Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information - Structural characterization and DFT study of $V^{IV}O(acac)_2$ in imidazolium ionic liquids

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SI1 - Characterization of the ionic liquids

bmimNTf$_2$ – The ionic liquid was prepared according to a literature procedure.[17]

δ_H: (300 MHz, CD_2Cl_2)/ppm 8.59 (1H, s, $N_2C\boldsymbol{H}$), 7.39 (2H, sextet, ^6J = 2.9 Hz, 2NC***H***), 4.18 (2H, t, ^3J = 7.4 Hz, $NC\boldsymbol{H}_2(CH_2)_2CH_3$), 3.92 (3H, s, $NC\boldsymbol{H}_3$), 1.99 (2H, m, $NCH_2C\boldsymbol{H}_2CH_2CH_3$), 1.37 (2H, sextet, ^6J = 7.4 Hz, $NCH_2CH_2C\boldsymbol{H}_2CH_3$) and 0.95 (3H, t, ^3J = 7.4 Hz, $N(CH_2)_3C\boldsymbol{H}_3$)

m/z (FAB+): 558 ($[(bmim)_2N(SO_2CF_3)_2]^+$, 45%) and 139 ($[bmim]^+$, 100)

m/z (FAB^-): 280 ($[N(SO_2CF_3)_2]^-$, 100%).

Water content (KF): 357 ± 7 ppm.

bbimNTf$_2$ – The compound was donated by a colleague.

δ_H: (300 MHz, CD_2Cl_2)/ppm 8.69 (1H, s, $N_2C\boldsymbol{H}$), 7.47 and 7.46 (2H, d, 2NC***H***), 4.22 (4H, t, ^3J = 7.4 Hz, $NC\boldsymbol{H}_2(CH_2)_2CH_3$), 1.88 (4H, quintet, ^5J = 3.8 Hz, $NCH_2C\boldsymbol{H}_2CH_2CH_3$), 1.37 (4H, quartet, ^4J = 7.6 Hz, $NCH_2CH_2C\boldsymbol{H}_2CH_3$) and 0.95 (6H, t, ^3J = 7.4 Hz, $N(CH_2)_3C\boldsymbol{H}_3$).

Water content (KF): 143 ± 13 ppm.

C_3OmimNTf$_2$ – The ionic liquid was donated by a colleague.

δ_H: (300 MHz, CD_2Cl_2)/ppm 8.55 (1H, s, $N_2C\boldsymbol{H}$), 7.43 and 7.36 (2H, s, 2NC***H***), 4.33 (2H, t, ^3J = 4.8 Hz $NC\boldsymbol{H}_2(CH_2)_2CH_3$), 3.92 (3H, s, $NC\boldsymbol{H}_3$), 3.72 (2H, t, ^3J = 32.5 Hz, $NCH_2C\boldsymbol{H}_2OCH_3$), 3.35 (3H, s, $NCH_2CH_2OC\boldsymbol{H}_3$).

m/z (FAB^+): 562 ($\{[C_3Omim]_2([N(SO_2CF_3)_2]\}^+$, 15%) 282 $\{C_3Omim_2\}^{2+}$, 10%)

m/z (FAB^-): 280 ($[N(SO_2CF_3)_2]^-$, 100%).

bm$_2$imNTf$_2$ - The compound was donated by a colleague.

δ_H: (300 MHz, CD_2Cl_2)/ppm 2.58 (1H, s, $N_2C\boldsymbol{H}$), 7.25 (2H, quartet, ^4J = 2.9 Hz 2NC$\boldsymbol{H}$), 4.06 (2H, t, ^3J = 7.5 Hz, NC$\boldsymbol{H}_2(CH_2)_2CH_3$), 3.77 (3H, s, NC$\boldsymbol{H}_3$), 1.79 (2H, m, $NCH_2C\boldsymbol{H}_2CH_2CH_3$), 1.37 (2H, m, $NCH_2CH_2C\boldsymbol{H}_2CH_3$), 0.95 (3H, t, ^3J = 7.3 Hz, $N(CH_2)_3C\boldsymbol{H}_3$).

m/z (FAB$^+$) 586 ($[(bm_2im)_2NTf_2]^+$, 0.4%) and 153 ($[bm_2im]^+$, 100%);

m/z (FAB$^-$) 280 (NTf_2^-, 100%).

