SUPPORTING INFORMATION

Ionic liquid electrolytes for reversible magnesium electrochemistry

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Synthesis

Synthesis of *N*-ethyl-2-(2-methoxyethoxy)-*N*,*N*-bis(2-(2-methoxyethoxy)ethyl)-ethan-1-aminium iodide [$N_{2(20201)(20201)(20201)}$][I] (1)

Tris(2-(2-methoxyethoxy)ethyl)amine (20 g, 0.06 moles) and ethyl iodide (11.5 g, 0.062 moles) were mixed in acetonitrile (50 mL) and stirred overnight at 50 ˚C under N_2 to give a brown oil. The crude product was mixed with water and extracted from dichloromethane (6 × 30 mL). The aqueous layer was concentrated in vacuo to give a pale brown oil (15 g, yield 88%). ^{1}H NMR: δ 7.78-7.76 ppm, 1H, d ; δ 7.33-7.31 ppm, 1H, d ; δ 3.67 – 3.65 ppm, 2H, t ; δ 3.58 – 3.56 ppm, 2H, t ; δ 3.50-3.48 ppm, 4H, q ; δ 3.39 ppm, 3H, s ; δ 2.4 ppm, 3H, s. ^{13}C NMR : δ 145.2 ppm, ; δ 140.1 ppm ; δ130.5 ppm ; δ 126.7 ppm ; δ 72.2 ppm ; δ 66.3 ppm ; δ 64.3 ppm ; δ 62.1 ppm δ 59.9 ppm. MS $[ES]^+$ = 352.4 MS $[ES]^-$ = 126.9.

Synthesis *N*-ethyl-2-(2-methoxyethoxy)-*N*,*N*-bis(2-(2-methoxyethoxy)ethyl)ethan-1-aminium bis(trifluoromethylsulfonyl)imide [$N_{2(20201)(20201)(20201)}$][$NTf_2$] (IL1)

Lithium bis[(trifluoromethyl)sulfonyl]imide (10g, 0.035 moles) and compound **(1)** (11.9 g, 0.033 moles) was mixed in water and the solution was stirred for 12 hours at room temperature. The crude product was filtered and the filtrate was collected and concentrated *in vacuo*. To give a pale yellow oil (12 g, 80 %). ^{1}H NMR: δ 7.78-7.76 ppm, 1H, d ; δ 7.33-7.31 ppm, 1H, d ; δ 3.67 – 3.65 ppm, 2H, t ; δ 3.58 – 3.56 ppm, 2H, t ; δ 3.50-3.48 ppm, 4H, q ; δ 3.39 ppm, 3H, s ; δ 2.4 ppm, 3H, s. ^{13}C NMR: δ 145.2 ppm, ; δ 140.1 ppm ; δ130.5 ppm ; δ 126.7 ppm ; δ 72.2 ppm ; δ 66.3 ppm ; δ 64.3 ppm ; δ 62.1 ppm δ 59.9 ppm ; MS $[ES]^+$ = 352.4 MS $[ES]^-$ = 279.9. Rf (Ethyl acetate:Hexane 1:1) = 0.5.

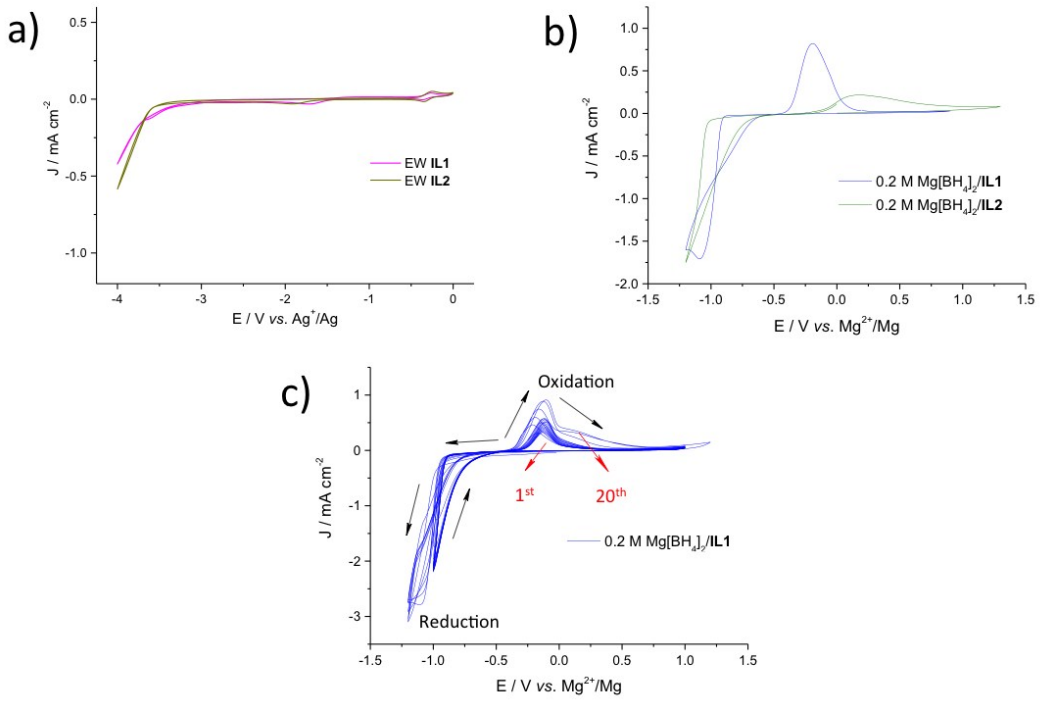
Synthesis *N*-ethyl-2-(2-methoxyethoxy)-*N*,*N*-bis(2-(2-methoxyethoxy)ethyl)ethan-1-aminium bis(trifluoromethylsulfonyl)imide [$N_{2(20201)(20201)(20201)}$][FSI] (IL2)

