Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2018 Please do not adjust margins

Journal Name

COMMUNICATION

Designing the ammonium cation to achieve a higher hydrophilicity of bistriflimide-based ionic liquids

A. Mão de Ferro,[a] P.M. Reis,[a,b] M.R.C. Soromenho,[a,b] C.E.S. Bernardes,[c] K. Shimizu,[c] A.A. Freitas,[c] J.M.S.S.Esperança,[*,a,b] J.N. Canongia Lopes,[*,a,c] L.P.N. Rebelo[a,b]

Supporting information

Synthesis of $[N_{2\,1\,1\,3OH}][NTf_2]$, $[N_{2\,1\,1\,2O1}][NTf_2]$ and $[N_{2\,1\,1\,4}][NTf_2]$

Materials:

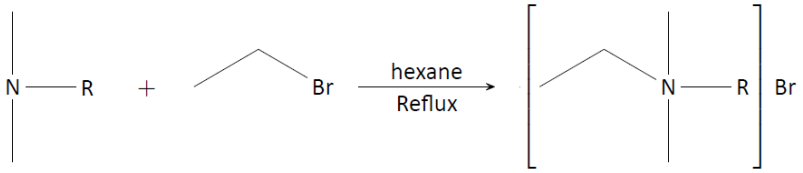
The reagents and solvents used for the synthesis of $[N_{2\,1\,1\,3OH}][NTf_2]$, $[N_{2\,1\,1\,2O1}][NTf_2]$ and $[N_{2\,1\,1\,4}][NTf_2]$ were purchased from different companies: N,N-dimethylbutylamine, dichloromethane and diethyl ether from Sigma-Aldrich with >99 % purity; 1-bromoethane and N,N-dimethylethylamine from Fluka with 98 and 99 % purity, respectively; 3-dimethylamino-1-propanol from Aldrich with 99 % purity; 2-chloroethyl methyl ether from Alfa Aesar with 98 % purity; lithium bistriflimide from Iolitec with 99 % purity and acetone from Scharlau with a purity better than 99.5 %. All reagents and solvents were used without further purification, except for chloroethyl methyl ether that was distilled prior to use.

Equipment:

^{1}H NMR spectra were obtained on an Ultrashield Bruker Avance II 400 spectrometer. Chemical shifts are reported in parts per million.

Experimental procedure and characterization:

The synthesis of $[N_{2\,1\,1\,3OH}][NTf_2]$, $[N_{2\,1\,1\,2O1}][NTf_2]$ and $[N_{2\,1\,1\,4}][NTf_2]$ started with the preparation of the respective halide anion version of each IL, *viz,* $[N_{2\,1\,1\,3OH}]Br$, $[N_{2\,1\,1\,2O1}]Cl$ and $[N_{2\,1\,1\,4}]Br$. The synthesis of the halide salts $[N_{2\,1\,1\,3OH}]Br$ and $[N_{2\,1\,1\,4}]Br$ followed a common procedure which consisted in mixing a R-dimethylamine (where R represents the functional groups propanol or butyl, respectively) with bromoethane (1.2 mol equiv.) in a pressure tube at room temperature, according to Scheme S1. Hexane was used as the reaction solvent.

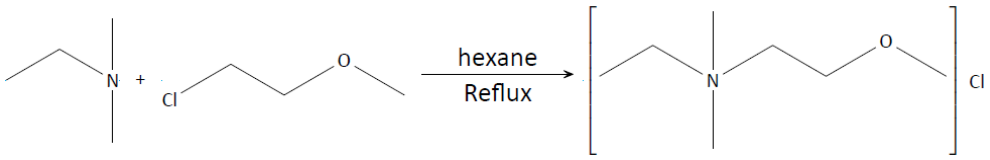


Scheme S1 Synthesis of $[N_{2\,1\,1\,R}]Br$ by N-alkylation reaction between R-dimethylamine and bromoethane

Please do not adjust margins

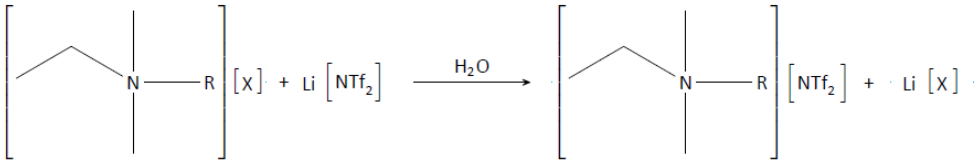
Please do not adjust margins

The reaction mixture was then warmed-up and hexane was left on reflux for 2 days. During this process, it was observed the formation of a product by precipitation of a white powder. Hexane was then decanted and the product was washed several times with diethyl ether. The final product was dried under vacuum, at 50ºC for 3 days.
The preparation of $[N_{2\,1\,1\,2O1}]Cl$ consisted in the alkylation reaction between N,N-dimethylethylamine and 2-chloroethyl methyl ether, according to Scheme S2. The same experimental conditions were used. Hexane was then decanted and the synthesized chloride salt was washed several times with diethyl ether. The final product was dried under vacuum, at 50ºC for 3 days.



