Supplementary Information

The effect of ether-functionalisation in ionic liquids analysed by DFT calculation, infrared spectra, and Kamlet-Taft parameter

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Table S1. Optimized geometry of the [$P_{1,2O2}$] cation conformers at the B3LYP/6-31G** level.

	conformer (a)			conformer (b)			conformer (c)		
	X	Y	Z	X	Y	Z	X	Y	Z
N	-0.761118	0.573314	-0.038563	-0.735818	0.479720	-0.155779	0.987344	-0.827750	0.154787
C	-0.531796	0.651426	-1.523158	-0.299930	-0.017060	-1.516821	2.250070	-1.610532	0.411112
C	0.256942	1.452920	0.692677	0.278667	1.513263	0.343742	-0.172109	-1.826288	0.263940
C	1.694395	1.397328	0.187245	1.584780	0.976990	0.919566	-1.496335	-1.439223	-0.382694
O	2.167131	0.072792	0.198504	2.255463	0.178635	-0.024225	-1.951436	-0.206431	0.118868
C	3.574294	-0.035670	-0.088654	3.580284	-0.204800	0.390902	-3.279044	0.137444	-0.321556
C	3.961609	-1.500782	-0.060374	4.207232	-1.037669	-0.709173	-3.658389	1.471292	0.290534
C	-0.638967	-0.878830	0.452706	-0.848800	-0.681143	0.831612	1.026562	-0.180329	-1.228171
C	-1.750966	-1.781800	-0.070626	-1.999845	-1.636614	0.517994	2.096901	0.901877	-1.351269
C	-3.137882	-1.240827	0.294051	-3.341807	-0.905677	0.388738	1.907682	1.990278	-0.288045
C	-3.291854	0.208095	-0.186151	-3.234193	0.242361	-0.623594	1.870037	1.371261	1.114982
C	-2.155852	1.098489	0.314645	-2.090839	1.184833	-0.263681	0.822525	0.265205	1.224451
H	3.761614	-1.939055	0.921237	3.623913	-1.943850	-0.896610	-3.642405	1.416750	1.382386
H	5.029915	-1.605169	-0.269033	5.217159	-1.338487	-0.417272	-4.668229	1.749479	-0.023263
H	3.411787	-2.067418	-0.817477	4.275825	-0.465604	-1.638358	-2.972803	2.260090	-0.032351
H	4.136193	0.537018	0.662669	3.516678	-0.770326	1.332214	-3.974887	-0.653829	-0.008701
H	3.780731	0.409427	-1.073319	4.168970	0.703219	0.584835	-3.296428	0.185157	-1.420189
H	1.780071	1.845119	-0.814709	2.175259	1.868606	1.187378	-1.410806	-1.419838	-1.480221
H	2.274015	2.041971	0.867843	1.408891	0.427668	1.856980	-2.193146	-2.257818	-0.139562
H	0.209165	1.158722	1.742876	-0.223490	2.092628	1.121714	-0.306508	-1.999287	1.334028
H	-0.099805	2.482563	0.603466	0.475910	2.169453	-0.506389	0.170691	-2.756031	-0.196851
H	0.431706	0.196946	-1.746970	0.715737	-0.394545	-1.427296	2.392112	-2.325465	-0.400009
H	-0.539143	1.699195	-1.826598	-0.325594	0.824345	-2.210372	2.142322	-2.141254	1.357879
H	-1.321991	0.117798	-2.043880	-0.979012	-0.792696	-1.859500	3.105806	-0.943238	0.465542
H	-2.220285	2.110145	-0.093203	-1.964307	1.989522	-0.991600	0.869615	-0.248230	2.188183
H	-2.174253	1.166819	1.406255	-2.270810	1.633663	0.717385	-0.188461	0.648722	1.084585
H	-3.358414	0.247413	-1.279495	-3.116323	-0.144056	-1.641849	2.861768	0.999856	1.396363
H	-4.223029	0.647363	0.186576	-4.150166	0.842193	-0.632534	1.609094	2.125123	1.865024
H	-3.920222	-1.866617	-0.143566	-4.125442	-1.605958	0.087745	2.712701	2.727178	-0.353466
H	-3.271947	-1.282877	1.382499	-3.637060	-0.502995	1.366229	0.969719	2.526964	-0.477744
H	-1.659412	-1.926945	-1.152742	-1.785348	-2.212514	-0.388900	3.102532	0.470781	-1.295781
H	-1.589375	-2.767981	0.376974	-2.032453	-2.366095	1.333932	2.005309	1.322147	-2.358149
H	-0.687065	-0.814944	1.543095	-0.991239	-0.220183	1.813757	0.039529	0.261298	-1.371040
H	0.360985	-1.207114	0.175251	0.116627	-1.188023	0.817052	1.165155	-0.988764	-1.950817

Table S2. Optimized geometry of the [$M_{1,2O2}$] cation conformers at the B3LYP/6-31G** level.

