Rational Electrolytes Design for Li-Metal Batteries Operated Under Extreme Conditions: A Combined DFT, COSMO-RS, and Machine Learning Study

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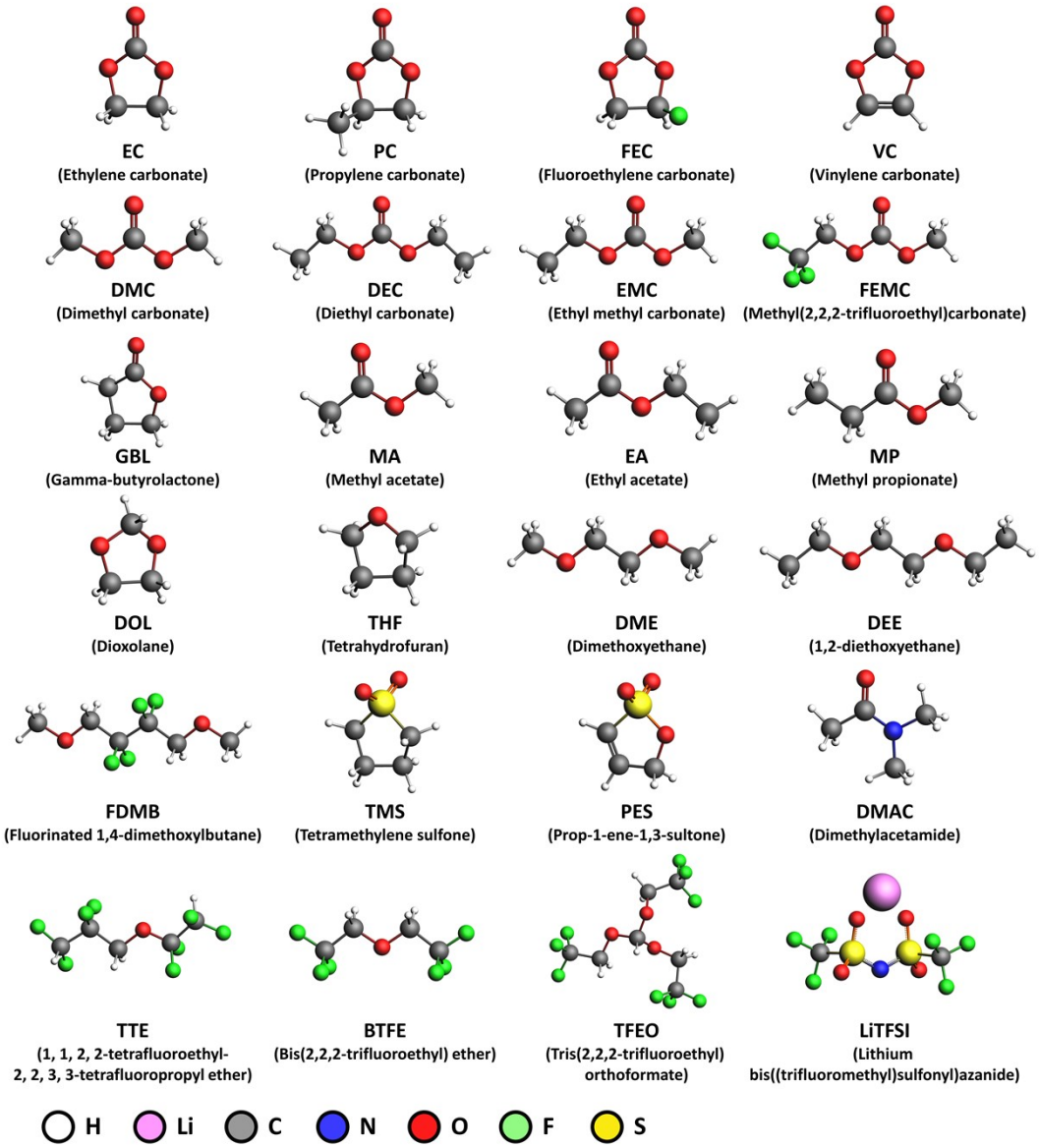

Figure S1. Optimized structures of 20 solvents, 3 diluents (TTE, BTFE, TFEO), and a lithium salt (LiTFSI). The common organic solvents include cyclic carbonates (EC, PC, FEC, VC), linear carbonate (DMC, DEC, EMC, FEMC), cyclic ester (GBL), linear ester (MA, EA, MP), cyclic ether (DOL, THF), linear ether (DME, DEE, FDMB), sulfone (TMS), sultone (PES), and amide (DMAC).

