

ELECTRONIC SUPPLEMENTARY INFORMATION

**Choline Chloride and Ethylene Glycol Based Deep Eutectic Solvent (DES)
versus Hydroxyl Functionalized Room Temperature Ionic Liquids
(RTILs): Assessing the Differences in the Microscopic Behaviour Between
DES and RTILs**

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Synthesis of DES and Hydroxyl ILs

1. *Synthesis of DES*: The DES (ethaline) was synthesized according to the previous reported literature method.^{1,2} Briefly, 10g of choline chloride (71.6 mmol) was mixed with 8.89g of ethylene glycol (143.2 mmol, density = 1.11) in a single neck round bottom flask. The mixture was stirred at 343k until a clear homogeneous mixture was formed. Then the mixture was cooled down to room temperature and kept under vacuum for 24 hours to reduce the water content of the mixture, the mixture was characterized by ¹H NMR.

¹H NMR (δ_{ppm}): 4.75 brs (1H, OH), 4.4 brs (4H, OH), 3.45 m (2H, N-CH₂), 3.05 m (10H, O-CH₂), 2.72 s (9H, N-(CH₃)₃).

2. *Synthesis of hydroxyl functionalized ionic liquids (Hydroxyl ILs)*: The hydroxyl ILs have been synthesized following the literature method.^{3,4} A brief overview of preparation and characterization of these hydroxyl ILs have been provide below.

2.1.1. *Synthesis of N-(2-hydroxyl ethyl)-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imidie, [OHEMPy][NTf₂]*: 12 gm (141 mmol) of 1-methylimidazole was mixed with 30mL of acetonitrile in a two-neck round bottom flask equipped with reflux condenser. To the solution, 13.6 gm of 2-chloroethanol (170 mmol, 1:1.2) was gradually added. The whole solution was stirred and condensed at 353K for 2 days in the same condition. Then the solution was condensed by evaporation in the rotary evaporator. The reaction product was washed several times with diethyl ether to obtained the solid product of the chloride salt. The white solid product was kept under high vacuum at 323K for 12 hours. Then, 18.71 gm of lithium bis(trifluoromethanesulfonyl)imide (65 mmol) was mixed with 30mL of water and gradually added to an aqueous solution of the chloride salt (9 gm, 54.3 mmol in 20 mL of water). The solution was stirred for 24 hours. Then two separate layer was formed and the aqueous solution

layer was decanted. The ionic liquid layer was dissolved in ethyl acetate and washed with water several times until no precipitation occurs in the washing residue after adding silver nitrate solution. After that, the solvent was evaporated and the viscous residue was mixed with activated charcoal in acetonitrile. The activated charcoal was removed by filtration to obtain a white solution. Then the solvent was evaporated. The ionic liquid was then dried under high vacuum at 308 K for 3 days. The product was a colorless liquid with 85% yield. The compound was characterized by $^1\text{H-NMR}$ and mass spectrometric studies.

$^1\text{H NMR}$ (δ_{H} , ppm): 5.27 t (1H, OH), 3.85 m (2H, N-CH₂), 3.52 m (4H, CH₂-N-CH₂), 3.45 m (2H, O-CH₂), 3.05 s (3H, N-CH₃), 2.1 m (4H, CH₂-CH₂). ESI-MS (+ve): 130.1244 [OHEMPy]⁺

2.2.1. *Synthesis of N-(2-hydroxyethyl)-N,N-dimethylpropan-1-aminium bis(trifluoromethanesulfonyl)imide, [OHC3CH][NTf₂]*: 10 gm (112.2 mmol) of N,N-dimethylethanolamine was mixed with 30mL of acetonitrile in a two-neck round bottom flask equipped with reflux condenser. To the solution, 10.8 gm of 1-bromopropane (134 mmol) was gradually added. The whole solution was stirred and condensed at 353K for 2 days in the same condition. Then the solution was condensed by evaporation in the rotary evaporator. The reaction product was washed several times with diethyl ether to obtain the solid bromide salt. The white solid product was kept under high vacuum at 323K for 12 hours. After that, 13.18 gm of lithium bis(trifluoromethanesulfonyl)imide (46 mmol) was mixed with 30mL of water and gradually added to an aqueous solution of the bromide salt (7 gm, 41.7 mmol in 20 mL of water). The solution was stirred for 24 hours. The two separate layers were formed and the aqueous solution layer was decanted. The ionic liquid layer was dissolved in ethyl acetate and washed with water several times until no precipitation occurs in the washing residue after adding silver nitrate solution. After that, the solvent was evaporated and the viscous residue was mixed with activated charcoal in acetonitrile. The activated charcoal was removed by filtration to

obtained a white solution. Then the solvent was evaporated. The ionic liquid was then dried under high vacuum at 308 K for 3 days. The product was a colorless liquid with 85% yield. The compound was characterized by $^1\text{H-NMR}$ and mass spectrometric studies.

