

## Supporting information

### **The Polarity of Ionic Liquids: relationship between relative permittivity and spectroscopic parameters of probe**

Xinyu Wang<sup>a, //</sup>, Songna Zhang<sup>a, //</sup>, JiaYao<sup>a</sup>, and Haoran Li<sup>\*a, b</sup>

<sup>a</sup>Department of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, Hangzhou 310027 (P.R. China);

<sup>b</sup>State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027 (P.R. China)

//These authors contribute equally.

\*Corresponding author. E-mail Address: [lihr@zju.edu.cn](mailto:lihr@zju.edu.cn), Fax: +86-571-87951895

# Content

**Table S1.** Glossary of terms of abbreviations used in this paper.

**Table S2.** Experimental and predicted values of the relative permittivity ( $\epsilon_r$  values) of the ILs, the molar electronic transition energy of the longest wavelength Vis absorption band of betaine dye no. 30 [ $E_T(30)$  values], and the hyperfine coupling constants of ATEMPO ( $A_N$  values) at 298.15K or room temperature.

**Table S1.** Glossary of terms of abbreviations used in this paper.

Abbreviation	Name	Abbreviation	Name
[BuNH <sub>3</sub> ] <sup>+</sup>	(n-butyl)ammonium	[Et <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	diethylphosphate
[2-BuNH <sub>3</sub> ] <sup>+</sup>	(2-butyl)ammonium	[EtMim] <sup>+</sup>	1-methyl-3-ethylimidazolium
[Bu <sub>3</sub> NH] <sup>+</sup>	tri(n-butyl)ammonium	[EtMMim] <sup>+</sup>	1,2-dimethyl-3-ethylimidazolium
[Bu <sub>4</sub> N] <sup>+</sup>	tetra(n-butyl)ammonium	[1-Et-4-HO(CH <sub>2</sub> ) <sub>2</sub> Py] <sup>+</sup>	1-ethyl-4-(2-hydroxyethyl)pyridinium
[BuNMe <sub>3</sub> ] <sup>+</sup>	n-butyl-trimethylammonium	[EtMeP] <sup>+</sup>	1-ethyl-2-methylpyrazolium
[BuEtNMe <sub>2</sub> ] <sup>+</sup>	(n-butyl)-ethyl-dimethylammonium	[Et <sub>3</sub> S] <sup>+</sup>	triethylsulfide
[BuOSO <sub>3</sub> ] <sup>-</sup>	butanesulfonate	[EtDMim] <sup>+</sup>	1-ethyl-2,3-dimethylimidazolium
[BES] <sup>-</sup>	2-[bis(2-hydroxyethyl)amino]ethanesulfonate	[FHMglyPip] <sup>+</sup>	N-glyceryl-N-methyl-4-hydroxypiperidinium
[BF <sub>4</sub> ] <sup>-</sup>	tetrafluoroborate	[FAP] <sup>-</sup>	trifluorotris(2,2,2-trifluoroethyl)phosphate
[Buim] <sup>+</sup>	1-(n-butyl)imidazolium	[GlyMim] <sup>+</sup>	1-methyl-3-glycerylimidazolium
[BuMim] <sup>+</sup>	1-methyl-3-(n-butyl)imidazolium	[GlyMMim] <sup>+</sup>	1,2-dimethyl-3-glycerylimidazolium
[2-BuMim] <sup>+</sup>	1-methyl-3-(2-butyl)imidazolium	[HO(CH <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> ] <sup>+</sup>	(2-hydroxyethyl)ammonium
[BuEtim] <sup>+</sup>	1-methyl-3-ethylimidazolium	[(HO(CH <sub>2</sub> ) <sub>2</sub> ) <sub>3</sub> NH] <sup>+</sup>	tri(2-hydroxyethyl)ammonium
[BuMMim] <sup>+</sup>	1,2-dimethyl-3-(n-butyl)imidazolium	[HCO <sub>2</sub> ] <sup>-</sup>	Formate
[BenzylMim] <sup>+</sup>	1-methyl-3-benzylimidazolium	[HexMim] <sup>+</sup>	1-(n-hexyl)-3-methylimidazolium
[Bupy] <sup>+</sup>	1-(n-butyl)pyridinium	[Hex <sub>4</sub> N] <sup>+</sup>	tetra(n-hexyl)ammonium
[1-Bu-4-MePy] <sup>+</sup>	1-(n-butyl)-4-methylpyridinium	[HOSO <sub>3</sub> ] <sup>-</sup>	hydrogen sulfate
[1-Bu-3-MePy] <sup>+</sup>	1-(n-butyl)-3-methylpyridinium	[HexOSO <sub>3</sub> ] <sup>-</sup>	(n-hexyl)sulfate
[BuMePyr] <sup>+</sup>	N-methyl-N-(n-butyl)pyrrolidinium	[HexMim] <sup>+</sup>	1-methyl-3-(n-hexyl)imidazolium
[BuMePy] <sup>+</sup>	N-methyl-N-(n-butyl)pyridinium	[HO(CH <sub>2</sub> ) <sub>2</sub> Mim] <sup>+</sup>	1-(2-hydroxyethyl)-3-methylimidazolium
[BuPrim] <sup>+</sup>	1-(n-butyl)-3-(n-propyl)imidazolium	[HexBuim] <sup>+</sup>	1-butyl-3-(n-hexyl)imidazolium
[CH <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup>	acetate	[HO(CH <sub>2</sub> ) <sub>3</sub> Mim] <sup>+</sup>	1-(3-hydroxypropyl)-3-methylimidazolium
[C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> ] <sup>-</sup>	benzoate	[HexMMim] <sup>+</sup>	1,2-dimethyl-3-(n-hexyl)imidazolium
[CHES] <sup>-</sup>	2-(cyclohexylamino)ethanesulfonate	[HexMPy] <sup>+</sup>	1-(n-hexyl)-3-methylpyridinium
[CF <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup>	trifluoroacetate	[HexMDMAPy] <sup>+</sup>	1-hexyl-3-methyl-4-dimethylaminopyridinium
[ClO <sub>4</sub> ] <sup>-</sup>	perchlorate	[Hex <sub>3</sub> PC <sub>14</sub> H <sub>29</sub> ] <sup>+</sup>	n-tetradecyl-tri(n-hexyl)phosphonium
[CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> ] <sup>-</sup>	propanoate	[HexDABCO] <sup>+</sup>	(N-hexyl)-1,4-diazabicyclo[2.2.2]octane
[(C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> PO <sub>2</sub> ] <sup>-</sup>	dibutyl phosphate	[HeptDABCO] <sup>+</sup>	(N-heptyl)-1,4-diazabicyclo[2.2.2]octane