Lithium bis[(fluoromethyl)sulfonyl]imide (10g, 0.035 moles) and compound **(1)** (11.9 g, 0.033 moles) was mixed in water and the solution was stirred for 12 hours at room temperature. The crude product was filtered and the filtrate was collected and concentrated *in vacuo*. To give a pale yellow oil (12 g, 80 %). ^{1}H NMR: δ 7.78-7.76 ppm, 1H, d ; δ 7.33-7.31 ppm, 1H, d ; δ 3.67 – 3.65 ppm, 2H, t ; δ 3.58 – 3.56 ppm,

2H, t ; δ 3.50-3.48 ppm, 4H, q ; δ 3.39 ppm, 3H, s ; δ 2.4 ppm, 3H, s. ^{13}C NMR : δ 145.2 ppm, ; δ 140.1 ppm ; δ130.5 ppm ; δ 126.7 ppm ; δ 72.2 ppm ; δ 66.3 ppm ; δ 64.3 ppm ; δ 62.1 ppm δ 59.9 ppm ; MS $[ES]^+$ = 352.4 MS $[ES]^-$ = 187.09.

Cyclic Voltammetry

Figure S1. a) Electrochemical window (EW) of **IL1** (pink curve) and **IL2** (olive curve); **b)** CV of 0.2 M $Mg[BH_4]_2$ in **IL1** (blue curve) and 0.2 M $Mg[BH_4]_2$ in **IL2** (green curve); and **c)** CV of 0.2 M $Mg[BH_4]_2$ in **IL1** over 20 cycles (coulombic efficiency calculated from area under CVs : 60 %).