Scheme S2 Synthesis of $[N_{2\,1\,1\,2O1}]Cl$ by alkylation reaction between N,N-dimethylethylamine and 2-chloroethyl methyl ether

The synthesis of $[N_{2\,1\,1\,3OH}][NTf_2]$, $[N_{2\,1\,1\,4}][NTf_2]$ and $[N_{2\,1\,1\,2O1}][NTf_2]$ was carried out by metathesis reaction of the corresponding halide salt with lithium bis(trifluoromethylsulfonyl)imide as shown in Scheme S3. Each of the previously prepared halide salts were dissolved in Millipore water and lithium bistriflimide (1.01 mole equiv.) was added. Appearance of a second phase signals the production of the desired ionic liquids. The reaction is left stirring at room temperature for 1h. Dichloromethane is added to the lower phase, containing the ammonium bistriflimide IL to enhance ionic liquid recovery and purification. This phase is extracted and washed several times with cold water. Dichloromethane is removed from the washed solution in a rotovapor under reduced pressure. The purified ionic liquids are dried under vacuum at 60ºC for 3 days. The water content of the dried ILs, measured by coulometric Karl Fischer titration, is always below 500 ppm.



Scheme S3 Synthesis of ammonium bistriflimide-based ILs by a counterion exchange between the halide salts $[N_{2\,1\,1\,R}][X]$ and $[Li][NTf_2]$ ([X] = Br or Cl).

$[N_{2\,1\,1\,3OH}][NTf_2]$
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 4.80 (s, 1H, $NCH_2CH_2CH_2O\mathbf{H}$); 3.48 (t, 2H, $NCH_2CH_2C\mathbf{H}_2OH$); 3.31 (m, 4H, $CH_3C\mathbf{H}_2NC\mathbf{H}_2CH_2CH_2OH$); 2.97 (s, 6H, $N(C\mathbf{H}_3)_2$); 1.79 (m, 2H, $NCH_2C\mathbf{H}_2CH_2OH$); 1.23 (t, 3H, $C\mathbf{H}_3CH_2N$).
^{19}FNMR (376 MHz, $(CD_3)_2SO$): δ -78.70
Elemental analysis calculated (found): %C 26.21 (25.70); % H 4.40 (4.55); % N 6.79 (6.37); %S 15.55 (15.60).

$[N_{2\,1\,1\,2O1}][NTf_2]$
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 3.73 (m, 2H, $NCH_2C\mathbf{H}_2OCH_3$); 3.47 (m, 2H, $NC\mathbf{H}_2CH_2OCH_3$); 3.37 (q, 2H, $N(CH_3)_2C\mathbf{H}_2CH_3$); 3.29 (s, 3H, N $CH_2CH_2OC\mathbf{H}_3$); 3.00 (s, 6H, $N(C\mathbf{H}_3)2CH_2CH_3$), 1.23 (t, 3H, N(CH3)2CH2C**H**3).
^{19}FNMR (376 MHz, $(CD_3)_2SO$): δ -78.70
Elemental analysis calculated (found): %C 26.21 (26.10); % H 4.40 (4.42); % N 6.79 (7.00); %S 15.55 (15.00).

$[N_{2\,1\,1\,4}][NTf_2]$
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 3.30 (qt, 2H, $NC\mathbf{H}_2CH_3$); 3.20 (m, 2H, $NC\mathbf{H}_2CH_2CH_2CH_3$); 2.96 (s, 6H, $N(C\mathbf{H}_3)_2$); 1.62 (m, 2H, $NCH_2C\mathbf{H}_2CH_2CH_3$); 1.31 (sxt, 2H, $CH_3CH_2NCH_2CH_2C\mathbf{H}_2CH_3$); 1.22 (t, 3H, $C\mathbf{H}_3CH_2N$); 0.93 (t, 3H, $NCH_2CH_2CH_2C\mathbf{H}_3$).
^{19}FNMR (376 MHz, $(CD_3)_2SO$): δ -78.80
Elemental analysis calculated (found): %C 29.27 (29.20); % H 4.91 (4.63); % N 6.83 (6.79); %S 15.63 (15.80).

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Synthesis of $[N_{2\ 1\ 2OH\ 2OH}][NTf_2]$, $[N_{1\ 2OH\ 2OH\ 2OH}][NTf_2]$, $[N_{2\ 2OH\ 2OH\ 2OH}][NTf_2]$ and $[N_{4\ 2OH\ 2OH\ 2OH}][NTf_2]$.