**Table S1.** Continued.

Abbreviation	Name	Abbreviation	Name
[CH <sub>3</sub> SO <sub>3</sub> ] <sup>-</sup>	methanesulfonate	[HexMeE <sub>1,4</sub> ] <sup>+</sup>	N-(n-butyl)-N-methylhexamethylenammonium
[DecMim] <sup>+</sup>	1-methyl-3-(n-decyl)imidazolium	[HexMeE <sub>1,6</sub> ] <sup>+</sup>	N-(2-hydroxyethyl)-N-methylhexamethylenammonium
[DCA] <sup>-</sup>	dicyanamide	[MeO(CH <sub>2</sub> ) <sub>2</sub> BuNMe <sub>2</sub> ] <sup>+</sup>	(2-methoxyethyl)-n-butyl dimethylammonium
[DBSA] <sup>-</sup>	4-dodecylbenzenesulfonate	[MeO(CH <sub>2</sub> ) <sub>2</sub> MeNEt <sub>2</sub> ] <sup>+</sup>	(2-methoxyethyl)-n-methyldiethylammonium
[DecDABCO] <sup>+</sup>	(N-decyl)-1,4-diazabicyclo[2.2.2]octane	[Me <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	dimethylphosphate
[EtNH <sub>3</sub> ] <sup>+</sup>	ethylammonium	[MeO(CH <sub>2</sub> ) <sub>2</sub> Mim] <sup>+</sup>	1-(2-methoxyethyl)-3-methylimidazolium
[Et <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup>	diethylammonium	[Mim] <sup>+</sup>	1-methylimidazolium
[EtOSO <sub>3</sub> ] <sup>-</sup>	ethylsulfate	[MMim] <sup>+</sup>	1,3-dimethylimidazolium
[1-MeO(CH <sub>2</sub> ) <sub>2</sub> -1-Me-pyrr] <sup>+</sup>	1-(2-methoxyethyl)-1-methylpyrrolidinium	[NEt <sub>4</sub> ] <sup>+</sup>	tetraethylammonium
[MePyrr] <sup>+</sup>	N-methylpyrrolidinium	[NPr <sub>4</sub> ] <sup>+</sup>	tetra(n-propyl)ammonium
[MeGlyPyrr] <sup>+</sup>	N-glyceryl-N-methylpyrrolidinium	[N(SO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	bis(methylsulfonyl)amide
[MeEtPyrr] <sup>+</sup>	N-ethyl-N-methylpyrrolidinium	[NonDABCO] <sup>+</sup>	[N-(n-nonyl)]-1,4-diazabicyclo[2.2.2]octane
[MePrPyrr] <sup>+</sup>	N-methyl-N-(n-propyl)pyrrolidinium	[N(O <sub>2</sub> SC <sub>2</sub> F <sub>5</sub> ) <sub>2</sub> ] <sup>-</sup>	bis(pentafluoroethanesulfonyl)imide
[MeBuPyrr] <sup>+</sup>	N-methyl-N-(n-butyl)pyrrolidinium	[Oct <sub>3</sub> NMe] <sup>+</sup>	n-methyl-trioctylammonium
[MePentPyrr] <sup>+</sup>	N-methyl-N-(n-pentyl)pyrrolidinium	[OctOSO <sub>3</sub> ] <sup>-</sup>	n-octylsulfate
[MeOctPyrr] <sup>+</sup>	N-methyl-N-(n-octyl)pyrrolidinium	[OctMim] <sup>+</sup>	1-methyl-3-(n-octyl)imidazolium
[MeCNPrPyrr] <sup>+</sup>	1-methyl-1-(3-cyano-1-propyl)pyrrolidinium	[OctMMim] <sup>+</sup>	1,2-dimethyl-3-(n-octyl)imidazolium
[MePS <sub>2</sub> Pyrr] <sup>+</sup>	1-methyl-1-[4,5-bis(methylthio)-1-(n-pentyl)pyrrolidinium]	[Oct <sub>2</sub> Mim] <sup>+</sup>	methyl-di(n-octyl)imidazolium
[MeBuPip] <sup>+</sup>	1-methyl-1-(n-butyl)piperidinium	[OctPy] <sup>+</sup>	1-(n-octyl)pyridinium
[MeOePip] <sup>+</sup>	N-(2-hydroxyethyl)-N-methylpiperidinium	[1-Oct-2-MePy] <sup>+</sup>	1-(n-octyl)-2-methylpyridinium
[MeGlyPip] <sup>+</sup>	N-glyceryl-N-methylpiperidinium	[1-Oct-3-MePy] <sup>+</sup>	1-(n-octyl)-3-methylpyridinium
[MePrPip] <sup>+</sup>	1-methyl-1-(n-propyl)piperidinium	[1-Oct-4-MePy] <sup>+</sup>	1-(n-octyl)-4-methylpyridinium
[MePentPip] <sup>+</sup>	1-methyl-1-(n-pentyl)piperidinium	[1-Oct <sub>3</sub> PMe] <sup>+</sup>	methyl-tri(n-octyl)phosphonium
[MeOctPip] <sup>+</sup>	1-methyl-1-(n-octyl)piperidinium	[OctDABCO] <sup>+</sup>	[N-(n-octyl)]-1,4-diazabicyclo[2.2.2]octane
[MeEtMor] <sup>+</sup>	N-ethyl-N-methylmorpholinium	[1O2Mim] <sup>+</sup>	3-(2-methoxyethyl)-1-methylimidazolium
[MePrMor] <sup>+</sup>	N-methyl-N-(1-propyl)morpholinium	[PentMim] <sup>+</sup>	1-(n-pentyl)-3-methylimidazolium
[MeBuMor] <sup>+</sup>	N-(n-butyl)-N-methylmorpholinium	[PrNH <sub>3</sub> ] <sup>+</sup>	(n-propyl)ammonium
[MePentMor] <sup>+</sup>	N-methyl-N-(n-pentyl)morpholinium	[Pr <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup>	di(n-propyl)ammonium
[MeHexMor] <sup>+</sup>	N-(n-hexyl)-N-methylmorpholinium	[PentNEt <sub>3</sub> ] <sup>+</sup>	n-pentyl-triethylammonium
[MeHeptMor] <sup>+</sup>	N-(n-heptyl)-N-methylmorpholinium	[Pent <sub>4</sub> N] <sup>+</sup>	tetra(n-pentyl)ammonium
[MeOctMor] <sup>+</sup>	N-methyl-N-(n-octyl)morpholinium	[PF <sub>6</sub> ] <sup>-</sup>	hexafluorophosphate
[MeNonMor] <sup>+</sup>	N-(n-nonyl)-N-methylmorpholinium	[PrMim] <sup>+</sup>	1-methyl-3-(n-propyl)imidazolium
[MeOeMor] <sup>+</sup>	N-(2-hydroxyethyl)-N-methylmorpholinium	[PrPy] <sup>+</sup>	1-(n-propyl)pyridinium
[MeGlyMor] <sup>+</sup>	N-glyceryl-N-methylmorpholinium	[1-Pr-4-MePy] <sup>+</sup>	1-(n-propyl)-4-methylpyridinium

