[Supplementary Information]

Differences in the Behavior of Dicationic and Monocationic Ionic Liquids as Revealed by Time Resolved-Fluorescence, NMR and Fluorescence Correlation Spectroscopy (FCS) Study

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1. Synthesis procedure of dicationic ionic liquids

1.1. Synthesis of 1,8-bis-(3-methylimidazolium-1-yl)octane bis-(trifluoromethylsulfonyl)amide ($[C_8(mim)_2][NTf_2]_2$)

1.1.1. 1,8-bis(3-methylimidazolium-1-yl)octane bromide, $[C_8(mim)_2][Br]_2$ (Precursor for target IL). Synthesis of $[C_8(mim)_2][NTf_2]_2$ was carried out by following the reported procedure proposed by Shirota and coworkers.[1] 1,8-Dibromooctane (1 mmol) was added drop wise to an acetonitrile solution of 1-methylimidazole (2.2 mmol) in reflux condition with rigorous stirring under a nitrogen atmosphere at 343 K . The reaction mixture was then condensed for 3 days in the same condition. The solution was then condensed by evaporation. The reaction product was washed by diethyl ether and a brown powder salt was precipitated. Finally, the salt was washed with diethyl ether several times. The purified product was obtained as a white solid. The product was dried under high vacuum at 308 K for several hours. The compound was characterized by ^{1}H-NMR and mass spectrometric studies.

$[C_8(mim)_2][Br]_2$: ^{1}H-NMR(DMSO-d_6): 2H(9.24 ppm, s), 2H(7.78 ppm, s), 2H(7.70 ppm, s), 4H(4.14 ppm, t), 6H(3.82 ppm, s), 4H(1.73 ppm, m), 8H(1.22 ppm, b)

1.1.2. $[C_8(mim)_2][NTf_2]_2$: $[C_8(mim)_2][Br]_2$ (1 mmol) was dissolved in water and aqueous lithium bis(trifluoromethylsulfonyl)amide (2.1 mmol) solution was gradually added to the solution. The mixture was stirred at room temperature for 1 day, the aqueous solution was decanted. The ionic liquid layer was dissolved in ethyl acetate and washed with water several times. The organic layer was dried with anhydrous Na_2SO_4, and filtered to remove the dry agent. After the solvent was evaporated, the residue was mixed with activated charcoal in acetonitrile. The activated charcoal was removed by filtration, and the solvent was evaporated. This decolorizing charcoal step was repeated 3-4 times. The ionic liquid was then dried under high vacuum at 308 K for 3 days. The product was a colorless liquid. The compound was characterized by ^{1}H-NMR and mass spectrometric studies.

$[C_8(mim)_2][NTf_2]_2$: ^{1}H-NMR(DMSO-d_6): 2H(9.02 ppm, s), 2H(7.69 ppm, s), 2H(7.64 ppm, s), 4H(4.08 ppm, t), 6H(3.79 ppm, s), 4H(1.71 ppm, m), 8H(1.21 ppm, b)

ESI -MS (+ve): 556 m/ z, $[C_8(mim)_2NTf_2]^+$

1.2. Synthesis of 1,9-Bis(3-methylimidazolium-1-yl)nonane bis-(trifluoromethylsulfonyl)amide ($[C_9(mim)_2][NTf_2]_2$)

1.2.1. 1,9-bis(3-methylimidazolium-1-yl)nonane bromide, $[C_9(mim)_2][Br]_2$ (Precursor for target IL).

1,9-Dibromononane (1 mmol) was added drop wise to an acetonitrile solution of 1-methylimidazole (2.2 mmol) in reflux condition with rigorous stirring under a nitrogen atmosphere at 343 K . The reaction mixture was then condensed for 3 days in the same condition. The solution was then condensed by evaporation. The residue was yellow oil. Next, the oil was washed with diethyl ether at several times. Diethyl ether was removed by evaporation, and the oil was mixed with activated charcoal in acetonitrile. The activated charcoal was removed by filtration, and the solvent was evaporated. This decolorizing charcoal step was repeated 2-3 times. The product was dried under high vacuum at 308 K for several hours. The compound was characterized by ^{1}H-NMR and mass spectrometric studies.