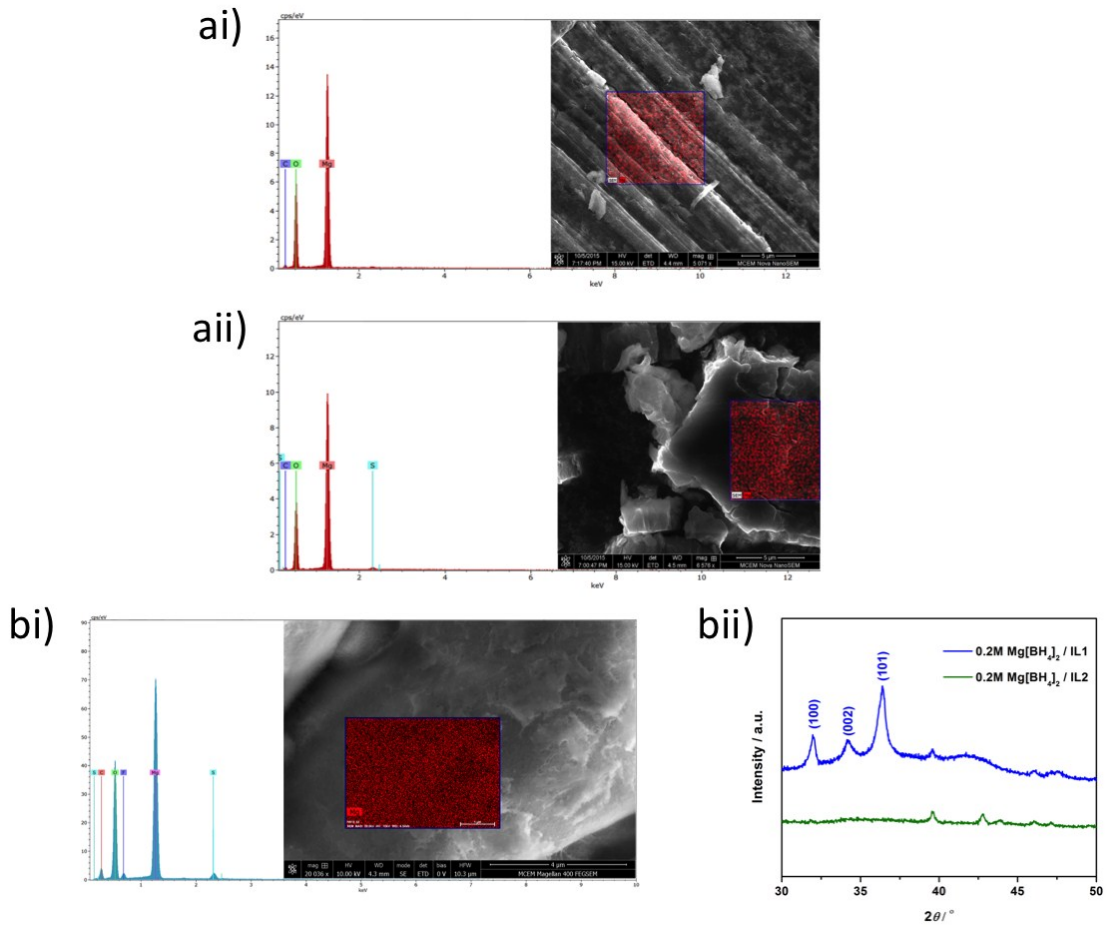


X-Ray Diffraction

Figure S2.

ai) SEM and EDX spectra of the electrodeposit obtained from 0.1 M $Mg[BH_4]_2$ in **IL1** and **aii)** 0.1 M $LiBH_4$ + 0.1 M $Mg[BH_4]_2$/**IL1** mixture after electrodeposition (12 h, working electrode = Pt);

bi) SEM and EDX spectra and **bii)** XRD pattern of 0.2 M $Mg[BH_4]_2$ in **IL2** (IL1 XRD shown for comparison).



Computational Details

The geometry, properties, and redox mechanisms the $Mg[NTf_2]_2$, $Mg[NTf_2]_2$/**IL1** and $Mg[BH_4]_2$/**IL1** complexes have been studied through the use of Density Functional Theory (DFT) *via* the M06-2X functional.[1] Two-layer 'ONIOM' basis sets have been applied for all models, using the 6-31+G(d,p) double-ζ Poples's basis set for magnesium and those atoms directly bounded with it, and the smaller 3-21+G(d) basis set for the rest.[2, 3] Furthermore, the redox mechanism for the decomposition of the

$[NTf_2]^-$ and $[FSI]^-$ anions have been studied at M06-2X/6-31+G(d) computational level. Also, for those systems with all-paired electrons (singlet multiplicity), the EDIIS/CDIIS self-consistent field (SCF) procedure was used,[4] while for radical states (doublet multiplicity), the quadratically convergent (QC) SCF procedure was employed.[5]

In all cases, frequency calculations were performed in order to confirm the nature of the stationary points and to obtain the zero point energy (ZPE) as well as the thermal correction terms. With the aim to obtain more accurate values for the theoretical description of the FT-IR and Raman spectra, re-optimization at the M06-2X/6-31+G(d,p) computational level for all atoms were carried out in the Mg^{2+}-oxidized complex in **IL1**, correcting the harmonic vibrational frequencies by the scaling factor f = 0.967 proposed by Truhlar and co-workers.[6] Furthermore, the solvent effect was taken into account by optimizing the systems through the use of the Polarizable Continuum Model (PCM)[7] using the standard parameters for THF (ε = 7.4257).

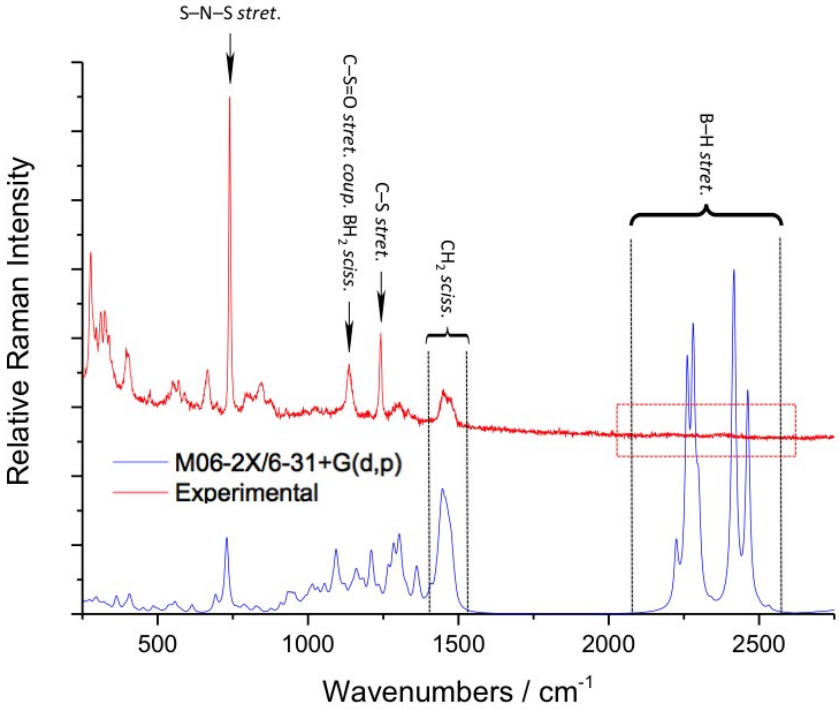
Finally, Natural Bond Orbital (NBO)[8, 9] theory was applied to help analyse the interactions, using the NBO6.0 program.[10] In this regard, the presence of charge transfers between natural orbitals of different fragments support the presence of attractive bonding interactions.[11]