**Table S1.** Continued.

Abbreviation	Name	Abbreviation	Name
[MeNH <sub>3</sub> ] <sup>+</sup>	(n-methyl)ammonium	[Pr21(OH)] <sup>+</sup>	1-(2-hydroxyethyl)-1-methylpyrrolidinium
[Me <sub>2</sub> NCO <sub>2</sub> ] <sup>-</sup>	N,N-dimethylcarbamate	[PentDABCO] <sup>+</sup>	[N-(n-pentyl)]-1,4-diazabicyclo[2.2.2]octane
[MeNBu <sub>3</sub> ] <sup>+</sup>	tri(n-butyl)-methylammonium	[SCN] <sup>-</sup>	thiocyanate
[Me <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup>	dimethylammonium	[SbF <sub>6</sub> ] <sup>-</sup>	Hexafluoroantimonate
[NO <sub>3</sub> ] <sup>-</sup>	nitrate	[Tf <sub>2</sub> N] <sup>-</sup>	bis(trifluoromethylsulfonyl)imide
[N114,1O2] <sup>+</sup>	N-(2-methoxyethyl)-Nbutyl-N,N-diethylammonium	[TOTO] <sup>-</sup>	2,5,8,11-tetraoxatridecan-13-oate
[N1124] <sup>+</sup>	N-butyl-N-ethyl-N,N-diethylammonium	[TfO] <sup>-</sup>	trifluoromethanesulfonatetritate
[NBu <sub>4</sub> ] <sup>+</sup>	tetra(n-butyl)ammonium	[TOS] <sup>-</sup>	p-toluenesulfonate
[N(NC) <sub>2</sub> ] <sup>-</sup>	nicyanamide	[WO <sub>4</sub> ] <sup>2-</sup>	wolframate

**Table S2.** Experimental and predicted values of the relative permittivity ( $\epsilon_r$  values) of the ILs, the molar electronic transition energy of the longest wavelength Vis absorption band of betaine dye no. 30 [ $E_T(30)$  values], and the hyperfine coupling constants of ATEMPO ( $A_N$  values), both probes dissolved in the ILs given and measured at 298.15K or room temperature. -  $E_T(30)^a$ ,  $\epsilon_r^a$  and  $A_N^a$  are directly measured experimental values; -  $E_T(30)^b$  values are estimated values:  $b_1$  derived from  $E_T(33)$  values,<sup>123, 112-124</sup>  $b_2$  estimated from linear correlations with  $A_N$ ,<sup>61</sup> and  $b_3$  were calculated by means of the modified Onsager reaction-filed model,<sup>130</sup> -  $\epsilon_r^b$  values are estimated from measurements of the spectra of a number of probes, the speeds of sound, densities or heats of vaporization<sup>15, 48, 53, 54</sup> -  $A_N^b$  values are derived from Eq. (2) according to the modified Onsager reaction-filed model.<sup>130</sup>