$[C_9(mim)_2][Br]_2$: ^{1}H-NMR(DMSO-d_6): 2H(9.21 ppm, s), 2H(7.78 ppm, s), 2H(7.69 ppm, s), 4H(4.12 ppm, t), 6H(3.81 ppm, s), 4H(1.72 ppm, m), 10H(1.20 ppm, b)

1.2.2. $[C_9(mim)_2][NTf_2]_2$: $[C_9(mim)_2][Br]_2$ (1 mmol) was dissolved in water and aqueous lithium bis(trifluoromethylsulfonyl)amide (2.1 mmol) solution was gradually added to the solution. The mixture was stirred at room temperature for 1 day, the aqueous solution was decanted. The ionic liquid layer was dissolved in ethyl acetate and washed with water several times. The organic layer was dried with anhydrous Na_2SO_4, and filtered to remove the dry agent. After the solvent was evaporated, the residue was mixed with activated charcoal in acetonitrile. The activated charcoal was removed by filtration, and the solvent was evaporated. This decolorizing charcoal step was repeated 3-4 times. The ionic liquid was then dried under high vacuum at 308 K for 3 days. The product was a colorless liquid. The compound was characterized by ^{1}H-NMR and mass spectrometric studies.

$[C_9(mim)_2][NTf_2]_2$: ^{1}H-NMR(DMSO-d_6): 2H(9.03 ppm, s), 2H(7.69 ppm, s), 2H(7.63 ppm, s), 4H(4.08 ppm, t), 6H(3.79 ppm, s), 4H(1.71 ppm, m), 10H(1.20 ppm, b)

ESI -MS (+ve): 570 m/ z, $[C_9(mim)_2NTf_2]^+$

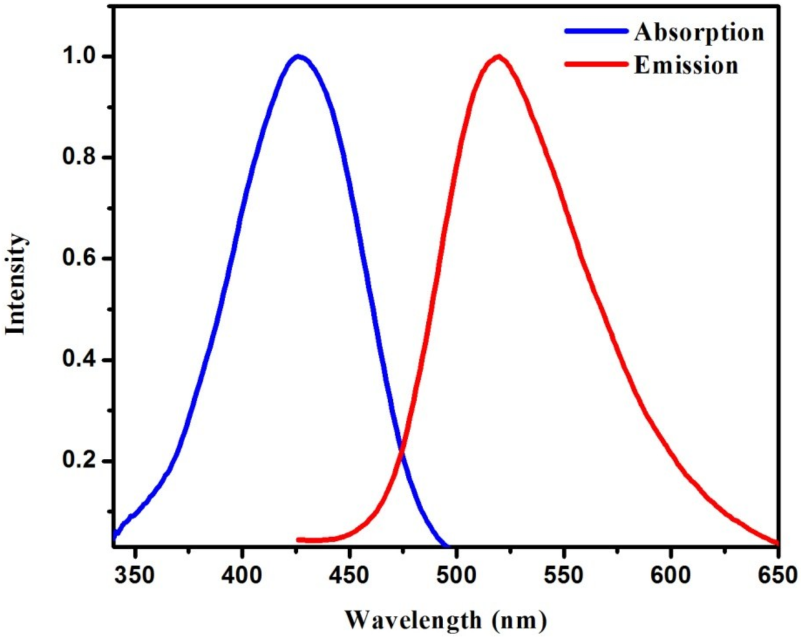

Fig. S1 Normalized absorption and emission (λ_{exc}= 375 nm) spectra of C153 in $[C_9(mim)_2][NTf_2]_2$.