	conformer (a)			**conformer (b)**			**conformer (c)**		
	X	Y	Z	X	Y	Z	X	Y	Z
N	-0.770110	-0.570332	0.055183	-0.745118	-0.492677	0.191137	-1.015713	-0.812152	-0.150565
C	-2.173450	-1.050655	-0.316071	-2.134239	-1.126109	0.265388	-0.836037	0.284189	-1.211082
C	-0.636405	0.888258	-0.403591	-0.803145	0.664506	-0.800183	-1.038237	-0.143435	1.220341
C	-1.804662	1.743235	0.072546	-1.977340	1.602584	-0.520845	-2.040412	1.008124	1.272733
C	-3.263101	-0.077873	0.134950	-3.225041	-0.085002	0.506778	-1.820856	1.436261	-1.013684
O	-3.037123	1.216571	-0.384732	-3.204138	0.898117	-0.510471	-1.726773	1.976852	0.291443
C	-0.544321	-0.687631	1.539506	-0.315342	-0.011642	1.561814	-2.295441	-1.569794	-0.401287
C	0.232994	-1.453240	-0.695025	0.243951	-1.563269	-0.286514	0.127450	-1.831611	-0.259030
C	1.673809	-1.405577	-0.200128	1.556808	-1.055176	-0.876054	1.458342	-1.460163	0.383160
O	2.139789	-0.078671	-0.189496	2.210186	-0.200465	0.029711	1.923441	-0.234546	-0.123093
C	3.553575	0.029996	0.069861	3.535695	0.177894	-0.393841	3.260501	0.092853	0.307111
C	3.935821	1.496540	0.058418	4.123648	1.113253	0.643630	3.648638	1.428731	-0.294009
H	-3.355304	-0.053124	1.231563	-3.141885	0.371456	1.503705	-2.856029	1.139280	-1.239432
H	-4.217079	-0.428770	-0.266389	-4.194140	-0.586910	0.452719	-1.549772	2.231728	-1.712308
H	-2.307954	-2.042376	0.122843	-2.107218	-1.889967	1.046063	-0.963957	-0.192403	-2.186193
H	-1.808951	1.863893	1.165951	-1.834185	2.161560	0.415427	-3.079612	0.660915	1.172034
H	-1.696394	2.737867	-0.366861	-2.030666	2.331416	-1.333223	-1.947992	1.493807	2.247245
H	0.334189	1.242206	-0.060770	0.155579	1.181504	-0.744353	-1.250002	-0.914044	1.965855
H	-0.565043	-1.742556	1.815764	-0.376578	-0.854857	2.250719	-2.202387	-2.099495	-1.349903
H	0.425154	-0.251616	1.773773	0.712260	0.335664	1.486124	-2.449845	-2.283605	0.408671
H	-1.327810	-0.157808	2.075278	-0.974903	0.783507	1.899595	-3.136756	-0.883675	-0.448259
H	-0.133543	-2.479827	-0.608761	0.428396	-2.202948	0.578826	-0.232158	-2.751927	0.207592
H	2.250004	-2.034922	-0.897510	1.386532	-0.556933	-1.843007	2.142996	-2.288547	0.138561
H	1.767777	-1.873317	0.792091	2.154595	-1.955846	-1.090608	1.376939	-1.438799	1.481262
H	4.100104	-0.527733	-0.703545	3.475624	0.663471	-1.378792	3.943434	-0.703501	-0.021005
H	3.780896	-0.432170	1.041718	4.145869	-0.729484	-0.502455	3.286647	0.127318	1.405900
H	3.404309	2.048318	0.839276	4.188553	0.623022	1.618738	2.973376	2.221165	0.040929
H	5.008702	1.599934	0.242325	5.132027	1.411838	0.344249	4.663303	1.691365	0.017178
H	3.710875	1.951295	-0.910185	3.517721	2.018409	0.743831	3.626894	1.385216	-1.386308
H	0.174465	-1.149254	-1.741945	-0.270663	-2.149512	-1.051003	0.254931	-2.010483	-1.329256
H	-0.635065	0.856177	-1.494812	-0.922955	0.214650	-1.788523	-0.039137	0.264148	1.370796
H	-2.185450	-1.135411	-1.405061	-2.306479	-1.604745	-0.700942	0.192092	0.627230	-1.101723
N	-0.770110	-0.570332	0.055183	-0.745118	-0.492677	0.191137	-1.015713	-0.812152	-0.150565
C	-2.173450	-1.050655	-0.316071	-2.134239	-1.126109	0.265388	-0.836037	0.284189	-1.211082
C	-0.636405	0.888258	-0.403591	-0.803145	0.664506	-0.800183	-1.038237	-0.143435	1.220341

Table S3. Calculated IR active vibrations of the [$P_{1,2O2}$] cation conformers at the B3LYP/6-31G** level.