Water content (KF): 232 ± 5 ppm.

bmimOTf – The ionic liquid was prepared according to a literature procedure.[17]

δ_H: (300 MHz, CD_2Cl_2)/ppm 8.92 (1H, s, $N_2C\boldsymbol{H}$), 7.46 (2H, s, 2NC$\boldsymbol{H}$), 4.17 (2H, qd, ^4J = 3.6 Hz, NC$\boldsymbol{H}_2(CH_2)_2CH_3$), 3.91 (3H, d, NC$\boldsymbol{H}_3$), 1.83 (2H, qd, ^4J = 2.9 Hz, $NCH_2C\boldsymbol{H}_2CH_2CH_3$), 1.31 (2H, d, ^2J = 7.1 Hz, $NCH_2CH_2C\boldsymbol{H}_2CH_3$) and 0.90 (3H, t, ^3J = 3.6 Hz, $N(CH_2)_3C\boldsymbol{H}_3$)

m/z (FAB$^+$) 427 ($[(bmim)_2TfO]^+$, 2.0%) and 139 ($[bmim]^+$, 100%);

m/z (FAB$^-$) 437 ($[(bmim)(OTf)_2]^-$, 3.0%) and 149 (OTf^-, 100%).

Water content (KF): 1365 ± 16 ppm.

bmimBF$_4$ – The ionic liquid was prepared according to a literature procedure.[17]

δ_H (300 MHz, DMSO-d_6)/ppm 8.99 (1H, s, $N_2C\boldsymbol{H}$), 7.71 and 7.63 (2H, d, 2NC$\boldsymbol{H}$), 4.17 (2H, t, NC$\boldsymbol{H}_2(CH_2)_2CH_3$), 3.86 (3H, s, NC$\boldsymbol{H}_3$), 1.78 (2H, sextet, ^6J = 6.3 Hz, $NCH_2C\boldsymbol{H}_2CH_2CH_3$), 1.27 (2H, quartet, ^4J = 7.5 Hz, $NCH_2CH_2C\boldsymbol{H}_2CH_3$) and 0.89 (3H, t, ^3J = 7.4 Hz, $N(CH_2)_3C\boldsymbol{H}_3$).

m/z (FAB$^+$) 365 ($[(bmim)_2BF_4]^+$, 0.8%) and 139 ($[bmim]^+$, 100%);

m/z (FAB$^-$) 313 ($[(bmim)(BF_4)_2]^-$, 2%) and 87 (BF_4^-, 72%).

Water content (KF): 1570 ± 129 ppm.

bmimPF$_6$ - The ionic liquid was prepared according to a literature procedure.[17]

δ_H (400 MHz, DMSO-d_6)/ppm 8.97 (1H, s, $N_2C\boldsymbol{H}$), 7.63 and 7.57 (2H, m, 2NC$\boldsymbol{H}$), 4.14 (2H, t, NC$\boldsymbol{H}_2(CH_2)_2CH_3$), 3.84 (3H, s, NC$\boldsymbol{H}_3$), 1.77 (2H, quintet, $NCH_2C\boldsymbol{H}_2CH_2CH_3$), 1.26 (2H, sextet, $NCH_2CH_2C\boldsymbol{H}_2CH_3$) and 0.88 (3H, t, $N(CH_2)_3C\boldsymbol{H}_3$).

m/z (FAB$^+$) 423 ($[(bmim)_2PF_6]^+$, 1.5%) and 139 ($[bmim]^+$, 100%);

m/z (FAB$^-$) 429 ($[(bmim)(PF_6)_2]^-$, 2%) and 145 (PF_6^-, 100%).