$^1\text{H NMR}$ (δ_{H} , ppm): 5.22 t (1H, OH), 3.80 m (2H, O-CH₂), 3.44 t (2H, CH₂-CH₂-N), 3.36 t (2H, C₂H₅-CH₂-N), 3.12 s (6H, N-(CH₃)₂), 1.67 m (2H, CH₂-CH₃), 0.84 t (3H, CH₂-CH₃). ESI-MS (+ve): 132.1489 [OHCHC3]⁺.

Water content of all the concerned solvents have been measured through Karl Fischer titration after drying several hours. The water content of all the solvent systems have been found to be in accordance with previously reported literature report. We anticipate that water content at this level (for example, approximately 1 water molecules per 100 ethaline molecules) will not affected the experimental result significantly.

Table S1 Water content of the solvent systems used in this study.

SI No.	Systems	Water Content (in PPM)
1	Ethaline	800
2	[OHEMIM][NTf ₂]	250
3	[OHEMPy][NTf ₂]	360
4	[OHC3CH][NTf ₂]	342

3. *Sample Preparation:* Both DES and hydroxyl ILs are dried in the vacuum at 323K for 2 days so as to reduce the moisture contain before use. The viscosity values of all the solvents systems are almost comparable with previously reported literature values.^{2,3,4} The dried solvents were transferred into 2cm quartz cuvette and requisite amount of probe was added to prepare the solution (keeping absorbance below 0.4). All the cuvette were thoroughly sealed with septum and parafilm to avoid moisture intake.

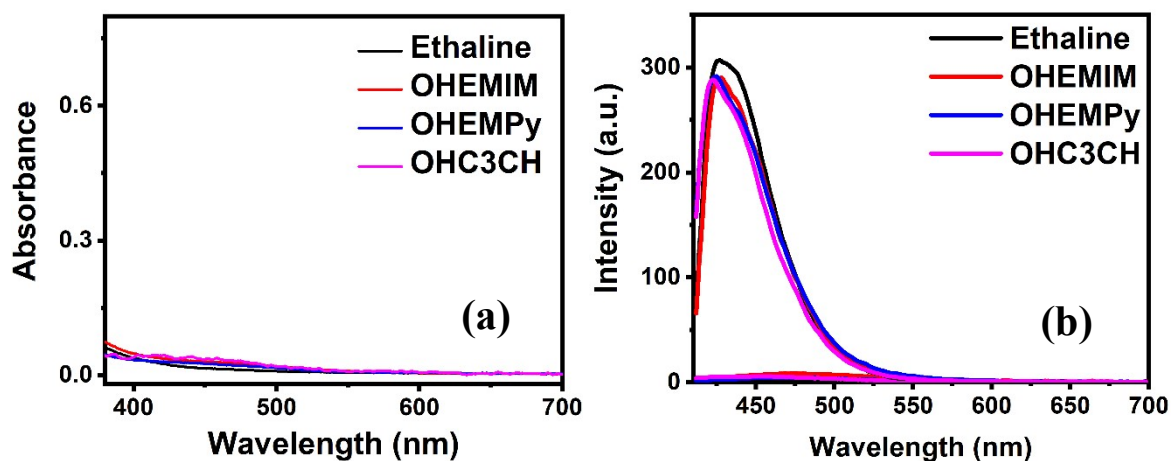


Figure S1: (a) Electronic absorption spectra of neat ethaline and hydroxyl (b) Comparison of Fluorescence spectra of neat solvents and solvents with MPTS (keeping the absorbance of MPTS at approximately 0.3).