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
<i>Ammonium salts</i>										
1	[EtNH <sub>3</sub> ] NO <sub>3</sub>	61.6	86			58.46	26.2		16.47	
		60	124			58.46				
2	[PrNH <sub>3</sub> ] NO <sub>3</sub>	60.6	86							
3	[Et <sub>2</sub> NH <sub>2</sub> ] NO <sub>3</sub>	65.5	127							
4	[Bu <sub>3</sub> NH] NO <sub>3</sub>	56.7	86							
5	[N114,1O2] NO <sub>3</sub>		113	53.98						
6	[HO(CH <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> ] NO <sub>3</sub>			58.50		59.52	60.9		16.52	
7	[BuNH <sub>3</sub> ] SCN	61.4	86							
8	[2-BuNH <sub>3</sub> ] SCN	61.6	86			61.58		38.8	16.63	
9	[Pr <sub>2</sub> NH <sub>2</sub> ] SCN	63.3	86							
10	[MeNH <sub>3</sub> ] HCO <sub>2</sub>			56.10		57.07	41		16.39	
						57.05	40.3		16.39	
11	[EtNH <sub>3</sub> ] HCO <sub>2</sub>			57.80		58.76	31.5		16.48	
							30.3			
12	[BuNH <sub>3</sub> ] HCO <sub>2</sub>			57.20		58.19	23		16.46	
						58.64	29.2		16.48	
13	[HO(CH <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> ] HCO <sub>2</sub>	59.5	83			59.52	61		16.52	

Table S2. Continued

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
						59.47	57.3		16.51	
14	[HO(CH <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> ] CH <sub>3</sub> CO <sub>2</sub>			58.50		59.49	58.3		16.51	
15	[(HO(CH <sub>2</sub> ) <sub>2</sub> ) <sub>3</sub> NH] CH <sub>3</sub> CO <sub>2</sub>			49.90		50.94	31		16.09	
16	[HO(CH <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> ] lactate			58.80		59.76	85.6		16.53	
17	[(HO(CH <sub>2</sub> ) <sub>2</sub> ) <sub>3</sub> NH] lactate			50.50		51.52	59.7		16.11	
18	[Me <sub>2</sub> NH <sub>2</sub> ] Me <sub>2</sub> NCO <sub>2</sub>	57.2	57							
19	[MeNBu <sub>3</sub> ] Tf <sub>2</sub> N	46.7	82			46.59		11.3	15.89	
		55.8	81							
20	[BuNMe <sub>3</sub> ] Tf <sub>2</sub> N	49.3	84			46.07	15.7		15.86	
		62.1	81							
21	[BuEtNMe <sub>2</sub> ] Tf <sub>2</sub> N	59	113	57.26						
22	[PentNEt <sub>3</sub> ] Tf <sub>2</sub> N			46.60		47.60	12.5		16.11	
23	[Oct <sub>3</sub> NMe] Tf <sub>2</sub> N	45.9	107			45.68		8.5	15.85	
24	[N1124] Tf <sub>2</sub> N	59	113							
25	[N114,1O2] Tf <sub>2</sub> N	58.8	113							
26	[BuEtNMe <sub>2</sub> ] Tf <sub>2</sub> N	49	113	48.29						
27	[HexMeE <sub>1,4</sub> ] Tf <sub>2</sub> N	55.76	97							
28	[NBu <sub>4</sub> ] Br					42.36		3.7	15.73	
29	[Hex <sub>4</sub> N] H <sub>5</sub> C <sub>6</sub> CO <sub>2</sub>	43.9	127			43.12		4.1	15.76	
30	[Pr <sub>4</sub> N] CHES	50.9	86			50.90		153.6	16.08	
31	[Bu <sub>4</sub> N] CHES	50.7	86			50.70		83.1	16.07	
32	[Pent <sub>4</sub> N] CHES	49.5	86			49.46		21.5	16.02	
33	[Pr <sub>4</sub> N] MOPSO	45.5	86			44.99		5.5	15.84	
34	[Bu <sub>4</sub> N] MOPSO	46.5	86			46.16		6.9	15.88	
35	[Pent <sub>4</sub> N] MOPSO	47.3	86			47.09		8.6	15.92	
36	[Pr <sub>4</sub> N] BES	49	86			48.93		16.2	16.00	
37	[NBu <sub>4</sub> ] BES	47.8	86			47.63		10	15.94	
38	[Pent <sub>4</sub> N] BES	49	86			48.93		16.2	16.00	
39	[NEt <sub>4</sub> ] TOTO	45.9	103			45.47		6	15.86	
40	[NPr <sub>4</sub> ] TOTO	44.8	103			44.18		4.8	15.80	
41	[NBu <sub>4</sub> ] TOTO	44	103			43.29		4.2	15.77	
42	[Choline] TOTO	48.4	103					-		

Table S2. Continued.

