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SUPPLEMENTARY INFORMATION

Triethylsulfonium-Based Ionic Liquids Enforce Lithium Salts Electrolytes

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Table S1. The atom-atom distances for the most characteristic non-covalent interactions determining the structure of the lithium salts dissolved in the sulfonium-based RTILs (systems 5-8).

$[Li][S_{222}][ClO_4]_2$		$[Li][S_{222}][OTF]_2$		$[Li][S_{222}][PF_6]_2$		$[Li][S_{222}][TOTF]_2$	
Interaction	r, Å	Interaction	r, Å	Interaction	r, Å	Interaction	r, Å
Li-S	3.213	Li-S	3.282	Li-S	3.575	Li-S	3.607
Li-Cl(1)	2.567	Li-O(1)	1.863	Li-F(1)	1.874	Li-O(1)	1.905
Li-Cl(2)	2.559	Li-O(2)	1.847	Li-F(2)	1.894	Li-O(2)	1.888
Li-O(1)	1.964	Li-F(1)	2.071	Li-F(3)	1.893	Li-O(3)	2.072
Li-O(2)	2.061	Li-F(2)	2.082	Li-F(4)	1.926	Li-N(1)	3.439
Li-O(3)	2.002	S-O(1)	3.086	Li-F(5)	2.531	Li-N(2)	2.069
Li-O(4)	2.028	S-O(2)	2.918	Li-P(1)	2.714		
S-O(1)	2.869			Li-P(2)	2.667		
S-O(2)	3.100			S-F(1)	2.884		
				S-F(2)	2.964		
				S-F(3)	3.096		
				S-F(4)	3.071		

Table S2. The non-covalent planar angles, in degrees, which are responsible for maintaining the local structure of the lithium salts dissolved in the sulfonium-based RTILs (systems 5-8).

$[Li][S_{222}][ClO_4]_2$		$[Li][S_{222}][OTF]_2$		$[Li][S_{222}][PF_6]_2$		$[Li][S_{222}][TOTF]_2$	
Interaction	angle, °	Interaction	angle, °	Interaction	angle, °	Interaction	angle, °
S-Li-O(1)	110.0	S-Li-O(1)	67.3	S-Li-F(1)	106.0	S-Li-O(1)	51.6
S-Li-O(2)	61.4	S-Li-O(2)	80.1	S-Li-F(2)	59.9	S-Li-O(2)	146.1
S-Li-O(3)	82.6	O-Li-O	144.1	S-Li-F(3)	51.9	S-Li-O(3)	73.0
S-Li-O(4)	68.6	F-Li-F	151.2	S-Li-F(4)	111.5	S-Li-N(1)	68.6
O-Li-O(1)	162.6			S-Li-F(5)	59.1	N-Li-N(2)	161.6
O-Li-O(2)	136.4			S-Li-F(6)	54.8	O-Li-O	96.9
O-Li-O(3)	120.8			F-Li-F(1)	139.1	O-Li-N	71.6
O-Li-O(4)	104.8			F-Li-F(2)	138.7		
O-Li-O(5)	72.9			F-Li-F(3)	115.2		
O-Li-O(6)	72.9			F-Li-F(4)	118.5		
				F-Li-F(5)	74.8		
				F-Li-F(6)	73.4		

Table S3. The atom-atom distances for the most characteristic non-covalent interactions determining the structure of the sulfonium-based RTILs. (systems 1-4).

$[Li][S_{222}][ClO_4]_2$		$[Li][S_{222}][OTF]_2$		$[Li][S_{222}][PF_6]_2$		$[Li][S_{222}][TOTF]_2$	
Interaction	angle, °	Interaction	angle, °	Interaction	angle, °	Interaction	angle, °
Cl-S	3.257	S-S	3.753	P-S	3.729	N-S	3.220
O-S(1)	2.716	O-S(1)	2.704	F-P(1)	2.928	O-S(1)	3.023
O-S(2)	3.130			F-P(2)	2.923	O-S(2)	3.105

Table S4. The non-covalent planar angles, in degrees, which are responsible for maintaining the local structure of the sulfonium-based RTILs.