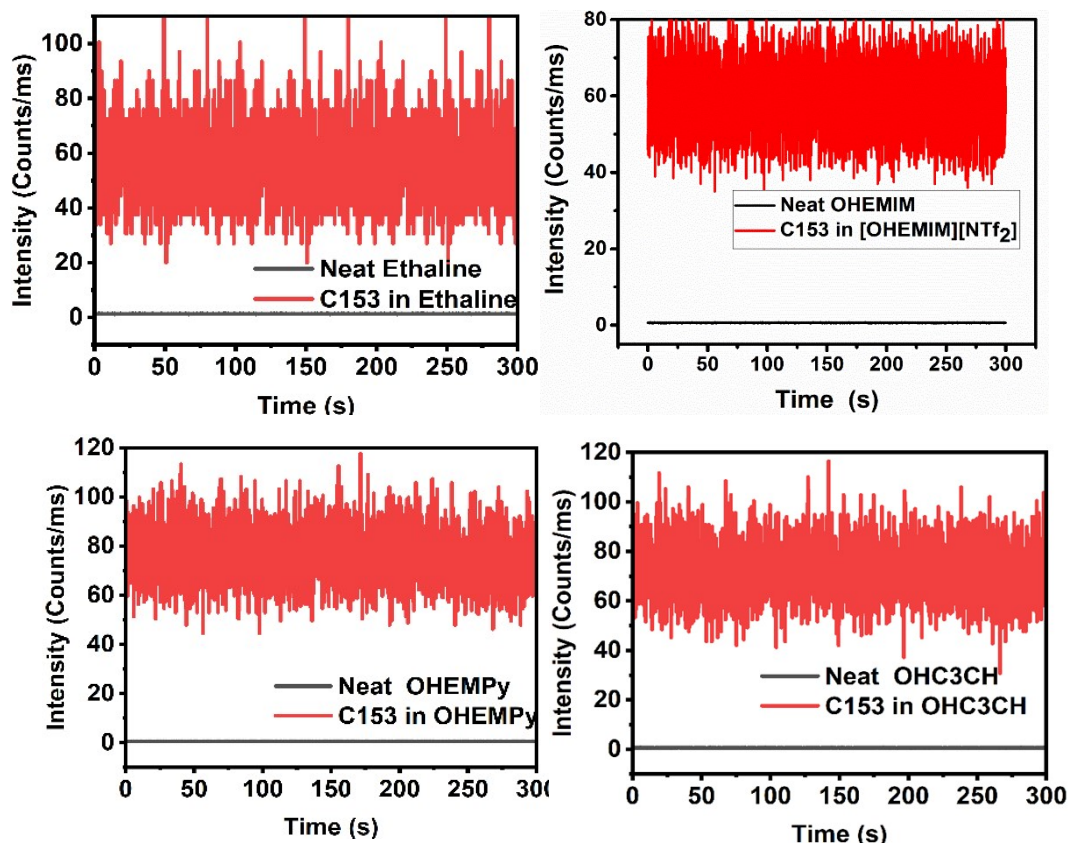


Figure S2: Fluorescence intensity time trace of neat [OHEMIM][NTf₂] and C153 in [OHEMIM][NTf₂].