All calculations were carried out through the facilities provided by the Gaussian09 package (revision D.01).[12]

Theoretical Framework

$E^{abs} = -\Delta G / nF$, being ΔG the Gibbs free energy difference between a [Red]/[Ox] couple, n the number of electrons transferred along the redox process, and F the Faraday constant (23.601 kcal per volt gram equivalent). E^{rel} *vs*. NHE = E^{abs} – 4.28 V; E^{rel} *vs*. Ag^+/Ag = E^{rel} *vs*. NHE – 0.80 V.

Figure S3. Experimentally measured([a]) (red curve) and the theoretically predicted([b,c]) (blue curve) Raman spectra for the $Mg[BH_4]_2$/**IL1** complex.

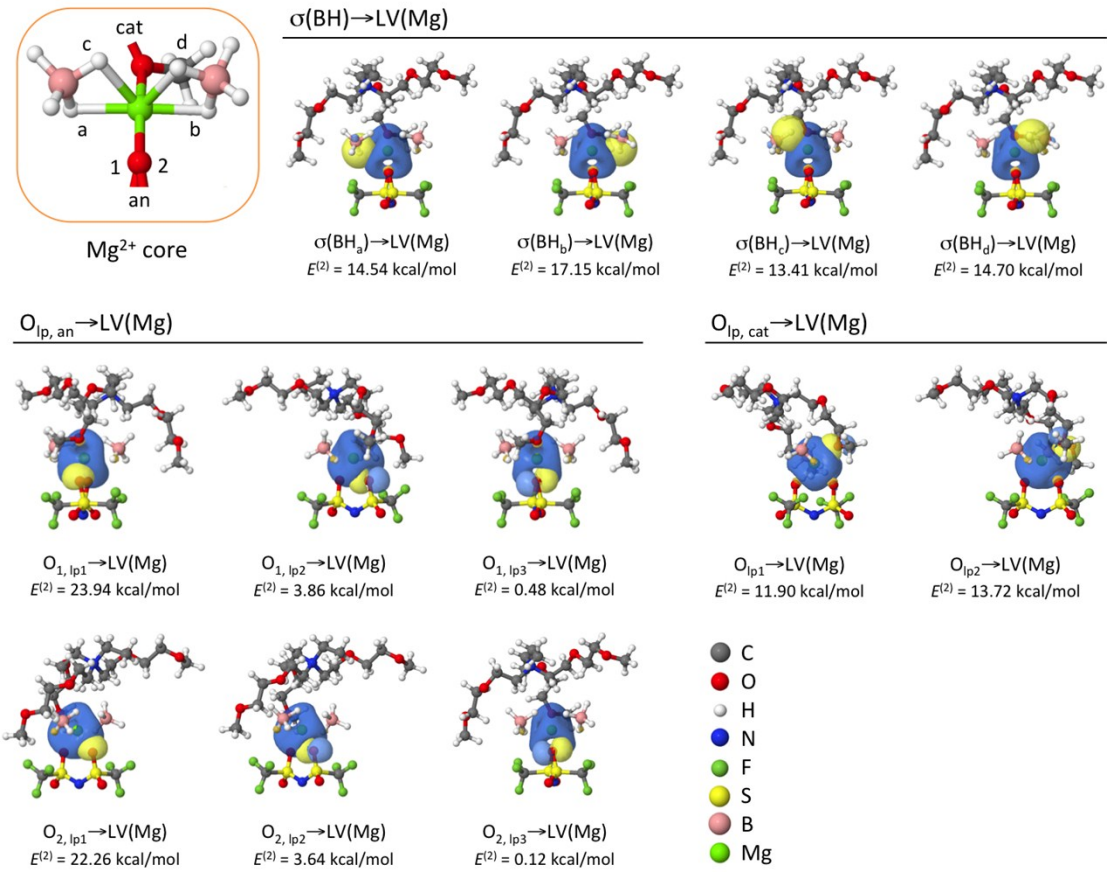


([a]) 0.1 M $Mg[BH_4]_2$/**IL1**.

([b]) M06-2X/6-31+G(d,p) computational level. See **Computational Details** section.