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SI2 – Spectra of $VO(acac)_2$ in $bmimBF_4$ with different amounts of water

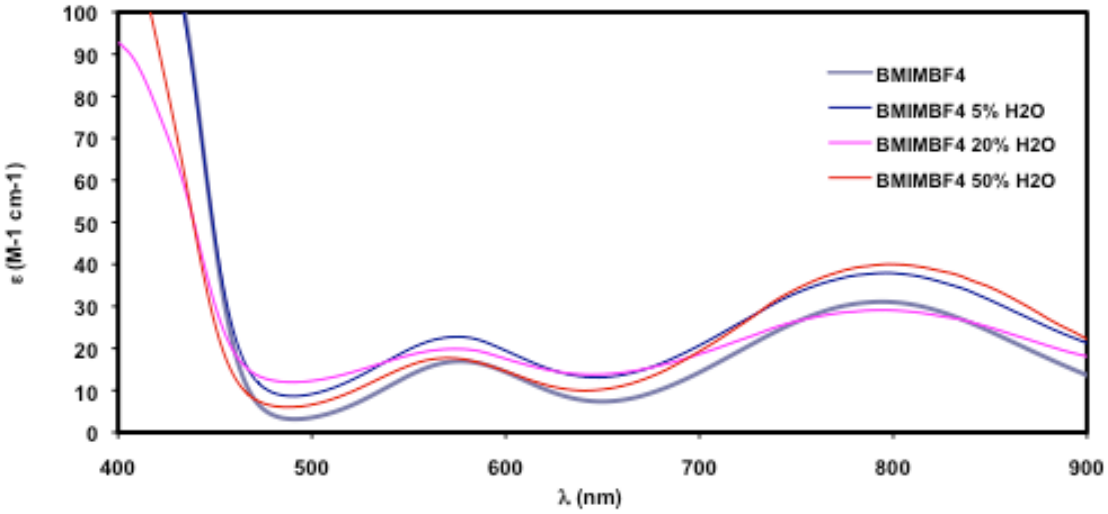

Figure SI2 -1 – Vis spectra of $VO(acac)_2$ dissolved in $bmimBF_4$ with different amounts of water.

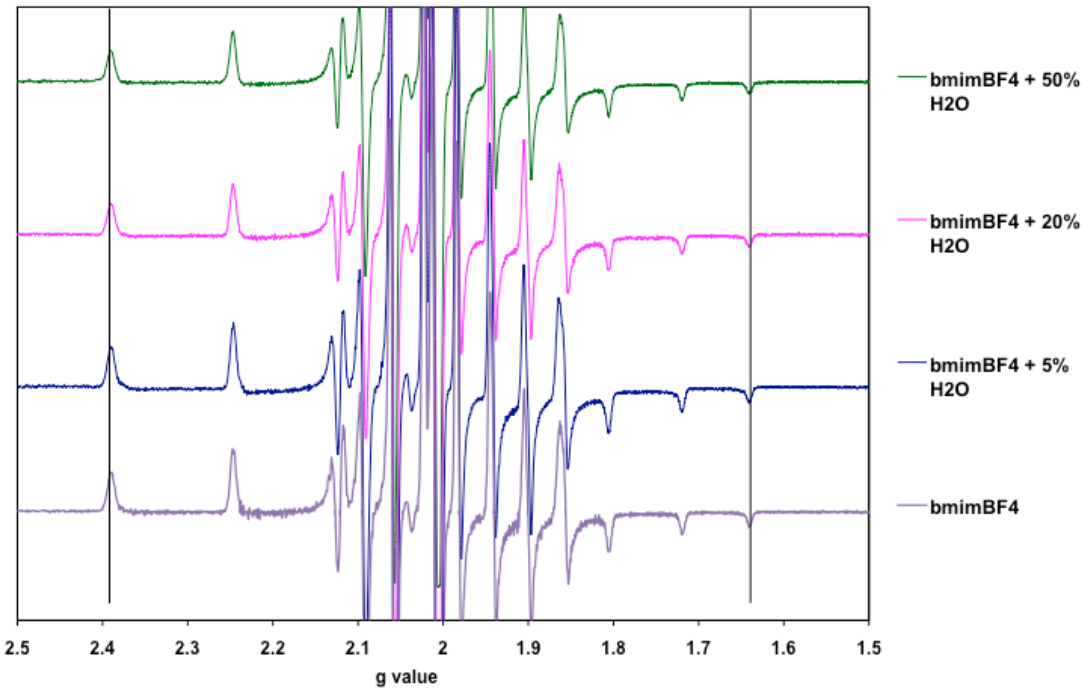

Figure SI2 – 2 - EPR spectra of $VO(acac)_2$ dissolved in $bmimBF_4$ with different amounts of water, measured at 77K.