conformer (a)		**conformer (b)**		**conformer (c)**	
Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
35	0.64	30	0.72	36	0.38
62	0.23	87	0.88	71	0.52
76	0.96	97	0.24	83	0.6
118	8.55	120	8.29	113	7.51
155	0.41	149	0.72	148	1.96
189	2.14	207	0.48	209	1.9
230	0.07	215	1.12	214	0.05
256	1.03	254	1.95	253	0.8
258	2.45	269	1.44	263	1.18
278	0.73	274	0.28	273	0.21
318	0.01	302	1.7	303	2
338	1.53	341	1.85	333	0.76
353	0.35	358	1.57	339	0.57
419	0.54	409	1.28	408	1.24
425	1.91	425	2.44	420	2.99
441	1.13	442	1.11	433	0.16
467	1	466	0.48	469	0.7
480	0.15	480	0.1	482	0.15
539	1.06	542	1.08	541	1.96
597	0.55	585	1.56	591	0.76
692	0.45	687	0.72	682	0.76
787	4.02	798	2.94	790	2.82
826	0.56	829	22.07	827	2.6
831	12.42	835	0.6	832	3.67
838	5.45	843	2.27	842	10.7
857	10.18	860	8.14	860	10.74
880	35.63	876	21.36	877	21.95
890	0.64	902	2.79	897	4.42
943	9.08	934	7.68	935	3.81
966	23.89	957	28.25	954	17.52
969	5.33	976	21.31	990	19.89
986	12.65	996	4.98	995	6.39
1010	5.38	1012	7.33	1011	5.27
1038	11.92	1043	12.74	1038	2.18
1046	8.3	1050	12.92	1041	2.8
1059	59.6	1061	49.62	1065	79.66
1091	1.23	1092	0.05	1093	0.83
1115	2.29	1114	10.63	1116	8.84
1141	12.7	1147	52.86	1145	24.83
1150	105.47	1156	12.32	1155	32.06
1165	78.01	1161	111.44	1168	120.39
1183	4.04	1189	10.48	1187	6.54
1200	3.05	1198	3.31	1194	2.9
1209	1.13	1211	2.38	1207	1.18
1218	2.22	1215	9.23	1212	1.73
1255	0.92	1257	0.28	1246	2.51
1276	2.28	1289	5.14	1281	5.27
1303	5.39	1302	1.2	1297	5.99
1305	4.74	1310	2.21	1309	3.93
1316	0.43	1315	5.9	1317	0.94
1336	8	1339	7.81	1347	6.72
1366	4.21	1366	1.86	1359	7.64
1371	6.48	1377	7.61	1367	1.43

conformer (a)		**conformer (b)**		**conformer (c)**	
Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
1390	39.92	1391	12.7	1393	24.08
1399	11.44	1400	21.6	1399	16.02
1401	1.26	1401	13.92	1403	2.9
1405	0.95	1406	0.09	1410	2.88
1419	2.29	1419	0.92	1417	0.77
1427	19.46	1435	30.67	1429	22.07
1443	9.1	1442	4.72	1438	4.21
1461	3.42	1462	1.43	1466	5.25
1471	8.36	1470	6.86	1468	1.26
1489	2.79	1487	2.5	1491	0.71
1493	12.11	1492	10.43	1497	10.78
1499	9.91	1501	10.72	1498	9.73
1500	6.84	1502	15.44	1500	10.06
1506	11.89	1505	15.37	1505	31.59
1511	9.85	1511	8.6	1509	8.7
1512	6.24	1516	6.05	1513	4.72
1517	20.13	1521	8.77	1520	21.16
1528	2.06	1524	7.08	1525	5.42
1535	10.11	1531	5.65	1529	6.99
1542	18.07	1537	20.9	1533	8.25
1551	3.27	1551	2.9	1549	1.07
2993	16.42	2993	18.17	2991	19.56
3007	49.94	3009	45.36	3010	45.52
3023	29.04	3023	33.18	3020	29.48
3047	26.15	3049	8.7	3050	25.7
3050	7.32	3049	26.31	3052	6.1
3060	8.95	3062	8.55	3061	9.04
3062	9.83	3066	8.2	3064	15.68
3067	13.77	3068	12.24	3068	13.42
3078	2.29	3079	1.7	3089	2.5
3088	1.23	3083	8.16	3091	5.6
3095	6.77	3097	4.81	3092	2.91
3101	2.26	3103	8.22	3098	11.94
3106	6.3	3108	6.42	3106	6.48
3109	12.03	3110	9.99	3108	7.4
3119	16.55	3121	14.04	3120	18.58
3137	22.61	3140	21.16	3138	22.53
3140	4.12	3141	5.89	3144	12.29
3142	12.65	3144	12.64	3151	2.88
3150	7.15	3157	3.59	3158	2.82
3193	5.43	3159	3.81	3166	10.09
3195	4.29	3199	12.65	3180	1.42
3217	0.74	3231	6.06	3215	2.14

Table S4. Calculated IR active vibrations of the [$M_{1,2O2}$] cation conformers at the B3LYP/6-31G** level.

conformer (d)		**conformer (e)**		**conformer (f)**	
Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
34	1.09	28	1.78	31	0.08
69	0.19	52	0.24	71	0.66
75	0.72	90	2.08	77	0.08
119	11.34	114	8.07	116	7.2
154	2.07	161	5.73	151	4.98
190	1.8	212	0.36	208	1.16
239	0.41	239	0.28	218	4.08
257	2.39	253	1.91	251	1.24
262	1.5	254	2.02	261	0.76
274	1.17	277	1.14	268	1.7
321	1.15	307	0.41	303	2.27
333	3.64	354	8.8	335	1.49
383	3.38	388	2.11	360	11.79
426	3.66	420	3.46	417	1.9
431	0.77	428	1.2	427	1.97
449	2.06	456	3.48	443	0.82
466	3.03	471	1.76	473	3.4
505	0.31	510	0.08	503	0.15
567	3.72	569	1.18	567	0.61
627	2.58	627	6.4	627	6.74
697	0.34	696	0.62	686	0.53
801	9.52	823	5.96	801	4.49
824	1.02	826	14.5	830	1.1
845	4.32	839	8.42	842	5.42
846	18.67	855	3.25	851	23.77
893	21.62	898	48.6	893	29
902	43.23	908	3.15	904	9.1
958	24.79	929	16.18	935	1.43
961	10.37	967	30.52	982	38.37
999	16.75	1004	13.7	1008	1.99
1015	5.23	1014	7.65	1010	16.45
1032	9.73	1031	12.94	1016	12.34
1057	45.13	1058	63.4	1056	11.69
1058	31.54	1063	9.76	1064	69.19
1083	22.51	1083	7.69	1081	6.02
1102	2.19	1114	31.54	1119	13.87
1144	88.48	1143	43.84	1147	36.34
1157	6.68	1156	59.21	1159	82.79
1164	133.18	1164	94.58	1164	79.12
1177	0.18	1182	25.43	1180	25.15
1193	6.5	1190	15.01	1189	13.82
1200	27.35	1205	9.69	1202	20.86
1227	1.89	1227	4.74	1218	2.5
1258	16.45	1263	15.5	1259	15.09
1277	1.21	1278	6.33	1268	6.4
1298	4.53	1306	1.51	1297	7.36
1304	3.54	1309	2.92	1310	4.79
1328	10.94	1322	16.63	1328	1.87
1333	5.14	1333	2.11	1339	3.78
1365	5.97	1372	1.78	1357	7.32
1379	7.68	1374	9.01	1375	6.55
1391	34.33	1393	37.44	1396	44.06
1397	19.77	1400	6.8	1408	2.32