Materials:

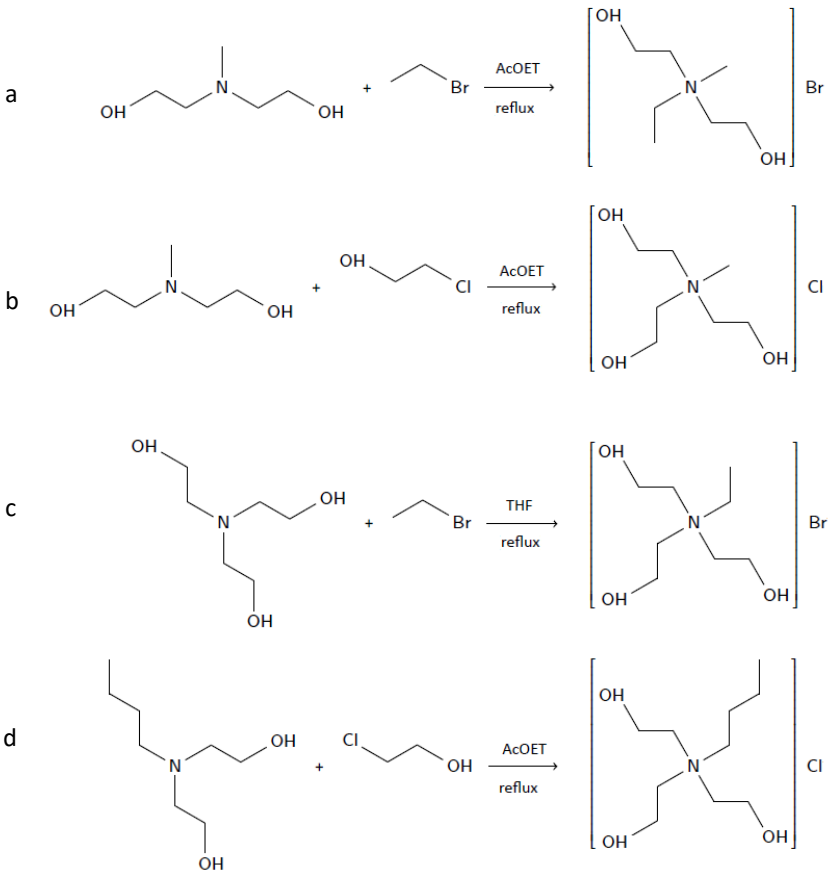
The reagents and solvents used for the synthesis of $[N_{2\ 1\ 2OH\ 2OH}][NTf_2]$, $[N_{1\ 2OH\ 2OH\ 2OH}][NTf_2]$, $[N_{2\ 2OH\ 2OH\ 2OH}][NTf_2]$ and $[N_{4\ 2OH\ 2OH\ 2OH}][NTf_2]$ were purchased from different companies: 1-bromoethane from Fluka (98 %); lithium bistriflimide from Iolitec (99 %), Sulfuric acid from Merck (98 %), and N-methyldiethanolamine (≥ 99 %), N-butyldiethanolamine (≥ 98.6 %), triethanolamine (≥ 99 %), 2-chloroethanol (99 %), ethyl acetate (99.8 %), tetrahydrofuran (99.9 %), hexane (95 %), dichloromethane (≥ 99.9 %) and diethyl ether (≥ 99.8 %) from Sigma-Aldrich.

Equipment:

^{1}H NMR spectra were obtained on an Ultrashield Bruker Avance II 400 spectrometer. Chemical shifts are reported in parts per million.

Experimental procedure and characterization:

The synthesis of $[N_{2\ 1\ 2OH\ 2OH}][NTf_2]$, $[N_{1\ 2OH\ 2OH\ 2OH}][NTf_2]$, $[N_{2\ 2OH\ 2OH\ 2OH}][NTf_2]$ and $[N_{4\ 2OH\ 2OH\ 2OH}][NTf_2]$ follows the same procedure as the previous ionic liquids and starts with the preparation of the homologue halide salt - same cation but with chloride or bromide as anion, according to Scheme S4.



Scheme S4 Synthesis of (a) $[N_{2\ 1\ 2OH\ 2OH}]Br$, (b) $[N_{1\ 2OH\ 2OH\ 2OH}]Cl$, (c) $[N_{2\ 2OH\ 2OH\ 2OH}]Br$ and (d) $[N_{4\ 2OH\ 2OH\ 2OH}]Cl$, by an alkylation reaction between N-alkyl-diethanolamine or triethanolamine and bromoethane or 2-chloroethanol.