SI3 – DFT studies

Table SI-1. Cartesian atomic coordinates (Å) of the calculated equilibrium structures (first column – nuclear charge of the element, second–fourth columns – x, y and z coordinates, respectively).

OTf^-

8	-0.019293	-1.689591	-0.232522
16	0.513620	-2.403924	0.942760
8	1.950483	-2.204480	1.209515
6	0.451838	-4.173854	0.395458
8	-0.358604	-2.409333	2.132189
9	0.908927	-5.009122	1.346690
9	1.198444	-4.385018	-0.704265
9	-0.802006	-4.563570	0.099985

[mmim]•OTf

8	-0.378394	-0.844498	-1.729729
16	-0.411296	0.306916	-0.832473
8	0.817335	1.146431	-0.801045
6	-0.469004	-0.412072	0.868480
8	-1.640963	1.143155	-0.886281
9	-0.502808	0.564509	1.787874
9	0.608814	-1.163582	1.101407
9	-1.557330	-1.167890	1.026286
6	0.270006	5.926146	-0.841462
6	-1.090350	5.923300	-0.893550
6	2.042760	4.097377	-0.878567
7	0.676417	4.610659	-0.910593
6	-0.400823	3.831577	-1.003190
7	-1.485119	4.606189	-0.993402
6	-2.848280	4.088407	-1.066218
1	2.540190	4.449944	0.027203
1	2.585993	4.444522	-1.760152
1	1.984409	3.006166	-0.872834
1	-0.394026	2.745071	-1.062160
1	-3.415085	4.440846	-0.202123
1	-2.787052	2.997365	-1.054088
1	-3.322747	4.432717	-1.987680
1	-1.800460	6.734599	-0.865221
1	0.972542	6.740357	-0.758964

1

6	-1.500663	-0.431223	-2.593561
6	5.060383	-1.265769	-3.014772
6	4.421698	-0.999383	-1.681605
6	5.149424	-1.182492	-0.501427
6	4.573857	-1.037206	0.764874
6	5.372147	-1.343866	1.999776
6	-0.653267	-0.353566	-1.355766

6	-1.249223	-0.368802	-0.090660
6	-0.501062	-0.390604	1.090745
6	-1.188638	-0.507350	2.421085
8	2.260669	1.646467	-0.278555
8	3.369108	-0.670282	0.975443
8	3.200745	-0.628798	-1.729817
8	0.605383	-0.297333	-1.563190
8	0.773679	-0.338162	1.142128
23	2.061848	0.097992	-0.289617
1	-2.567390	-0.490375	-2.368485
1	-1.204021	-1.306580	-3.180817
1	-1.308873	0.449614	-3.215220
1	-0.824075	-1.400279	2.939652
1	-2.275208	-0.560523	2.328322
1	-0.918630	0.353908	3.041103
1	4.484913	-2.031787	-3.545053
1	6.098963	-1.590320	-2.924874
1	5.015348	-0.355762	-3.622185
1	6.391336	-1.662294	1.771910
1	4.865923	-2.128197	2.572253
1	5.403320	-0.453824	2.636883
1	-2.328692	-0.426694	-0.024377
1	6.180099	-1.507950	-0.570554

trans-**[1•OTf]**$^-$

23	0.380859	1.088913	-0.278444
6	3.845532	0.137267	2.061362
8	0.331606	2.653371	-0.389281
8	1.870191	0.870471	1.034758
8	1.661357	0.646117	-1.744595
8	0.480775	-1.300159	-0.120636
1	4.580305	-0.284818	-0.477972
1	3.404727	0.666859	-3.652563
1	3.009147	-1.023750	-3.342626
1	4.582696	-0.380653	-2.809436
6	3.521494	-0.147559	-2.930351
1	3.704329	0.946252	2.783670
6	2.859307	0.235445	-1.629946
1	4.909612	0.008550	1.844581
6	3.571236	0.108518	-0.435324
1	3.451739	-0.787711	2.498404
6	3.031707	0.406090	0.826328
8	-1.085053	0.574956	-1.532129
8	-0.867212	0.777430	1.247799
6	-2.241390	0.134734	-1.236754
6	-2.031328	0.275774	1.218301
6	-3.089091	-0.254877	-2.422593
6	-2.755347	-0.019846	0.051697