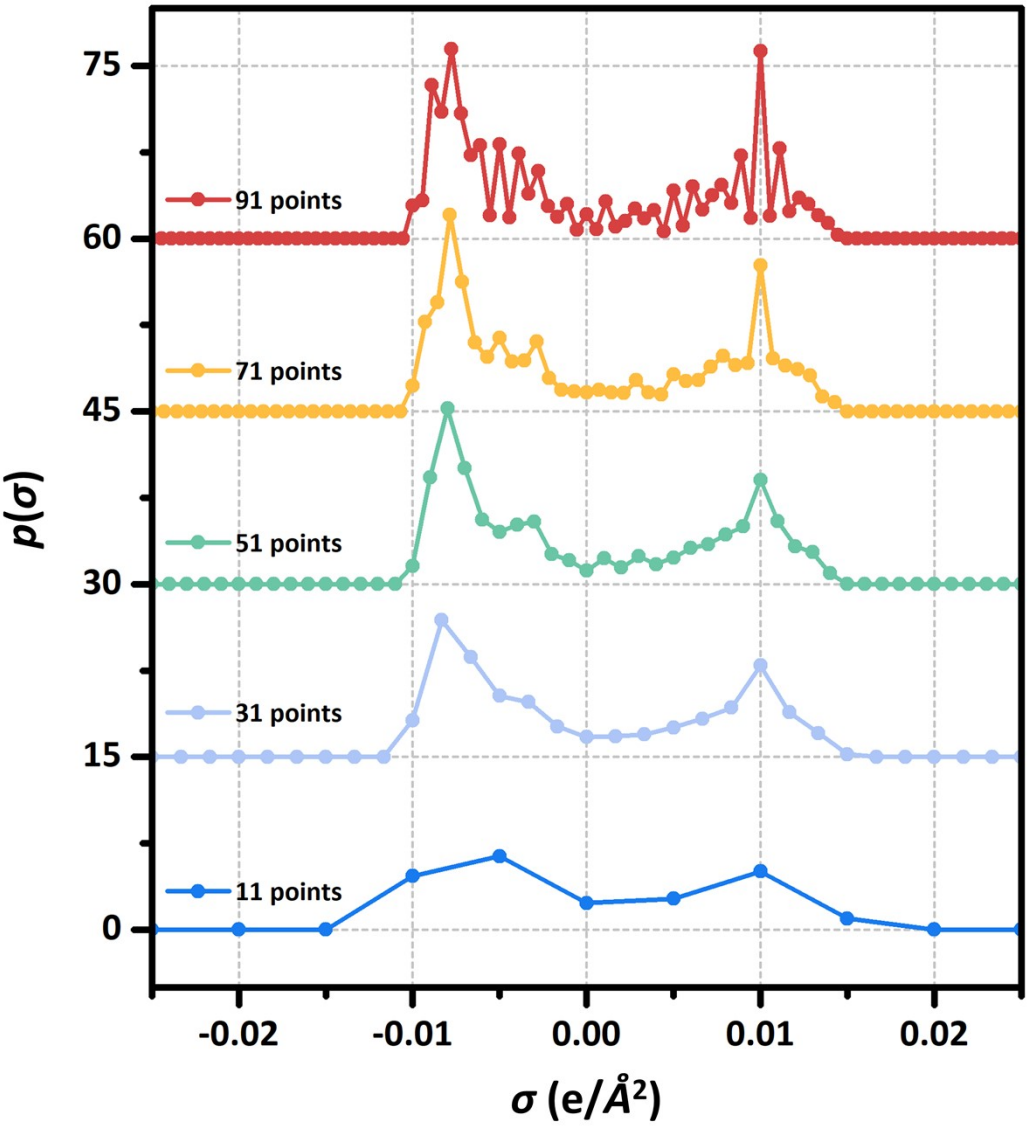

Figure S2. The σ-profiles of EC with various numbers of points, 11, 31, 51, 71, and 91, within the screening charge range of 0.025 to -0.025 e $Å^{-2}$

Table S1. The melting point (mp in K), boiling point (bp in K), and enthalpy of fusion (ΔH_f in kJ mol^{-1}) of 20 common organic solvents. [a] From Sigma-Aldrich; [b] From indagoochem; [c] Predicted from QSPR in AMS.