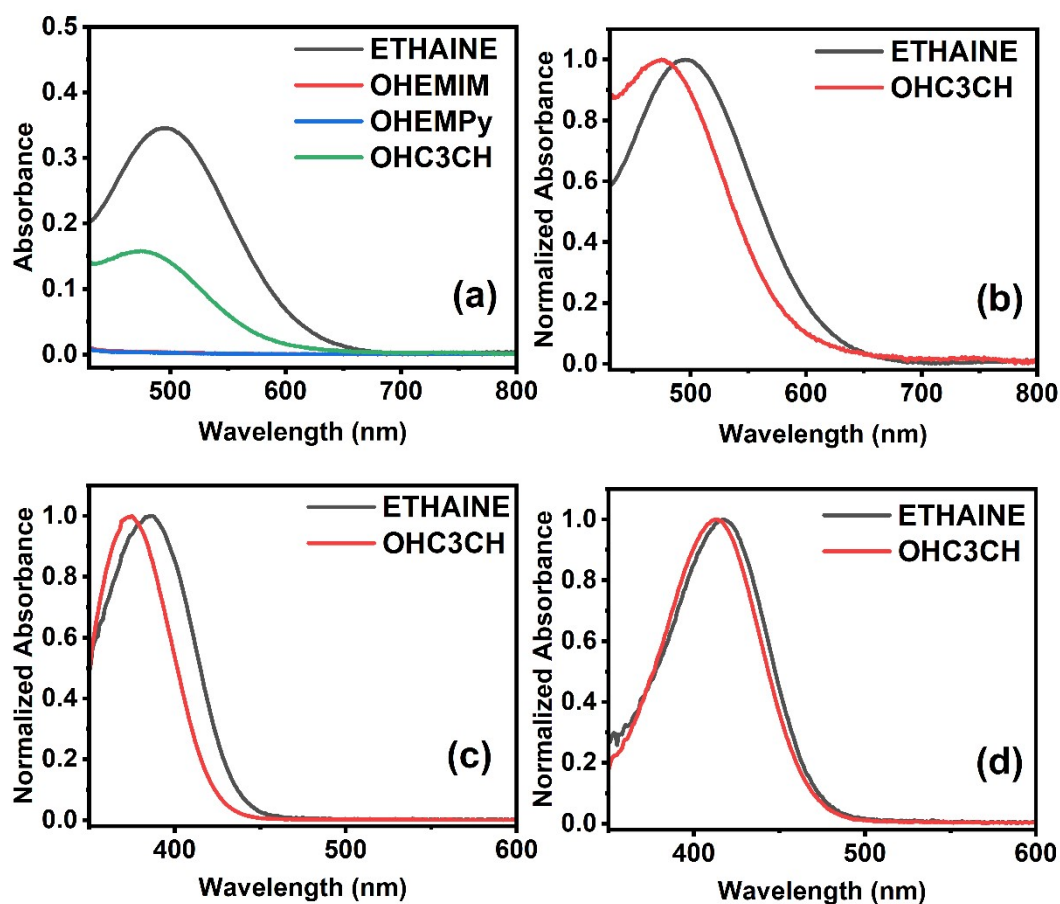


Figure S3: (a) Electronic absorption spectra of Reichardt's dye 30 in all the concerned solvent systems, (b) Normalized electronic absorption spectra of Reichardt's dye 30 showing the shift in λ_{max}^{abs} , (c) Normalized electronic absorption spectra of 4-nitroaniline and (d) N,N-dimethyl-4-nitroaniline dye showing the shift in λ_{max}^{abs} .

Table S2 E_T (30) and Kamlet-Taft parameters of concerned solvent systems

Systems	E_T (30) in kcal/mol	π^*	α	β
Ethaline	57.78	1.19	0.84	0.45
[OHC3CH][NTf ₂]	60.19	1.13	1.05	0.24

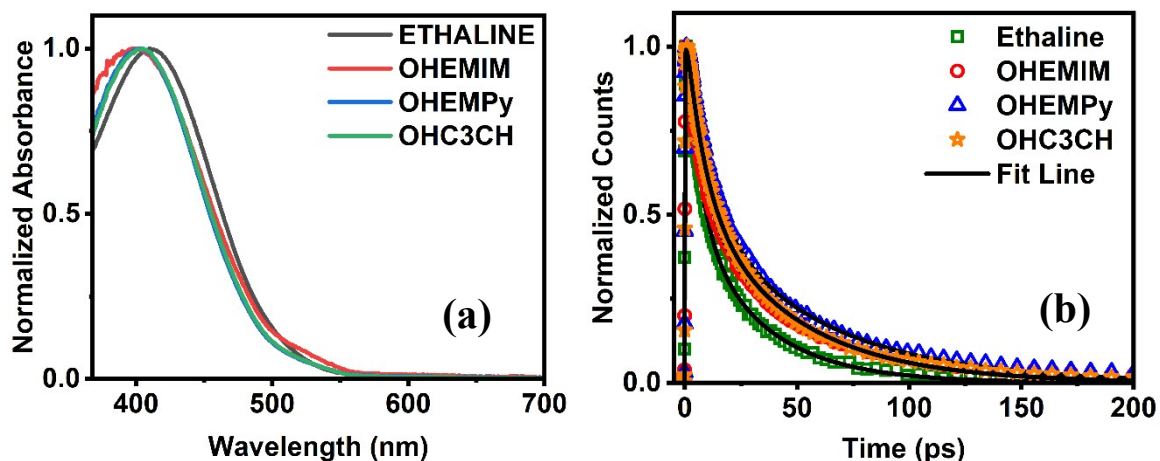


Figure S4: (a) Normalized absorbance spectra of 2-amino-7-nitrofluorene (ANF) in all the concerned solvent systems. (b) Femto-second fluorescence up-conversion decay plot of ANF in all the concerned solvent systems.

