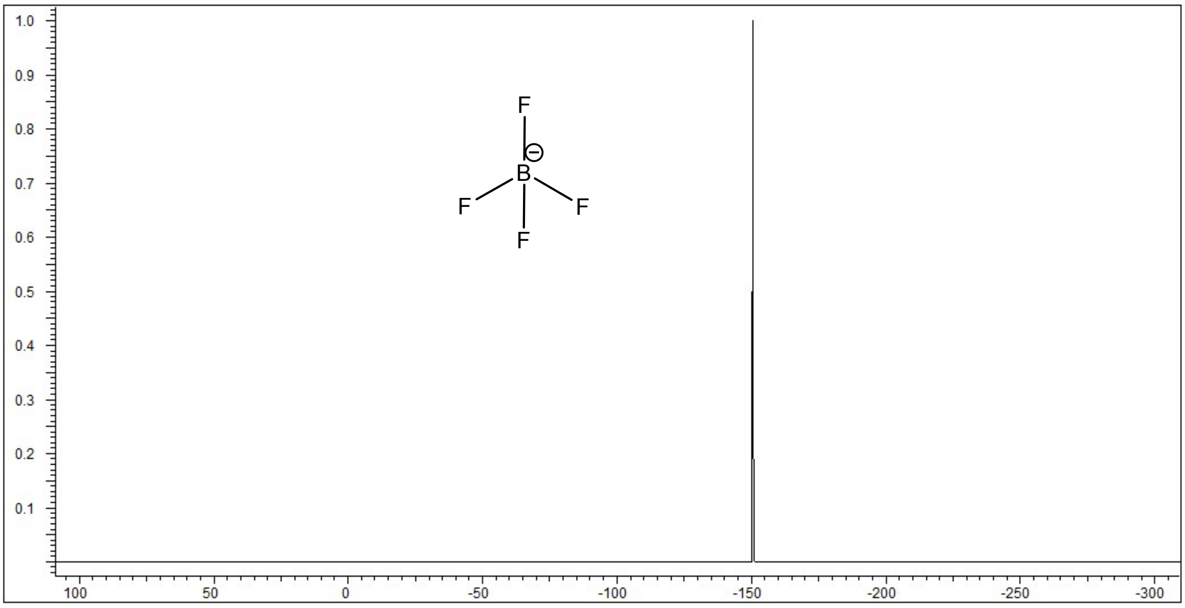
(a) ^{1}H NMR spectrum of pure [C_4C_1im][BF_4] in neat condition at 200 MHz using $CDCl_3$ capillary:



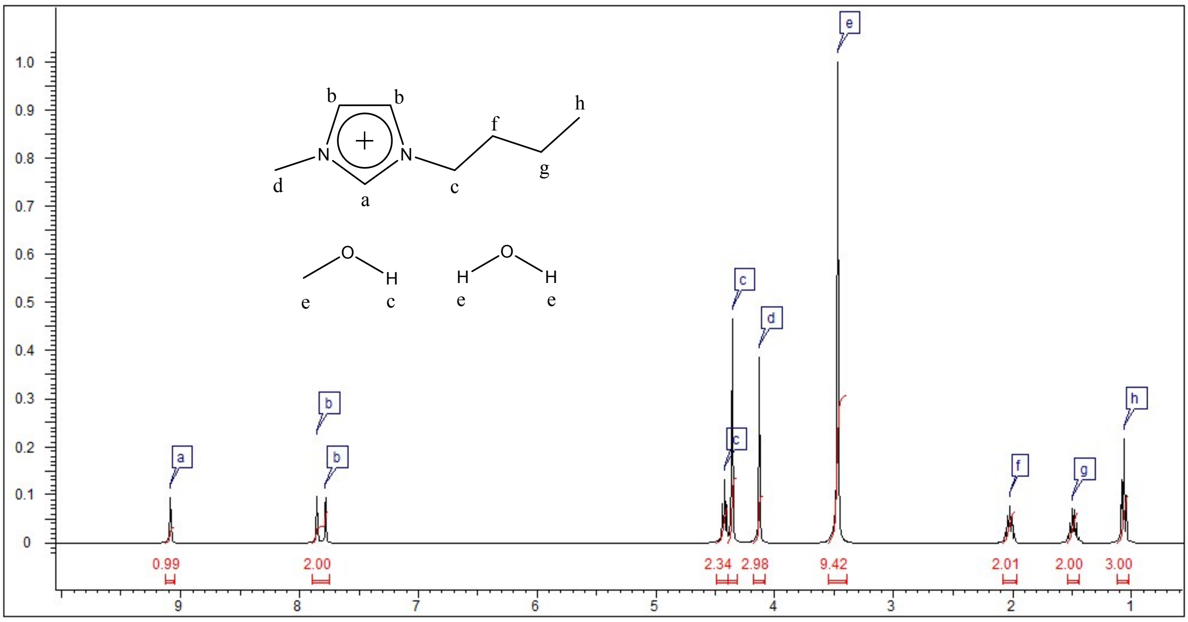
(b) ^{13}C NMR spectrum of pure [C_4C_1im][BF_4] in neat condition at 500 MHz using $CDCl_3$ capillary:



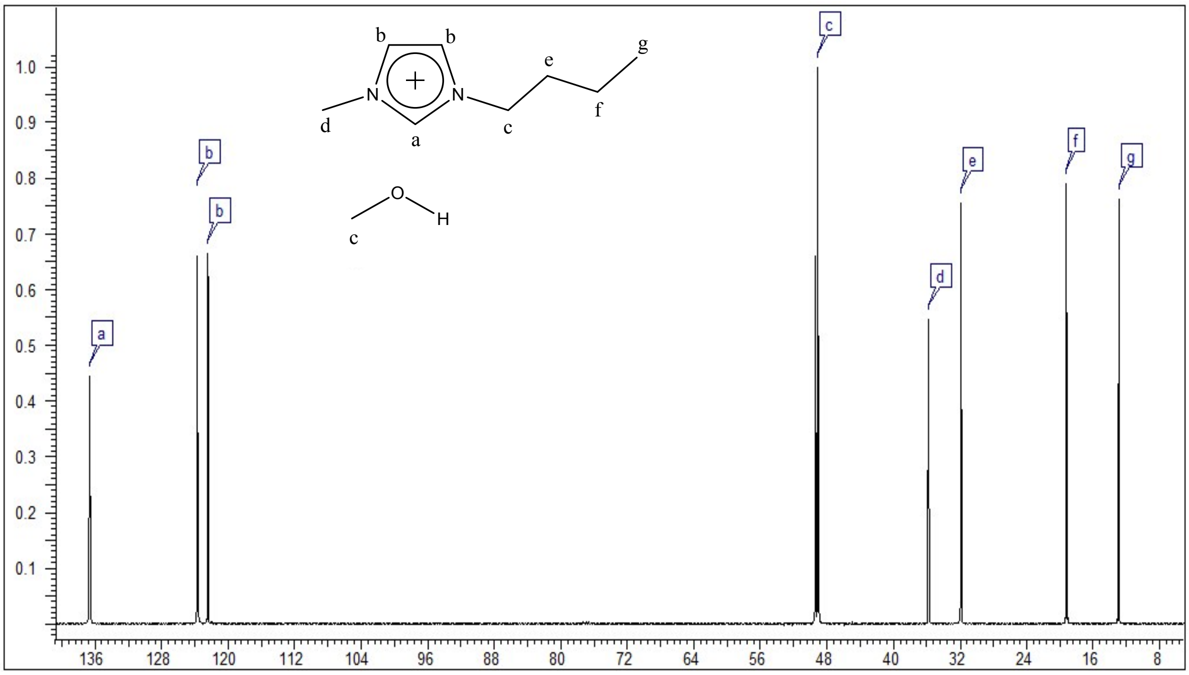
(c) ^{19}F NMR spectrum of pure $[C_4C_1im][BF_4]$ in neat condition at 500 MHz using $CDCl_3$ capillary:



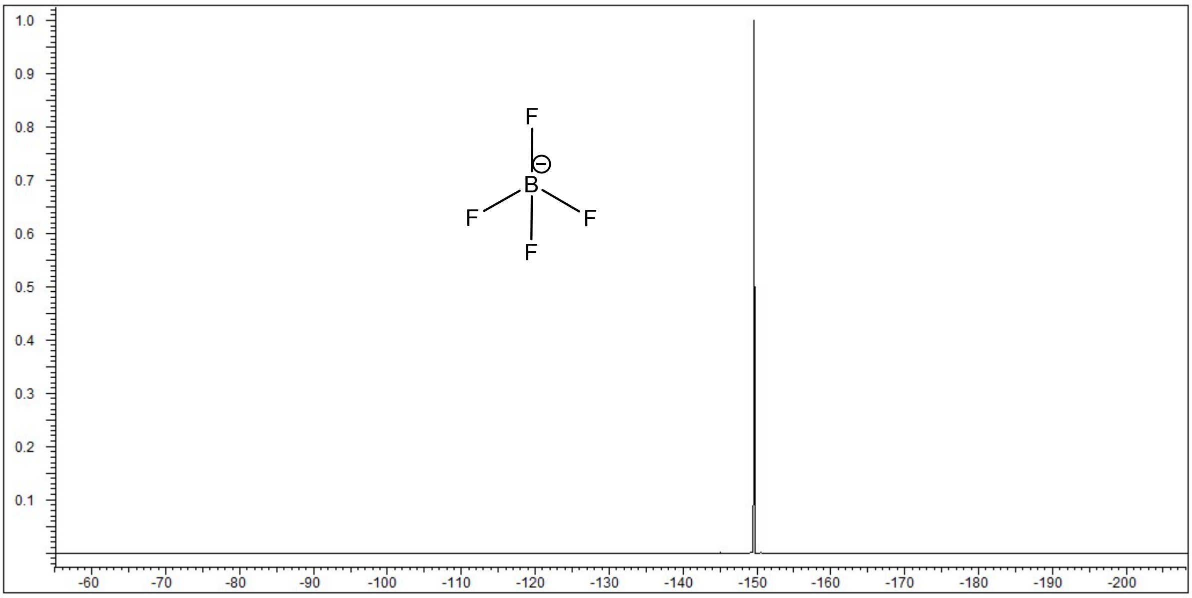
(d) ^{1}H NMR spectrum of the mixture of $[C_4C_1im][BF_4]$, water and methanol in neat condition at 200 MHz using $CDCl_3$ capillary:



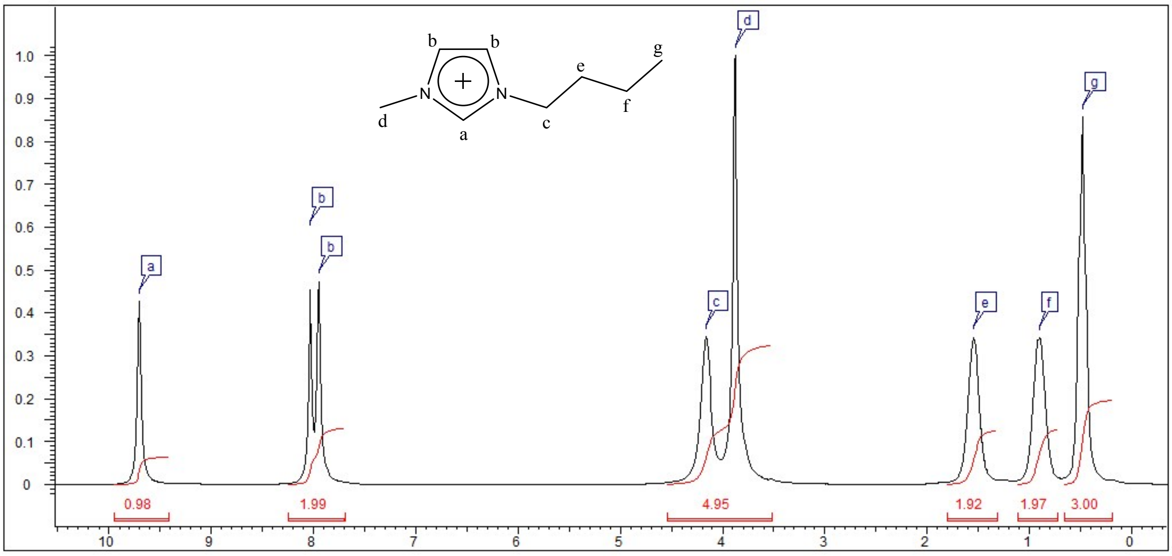
(e) ^{13}C NMR of the mixture of [C_4C_1im][BF_4] with water and methanol:



(f) ^{19}F NMR of the mixture of [C_4C_1im][BF_4] with water and methanol:



(g) ^{1}H NMR spectrum of pure $[C_4C_1im][N(CN)_2]$ in neat condition at 200 MHz using $CDCl_3$ capillary



(h) ^{13}C NMR spectrum of pure $[C_4C_1im][N(CN)_2]$ in neat condition at 200 MHz using $CDCl_3$ capillary