conformer (d)		**conformer (e)**		**conformer (f)**	
Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
1408	1.66	1411	4.48	1414	1.04
1425	11.1	1427	10.29	1419	0.42
1430	13.13	1432	23.23	1428	25.62
1448	10.31	1449	7.67	1444	6.18
1460	5.43	1461	0.82	1465	3.68
1471	11.23	1471	16.1	1468	5.98
1485	2.97	1483	2.93	1490	3.66
1491	0.18	1495	2	1494	2.43
1500	8.65	1499	10.37	1498	15.09
1503	19.41	1504	18.82	1500	17.1
1503	9.47	1511	3.37	1502	8.1
1512	5.8	1512	10.29	1514	4.75
1521	16.07	1521	5.29	1519	7.76
1523	11	1528	4.54	1520	17.28
1529	1.68	1530	6.2	1526	18.39
1538	24.79	1540	27.38	1529	7.28
1550	2.32	1550	4.88	1549	1.61
2993	18.88	2995	17.56	2990	20.77
3011	45.88	3011	44.64	3011	46.77
3015	11.68	3024	18.77	3013	16.63
3020	37.81	3025	25.99	3018	55.49
3023	34.31	3029	37.02	3019	23.74
3051	25.88	3052	24.69	3051	26.22
3061	8.97	3061	9.22	3062	7.87
3087	0.37	3092	0.55	3089	1.72
3093	4.52	3098	3.34	3095	1.17
3102	3.89	3100	6.54	3098	7.63
3110	2.71	3105	8.79	3101	8.8
3127	4.06	3129	3.81	3126	4.67
3129	2.64	3132	3.18	3128	2.78
3139	22.53	3138	21.89	3140	20.42
3143	11.6	3144	11.41	3144	11.63
3151	0.6	3155	0.28	3151	2.54
3156	5.68	3161	5.52	3174	1.01
3195	2.76	3168	1.4	3180	15.26
3197	6.07	3200	10.24	3182	1.51
3216	0.47	3228	8.84	3215	1.82

Table S5. Calculated IR active vibrations of the [$P_{1,2O2}$] cation conformers at the B3LYP/6-311++G** level.

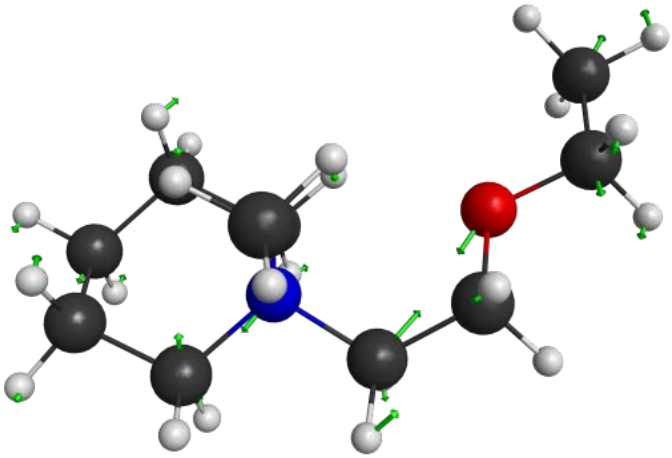
conformer (a)		**conformer (b)**		**conformer (c)**	
Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
39	0.49	22	0.66	36	0.23
61	0.31	81	0.73	74	0.34
74	0.92	103	0.44	80	0.77
122	8.84	115	8.3	120	7.94
154	0.32	141	0.46	142	1.78
189	2.19	153	1.28	210	1.94
228	0.03	214	1.05	219	0.01
250	1.3	246	2.24	249	0.81
258	2.15	257	1.23	260	1.04
277	0.43	263	0.39	283	0.32
319	0.03	279	1.91	302	1.46
336	1.44	338	1.74	330	0.84
353	0.32	355	0.97	337	0.4
415	0.44	396	0.49	406	0.8
424	2.41	424	3.36	421	3.55
440	1.1	436	0.86	431	0.08
464	0.76	463	0.44	469	0.81
479	0.15	477	0.08	480	0.12
539	1.32	539	1.01	539	1.99
594	0.78	578	2.03	587	0.7
691	0.5	683	0.67	679	0.66
786	4.59	789	2.91	783	2.83
825	0.5	823	22.13	825	4.48
828	11.31	833	1.1	830	2.73
833	5.81	836	1.61	838	8.26
854	11.37	856	9.3	858	11.34
877	34.1	872	19.71	874	21.82
885	1.73	900	1.93	893	6.38
941	7.89	928	11.04	931	4.44
962	29.29	949	26.89	949	16.88
965	6.93	970	21.49	984	20.67
985	8.25	992	6.97	991	4.78
1009	6.2	1009	8.12	1008	5.99
1035	13.38	1039	19.66	1034	1.94
1043	13.2	1046	18.79	1038	3.07
1050	67.48	1052	44.17	1057	97.22
1090	1.4	1089	0.19	1089	1.18
1108	4.23	1107	21.5	1108	13.23
1135	106.2	1137	115.3	1138	44.86
1141	52.99	1144	43.43	1145	73.97
1156	24.53	1155	8.45	1156	46.92
1175	4.18	1180	6.88	1179	6.22
1193	1.84	1191	2.91	1188	0.8
1208	1.21	1208	2.79	1204	1.17
1215	1.78	1210	6.82	1209	1.21
1251	0.66	1252	0.41	1241	1.43
1275	2.26	1286	3.8	1279	5.59
1301	4.67	1298	1.3	1296	5.24
1304	5.35	1307	1.95	1308	4.01
1316	0.85	1312	7.48	1316	1.87
1336	6.4	1330	5.77	1342	5.81
1363	6.29	1363	2.87	1357	8.3
1369	3.84	1372	4.77	1365	0.8