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
43	[MeO(CH <sub>2</sub> ) <sub>2</sub> BuNMe <sub>2</sub> ] Tf <sub>2</sub> N	58.8	113	56.50						
44	[MeO(CH <sub>2</sub> ) <sub>2</sub> BuNMe <sub>2</sub> ] N(CN) <sub>2</sub>	49	113	49.06						
45	[HexMeE <sub>1,4</sub> ] N(CN) <sub>2</sub>	54.5	97							
46	[HexMeE <sub>1,e</sub> ] N(CN) <sub>2</sub>	57.44	97							
47	[MeO(CH <sub>2</sub> ) <sub>2</sub> MeNEt <sub>2</sub> ] BF <sub>4</sub>				48.38		-	16.02		
48	[N114,1O2] BF <sub>4</sub>			54.09						
49	[N114,1O2] PF <sub>6</sub>			56.39						
50	[MeO(CH <sub>2</sub> ) <sub>2</sub> MeNEt <sub>2</sub> ] N(SO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>				48.38		-	16.02		
51	[N1124] DCA	49	113							
52	[N114,1O2] DCA	49	113							
<i>Imidazolium salts</i>										
53	[EtMim] N(CN) <sub>2</sub>	51.7	57	51.6		52.67	19.1		16.18	
				52.8						
54	[BuMim] N(CN) <sub>2</sub>	51.4	113			52.34	16.5		16.16	
55	[HexMim] N(CN) <sub>2</sub>	51.1	94			52.01	14.5		16.10	
56	[HO(CH <sub>2</sub> ) <sub>2</sub> Mim] N(CN) <sub>2</sub>			56.0						
				56.7						
57	[GlyMim] N(CN) <sub>2</sub>	57.6	97				-			
58	[GlyMMim] N(CN) <sub>2</sub>	57	97				-			
59	[EtMim] BF <sub>4</sub>	53.7	35	45.87	51.65		12.8	15.91	16.14	
		47.5~49.1	57				12.8±0.6			
60	[PrMim] BF <sub>4</sub>	53.1	35		54.18		63.9		16.24	
61	[HexMim] BF <sub>4</sub>	53.6	57							
62	[BuMim] BF <sub>4</sub>	52.5	74	53.86	51.89		13.9	16.26	16.15	
							12.2			
							11.7±0.6			
		52.7	35							
		54.6	57							
		48.9	108							
		47.1~48.9	57							
		52.5	110							
		52.31	125							

Table S2. Continued.

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
		53.03	113							
63	[OctMim] BF <sub>4</sub>	52.4	57			52.78	20.1		16.18	
64	[OctMMim] BF <sub>4</sub>	48.3	74			47.88	5.6		15.98	
65	[MeO(CH <sub>2</sub> ) <sub>2</sub> Mim] BF <sub>4</sub>	53.3	35			54.39	94.2		16.25	
66	[HO(CH <sub>2</sub> ) <sub>2</sub> Mim] BF <sub>4</sub>			51.00		53.06	23.3		16.19	
67	[BuMMim] BF <sub>4</sub>	49.4	98			51.76	13.3		16.14	
68	[BuMMMim] BF <sub>4</sub>			51.30		51.44	12.0		16.13	
69	[1O2Mim] BF <sub>4</sub>			55.95						
70	[BuMim] NO <sub>3</sub>	51.8	78	51.79		52.78	20.1		16.18	
		52.1	85							
71	[EtMim] NO <sub>3</sub>	51.5	123	52.56						
				52.3						
				53.5						
72	[HOEtMim] NO <sub>3</sub>			55.62						
				57						
				57.6						
73	[1O2Mim] NO <sub>3</sub>			49.60						
74	[HexMim] HCO <sub>2</sub>	56	79	56.63						
75	[HexBuim] HCO <sub>2</sub>	56.6	79	57.26						
76	[EtMim] CH <sub>3</sub> CO <sub>2</sub>	49.8	98	51.7		50.55	9.4		16.09	
		50.57	125	53.1						
		50.8	75							
77	[BuMim] CH <sub>3</sub> CO <sub>2</sub>	49.2	65			49.85	8		16.06	
		49.9	125							
		50.6	75							
78	[HexMim] CH <sub>3</sub> CO <sub>2</sub>	48.81	125							
79	[HexBuim] CH <sub>3</sub> CO <sub>2</sub>	55.5	79	55.96						
80	[OctMim] CH <sub>3</sub> CO <sub>2</sub>	48.99	125							
81	[BuEtim] CH <sub>3</sub> CO <sub>2</sub>	50.1	125							
82	[BuPrim] CH <sub>3</sub> CO <sub>2</sub>	48.56	125							
83	[PentMim] CH <sub>3</sub> CO <sub>2</sub>	50.5	75							
84	[HexMim] CH <sub>3</sub> CO <sub>2</sub>	50.3	75							

Table S2. Continued

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
85	[HO(CH <sub>2</sub> ) <sub>2</sub> Mim] CH <sub>3</sub> CO <sub>2</sub>	52.3	111	52.4		52.12		15.1	16.15	
				53.7						
86	[HO(CH <sub>2</sub> ) <sub>3</sub> Mim] CH <sub>3</sub> CO <sub>2</sub>	51.1	111			52.01		14.5	16.15	
87	[HexMim] CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub>	47	79	45.78						
88	[HexBuim] CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub>	54.9	79	55.24						
89	[BuMim] CF <sub>3</sub> CO <sub>2</sub>	51.1	78			52.01		14.5	16.15	
90	[EtMim] ClO <sub>4</sub>	52.4	123	52.45		53.43		29.7	16.21	
				52.2						
				53.3						
91	[BuMim] ClO <sub>4</sub>	52.9	98			53.97		48.2	16.23	
92	[HO(CH <sub>2</sub> ) <sub>2</sub> Mim] ClO <sub>4</sub>	60.3	123	62.1						
				62.2						
93	[BuMim] SbF <sub>6</sub>	52.5	98			53.54		32.2	16.21	
94	[BuMim] PF <sub>6</sub>	52.3	74		54.77	51.91	14.0		16.3	16.15
							11.8			
							11.4±0.6			
		52.5	98							
		52.7	35							
		53.2	57							
		49	85							
		53.1	110							
		52.6	57							
		52.4	112							
95	[EtMim] PF <sub>6</sub>	52.6	123	52.45						
				52.2						
				53.3						
96	[HexMim] PF <sub>6</sub>	52	57			53.11		24	16.20	
						50.33	8.9	11.1	16.08	
							8.9±0.9			
97	[OctMim] PF <sub>6</sub>	51.2	74			52.12		15.1	16.15	
		50	57							
		51.3	57							