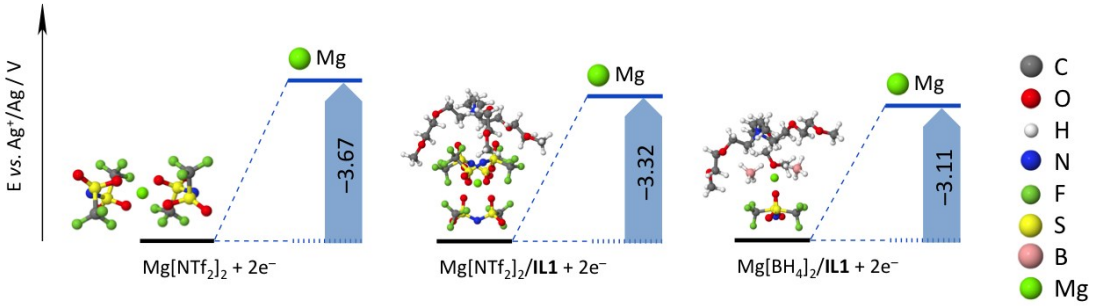
([c]) For both FT-IR (see **Fig. 2b** from the main text) and Raman theoretically predicted spectra: Lorentzian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 8 cm^{-1}. 2750-250 cm^{-1} spectral area.

Figure S4. Main NBO contributions([a]) in the Mg^{2+} environment for the $Mg[BH_4]_2$/**IL1** complex.



([a]) M06-2X functional, two-layer 'onion' basis sets model. See **Computational Details** section.

Figure S5. Calculated potentials (in V *vs*. Ag^+/Ag) at 298.15 K([a]) for the two-electron reduction steps for the indicated processes.



([a]) M06-2X functional, two-layer 'onion' basis sets model. See **Computational Details** section.

Cartesian Coordinates DFT Calculations

$Mg[NTf_2]_2$/**IL1**
PCM: THF
DFT: Functional M06-2X
Basis Set: 6-31+G(d,p) for atoms 1-7, 3-21+G(d) for atoms 8-108
SCF Energy: –6825.220726 a.u.
Charge, Multiplicity: 0, 1
Symmetry: C_1

Mg	-1.962904	-0.040203	-0.128777
O	-3.309344	-1.445377	0.384817
O	-3.456419	1.303581	-0.216862
O	-0.491752	-1.413401	0.043347
O	-1.589589	0.563598	1.773441
O	-2.070770	-0.604868	-2.071311
O	-0.559890	1.330236	-0.650305
N	-5.483113	-0.124795	0.355925
S	-4.766512	-1.531324	0.270946
S	-4.828954	1.312622	0.293216
O	-5.447752	-2.556439	1.039999
O	-5.739626	2.315273	-0.226722
C	-5.015318	-1.955346	-1.513212
C	-4.597935	1.684041	2.094024
F	-6.303683	-2.362693	-1.754734
F	-4.752691	-0.837133	-2.278156
F	-4.148395	-2.957774	-1.886126
F	-5.779764	2.066388	2.678776
F	-3.668527	2.684968	2.263746
F	-4.140044	0.544259	2.724297
S	-1.264179	-0.332827	-3.258138
S	-0.032864	1.849322	-1.912305
S	0.528463	-1.714057	1.045775
S	-0.463706	0.393088	2.687220
N	-0.529325	1.068568	-3.191940
O	-1.849477	-0.576553	-4.562593
C	0.181848	-1.484871	-3.061504
O	1.386569	2.183381	-1.941803
C	-0.941488	3.435666	-2.124172
N	0.389775	-0.897383	2.388880
O	1.906484	-1.802562	0.577045
C	-0.012533	-3.368065	1.655751
O	-0.699465	0.571910	4.109333
C	0.722140	1.737554	2.182813
F	0.898886	-1.577442	-4.228801
F	0.989384	-0.919433	-2.089464
F	-0.204909	-2.734759	-2.650301
F	-2.291565	3.181422	-2.181018
F	-0.553735	4.090299	-3.265781
F	-0.688541	4.243167	-1.035189
F	0.835111	-3.879251	2.602986
F	-1.266509	-3.215951	2.215357
F	-0.124470	-4.238876	0.596891
F	1.501979	1.295827	1.117893
F	1.570968	2.039888	3.218370
F	0.031513	2.852947	1.783651
N	4.801204	0.529378	-1.535319