Please do not adjust margins

The reaction mixture was then warmed-up to obtain solvent reflux for 3 days. All the obtained halide products were washed several times with diethyl ether. The solvent is decantated and the final product is dried under vacuum, at 50ºC for 3 days.
The synthesis of $[N_{4\ 2OH\ 2OH\ 2OH}][NTf_2]$ was carried out by metathesis reaction of the corresponding halide salt with lithium bis(trifluoromethylsulfonyl)imide. The synthesis of $[N_{2\ 1\ 2OH\ 2OH}][NTf_2]$, $[N_{1\ 2OH\ 2OH\ 2OH}][NTf_2]$ and $[N_{2\ 2OH\ 2OH\ 2OH}][NTf_2]$ followed a different procedure which consisted in the production of an hydroxide salt by passing the halide salt over an anionic exchange resin column (amberlite). The hydroxide salt produced was reacted with a solution of $HNTf_2$. The titration with the acid finished when the pH of the solution reaches 7. Water was removed by evaporation in a rotovapor. The $HNTf_2$ was also synthetized in-house by adding H_2SO_4 to pure $LiNTf_2$ followed by the distillation of the $HNTf_2$, forming a white powder.
Before any experiment, the obtained ILs were dried under vacuum at 60 ºC for at least 3 days. Coulometric Karl Fischer titration revealed water contents below 500 ppm for all ionic liquids. ^{1}H NMR and elemental analysis was performed to reach the purity of each sample.

$[N_{2\ 1\ 2OH\ 2OH}][NTf_2]$
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 5.25 (t, 2H, $N(CH_3)(CH_2CH_3)(CH_2CH_2O\mathbf{H})_2$); 3.82 (m, 4H, $N(CH_3)(CH_2CH_3)(CH_2C\mathbf{H}_2OH)_2$); 3.36-3.50 (m, 6H, $N(CH_3)(C\mathbf{H}_2CH_3)(C\mathbf{H}_2CH_2OH)_2$); 3.05 (s, 3H, $N(C\mathbf{H}_3)(CH_2CH_3)(CH_2CH_2OH)_2$); 1.25 (t, 3H, $N(CH_3)(CH_2C\mathbf{H}_3)(CH_2CH_2OH)_2$).
^{19}FNMR (376 MHz, $(CD_3)_2SO$): δ -78.70
Elemental analysis calculated (found): %C 25.23 (25.30); %H 4.24 (4.78); %N 6.54 (6.54); %S 14.97 (15.10).

$[N_{1\ 2OH\ 2OH\ 2OH}][NTf_2]$
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 5.25 (t, 3H, $N(CH_3)(CH_2CH_2O\mathbf{H})_3$); 3.85 (m, 6H, $N(CH_3)(CH_2C\mathbf{H}_2OH)_3$); 3.53 (t, 6H, $N(CH_3)(C\mathbf{H}_2CH_2OH)_3$); 3.15 (s, 3H, $N(C\mathbf{H}_3)(CH_2CH_2OH)_3$).
^{19}FNMR (376 MHz, $(CD_3)_2SO$): δ -78.70
Elemental analysis calculated (found): %C 24.33 (24.10); %H 4.08 (4.05); %N 6.30 (6:11); %S 14.43 (14.70).

$[N_{2\ 2OH\ 2OH\ 2OH}][NTf_2]$
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 5.23 (t, 3H, $N(CH_2CH_3)(CH_2CH_2O\mathbf{H})_3$); 3.82 (m, 6H, $N(CH_2CH_3)(CH_2C\mathbf{H}_2OH)_3$); 3.44-3.56 (m, 8H, $N(C\mathbf{H}_2CH_3)(C\mathbf{H}_2CH_2OH)_3$); 1.25 (t, 3H, $N(CH_2C\mathbf{H}_3)(CH_2CH_2OH)_3$).
^{19}FNMR (376 MHz, $(CD_3)_2SO$): δ -78.70
Elemental analysis calculated (found): %C 26.20 (26.30); %H 4.40 (4.63); %N 6.11 (6.09); %S 13.99 (13.60).

$[N_{4\ 2OH\ 2OH\ 2OH}][NTf_2]$
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 5.23 (t, 3H, $N(CH_2CH_2CH_2CH_3)(CH_2CH_2O\mathbf{H})_3$); 3.82 (m, 6H, $N(CH_2CH_2CH_2CH_3)(CH_2C\mathbf{H}_2OH)_3$); 3.50 (t, 6H, $N(CH_2CH_2CH_2CH_3)(C\mathbf{H}_2CH_2OH)_3$); 3.40 (t, 2H, $N(C\mathbf{H}_2CH_2CH_2CH_3)(CH_2CH_2OH)_3$); 1.68 (m, 2H, $N(CH_2C\mathbf{H}_2CH_2CH_3)(CH_2CH_2OH)_3$); 1.30 (sxt, 2H, $N(CH_2CH_2C\mathbf{H}_2CH_3)(CH_2CH_2OH)_3$); 0.93 (t, 3H, $N(CH_2CH_2CH_2C\mathbf{H}_3)(CH_2CH_2OH)_3$).
^{19}FNMR (376 MHz, $(CD_3)_2SO$): δ -76.50
Elemental analysis calculated (found): %C 29.63 (29.32); %H 4.97 (4.84); %N 5.76 (5.60); %S 13.18 (13.58)