Table S2. Continued

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
		46.8	85							
98	[BuMMim] PF <sub>6</sub>			49.40		50.55	9.4		16.09	
99	[HOEtMim] PF <sub>6</sub>	61.7	123	60.76						
100	[1O2Mim] PF <sub>6</sub>			57.04						
101	[Buim] Tf <sub>2</sub> N	57.9	87			52.36		16.6	16.16	
102	[EtMim] Tf <sub>2</sub> N	52	123	52.45		51.52	12.3		16.13	
		53.1	57	52.2						
		47.6	57	53.3						
		52.6	110							
						51.51	12.25	11.5	16.13	
103	[PrMim] Tf <sub>2</sub> N	51.9	80			51.76	13.3		16.14	
						51.02		10.6	16.11	
104	[BuMim] Tf <sub>2</sub> N	50	57			51.91	14.0		16.15	
		51.5	74							
		51.6	57							
		52.5	110							
		47.1	57							
						51.31	11.52	9.4	16.12	
		51.5	112							
		50.8	75							
		51.6	113							
105	[HexMim] Tf <sub>2</sub> N	51.9	57			52.89		21.3	16.19	
		51.8	112							
106	[HexMMim] Tf <sub>2</sub> N	49.3	112	48.34						
107	[OctMim] Tf <sub>2</sub> N	51.1	74			52.01		14.5	16.15	
		51	112	50.26						
108	[DecMim] Tf <sub>2</sub> N	51	80			51.89		13.9	16.15	
109	[MeO(CH <sub>2</sub> ) <sub>2</sub> Mim] Tf <sub>2</sub> N	54.1	80					-		
110	[BenzylMim] Tf <sub>2</sub> N	52.5	80			53.43		29.7	16.21	
111	[EtMMim] Tf <sub>2</sub> N	50	89			51.65	12.8	8	16.14	
		49	75							
						51.29	11.45		16.12	

Table S2. Continued

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
112	[OctMMim] Tf <sub>2</sub> N	47.7	74			47.13		5		15.95
113	[HO(CH <sub>2</sub> ) <sub>2</sub> Mim] Tf <sub>2</sub> N	61.4	80	62.1				-		
		60.8	123	62.2						
114	[HO(CH <sub>2</sub> ) <sub>3</sub> Mim] Tf <sub>2</sub> N	56.8	123					-		
115	[GlyMim] Tf <sub>2</sub> N	62.6	97					-		
116	[GlyMMim] Tf <sub>2</sub> N	61.2	96					-		
117	[BuMMim] Tf <sub>2</sub> N	48.6	74			51.91	14.0			16.15
		48.4	57							
		48.5	75							
118	[BuMMMim] Tf <sub>2</sub> N			51.90		52.10	15.0			16.15
119	[1O2Mim] Tf <sub>2</sub> N	54.5	113							
120	[EtDMim] Tf <sub>2</sub> N	51.8	113							
121	[Mim] Cl			53.90		51.87	13.8			16.14
122	[BuMim] Cl	50.27	125							
		50.6	57							
123	[HexMim] Cl	48.9	57			50.55		9.4		16.09
124	[OctMim] Cl	48.5	57							
125	[HO(CH <sub>2</sub> ) <sub>2</sub> Mim] Cl	55.6	123							
126	[HOEtMim] Cl		123	55.62						
				56.4						
127	[GlyMim] Cl	59	97					-		
128	[Mim] Br			54.40		52.36	16.6			16.16
129	[BuMim] Br	51.61	125							
130	[HexMim] Br	50.5	107			51.33		11.6		16.12
131	[EtMim] HOSO <sub>3</sub>			50.60		52.59	18.4			16.17
132	[HexMim] HOSO <sub>3</sub>	63.6	79	65.67						
133	[HexBuim] HOSO <sub>3</sub>	65.5	79	68.03						
134	[EtMim] EtOSO <sub>3</sub>			51.60	43.81	53.64	35.0		15.82	16.08
						53.35	27.9	13.5		16.21
135	[EtMim] BuOSO <sub>3</sub>			51.40		53.45	30.0			16.21
136	[EtMim] HexOSO <sub>3</sub>	52.1	107			53.11		24		16.20