conformer (a)		**conformer (b)**		**conformer (c)**	
Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
1386	26.81	1384	8.02	1388	21.78
1392	3.98	1392	26.61	1391	0.63
1393	4.14	1393	2.95	1394	5.66
1401	1.01	1398	0.1	1405	1.66
1416	6.18	1412	1.24	1412	5.75
1418	17.49	1423	26.83	1419	20.05
1437	3.98	1438	1.81	1430	2.34
1453	2.5	1453	0.64	1455	3.73
1462	7.28	1462	4.9	1457	1.53
1480	1.51	1476	2.38	1481	1.46
1486	15.76	1482	7.96	1487	20.13
1487	7.56	1487	10.69	1488	11.5
1490	8.95	1490	14.67	1492	2.17
1497	7.71	1492	20.08	1496	29.56
1498	11.7	1499	10.37	1500	2.63
1504	11.06	1502	8.52	1500	11.24
1509	26.5	1507	17.33	1509	21.98
1517	2.18	1509	12.98	1514	9.17
1525	10.37	1515	4.82	1521	5.83
1528	15.95	1521	12.86	1522	11.59
1535	5.15	1532	5.58	1533	1.42
2983	20.26	2983	20.98	2982	21.44
2999	50.08	2999	46.38	2999	46.48
3009	26.73	3009	31.3	3007	29.36
3029	6.74	3027	8.11	3029	4.45
3034	21.87	3035	22.17	3034	21.28
3042	9.4	3044	8.96	3042	9.25
3047	7.33	3048	9.55	3044	14.24
3049	16.28	3051	10.97	3049	16.75
3060	2.82	3063	1.24	3073	2.08
3070	0.11	3067	7.41	3076	2.8
3077	6.15	3080	4.49	3077	2.01
3084	4	3087	5.31	3082	16.16
3085	5.53	3087	10.99	3086	7.41
3088	12.44	3088	8.63	3087	5.02
3097	18.26	3098	17.82	3095	20.14
3112	21.85	3114	20.45	3111	20.88
3116	15.93	3117	16.9	3115	17.24
3117	5.22	3124	3.55	3129	3.06
3129	7.36	3134	6.52	3138	3.85
3164	6.21	3139	4.16	3146	9.69
3171	2.33	3174	11.33	3158	1.91
3191	0.99	3203	3.81	3195	2.29

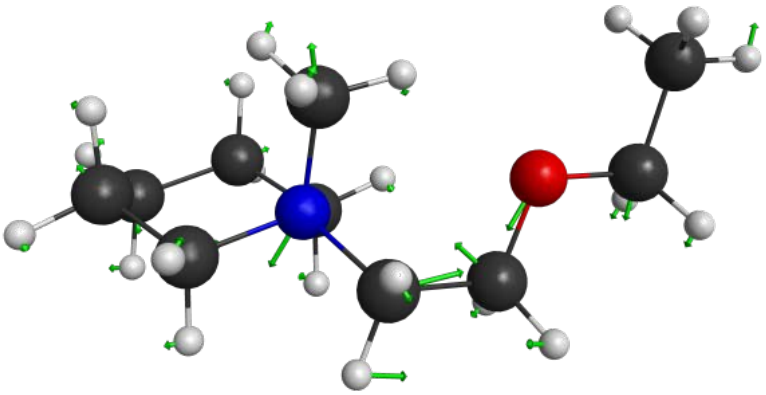
Table S6. Calculated IR active vibrations of the [$P_{1,2O2}$] cation conformers at the MP2/6-311G* level.