Simulation details

Tab. S1 Simulation conditions and size of the equilibrated boxes.

mixture	$N_{IL}{}^a+N_{solv}$	V_{box} nm^3	l_{box} nm
pure $[N_{1\ 1\ 1\ 2OH}][NTf_2]$	350+0	148.3	5.29
20 mol % $[N_{1\ 1\ 1\ 2OH}][NTf_2]$ + butanol	150+600	167.9	5.52
20 mol % $[N_{1\ 1\ 1\ 2OH}][NTf_2]$ + pentanol	150+600	186.6	5.71
20 mol % $[N_{1\ 1\ 1\ 2OH}][NTf_2]$ + hexanol	150+600	205.2	6.00
pure $[N_{1\ 2OH\ 2OH\ 2OH}][NTf_2]$	350+0	168.5	5.52
5 mol % $[N_{1\ 2OH\ 2OH\ 2OH}][NTf_2]$ + water	160+3040	166.0	5.50

[a] ion pairs

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Experimental results

Tab. S2 Experimental could-point temperature data at atmospheric pressure for $[N_{1\,1\,1\,2OH}][NTf_2]$, $[N_{2\,1\,1\,3OH}][NTf_2]$, $[N_{2\,1\,1\,2O1}][NTf_2]$ and $[N_{2\,1\,1\,4}][NTf_2]$ with C2 to C6 alkyl alcohols. W_{IL} and X_{IL} are the ionic liquid mass fraction and molar fraction, respectively.

$[N_{1\,1\,1\,2OH}][NTf_2]$

1-butanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.097	0.020	259.6	0.332	0.087	274.3	0.600	0.225	274.3
0.134	0.029	266.0	0.384	0.107	274.6	0.640	0.256	273.6
0.184	0.042	270.4	0.435	0.129	274.9	0.677	0.288	272.5
0.209	0.049	272.4	0.484	0.153	275.0	0.717	0.328	270.6
0.246	0.059	272.8	0.505	0.164	274.8	0.767	0.388	267.0
0.288	0.072	273.7	0.550	0.191	274.6	0.820	0.468	260.2

1-pentanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.094	0.023	270.2	0.448	0.157	301.9	0.698	0.346	300.2
0.161	0.042	294.2	0.501	0.187	302.1	0.753	0.412	298.2
0.207	0.057	297.7	0.504	0.189	302.0	0.796	0.472	295.9
0.263	0.076	299.4	0.558	0.224	301.7	0.827	0.522	293.2
0.319	0.097	300.6	0.588	0.247	301.4	0.873	0.612	285.7
0.385	0.125	301.5	0.621	0.273	301.2	0.919	0.723	272.2

1-hexanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.050	0.014	296.7	0.402	0.152	324.6	0.717	0.402	323.3
0.086	0.025	308.0	0.431	0.168	324.8	0.763	0.462	321.7
0.124	0.036	314.6	0.467	0.189	324.9	0.803	0.520	319.0
0.198	0.061	319.6	0.560	0.253	325.2	0.850	0.602	313.6
0.261	0.086	322.3	0.624	0.306	325.2	0.895	0.693	302.9
0.320	0.111	323.6	0.669	0.350	324.4	0.930	0.780	287.6

$[N_{2\,1\,1\,3OH}][NTf_2]$

1-propanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.062	0.009	211.6	0.296	0.058	234.7	0.472	0.115	236.0
0.069	0.011	221.6	0.338	0.069	235.0	0.510	0.132	236.0
0.111	0.018	231.4	0.360	0.076	235.4	0.552	0.152	236.0
0.150	0.025	234.3	0.397	0.088	235.6	0.600	0.180	235.0
0.198	0.035	234.3	0.442	0.104	235.8	0.653	0.215	232.5
0.242	0.044	234.2	0.443	0.104	236.2	0.705	0.259	229.6

1-butanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.056	0.010	270.3	0.338	0.084	291.8	0.661	0.259	289.5
0.108	0.021	282.3	0.396	0.105	292.2	0.722	0.318	285.7
0.168	0.035	288.3	0.461	0.133	292.1	0.782	0.392	278.9
0.226	0.050	290.2	0.514	0.160	292.0	0.826	0.461	272.7
0.279	0.065	291.3	0.593	0.208	291.5	0.873	0.553	250.1