Table S1 Viscosity (η) of $[C_4(mim)][NTf_2]$, $[C_8(mim)_2][NTf_2]_2$ and $[C_9(mim)_2][NTf_2]_2$ at 298 K.

	$[C_4(mim)][NTf_2]$	$[C_8(mim)_2][NTf_2]_2$	$[C_9(mim)_2][NTf_2]_2$
No. of repeats	η (cP)[a]	η (cP)[a]	η (cP)[a]
R1	51	646	688
R2	52	649	686
R3	51	645	690

[a] Experimental error=±2%,

Table S2 Van der Walls volumes (V), shape factors (f) and boundary condition parameter (C_{slip}) of perylene and MPTS

Solute	V (Å^3)	f	C_{slip}
perylene	225	1.76	0.085
MPTS	343	1.33	0.11

2. Gierer-Wirtz (GW) theory

To explain solvent size dependent rotational behavior of the perylene molecule, quasi hydrodynamic theory (GW theory)[2] have been employed as it takes into consideration both the size of solute and solvent. The boundary condition parameter is modified by using the following equation 1.

$$C_{GW} = \sigma C_0 \tag{1}$$

Where, σ= sticking factor, denoted by the following equation.

$$\sigma = \left[1 + 6\left(\frac{V_S}{V_P}\right)^{1/3} C_0\right]^{-1} \tag{2}$$

and C_0 is given by following equation 4.

$$C_0 = \left[\frac{6\left(\frac{V_S}{V_P}\right)^{1/3}}{\left[1 + 2\left(\frac{V_S}{V_P}\right)^{1/3}\right]^4} + \frac{1}{\left[1 + 4\left(\frac{V_S}{V_P}\right)^{1/3}\right]^3}\right]^{-1}$$

(3)

Where, V_S and V_p is the van der Waals volume of solvent and solute respectively. The van der Waals volume for $[C_8(mim)_2][NTf_2]_2$ and $[C_4(mim)][NTf_2]$ are 356 cm^3/mol and 209 cm^3/mol respectively.[42] However, in the present case, the C_{GW} (calculated boundary condition parameter using GW theory) is estimated to be 0.11 for $[C_8(mim)_2][NTf_2]_2$, which is higher than the value predicted by SED theory (C_{slip}=0.085). This means that GW theory is unable to explain the faster rotation of perylene in DILs.

Table S3 Reorientation time (τ_r) and viscosity (η) of perylene and MPTS in [C_8(mim)][NTf_2].

			Perylene		MPTS	
System	Temp. (K)	Viscosity (cP)[a]	τ_r (ns)[b]	C_{rot}	τ_r (ns)[b]	C_{rot}
[C_8(mim)][NTf_2]	293	109	1.72	0.16	18.32	1.48
	298	83	1.43	0.18	14.02	1.50
	303	65	1.24	0.20	11.10	1.54
	308	54	1.10	0.22	9.16	1.56