conformer (a)		**conformer (b)**		**conformer (c)**	
Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
49	0.41	43	0.36	46	0.17
79	0.9	79	0.75	77	0.49
83	0.49	91	0.96	86	0.95
129	8.27	132	9.53	130	6.76
154	1.82	155	0.72	155	3.42
193	2.36	204	0.22	222	2.03
242	0.08	214	1.25	229	0.05
274	1.86	261	1.98	266	0.67
278	1.56	275	1.61	276	1.11
296	0.36	280	0.69	302	1.28
335	0.86	322	1.25	316	1.5
357	0.94	354	2.26	346	1.18
369	0.57	375	0.46	358	0.4
419	0.61	419	1.16	419	0.95
431	2.09	430	2.92	427	3.42
446	0.98	453	0.93	444	0.13
473	0.72	475	0.35	483	0.58
487	0.1	492	0.13	490	0.15
553	1.31	560	0.98	557	2.19
608	0.83	602	2.27	611	0.59
714	0.46	712	0.54	706	0.95
805	1.08	816	0.8	811	0.66
841	0.59	841	0.36	840	0.56
848	9.29	850	12.11	850	7.16
862	2.44	864	1.26	865	2.99
876	0.12	880	1.4	882	1.24
908	35.41	908	25.98	907	29.02
917	6.05	930	5.93	925	2.75
963	6.39	955	4.7	956	5.48
987	15.64	979	16.75	977	11.42
1007	1.69	1006	21.25	1019	8.89
1019	19.87	1023	10.03	1026	12.92
1031	4.59	1036	11.55	1039	7.63
1065	12.37	1072	14.18	1061	7.41
1083	15.6	1085	6.77	1075	3.36
1095	53	1093	50.29	1097	78.08
1128	0.78	1126	2.79	1126	3.15
1136	2.67	1137	17.29	1135	14.29
1165	15.57	1171	29.74	1167	27.67
1175	69.62	1174	12.83	1178	16.77
1192	91.45	1186	110.6	1190	110.5
1209	4.41	1210	8.41	1212	7.82
1223	2.79	1221	2.61	1216	1.55
1229	1	1230	1.57	1229	0.5
1238	2.78	1236	10.36	1234	0.87
1277	0.86	1282	1.07	1269	1.35
1305	2.35	1313	4.26	1314	4.25
1325	5.68	1321	0.94	1320	6.05
1335	3.43	1333	1.69	1336	5.61
1339	2.75	1338	8.27	1342	0.98
1365	5.53	1362	7.26	1374	6.5
1381	3.32	1380	1.77	1382	1.49
1393	7.12	1398	5.75	1386	6.53

conformer (a)		conformer (b)		conformer (c)	
Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})	Frequency (cm^{-1})	Intensity (km mol^{-1})
1409	6.97	1404	2.81	1409	1.42
1416	1.69	1417	2.81	1419	16.3
1420	4.55	1420	17.73	1421	2.53
1423	16.88	1421	2.15	1427	6.4
1435	3.37	1434	1	1437	0.03
1448	23.3	1452	36.84	1450	27.41
1459	14.92	1458	8.7	1455	11.39
1477	9.97	1481	3.75	1485	5.41
1491	4.42	1490	9.73	1489	2.5
1513	2.45	1510	1.29	1513	4.25
1519	13.18	1518	7.22	1520	4.17
1523	11.46	1525	18.1	1522	21.66
1525	14.54	1526	10.46	1525	15.03
1530	13.28	1529	17.1	1529	33.44
1533	20.01	1531	23.86	1532	11.85
1537	5.59	1538	5.4	1537	6.22
1547	36.88	1548	8.47	1549	40.25
1555	2.38	1553	20.73	1554	0.78
1557	6.14	1556	6.29	1556	5.57
1562	16.16	1560	15.82	1560	2.6
1575	3.6	1575	4.91	1576	3.17
3041	20.25	3041	18.64	3041	18.78
3056	40.37	3056	39.05	3057	39.57
3084	7.85	3084	10.47	3085	7.7
3086	24.32	3086	24.18	3086	23.7
3094	7.11	3094	6.67	3094	6.9
3098	7.83	3101	6.09	3099	10.49
3100	6.97	3102	2.82	3101	6.27
3101	2.62	3103	5.16	3111	4.9
3111	20.61	3106	7.77	3111	21.53
3112	2.34	3112	21.62	3113	3.3
3117	7.7	3117	4.22	3117	2.29
3121	1.84	3128	7.61	3121	9.6
3146	7.07	3148	5.07	3146	6.51
3150	1.49	3153	1.31	3150	1.42
3160	13.34	3161	12.82	3160	18.85
3172	6.22	3174	5.57	3182	2.02
3186	3.47	3187	3.57	3188	14.69
3189	13.66	3189	12.91	3193	4.13
3194	14.73	3191	1.31	3193	11.89
3217	6.76	3194	15.03	3208	9.56
3227	1.98	3237	9.26	3217	0.79
3258	0.64	3269	4.86	3259	1.37



Conformer (a), frequency: 969 cm^{-1}



Conformer (b), frequency: 976 cm^{-1}

Figure S1. Atomic movements of selected vibration lines of the [$P_{1,2O2}$] cation conformers.