C	5.820056	0.787779	-2.657109
C	3.627032	-0.320271	-2.037628
C	5.511167	-0.197874	-0.396486
C	4.209719	1.850829	-1.050182
C	5.228262	1.550205	-3.841024
H	6.204120	-0.188879	-2.960788
H	6.648951	1.335240	-2.200516
C	4.039237	-1.564498	-2.852347
H	2.994374	0.350367	-2.621076
H	3.063417	-0.633712	-1.156921
C	4.687991	-0.238619	0.895287
H	6.472823	0.295893	-0.233248
H	5.702826	-1.223914	-0.724074
C	5.247739	2.838870	-0.505706
H	3.685636	2.304224	-1.891191
H	3.451172	1.609380	-0.299588
H	5.991178	1.592803	-4.626135
H	4.964672	2.580421	-3.584432
H	4.351128	1.052482	-4.266024
O	3.168608	-2.681211	-2.495500
H	5.082220	-1.858745	-2.680836
H	3.895029	-1.402336	-3.922546
O	5.264917	-1.371912	1.615871
H	3.624568	-0.419370	0.717091
H	4.810969	0.679713	1.487754
O	4.509252	4.060016	-0.198058
H	5.774795	2.472169	0.384825
H	5.978799	3.130093	-1.263149
C	3.596700	-3.362455	-1.262430
C	4.975862	-1.373373	3.056742
C	3.796521	4.067427	1.091240
C	2.525942	-4.400901	-0.969862
H	4.578006	-3.826468	-1.425664
H	3.652177	-2.663331	-0.422456
C	3.482020	-1.520653	3.331265
H	5.523360	-2.227378	3.458929
H	5.352370	-0.445385	3.505958
C	2.498881	4.815651	0.829703
H	3.586793	3.046583	1.432411
H	4.406785	4.581712	1.839173
O	2.696857	-4.765117	0.438934
H	1.533444	-3.970763	-1.130384
H	2.648591	-5.283165	-1.612047
O	3.379857	-1.549136	4.787852
H	2.907404	-0.672585	2.938493
H	3.091367	-2.448286	2.896988
O	1.848025	4.942778	2.129290
H	2.711327	5.805322	0.403671
H	1.862186	4.251566	0.135052
C	2.281576	-6.138586	0.746052
C	1.995732	-1.679520	5.261723
C	0.606125	5.721696	2.059084
H	2.407442	-6.256257	1.823542
H	1.232696	-6.299298	0.473454
H	2.919544	-6.851838	0.209669
H	2.051762	-1.689127	6.350728
H	1.391807	-0.834398	4.917987
H	1.558748	-2.615330	4.894447
H	0.154327	5.663133	3.050073

H	0.833331	6.764321	1.804829
H	-0.071678	5.293631	1.313166

$Mg[BH_4]_2$/**IL1**
PCM: THF
DFT: Functional M06-2X
Basis Set: 6-31+G(d,p) for atoms 1-14, 3-21+G(d) for atoms 15-88
SCF Energy: –3243.261026 a.u.
Charge, Multiplicity: 0, 1
Symmetry: C_1

H	-0.246756	0.910059	0.343474
H	0.200504	2.831909	0.353348
H	0.763607	1.638287	-1.195254
H	1.663143	1.520628	0.586284
B	0.603610	1.746076	-0.003173
Mg	1.119924	-0.385986	0.985684
H	0.965929	-2.259073	1.623197
H	-0.878118	-2.467394	2.324251
B	-0.227503	-2.363657	1.305102
H	-0.607479	-1.349070	0.702343
H	-0.332130	-3.294585	0.542304
O	3.149844	-0.615503	1.428111
O	1.622642	-1.049599	-0.931900
O	0.958879	0.244125	2.940264
N	4.145884	-1.338043	-0.798153
S	4.381657	-0.836966	0.672960
S	2.818473	-1.494421	-1.636440
O	5.470313	-1.534193	1.337088
O	2.987190	-1.106901	-3.028319
C	5.009891	0.872303	0.366970
C	2.655667	-3.330949	-1.660208
F	6.269486	0.843796	-0.183310
F	4.167944	1.535370	-0.500991
F	5.058703	1.577511	1.550136
F	3.676382	-3.906980	-2.380554
F	1.455488	-3.692026	-2.232288
F	2.697314	-3.822160	-0.373094
C	-5.248126	1.224287	-0.497518
N	-3.798744	1.409738	-0.015844
C	-2.945213	2.087646	-1.089535
C	-3.856554	2.284644	1.245778
C	-3.127683	0.063523	0.268014
C	-3.805395	-0.780321	1.341373
O	-5.029545	-1.405991	0.834722
C	-4.798699	-2.659949	0.104812
C	-6.190427	-3.122846	-0.323386
O	-6.110907	-4.261715	-1.234940
C	-5.737609	-5.519818	-0.572469
C	-3.543764	3.375244	-1.678214
O	-2.459460	4.015701	-2.420654
C	-1.541270	4.807965	-1.580320
C	-0.150834	4.604563	-2.158438
O	0.748334	5.361489	-1.287622
C	2.155238	4.997135	-1.492960
C	-2.529973	2.413110	1.997359
O	-2.535579	1.482922	3.140521
C	-1.434993	0.515683	3.230589