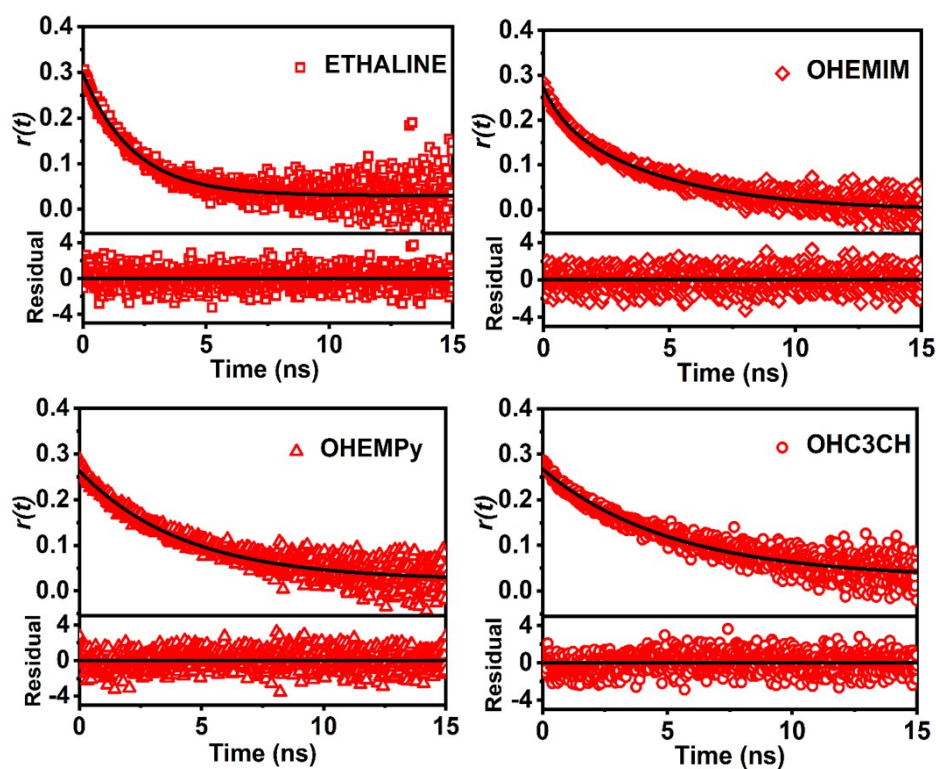


Figure S5: Time-resolved fluorescence anisotropy decay for C153 in DES and hydroxyl ILs at 298 K with residual plot. The reduced χ^2 value for each fitting are in the range of 1.03-1.07.