6	-2.630981	-0.040786	2.559573
1	-2.613374	-1.098131	-2.935292
1	-3.128361	0.577209	-3.132959
1	-4.105132	-0.540070	-2.137293
1	-3.749288	-0.437846	0.161831
1	-2.147103	-0.960222	2.909265
1	-3.711608	-0.200858	2.507577
1	-2.402641	0.759496	3.268909
16	0.555260	-2.350499	0.932960
8	1.829198	-2.410357	1.665861
6	0.592254	-3.880231	-0.106859
8	-0.665174	-2.514821	1.738190
9	0.657677	-4.976372	0.664245
9	1.656954	-3.892089	-0.920721
9	-0.505280	-3.985446	-0.868785

cis-**[1•OTf]**$^{-}$

23	-0.132765	-0.223381	-0.001535
8	0.742453	-0.388244	1.293617
8	-0.201812	1.793523	0.004847
8	1.334855	-0.126951	-1.354498
8	-0.442268	-2.203192	-0.454145
8	-1.940081	-0.254285	0.838235
8	-1.304175	0.070376	-1.835132
6	0.209212	4.053814	-0.460962
6	0.504443	2.589096	-0.684236
6	1.496935	2.227280	-1.604663
6	1.843830	0.898195	-1.892543
6	2.907362	0.612736	-2.922707
6	-4.167257	-0.735448	1.389647
6	-3.093890	-0.496817	0.353577
6	-3.424752	-0.546964	-0.997727
6	-2.498878	-0.268576	-2.028158
6	-2.940928	-0.394984	-3.465570
1	0.333634	4.288886	0.601409
1	-0.838236	4.251420	-0.713117
1	0.851812	4.709574	-1.054259
1	2.018431	3.017710	-2.132615
1	3.695139	0.004624	-2.466708
1	3.343087	1.522364	-3.344605
1	2.468176	0.010752	-3.724892
1	-4.207113	0.117647	2.075747
1	-3.901842	-1.615265	1.986107
1	-5.154296	-0.888446	0.944666
1	-4.443909	-0.798640	-1.269701
1	-2.566688	0.454887	-4.044655
1	-4.027041	-0.470515	-3.575011
1	-2.473515	-1.303612	-3.861746

16	-0.109533	-3.166147	-1.567751
8	1.317946	-3.406151	-1.769550
8	-0.948176	-3.014921	-2.760560
6	-0.731093	-4.719136	-0.776491
9	-0.077141	-4.984472	0.358068
9	-0.553465	-5.757705	-1.606909
9	-2.036402	-4.638102	-0.496536

trans-**mmim•[1•OTf]**

23	-0.889872	-1.694432	-0.216123
6	2.239521	-0.936016	2.651892
8	-0.598694	-3.170368	-0.658595
8	0.780616	-1.367588	0.853028
8	-1.887760	-1.950015	1.471483
8	-1.152073	0.602749	0.413051
1	0.097183	-1.557777	4.091698
1	-3.010834	-3.056815	3.539703
1	-3.251537	-1.316429	3.662111
1	-2.074985	-2.116059	4.736022
6	-2.498049	-2.108593	3.729313
1	3.035403	-1.398210	2.059305
6	-1.459148	-1.882904	2.665591
1	2.372663	-1.195388	3.704604
6	-0.135040	-1.610336	3.034910
1	2.311572	0.152544	2.544099
6	0.889972	-1.339726	2.127606
8	-2.659845	-1.336807	-1.032225
8	-0.024439	-0.763631	-1.788275
6	-2.933753	-0.718791	-2.106005
6	-0.612810	-0.189257	-2.772415
6	-4.400005	-0.598670	-2.418205
6	-1.990059	-0.157015	-2.980282
6	0.294053	0.520449	-3.737806
1	-4.886316	-0.027054	-1.620536
1	-4.852076	-1.595590	-2.420018
1	-4.588368	-0.110256	-3.376494
1	-2.356835	0.359772	-3.858871
1	0.665854	1.423251	-3.239782
1	-0.220235	0.810996	-4.656293
1	1.151614	-0.112163	-3.989224
16	-0.219054	1.756872	0.468285
8	0.710808	1.772741	1.609733
6	-1.365664	3.173440	0.774626
8	0.418037	2.088980	-0.830867
9	-0.672614	4.315000	0.833334
9	-2.011881	3.010278	1.928591
9	-2.262060	3.273543	-0.207675
6	4.691940	-1.027309	-0.546834