C	-0.054827	1.191588	3.324046
C	1.297207	-0.688429	3.991147
C	-5.362785	0.439786	-1.801540
H	-5.660269	2.233504	-0.597061
H	-5.766672	0.702026	0.309145
H	-2.787968	1.357405	-1.886760
H	-1.966118	2.291026	-0.641729
H	-4.607825	1.849819	1.909732
H	-4.219338	3.261060	0.919542
H	-3.088620	-0.473414	-0.684221
H	-2.096192	0.294370	0.536617
H	-3.094212	-1.558080	1.656179
H	-4.086491	-0.197598	2.221455
H	-4.167360	-2.492426	-0.778282
H	-4.302190	-3.377831	0.769002
H	-6.793334	-3.381345	0.556017
H	-6.687655	-2.325766	-0.880822
H	-5.868848	-6.300767	-1.321468
H	-4.693447	-5.496210	-0.243272
H	-6.397404	-5.706548	0.283739
H	-3.934272	4.061949	-0.919026
H	-4.326493	3.168340	-2.410869
H	-1.847398	5.858122	-1.605256
H	-1.552320	4.448582	-0.543391
H	0.105220	3.539829	-2.132894
H	-0.087754	4.977188	-3.188191
H	2.734956	5.614025	-0.805627
H	2.302450	3.934351	-1.266703
H	2.454799	5.205505	-2.527729
H	-2.451651	3.424469	2.406613
H	-1.662736	2.240372	1.352422
H	-1.667876	-0.070280	4.122574
H	-1.434980	-0.158489	2.368940
H	0.028809	2.025205	2.619885
H	0.154287	1.558285	4.335118
H	2.148365	-1.272519	3.635963
H	1.580052	-0.124109	4.885695
H	0.455197	-1.355724	4.203008
H	-6.425096	0.394673	-2.067706
H	-5.013117	-0.588781	-1.690290
H	-4.837540	0.915802	-2.634715

IL1

PCM: THF

DFT: Functional M06-2X

Basis Set: 6-31+G(d,p) for atoms 1-2, 3-21+G(d) for atoms 3-77

SCF Energy: –2988.276228 a.u.

Charge, Multiplicity: 0, 1

Symmetry: C_1

O	1.352474	0.711372	0.008811
O	-0.256657	-1.330576	1.402875
O	1.611568	5.397464	-2.077268
N	1.274899	0.373626	2.548334
S	2.007040	0.966428	1.273509
S	0.005095	-0.573850	2.603597
O	2.536330	2.300924	1.554768
O	-0.084960	-1.214002	3.913327

C	3.498766	-0.116031	1.203620
C	-1.342524	0.701939	2.604228
F	4.310491	0.020757	2.307709
F	3.102847	-1.440128	1.125768
F	4.241269	0.186653	0.080062
F	-1.429324	1.398035	3.786458
F	-2.576069	0.126332	2.343665
F	-1.104407	1.618100	1.584655
C	-2.409557	-1.501128	-2.839014
N	-1.280380	-0.695291	-2.169684
C	-0.151667	-1.609714	-1.700671
C	-0.798467	0.312881	-3.217537
C	-1.775588	0.008052	-0.896350
C	-2.953238	0.948356	-1.102093
O	-4.219598	0.219274	-1.246811
C	-4.775371	-0.277708	0.015988
C	-6.055937	-1.011459	-0.381448
O	-6.537252	-1.864032	0.703818
C	-7.075034	-1.107503	1.843558
C	0.530079	-2.414382	-2.810578
O	1.546090	-3.231708	-2.146367
C	2.819245	-2.528888	-1.924941
C	3.647544	-3.443352	-1.038479
O	4.928635	-2.758864	-0.877807
C	5.763041	-3.371034	0.160356
C	0.288003	1.267267	-2.750700
O	-0.339818	2.228346	-1.839840
C	0.579947	3.268981	-1.357089
C	0.510302	4.463221	-2.313706
C	1.521749	6.083512	-0.779770
C	-2.926208	-2.661126	-1.992710
H	-2.007665	-1.856765	-3.793077
H	-3.208443	-0.782383	-3.033867
H	-0.583652	-2.297429	-0.971234
H	0.561362	-0.983453	-1.160904
H	-1.676783	0.881361	-3.532222
H	-0.452202	-0.269190	-4.075113
H	-2.023983	-0.790249	-0.191946
H	-0.916879	0.558933	-0.515364
H	-3.007045	1.618499	-0.233519
H	-2.853779	1.566906	-1.994351
H	-4.086967	-0.978454	0.504792
H	-4.959980	0.569564	0.688202
H	-6.836574	-0.299535	-0.678719
H	-5.840875	-1.683281	-1.215340
H	-7.526102	-1.844982	2.507757
H	-6.276538	-0.574732	2.370851
H	-7.836170	-0.396070	1.499582
H	1.005052	-1.783773	-3.572422
H	-0.153022	-3.118942	-3.291580
H	3.316887	-2.354838	-2.885954
H	2.653869	-1.572693	-1.415992
H	3.160211	-3.574595	-0.065731
H	3.794488	-4.422391	-1.510674
H	6.680580	-2.783054	0.200056
H	5.246147	-3.331968	1.127141
H	5.993343	-4.412361	-0.098120
H	0.677560	1.781594	-3.639930
H	1.117997	0.767415	-2.241302