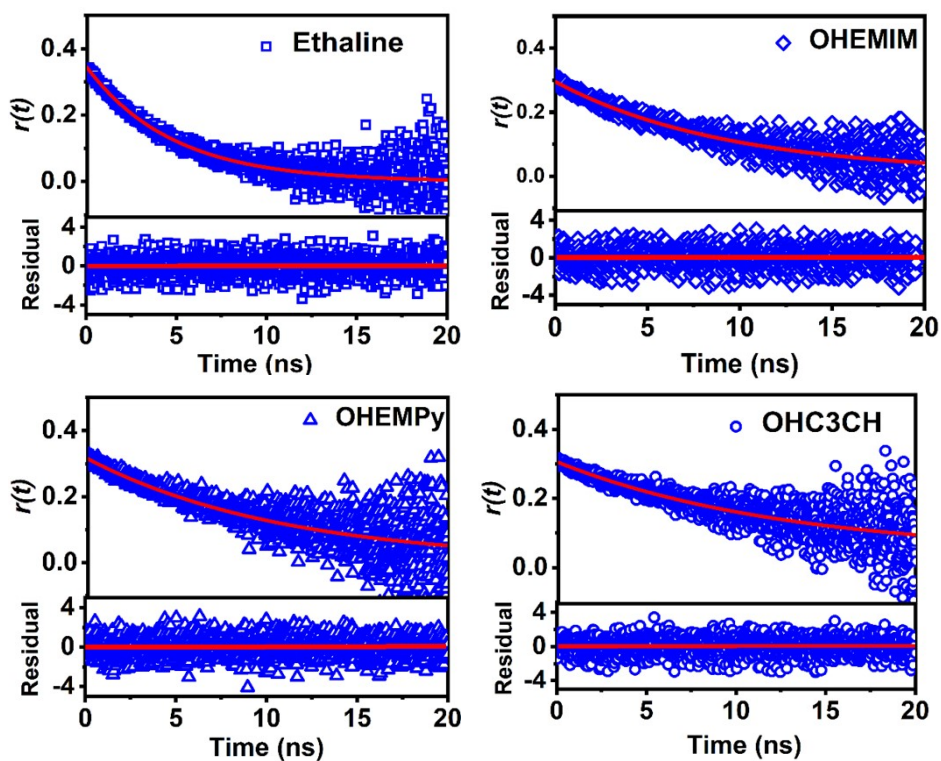


Figure S6: Time-resolved fluorescence anisotropy decay for MPTS in DES and hydroxyl ILs at 298 K with residual plot. The reduced χ^2 value for each fitting are in the range of 1.07-1.08

Table S3 Rotational relaxation parameter^a of different probes in both DES and hydroxyl ILs.

System	η (cP)/T (K)	C153		Perylene		MPTS	
		τ_r (ns)	C_{obs} (avg.)	τ_r (ns)	C_{obs} (avg.)	τ_r (ns)	C_{obs} (avg.)
Neat Ethaline	38.5/(298)	2.44 ± 0.1		0.95 ± 0.04		4.79 ± 0.2	
	30.6/(303)	1.90 ± 0.09		0.80 ± 0.04		4.02 ± 0.21	
	24.7/(308)	1.55 ± 0.08	0.65 ± 0.03	0.68 ± 0.03	0.30 ± 0.01	3.3 ± 0.2	1.27 ± 0.06
	20.5/(313)	1.27 ± 0.08		0.57 ± 0.03		2.84 ± 0.2	
	16.9/(318)	1.1 ± 0.06		0.51 ± 0.03		2.41 ± 0.19	
	14.7/(323)	0.95 ± 0.05		0.44 ± 0.02		2.11 ± 0.19	
[OHEMIM][NTf ₂]	72.7/(298)	4.02 ± 0.15		1.53 ± 0.06		7.12 ± 0.27	
	57.6/(303)	3.42 ± 0.15		1.3 ± 0.06		5.92 ± 0.26	
	45.5/(308)	2.85 ± 0.14	0.61 ± 0.03	1.07 ± 0.04	0.25 ± 0.01	4.95 ± 0.26	1.06 ± 0.05

	37.2/(313)	2.34 ±0.13		0.92 ± 0.03		4.40 ± 0.24	
	30.6/(318)	1.98 ± 0.14		0.81 ±0.02		3.82 ± 0.22	
	26.5/(323)	1.75 ±0.11		0.72 ±0.03		3.39 ± 0.22	
[OHEMPy][NTf ₂]	92.4/(298)	4.30 ± 0.15		1.69 ± 0.06		7.64 ± 0.29	
	71.8/(303)	3.60 ± 0.14		1.39 ±0.05		6.45 ± 0.27	
	58.4/(308)	3.15 ± 0.14	0.55 ± 0.02	1.18 ± 0.04	0.22 ± 0.01	5.69 ± 0.28	0.95 ± 0.05
	47.3/(313)	2.62 ± 0.12		0.98 ± 0.04		5.12 ± 0.27	
	39.1/(318)	2.23 ± 0.12		0.83 ± 0.02		4.52 ± 0.24	
	31.4/(323)	1.83 ± 0.12		0.76 ± 0.03		3.72 ± 0.24	
[OHC3CH][NTf ₂]	98.5/(298)	4.76 ± 0.18		1.81 ± 0.06		8.91 ± 0.32	
	77.5/(303)	3.92 ± 0.16		1.43 ± 0.06		7.88 ± 0.33	
	63.4/(308)	3.4 ± 0.16	0.55 ± 0.02	1.2 ± 0.05	0.21 ± 0.01	7.19 ± 0.32	1.07 ± 0.05
	52.1/(313)	2.85 ± 0.14		1.02 ± 0.04		6.3 ± 0.28	
	42.3/(318)	2.32 ± 0.14		0.9 ± 0.03		5.28 ± 0.26	
	34.2/(323)	2.03 ± 0.13		0.77 ± 0.03		4.48 ± 0.24	