Table S2. Continued

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
137	[EtMim] OctOSO <sub>3</sub>	51.1	107			52.01		14.5		16.15
138	[BuMim] OctOSO <sub>3</sub>	51.4	107			52.34		16.5		16.16
139	[MMim] Me <sub>2</sub> PO <sub>4</sub>			51.40		53.43	29.6			16.21
140	[EtMim] Et <sub>2</sub> PO <sub>4</sub>			50.40		52.40	16.9			16.17
141	[BuMim] (C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> PO <sub>2</sub>	48.24	125							
142	[EtMim] TfO			50.30	55.23	52.34	16.5		16.32	16.16
						52.14	15.2	15.8		16.16
143	[BuMim] TfO	52.3	74			51.74	13.2			16.14
		52.1	110							
144	[HexMim] TfO	52.5	112	51.84						
145	[BuMim] <sub>2</sub> WO <sub>4</sub>				49.52	51.08		10.8	16.07	16.11
146	[EtMim] DCA	51.7	123	52.45						
		51.6	113							
147	[BuMim] DCA	51.4	113							
148	[1O2Mim] DCA	52.4	113							
149	[HOEtMim] DCA	56.1	113							
150	[BuMim] [propionate]	49.1	101							
151	[BuMim] [butyrate]	49.3	101							
152	[BuMim] [glycolate]	50.5	101							
153	[BuMim] [H-malate]	48.6	101							
154	[BuMim] [H-maleate]	47.6	101							
155	[BuMim] <sub>2</sub> [maleate]	48.8	101							
156	[BuMim] <sub>2</sub> [malate]	49.8	101							
157	[BuMim] [H-succinate]	48.2	101							
158	[BuMim] <sub>2</sub> [succinate]	49.4	101							
<i>Pyridinium salts</i>										
159	[PrPy] BF <sub>4</sub>	52.1	35			49.21		13.4		16.01
160	[BuPy] BF <sub>4</sub>	51.4	35			48.52		10.6		15.99
		44.9	85							
161	[1-Pr-4-MePy] BF <sub>4</sub>	52.4	35			49.50		15		16.03
162	[1-Bu-4-MePy] BF <sub>4</sub>	51.1	35			48.26		9.8		15.97
163	[1-Oct-3-MePy] BF <sub>4</sub>	50.1	107			47.25		7.6		15.93

Table S2. Continued

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
164	[BuPy] Tf <sub>2</sub> N	51.7	57			49.54	15.3		16.03	
165	[BuMPy] Tf <sub>2</sub> N	50.2	112	49.33						
166	[HexMPy] Tf <sub>2</sub> N	50.4	112	49.60						
167	[OctPy] Tf <sub>2</sub> N	49.8	95			46.94	7.1		15.92	
		50.7	96							
168	[1-Oct-2-MePy] Tf <sub>2</sub> N	48.6	95			44.90	4.9		15.84	
169	[OctMePy] Tf <sub>2</sub> N	48.99	112	48.03						
170	[1-Oct-3-MePy] Tf <sub>2</sub> N	49.4	95			46.51	6.5		15.90	
		49	112							
171	[1-Oct-4-MePy] Tf <sub>2</sub> N	49.4	95			46.51	6.5		15.90	
172	[1-Bu-3-MePy] Tf <sub>2</sub> N	49.7	95			46.87	7		15.92	
			112	50.20						
173	[HexMDMeAPy] Tf <sub>2</sub> N	48.3	112	47.27						
174	[MeOctEtMPy] [OTf]	60.2	123							
175	[1-Et-4-HO(CH <sub>2</sub> ) <sub>2</sub> Py] EtOSO <sub>3</sub>			52.90		50.88	35		16.08	
<i>Pyrrolidinium salts</i>										
176	[1-MeO(CH <sub>2</sub> ) <sub>2</sub> -1-Me-pyrr] CF <sub>3</sub> CO <sub>2</sub>	42.7	78			42.02	4.1		15.71	
177	[1-MeO(CH <sub>2</sub> ) <sub>2</sub> -1-Me-pyrr] CH <sub>3</sub> CO <sub>2</sub>	47.5	78			47.44	16.1		15.93	
178	[1-MeO(CH <sub>2</sub> ) <sub>2</sub> -1-Me-pyrr] CH <sub>3</sub> SO <sub>3</sub>	56	78				-			
179	[1-MeO(CH <sub>2</sub> ) <sub>2</sub> -1-Me-pyrr] CF <sub>3</sub> SO <sub>3</sub>	60.2	78							
180	[MePyrr] HCO <sub>2</sub>			49.60		50.62	23.1		16.07	
181	[1-MeO(CH <sub>2</sub> ) <sub>2</sub> -1-Me-pyrr] NO <sub>3</sub>	57.9	78				-			
182	[MeGlyPyrr] NO <sub>3</sub>	57.86	97				-			
183	[1-MeO(CH <sub>2</sub> ) <sub>2</sub> -1-Me-pyrr] TfO	60.2	78				-			
184	[MeEtPyrr] N(CN) <sub>2</sub>	48.7	124			48.69	41.5		15.98	
185	[MeGlyPyrr] N(CN) <sub>2</sub>	58.28	97							
186	[BuMePyrr] N(CN) <sub>2</sub>			46.60		47.65	18		15.93	
187	[MePrPyrr] Tf <sub>2</sub> N	52.4	90							
188	[MeBuPyrr] Tf <sub>2</sub> N	48.3	98			47.24	14.7		15.92	
		49	90							
189	[MePentPyrr] Tf <sub>2</sub> N	49	90			46.86	12.5		15.90	