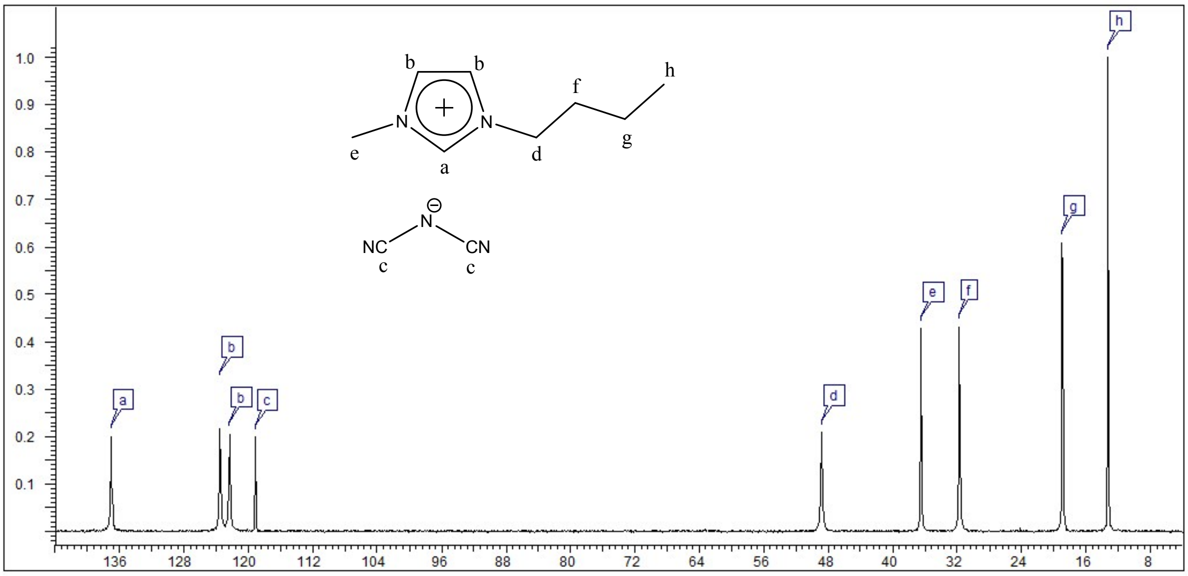


Figure S2: ^{1}H, ^{13}C and ^{19}F NMR spectra (a-h) of pure ionic liquids and mixture of $[C_4C_1im][BF_4]$ with methanol and water in neat conditions using $CDCl_3$ capillary as anti locking solvent.

5. Calculation of solvatochromic parameters

E_T^N parameter:

The E_T^N values for a given solvents is defined as the normalized value of $E_T(30)$ parameter using water ($E_T^N = 1$) and TMS ($E_T^N = 0$) as reference solvents.

$$E_T^N = [E_T(30)_{\text{solvent}} - E_T(30)_{\text{TMS}}]/[E_T(30)_{\text{water}} - E_T(30)_{\text{TMS}}]$$

$$= [E_T(\text{solvent}) - 30.7]/32.4 \qquad (1)$$

$E_T(30)$ value for a given solvent can be calculated from the molar transition energy (in kcal mol^{-1}) of the Reichardt's dye no. 30 (**Figure S1 c**), at NTP, (298 K temperature and 1 bar pressure), using equation (2).[5,6]

$$E_T(30) = hc\,\nu(\mathbf{c})_{\text{max}} N_A = 2.8591\,\nu(\mathbf{c})_{\text{max}} \qquad (2)$$

π^* parameter:

This parameter is a measure of dipolarity/polarizability of solvents and is calculated by the solvatochromic shifts of the λ_{max} values of *N,N*-diethyl-4-nitroaniline dye (**Figure S1 d**) using equation (3).[6]

$$\nu(\mathbf{d})_{\text{max}} = 27.52 - 3.182\pi^* \qquad (3)$$

α parameter:

The α value of solvents is obtained by using $E_T(30)$ and π^* parameters of the solvents as shown by equation (4)[6]

$$\alpha = 0.0649\,E_T(30) - 0.72\pi^* - 2.03 \qquad (4)$$

β parameter:

The hydrogen bond acceptor basicity or β parameter of solvents is determined by equation (5) using the spectroscopic shift of 4-nitroaniline (**Figure S1 e**) with respect to *N,N*-diethyl-4-nitroaniline (**Figure S1 d**).[6]

$$\nu(\mathbf{e})_{\max} = 1.035\nu(\mathbf{d})_{\max} - 2.8\beta + 2.64 \qquad (5)$$

6. Sample Preparation

Sample preparations were carried out under the inert atmosphere of nitrogen gas in glove box. First a stock solution of Reichardt's dye was prepared in DCM. The stock solution thus prepared was added drop wise to the ionic liquids. After the addition of stock solution, DCM was removed from the ionic liquid with the help of high vacuum at 50°C. The binary mixtures of ionic liquids were prepared by the addition of appropriate amount of the molecular solvent or pseudo-solvent to the ionic liquid in the glove box. For the mixtures not containing ionic liquids, preparation of stock solutions were not needed and dye was directly introduced into the solvents. The binary mixture containing the probe molecules was then transferred to the cuvette for the measurement of λ_{max}. All this procedures were performed in the inert atmosphere of glove box under the nitrogen gas. After introducing the samples into the cuvette the λ_{max} values were obtained with the help of UV-visible spectrophotometer. Temperature of the sample was kept constant at 298.15 K using the Peltier setup with an accuracy of ±0.01 K. All the binary mixtures were prepared on mole fraction basis.

7. Determination of λ_{max} for Reichardt's dye with the help of UV-vis spectrophotometer

The wavelength of maximum absorption (λ_{max}) was determined by using the Cary-50 UV-vis spectrophotometer, with an accuracy of $\lambda_{max} \pm 1$ nm. The representative spectra obtained for methanol is shown in the **Figure S3**.

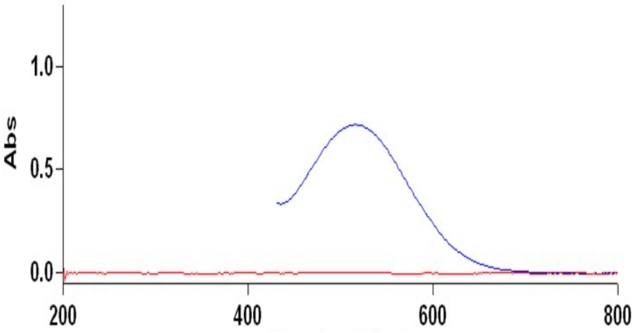


Figure S3: A representative UV-vis spectra obtained for methanol.

For comparison, plots of reported and measured $E_T(30)$ values are shown for water-DMSO and methanol-DMSO binary mixtures **in Figure S4.**

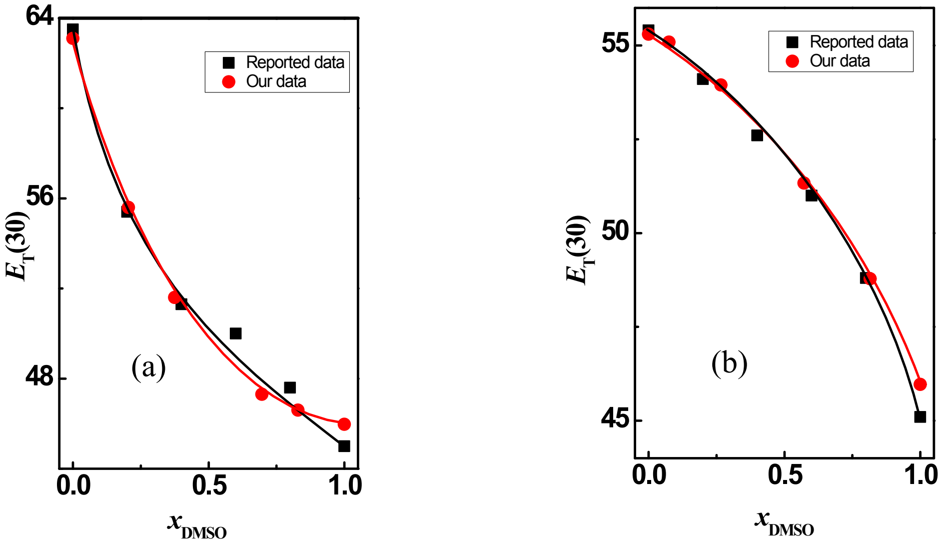


Figure SI 4: Comparison of the data with earlier reported data for (a) water-DMSO and (b) methanol-DMSO mixtures.

8. References

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