Table S4 Hydrodynamic radii ($r \times 10^{-10}$ m) of the cationic species of both DES and hydroxyl ILs calculated using Stokes-Einstein equation

Temp (K)	Ethaline (Ch ⁺)/(3.06) ^a	<i>OHEMIM</i> ⁺ /(3.09) ^a	<i>OHEMPy</i> ⁺ /(3.24) ^a	<i>OHC3CH</i> ⁺ /(3.33) ^a
298	2.44 ± 0.09	1.75 ± 0.06	1.76 ± 0.06	1.55 ± 0.05
303	2.47 ± 0.09	1.71 ± 0.05	1.79 ± 0.05	1.57 ± 0.05
308	2.56 ± 0.09	1.72 ± 0.06	1.79 ± 0.06	1.55 ± 0.05
313	2.57 ± 0.08	1.71 ± 0.05	1.84 ± 0.06	1.55 ± 0.06
318	2.69 ± 0.09	1.72 ± 0.05	1.85 ± 0.07	1.57 ± 0.06
323	2.55 ± 0.08	1.68 ± 0.05	1.97 ± 0.07	1.59 ± 0.06

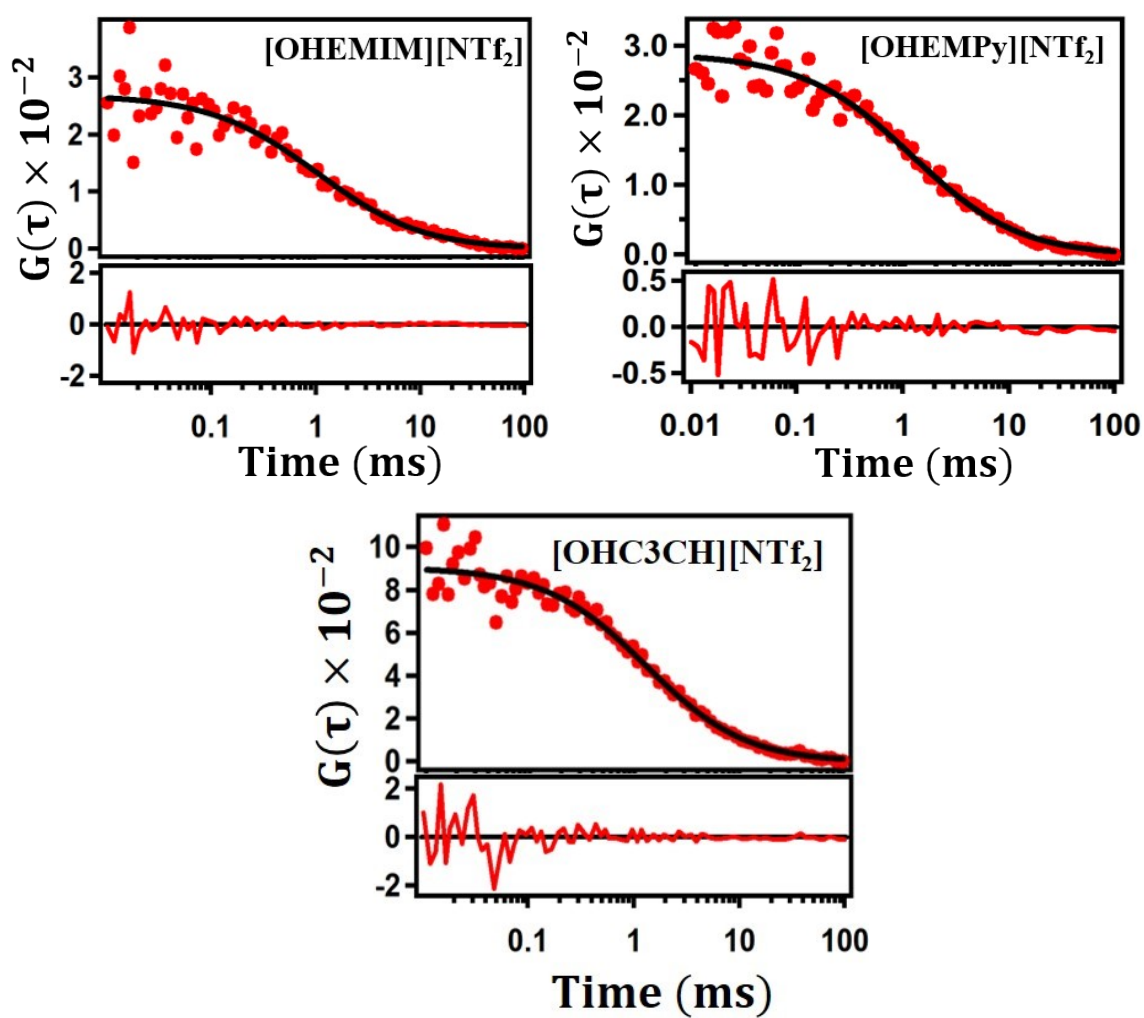


Figure S7: Fluorescence correlation curve for C153 in hydroxyl ILs along with the fit residual. The solid black curve represents the fit to the points through anomalous diffusion model.

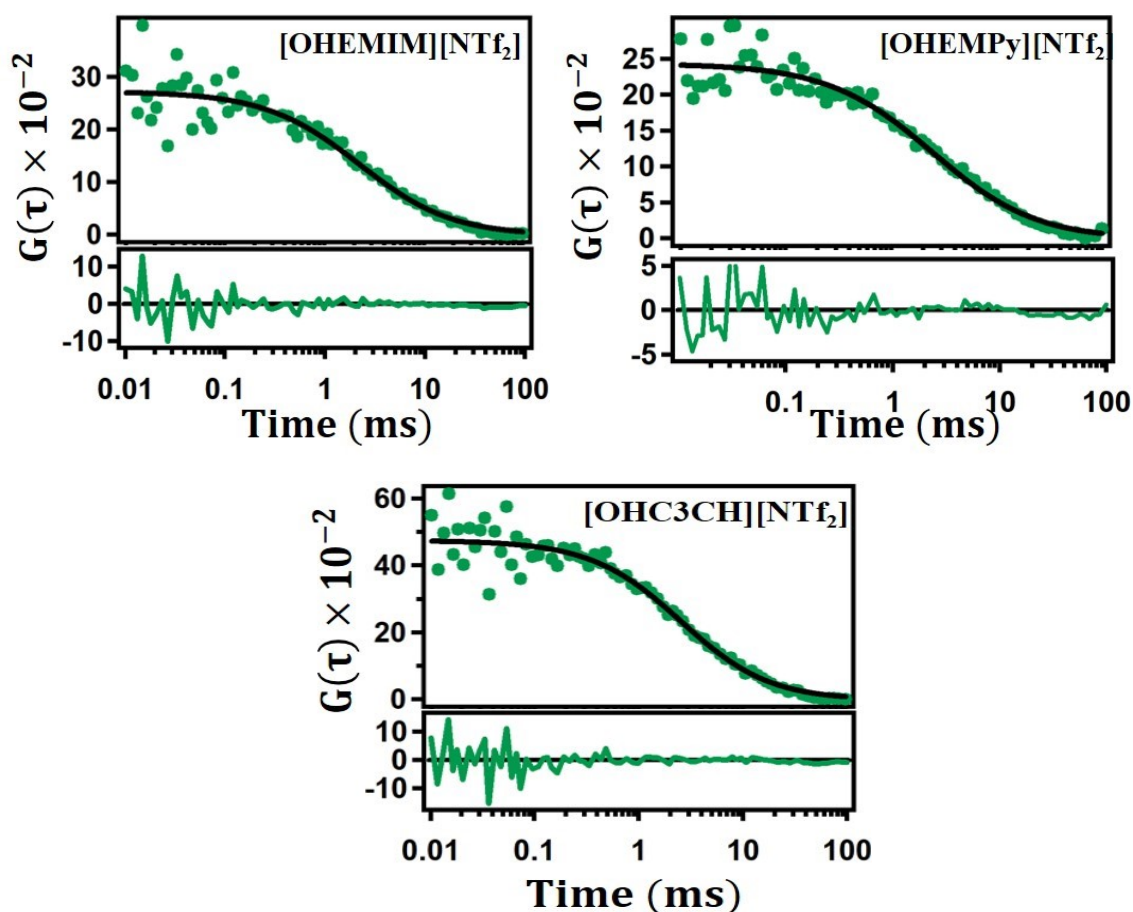


Figure S8: Fluorescence correlation curve for C153 in hydroxyl ILs along with the fit residual. The solid black curve represents the fit to the points through anomalous diffusion model.

References:

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