H	0.241964	3.518631	-0.348786
H	1.603707	2.880526	-1.304752
H	0.631091	4.131078	-3.348162
H	-0.451683	4.982665	-2.212051
H	2.295731	6.851491	-0.793049
H	0.534185	6.547614	-0.663836
H	1.706174	5.385962	0.043950
H	-3.780778	-3.100778	-2.519536
H	-3.284685	-2.333974	-1.013894
H	-2.180630	-3.450566	-1.860024

$[NTf_2]^-$
PCM: THF
DFT: Functional M06-2X
Basis Set: 6-31+G(d) for all atoms
SCF Energy: –1826.928752 a.u.
Charge, Multiplicity: –1, 1
Symmetry: C_2

O	1.215334	0.863995	1.282058
O	-1.215334	-0.863995	1.282058
N	0.000000	0.000000	-0.851217
S	0.841741	1.135816	-0.099594
S	-0.841741	-1.135816	-0.099594
O	1.854131	1.641752	-1.016049
O	-1.854131	-1.641752	-1.016049
C	-0.383056	2.520644	0.015450
C	0.383056	-2.520644	0.015450
F	-0.777602	2.902086	-1.197185
F	-1.449626	2.138228	0.713313
F	0.180356	3.562450	0.627899
F	0.777602	-2.902086	-1.197185
F	-0.180356	-3.562450	0.627899
F	1.449626	-2.138228	0.713313

$[NTf_2]^{2-}\bullet$
PCM: THF
DFT: Functional M06-2X
Basis Set: 6-31+G(d) for all atoms
SCF Energy: –1826.997064 a.u.
Charge, Multiplicity: –2, 2
Symmetry: C_1

O	-0.068156	1.633042	-1.286185
O	-0.289330	-2.236633	-1.952362
N	-0.489528	1.113867	1.175583
S	0.162490	2.045772	0.106816
S	-0.106830	-2.002503	-0.468231
O	-0.006886	3.473715	0.441244
O	0.338295	-3.254390	0.260319
C	2.012617	1.886369	0.219723
C	-1.928794	-2.018856	0.038205
F	2.445514	2.208025	1.447293
F	2.408930	0.634955	-0.035580
F	2.633989	2.696554	-0.651148
F	-2.075398	-1.920728	1.371973
F	-2.538405	-3.155635	-0.343720

F	-2.608398	-1.000325	-0.516833

[FSI]$^{-}$
PCM: THF
DFT: Functional M06-2X
Basis Set: 6-31+G(d) for all atoms
SCF Energy: –1351.505770 a.u.
Charge, Multiplicity: –1, 1
Symmetry: C_2

O	1.021161	1.251417	1.121221
O	-1.021161	-1.251417	1.121221
N	0.000000	0.000000	-0.885355
S	0.231835	1.360077	-0.087249
S	-0.231835	-1.360077	-0.087249
O	0.511276	2.412243	-1.036076
O	-0.511276	-2.412243	-1.036076
F	1.251698	-1.709288	0.457252
F	-1.251698	1.709288	0.457252

[FSI]$^{2-}$•
PCM: THF
DFT: Functional M06-2X
Basis Set: 6-31+G(d) for all atoms
SCF Energy: –1351.582168 a.u.
Charge, Multiplicity: –2, 2
Symmetry: C_1

O	-1.162107	1.326784	-0.884251
O	1.118362	-1.354174	-0.978154
N	0.235682	0.161337	0.946207
S	-0.139085	1.450042	0.150079
S	0.107814	-1.348140	0.110722
O	-0.207640	2.608939	1.031639
O	0.364993	-2.316699	1.202544
F	-1.502387	-2.355879	-0.860642
F	1.197687	1.801150	-0.751717

REFERENCES

1. Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.
2. M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.
3. M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.
4. K. N. Kudin, G. E. Scuseria and E. Cancès, *J. Chem. Phys.*, 2002, **116**, 8255.
5. G. B. Bacskay, *Chem. Phys.*, 1981, **61**, 385.
6. I. M. Alecu, J. Zheng, Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.*, 2010, **6**, 2872.
7. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.
8. E. D. Glendening, C. R. Landis and F. Weinhold, *WIREs Comput. Mol. Sci.*, 2012, **2**, 1.
9. F. Weinhold and C. R. Landis, *Valency and Bonding. A Natural Bond Orbital Donor-Aceptor Perspective*, Cambridge Press, Cambridge, UK, 2005.

10. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, *Journal*, 2013.
11. L. M. Azofra, *Chem. Phys.*, 2015, **453–454**, 1.
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian09 (Revision D.01)*, Gaussian Inc., Wallingford CT, 2009.