1-pentanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.069	0.016	301.2	0.37	0.111	318.3	0.616	0.255	317.9
0.118	0.028	308.4	0.418	0.133	318.6	0.681	0.313	315.9
0.184	0.046	313.7	0.419	0.133	318.6	0.748	0.388	311.3
0.238	0.062	316.4	0.496	0.174	318.6	0.835	0.519	300.4
0.317	0.090	317.9	0.589	0.235	318.3	0.894	0.644	285.4

1-hexanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.076	0.020	329.7	0.369	0.126	342.9	0.621	0.289	342.1
0.106	0.029	333.4	0.443	0165	343.2	0.656	0.321	341.2
0.169	0.048	337.9	0.483	0.188	343.1	0.689	0.354	340.4
0.224	0.067	340.7	0.524	0.214	343.0	0.716	0.385	338.8
0.264	0.081	341.9	0.564	0.242	342.9	0.823	0.535	330.4
0.312	0.101	342.4	0.586	0.260	342.7	0.871	0.626	321.2

$[N_{2\,1\,1\,2O1}][NTf_2]$

ethanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.094	0.011	231.1	0.245	0.035	237.4	0.52	0.108	241.1
0.152	0.02	236.3	0.371	0.062	239.6	0.618	0.153	240.4
0.198	0.027	236.8	0.446	0.083	239.7	0.743	0.244	238.8
0.226	0.032	237.4	0.503	0.101	241.1	0.835	0.362	234.0

1-propanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.078	0.012	277.8	0.497	0.126	294.7	0.809	0.382	285.8
0.163	0.028	288.7	0.625	0.196	295.1	0.858	0.469	277.9
0.241	0.044	291.9	0.756	0.311	290.4	0.924	0.639	257.8
0.375	0.080	294.6	-	-	-	-	-	-

1-butanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.067	0.013	309.7	0.413	0.112	322.7	0.742	0.340	317.5
0.135	0.027	315.5	0.510	0.158	323.2	0.801	0.420	313.0
0.229	0.051	320.6	0.516	0.161	323.5	0.865	0.536	302.3
0.331	0.082	321.9	0.572	0.193	323.5	0.923	0.682	282.9
0.384	0.101	322.3	0.646	0.247	322.4	-	-	-

1-pentanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.106	0.025	332.3	0.518	0.187	340.4	0.741	0.380	334.7
0.201	0.051	337.6	0.572	0.222	340.6	0.790	0.445	329.6
0.302	0.085	339.8	0.597	0.241	340.5	0.866	0.579	315.1
0.413	0.131	340.7	0.678	0.311	337.4	0.917	0.703	278.2
0.515	0.185	340.5	-	-	-	-	-	-

1-hexanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.061	0.016	331.1	0.439	0.162	353.5	0.79	0.482	342.4
0.094	0.025	337.2	0.519	0.211	353.9	0.82	0.530	340.6
0.270	0.084	351.2	0.57	0.247	353.8	0.832	0.550	339.4
0.300	0.096	351.7	0.626	0.293	352.8	0.86	0.603	333.2
0.330	0.109	352.3	0.678	0.343	350.4	0.897	0.684	321.5
0.364	0.124	352.7	0.726	0.396	346.4	0.93	0.768	305.3
0.404	0.144	353.4	0.755	0.432	344.9	0.96	0.854	282.3

$[N_{2\,1\,1\,4}][NTf_2]$

ethanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.313	0.049	205.1	0.703	0.210	205.7	0.561	0.125	205.9
0.418	0.075	206.6	0.648	0.171	206.3	0.486	0.096	206.1

1-propanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.066	0.010	273.0	0.363	0.077	283.1	0.712	0.266	278.9
0.125	0.020	281.9	0.458	0.110	283.0	0.794	0.361	278.4
0.162	0.028	280.5	0.564	0.159	281.7	0.887	0.535	268.4
0.181	0.031	281.7	0.650	0.214	284.9	0.939	0.692	239.6
0.31	0.062	283.3	-	-	-	-	-	-

1-butanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.048	0.009	299.9	0.398	0.107	317.2	0.772	0.380	308.6
0.121	0.024	308.3	0.479	0.142	317.0	0.839	0.484	298.9
0.154	0.032	311.9	0.590	0.207	316.1	0.896	0.609	280.7
0.240	0.054	316.3	0.692	0.288	312.6	0.929	0.702	272.6
0.331	0.082	317.3	-	-	-	-	-	-

1-pentanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.071	0.016	321.9	0.557	0.213	336.7	0.811	0.48	319.6
0.151	0.037	335.3	0.577	0.227	336.3	0.865	0.58	308
0.249	0.067	335.6	0.65	0.285	334.2	0.942	0.778	256.3
0.374	0.114	336.4	0.738	0.377	328.7			