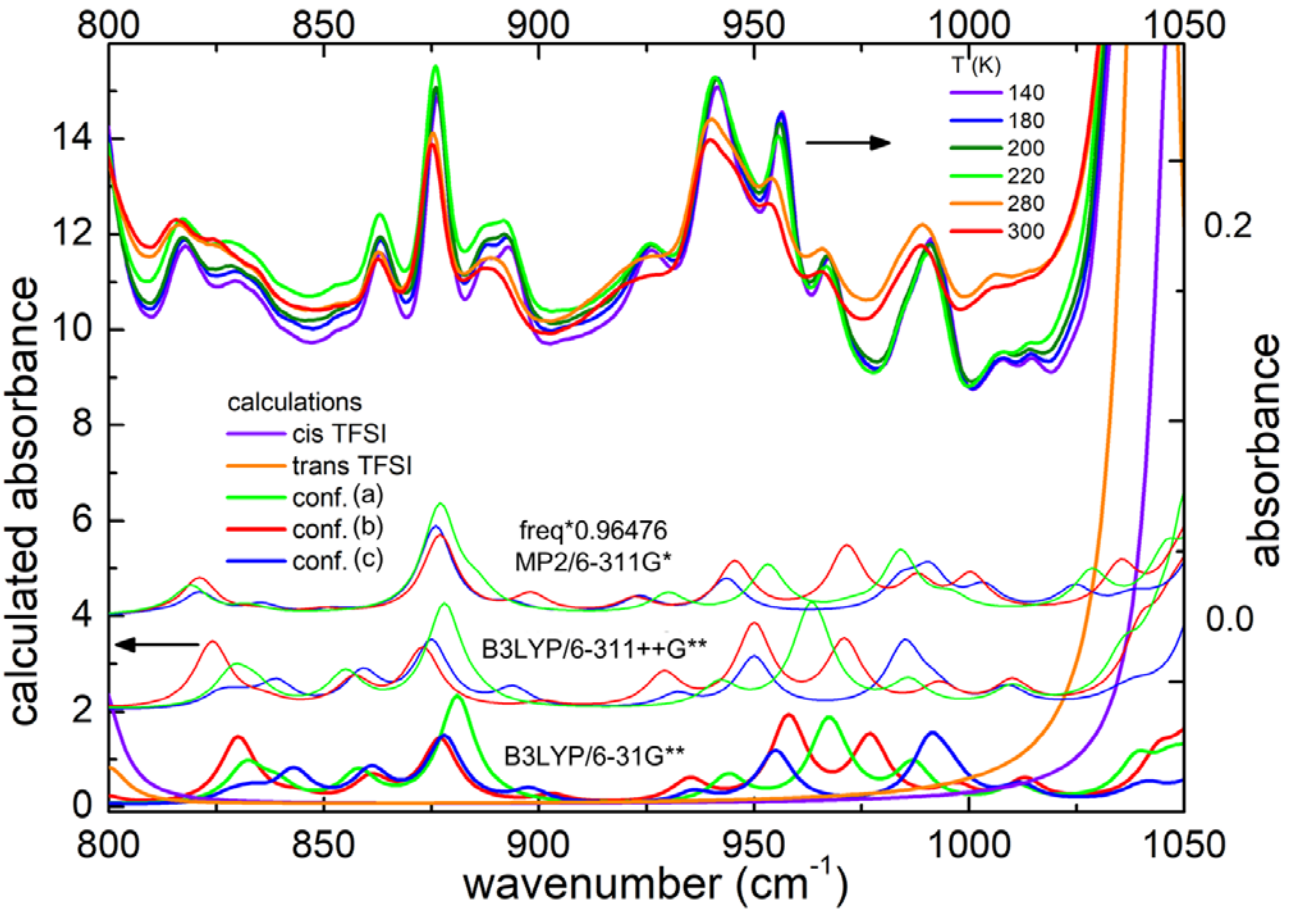


Figure S2. Comparison of the experimental absorbance spectra of [$P_{1,2O2}$][TFSI] with the absorbance spectra calculated at different levels of theory and basis sets.