Table S2. Continued

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
190	[MeHexPyrr] Tf <sub>2</sub> N	52	96							
191	[MeOctPyrr] Tf <sub>2</sub> N	57	90				-			
		51.8	96							
192	[MeGlyPyrr] Tf <sub>2</sub> N	64.1	97				-			
193	[MeCNPrPyrr] Tf <sub>2</sub> N	51.7	90				-			
194	[MPS <sub>2</sub> Pyrr] Tf <sub>2</sub> N	48.4	90			48.38	30		15.96	
<i>Piperidinium salts</i>										
195	[MeBuPip] N(CN) <sub>2</sub>	48.6	97			48.59	36.9		15.97	
196	[MeOePip] N(CN) <sub>2</sub>	55.65	97				-			
197	[MeGlyPip] N(CN) <sub>2</sub>	57	97				-			
198	[FHexMeGlyPip] N(CN) <sub>2</sub>	59.2	97				-			
199	[MePrPip] Tf <sub>2</sub> N	49	91			49.00	66.6		15.99	
200	[MeBuPip] Tf <sub>2</sub> N	48.6	91			48.59	36.9		15.97	
201	[MePentPip] Tf <sub>2</sub> N	48.9	91			48.89	55.5		15.98	
202	[MeOctPip] Tf <sub>2</sub> N	48.2	91			48.17	25.3		15.96	
203	[MeGlyPip] Tf <sub>2</sub> N	62.8	97				-			
204	[MeBCNPip] Tf <sub>2</sub> N	50.2	91							
205	[MPS <sub>2</sub> Pip] Tf <sub>2</sub> N	49.4	91							
206	[MeOctPip] N(O <sub>2</sub> SC <sub>2</sub> F <sub>5</sub> ) <sub>2</sub>	47.8	91			47.75	19.1		15.94	
<i>Morpholinium salts</i>										
207	[MeEtMor] N(CN) <sub>2</sub>	50.3	97				-			
208	[MePrMor] N(CN) <sub>2</sub>	50.2	97							
209	[MeBuMor] N(CN) <sub>2</sub>	49.5	97			49.50	3688.5		16.01	
210	[MePentMor] N(CN) <sub>2</sub>	49.5	97			49.50	3688.5		16.01	
211	[MeHexMor] N(CN) <sub>2</sub>	49.6	97							
212	[MeHeptMor] N(CN) <sub>2</sub>	49.2	97			49.20	110.3		16.00	
213	[MeOctMor] N(CN) <sub>2</sub>	49.1	97			49.10	83.1		15.99	
214	[MeNonMor] N(CN) <sub>2</sub>	49.2	97			49.20	110.3		16.00	
215	[MeOeMor] N(CN) <sub>2</sub>	55.8	97							
216	[MeGlyMor] N(CN) <sub>2</sub>	57.8	97							
217	[MeGlyMor] Tf <sub>2</sub> N	62.9	97							
<i>Guanidinium salts</i>										

Table S2. Continued

No.	Abbreviation	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	Ref.	$E_T(30)^b$ (kcal mol <sup>-1</sup> )			$\epsilon_r^a$ (F m <sup>-1</sup> )	$\epsilon_r^b$ (F m <sup>-1</sup> )	$A_N^a$ (Gauss)	$A_N^b$ (Gauss)
				$b_1$	$b_2$	$b_3$				
218	[N <sub>11</sub> N <sub>22</sub> N <sub>201,201</sub> ] Cl	44.7	126			43.13		2.9		15.78
219	[N <sub>11</sub> N <sub>22</sub> N <sub>44</sub> ] CF <sub>3</sub> CO <sub>2</sub>	42.3	126			39.73		2.2		15.64
220	[N <sub>22</sub> N <sub>44</sub> N <sub>66</sub> ] CF <sub>3</sub> CO <sub>2</sub>	43.7	126			41.86		2.6		15.73
221	[N <sub>11</sub> N <sub>22</sub> N <sub>201,201</sub> ] CF <sub>3</sub> CO <sub>2</sub>	45.1	126			43.50		3		15.80
222	[N <sub>11</sub> N <sub>22</sub> N <sub>44</sub> ] CF <sub>3</sub> SO <sub>3</sub>	46.1	126			44.80		3.4		15.86
223	[N <sub>22</sub> N <sub>44</sub> N <sub>66</sub> ] CF <sub>3</sub> SO <sub>3</sub>	46.8	126			45.62		3.7		15.89
224	[N <sub>11</sub> N <sub>22</sub> N <sub>201,201</sub> ] CF <sub>3</sub> SO <sub>3</sub>	49.6	126			49.03		5.7		16.03
225	[N <sub>11</sub> N <sub>22</sub> N <sub>44</sub> ] Tf <sub>2</sub> N	50	126			49.57		6.2		16.06
226	[N <sub>22</sub> N <sub>44</sub> N <sub>66</sub> ] Tf <sub>2</sub> N	43	126			40.87		2.4		15.69
227	[N <sub>11</sub> N <sub>22</sub> N <sub>201,201</sub> ] Tf <sub>2</sub> N	47.4	126			46.32		4		15.92
<i>Phosphonium salts</i>										
228	[1-Oct <sub>3</sub> PMe] Me <sub>2</sub> PO <sub>4</sub>	43.8	127			43.51		6.5		15.76
229	[Hex <sub>3</sub> PC <sub>14</sub> H <sub>29</sub> ] Tf <sub>2</sub> N	46.1	89			46.03		14.9		15.86
230	[Pr <sub>21</sub> (OH)] Tf <sub>2</sub> N			60.80						
231	[EtMeP] N(CN) <sub>2</sub>	50.4	94							
<i>Other salts</i>										
232	[PentDABCO] N(CN) <sub>2</sub>	48.4	77			48.35		17.4		15.97
233	[HexDABCO] N(CN) <sub>2</sub>	48.5	77			48.45		18.4		15.97
234	[HeptDABCO] N(CN) <sub>2</sub>	48.7	77			48.66		20.7		15.98
235	[OctDABCO] N(CN) <sub>2</sub>	48.7	77			48.66		20.7		15.98
236	[NonDABCO] N(CN) <sub>2</sub>	48.5	77			48.45		18.4		15.97
237	[DecDABCO] N(CN) <sub>2</sub>	48.5	77			48.45		18.4		15.97
238	[EtMeP] N(CN) <sub>2</sub>	50.4	94							
239	[Et <sub>3</sub> S] Tf <sub>2</sub> N			44.10		45.09	15.8			15.82
240	Na[TOTO]	41.8	103							