1-hexanol

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.050	0.013	326.1	0.394	0.139	354.4	0.653	0.319	351.0
0.153	0.043	350.1	0.469	0.180	354.0	0.714	0.384	347.2
0.191	0.056	352.2	0.502	0.201	354.5	0.820	0.531	329.5
0.255	0.078	354.1	0.552	0.235	353.9	0.879	0.644	322.8
0.327	0.108	354.4	0.607	0.277	352.5	0.926	0.757	301.3

Tab. S3 Experimental could-point temperature data at atmospheric pressure for $[N_{2\,1\,1\,3OH}][NTf_2]$, $[N_{2\,1\,1\,2O1}][NTf_2]$, $[N_{2\,1\,1\,4}][NTf_2]$, $[N_{2\,1\,2OH\,2OH}][NTf_2]$ and $[N_{4\,2OH\,2OH\,2OH}][NTf_2]$with water. W_{IL} and X_{IL} are the ionic liquid mass fraction and molar fraction, respectively.

$[N_{2\,1\,1\,3OH}][NTf_2]$
water

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.090	0.004	320.5	0.406	0.029	365.1	0.704	0.094	359.8
0.141	0.007	344.6	0.467	0.037	365.4	0.739	0.110	356.3
0.172	0.009	353.3	0.531	0.047	364.9	0.778	0.133	350.5
0.210	0.012	358.5	0.592	0.060	364.6	0.846	0.194	332.5
0.262	0.015	361.9	0.596	0.061	364.5	0.881	0.245	318.3
0.304	0.019	363.7	0.641	0.072	363.6	0.901	0.285	300.1
0.354	0.023	364.5	0.680	0.085	362.1	0.925	0.351	277.6

$[N_{2\,1\,1\,2O1}][NTf_2]$
water

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.049	0.002	361.2	0.343	0.022	433.0	0.743	0.112	422.9
0.086	0.004	391.8	0.426	0.031	433.3	0.655	0.077	429.8
0.122	0.006	407.5	0.954	0.473	352.9	0.560	0.053	432.8
0.190	0.010	422.9	0.904	0.292	379.0	0.477	0.038	433.5
0.252	0.014	427.9	0.839	0.185	396.2	-	-	-

$[N_{2\,1\,1\,4}][NTf_2]$
water

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.07	0.003	425.0	0.89	0.254	402.8	0.95	0.457	355.7
0.16	0.008	461.6	-	-	-	-	-	-

$[N_{2\,1\,2OH\,2OH}][NTf_2]$
water

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.151	0.007	301.5	0.804	0.147	298.2	0.120	0.006	281.9
0.201	0.010	307.8	0.237	0.013	309.5	0.746	0.110	309.5
0.500	0.040	316.2	0.284	0.016	312.2	0.856	0.199	279.5
0.609	0.062	315.8	0.407	0.028	315.0	0.347	0.022	314.4
0.697	0.088	312.5	-	-	-	-	-	-

$[N_{4\,2OH\,2OH\,2OH}][NTf_2]$
water

w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K	w_{IL}	x_{IL}	T/K
0.840	0.163	278.9	0.576	0.048	335.1	0.338	0.019	336.9
0.779	0.115	309.6	0.516	0.038	336.2	0.135	0.006	325.7
0.694	0.077	326.8	0.460	0.031	336.9	0.198	0.009	332.9
0.628	0.059	333.3	0.398	0.024	336.9	0.275	0.014	336.2