[a]Experimental error=±2%, [b]Experimental error=±5%

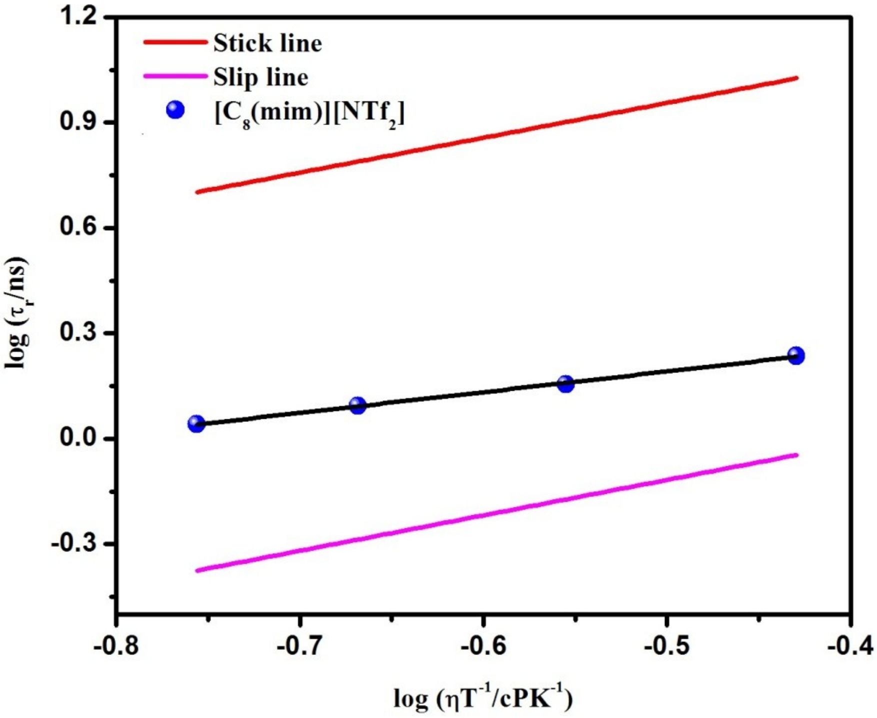

Fig. S2 log(τ_r) vs. log(η/T) plot of perylene in [C_8(mim)][NTf_2] with stick and slip boundary condition limits.

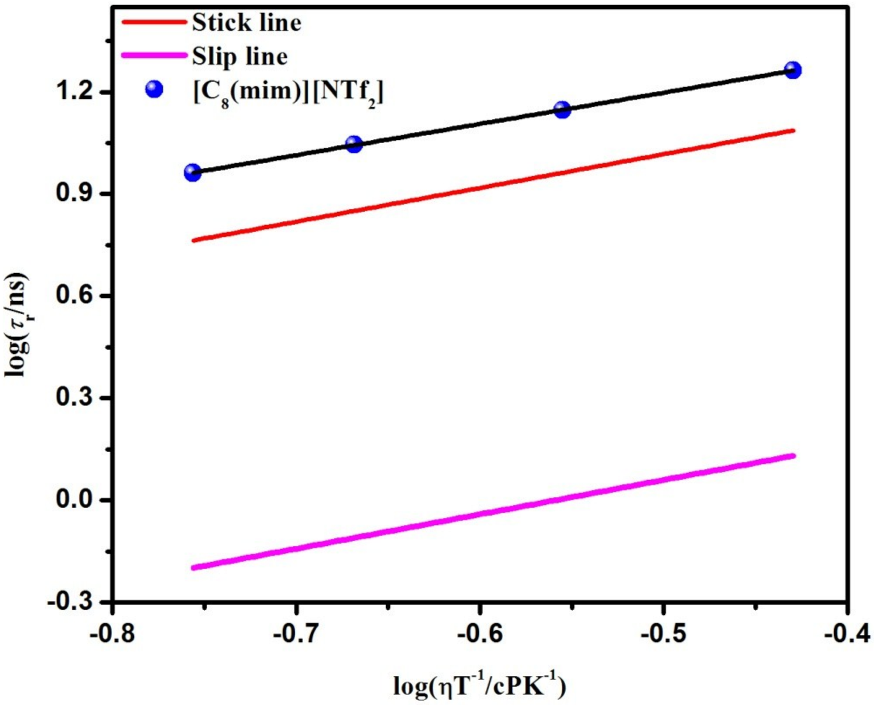

Fig. S3 log(τ_r) vs. log(η/T) plot of MPTS in [C_8(mim)][NTf_2] with stick and slip boundary condition limits.

References

(1) H. Shirota, T. Mandai, H. Fukazawa and T. Kato, *J. Chem. Eng. Data,* 2011, ***56,*** 2453-2459.

(2) A. Gierer and K. Wirtz, *Z. Naturforsch., A*: *Phys. Sci.* 1953, ***8***, 532−538.