$[Li][S_{222}][ClO_4]_2$		$[Li][S_{222}][OTF]_2$		$[Li][S_{222}][PF_6]_2$		$[Li][S_{222}][TOTF]_2$	
Interaction	angle, °	Interaction	angle, °	Interaction	angle, °	Interaction	angle, °
S-O-Cl(1)	81.1	S-O-S(1)	123.8	S-F-P(1)	105.4	S-N-S(1)	86.4
S-O-Cl(2)	73.0	S-O-S(2)	73.3	S-F-P(2)	105.5	S-N-S(2)	91.4
S-O-Cl(3)	56.0	S-F-C(1)	112.0	S-F-P(3)	91.3	S-N-S(3)	120.9
S-O-Cl(4)	163.8	S-F-C(2)				S-O-S(1)	92.9
						S-O-S(2)	102.2

Table S5. The total potential energies, corrections due to the basis set superposition errors, and cohesion energies of the simulated systems.

#	Corrected total energy, Hartree	Energy of lone ions, Hartree	BSSE, %	Cohesion energy, kJ mol^{-1}
1	-2463.024351981464	-2462.888094503994	7.6	-357
2	-1597.304769368906	-1597.164355229179	7.5	-368
3	-1576.440477492900	-1576.305990991169	12	-353
4	-1396.594631770183	-1396.457304672688	6.0	-360
5	-4297.852884573810	-4297.400066169365	9.1	-1188
6	-2566.403356874999	-2565.946311911832	8.6	-1199
7	-2524.672339907543	-2524.222775677016	13	-1179
8	-2164.993015861260	-2164.538442517457	7.3	-1192

Table S6. Comparison of calculated IR data (this study) with experimental IR band (in cm^{-1})

#system	group	**This Study**	Ref. 5	Ref. 58	Ref. 25	Ref. 59	Ref. 60	Ref. 61
1	C-H (stretching)	2912, 2974	2967, 2875 to 3021	2966, 2800 to 3000	2953, 3003	2979		
2	C-H (stretching)	2899, 3011	2967, 2875 to 3021	2966, 2800 to 3000	2953, 3003	2979		
3	C-H (stretching)	2905, 3013	2967, 2875 to 3021	2966, 2800 to 3000	2953, 3003	2979		
4	C-H (stretching)	2906, 2981	2967, 2875 to 3021	2966, 2800 to 3000	2953, 3003	2979		
5	C-H (stretching)	2907, 2965	2967, 2875 to 3021	2966, 2800 to 3000	2953, 3003	2979		
6	C-H (stretching)	2901, 2978	2967, 2875 to 3021	2966, 2800 to 3000	2953, 3003	2979		
7	C-H (stretching)	2908, 2976	2967, 2875 to 3021	2966, 2800 to 3000	2953, 3003	2979		
8	C-H (stretching)	2903, 2966	2967, 2875 to 3021	2966, 2800 to 3000	2953, 3003	2979		
1	SO2 (asymmetric bending)	623		608	601, 625			
1	SO2 (symmetric stretching)	1198		1146				
1	CF3 (symmetric bending)	682		757	743			
1	S-N-S (asymmetric stretching)	1026		1051				
1	S-N (stretching)	949			785			
5	SO2 (asymmetric stretching)	1221		1252	1325	1238		
5	SO2 (symmetric stretching)	1151			1132	1152		
5	S-N-S (asymmetric stretching)	1010			1060	1058		
5	C-SO2-N (bonding)	1373			1335		1332	
5	CF3 (asymmetric bending)	528			574		515 , 574	
5	CF3 (symmetric stretching)	1127					1195	
5	CF3 (symmetric bending)	1151				1227, 1234		
5	SO2 (asymmetric bending)	567, 637					600 to 630	
6	SO3	902				933		
7	P-F	511, 588, 652						561
7	P-F (asymmetric stretching)	852						850