MD-based Radial distribution functions and Aggregation Analyses

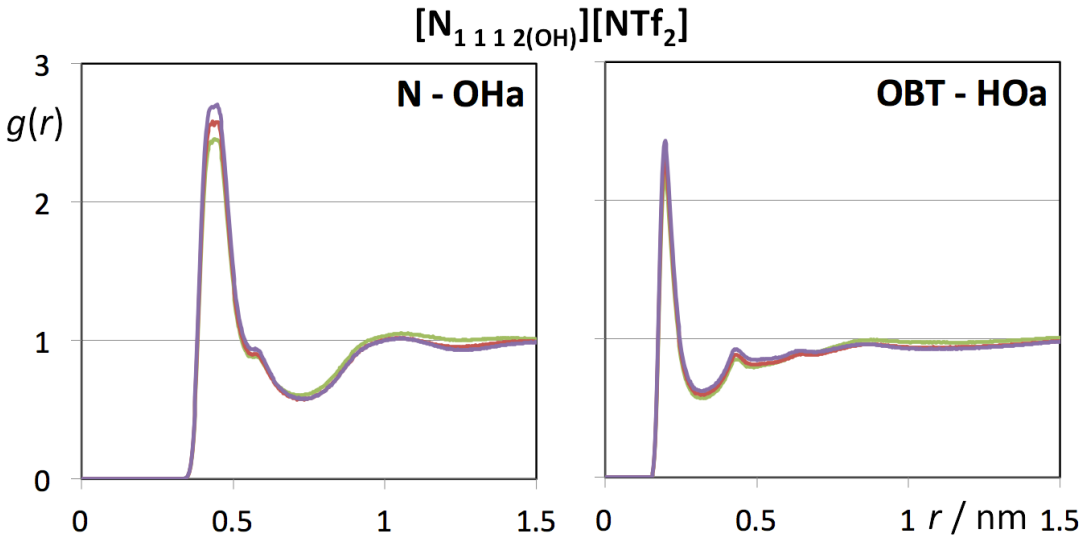


Figure S1 Pair radial distribution functions, g(r), between selected pairs of interaction centres in the $[N_{1\,1\,1\,2OH}][NTf_2]$ ionic liquid and 1-butanol (green), 1-pentanol (red) or 1-hexanol (purple). All (BIL + n-alcohol) systems are at 400 K and have compositions of 0.2 IL mole fraction. The N and OHa centres correspond to the nitrogen of the cation and the oxygen in the alcohol, respectively; the OBT and HOa centres correspond to the oxygen atoms in the anion and the hydroxyl group hydrogen atom in the alcohol, respectively. Both graphs show the existence of hydrogen bonding between the hydroxyl group of the alcohol and the charged moieties of the ions.

This journal is © The Royal Society of Chemistry 20xx

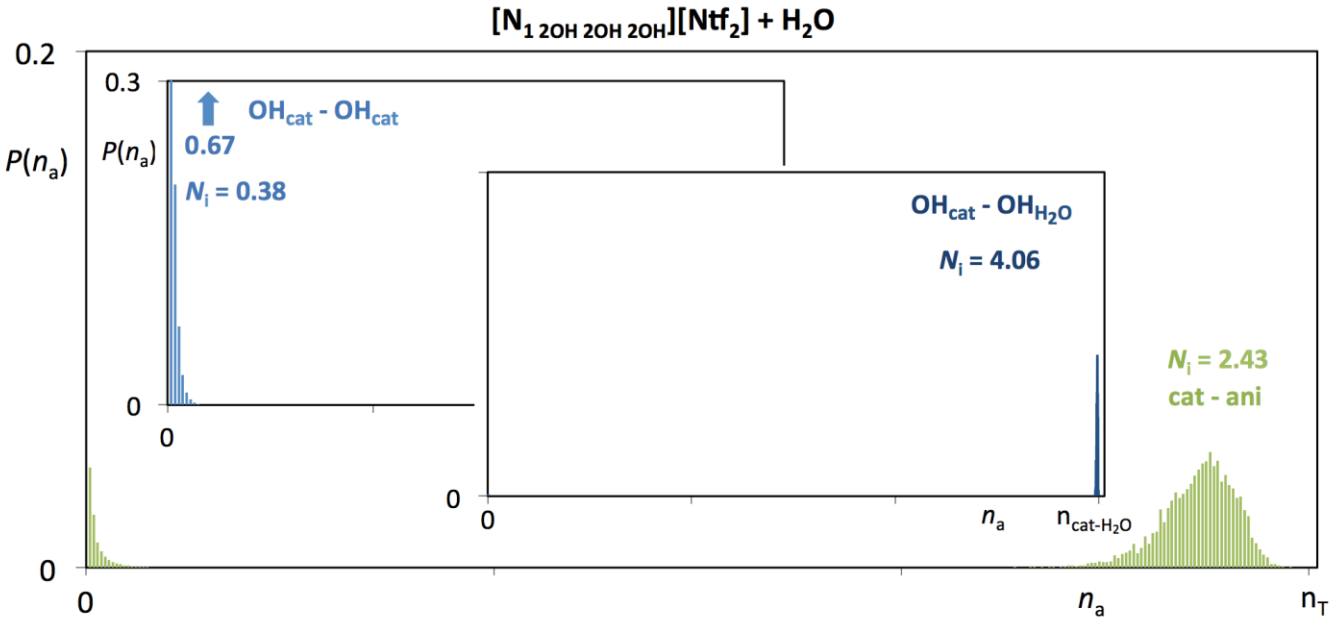


Figure S2 Discrete probability distribution functions, $P(n_a)$, of different types of aggregate in a ($[N_{1\ 2OH\ 2OH\ 2OH}][NTf_2]$ + H_2O) aqueous mixture at xIL = 0.05 at 400 K. The depicted aggregates are: cat-ani (green) as the polar network; OH_{cat}-OH_{cat} (light blue) as the choline H-Bonding; and OH_{cat}-OH_{H2O} (dark blue) as the H-Bonding network in the aqueous mixture. The value n_T corresponds to the number of ions in the simulation box (320); n_{CAT} is the number of cations (160); $n_{CAT+H2O}$ is the number of cations plus water molecules (3200). The N_i values correspond to the average number of neighbors of a given ion or molecule within the aggregate under analysis.