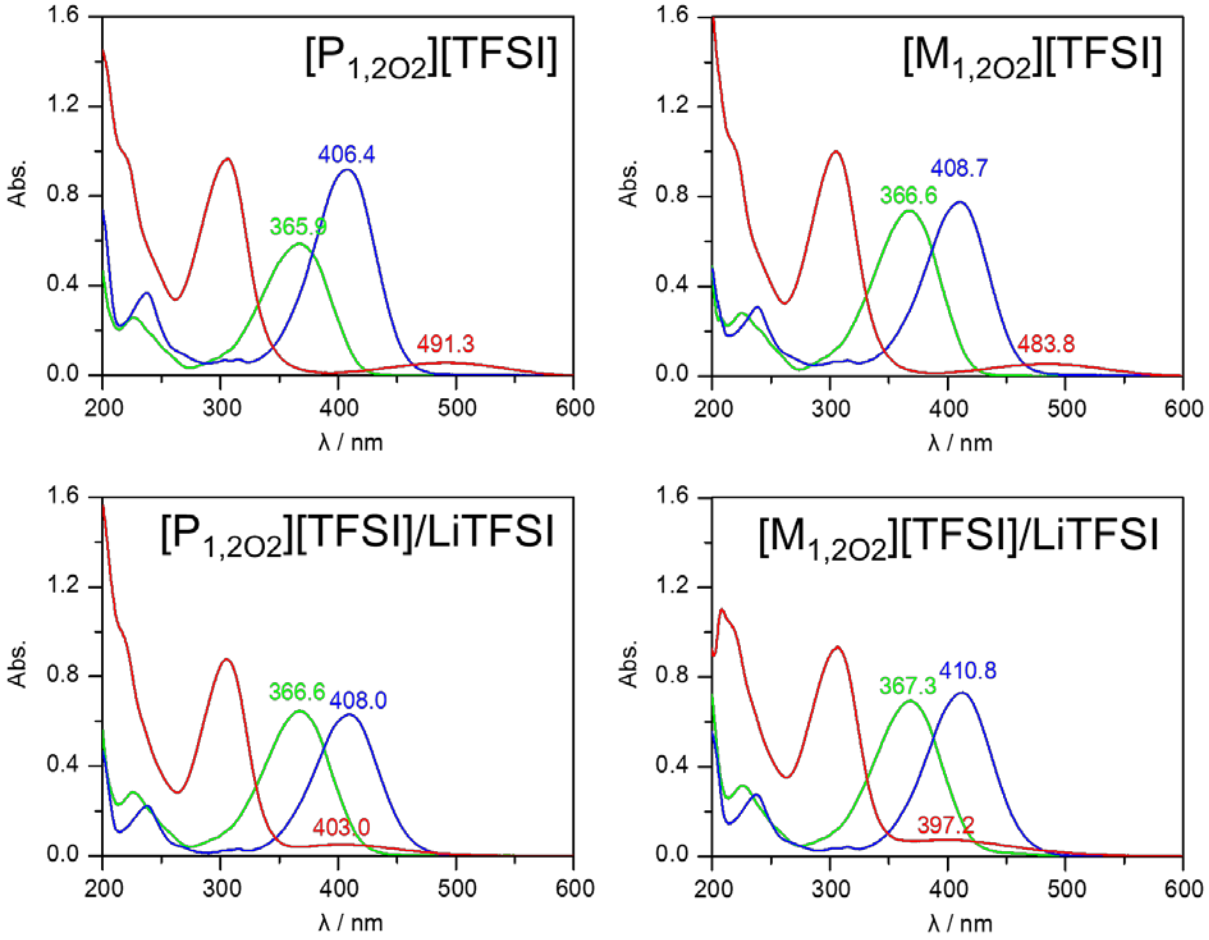


Figure S3. UV-vis spectra of the solvatochromism of *N*,*N*-diethyl-4-nitroaniline, dye_{NN} (blue), 4-nitroaniline, dye_{4N} (green), and Reichardt' dye 33, dye_{Rei} (red) added to $[P_{1,2O2}][TFSI]$, $[M_{1,2O2}][TFSI]$, and their mixtures with LiTFSI. The ν_{dye}s in equation (1)-(4) in the main text are given as $1 / (\lambda_{max\,(dye)} \times 10^{-4})$.

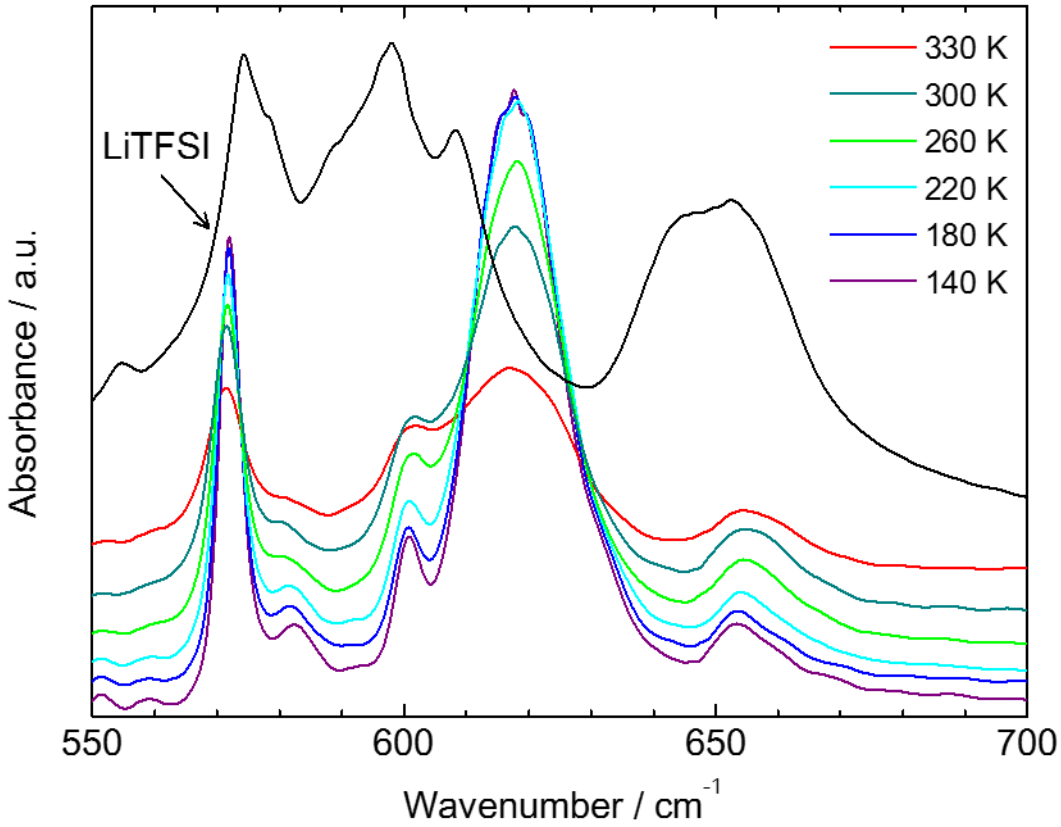


Figure S4. Temperature dependence of the absorbance of the [$M_{1,2O2}$][TFSI]/LiTFSI mixture.