6	4.888583	0.266779	-0.177214
6	2.710583	-2.364673	-1.363552
7	3.380112	-1.135839	-0.949681
6	2.789297	0.054179	-0.820464
7	3.692494	0.924166	-0.361452
6	3.439202	2.331830	-0.066155
1	2.519862	-2.989022	-0.489950
1	3.344234	-2.886624	-2.083325
1	1.752762	-2.102002	-1.810672
1	1.750198	0.271383	-1.047834
1	3.432056	2.479955	1.014793
1	2.453524	2.592200	-0.456021
1	4.220594	2.935314	-0.532570
1	5.766472	0.773425	0.191066
1	5.364921	-1.869944	-0.562573

cis-**mmim•[1•OTf]**

6	4.594698	-1.628130	-0.939352
6	4.330997	-0.523799	-1.686945
6	3.167542	-3.394154	0.162947
7	3.393599	-2.267908	-0.729895
6	2.424044	-1.563620	-1.313056
7	2.972771	-0.508400	-1.912630
6	2.220980	0.527114	-2.610895
1	2.992128	-3.007928	1.168867
1	4.037559	-4.051773	0.133891
1	2.287717	-3.942107	-0.175528
1	1.353018	-1.771016	-1.313247
1	2.362180	1.473597	-2.088005
1	1.163085	0.264138	-2.586730
1	2.573497	0.600207	-3.642167
1	4.983588	0.243390	-2.071513
1	5.520969	-2.006466	-0.537520
23	-1.199985	-0.435452	-0.723598
8	-0.426099	-1.394023	-1.739971
8	-3.063081	-0.823339	-1.257667
8	-1.388851	-1.700922	0.782911
8	0.550559	0.306268	0.139911
8	-1.174400	1.188234	-1.874387
8	-2.114501	0.869171	0.671057
6	-5.310137	-1.491587	-1.209396
6	-3.939913	-1.462405	-0.588350
6	-3.718684	-2.109119	0.632967
6	-2.464759	-2.194776	1.250467
6	-2.312695	-2.924708	2.555070
6	-1.159740	3.349808	-2.793149
6	-1.402407	2.423403	-1.629067
6	-1.852499	2.942060	-0.418788

6	-2.187240	2.127639	0.682883
6	-2.662254	2.757126	1.965339
1	-5.240631	-1.907899	-2.219666
1	-5.681590	-0.466186	-1.310248
1	-6.023235	-2.076705	-0.624818
1	-4.559413	-2.594308	1.114004
1	-1.598631	-3.746306	2.433996
1	-3.259175	-3.321389	2.928537
1	-1.884981	-2.234855	3.289852
1	-1.807721	3.059969	-3.627482
1	-0.125887	3.247028	-3.140649
1	-1.348476	4.395663	-2.540604
1	-1.982742	4.014350	-0.332746
1	-3.621355	2.316913	2.256352
1	-2.764481	3.842813	1.895378
1	-1.941293	2.507834	2.751425
16	1.185130	0.200048	1.510697
8	2.148129	-0.908216	1.592732
8	0.291987	0.414276	2.640954
6	2.247693	1.712892	1.446833
9	3.083059	1.663406	0.391752
9	2.986656	1.802082	2.551722
9	1.507526	2.813596	1.336361