Solvents	Melting Point (K)	Boiling Point (K)	Enthalpy of fusion (kJ mol^{-1})
EC	309.48 [1]	519.15 [1]	13.02 [2]
PC	224.35 [1]	514.75 [1]	8.96 [2]
FEC	290.45 [3]	485.15 [4]	15.95 [c]
VC	293.65 [a]	435.15 [a]	15.79 [c]
DMC	272.15 [1]	363.26 [1]	11.58 [2]
DEC	230.15 [1]	399.05 [1]	9.24 [2]
EMC	259.15 [1]	380.65 [1]	11.24 [2]
FEMC	229.00 [5]	363.00 [5]	16.64 [c]
GBL	229.79 [1]	477.75 [1]	9.57 [1]
MA	174.90 [1]	329.85 [1]	7.49 [1]
EA	189.35 [1]	350.25 [1]	10.48 [1]
MP	185.65 [1]	351.75 [1]	17.02 [c]
DOL	175.94 [1]	348.45 [1]	6.57 [1]
THF	164.77 [1]	339.15 [1]	8.54 [1]
DME	204.15 [1]	358.15 [1]	14.01 [c]
DEE	199.15 [a]	394.15 [a]	15.44 [c]
FDMB	224.15 [c]	405.82 [c]	21.17 [c]
TMS	301.60 [1]	559.15 [1]	1.372 [6]
PES	355.65 [b]	529.75 [b]	16.95 [c]
DMAC	254.15 [1]	439.05 [1]	15.78 [c]

Table S2. The calculated bubble point temperature (K) in the upper triangular matrix and eutectic temperature (K) in the lower triangular matrix for 190 binary mixtures at their eutectic compositions.

	EC	PC	FEC	VC	DMC	DEC	EMC	FEMC	GBL	MA	EA	MP	DOL	THF	DME	DEE	FDMB	TMS	PES	DMAC
EC		515.003	499.843	457.788	374.683	401.474	387.781	366.859	481.843	330.266	350.873	352.264	349.057	339.463	359.327	394.666	408.421	550.371	522.307	447.906
PC	219.031		508.773	492.929	419.381	425.69	429.616	400.496	494.838	336.618	360.378	361.546	356.334	343.383	374.265	403.349	442.191	541.879	515.14	484.915
FEC	259.525	213.205		454.192	381.625	404.798	394.016	366.145	483.011	331.608	352.567	353.66	351.415	341.501	362.497	396.199	409.272	538.482	492.68	455.247
VC	266.832	216.803	264.092		377.683	402.466	390.483	366.51	467.392	330.788	351.793	353.002	349.882	340.446	361.35	395.342	407.784	508.63	443.907	441.807
DMC	256.537	212.974	244.566	248.361		384.995	371.735	364.918	409.449	330.984	351.112	352.418	349.183	339.654	358.432	387.596	388.042	425.147	367.272	387.966
DEC	227.172	204.173	222.21	223.001	217.518		391.883	381.795	420.483	334.807	358.165	359.499	352.766	343.288	369.578	395.216	402.361	445.989	399.617	406.449
EMC	250.233	211.933	240.612	242.519	234.294	213.263		371.511	419.068	331.739	352.912	354.123	350.033	340.39	361.706	390.645	395.498	438.656	382.748	398.829
FEMC	226.115	201.528	226.593	225.943	215.448	200.314	211.524		398.564	334.135	354.595	355.609	352.14	343.135	362.612	383.131	379.324	427.68	363.506	383.44
GBL	223.053	197.138	210.197	216.248	215.694	203.883	213.435	195.212		335.888	359.992	361.323	354.597	342.517	373.057	403.382	434.828	520.54	479.938	463.587
MA	174.453	168.149	172.94	173.874	173.075	169.128	172.41	168.138	168.752		334.987	333.99	338.101	333.468	332.906	333.772	331.717	360.159	329.933	330.929
EA	188.833	181.696	187.326	187.977	186.776	180.953	185.626	180.35	181.762	162.522		350.932	348.458	341.629	352.483	358.918	354.385	386.295	350.39	352.713
MP	185.4	181.234	184.671	184.992	184.282	180.632	183.611	180.522	181.166	165.505	173.378		348.767	341.039	353.642	360.465	355.278	390.003	351.873	353.902
DOL	175.24	167.27	172.153	174.171	173.628	169.278	172.906	166.388	169.119	153.23	162.162	165.311		341.136	349.248	351.313	350.704	379.526	348.614	349.436
THF	164.522	161.099	162.417	163.669	163.871	161.088	163.422	158.546	162.17	151.184	157.018	159.721	151.241		340.894	342.778	340.538	364.098	339.267	339.649
DME	203.343	194.083	200.731	201.633	200.434	192.55	198.737	190.633	194.618	168.968	179.144	179.339	169.289	161.636		372.793	366.594	398.404	358.454	362.6
DEE	198.854	194.326	197.798	197.985	197.104	190.726	195.789	190.544	193.887	169.928	179.228	179.395	170.303	161.453	187.061		395.715	430.076	394.655	396.467
FDMB	222.753	206.572	222.065	222	216.868	205.937	214.407	210.506	203.88	172.769	185.252	183.566	172.797	163.513	196.197	194.846		466.865	406.241	416.054
TMS	224.662	173.93	185.61	203.263	207.106	187.331	202.979	165.396	184.176	147.909	164.353	169.296	148.016	147.436	181.99	185.313	189.229		555.475	501.2
PES	289.634	222.795	278.747	283.627	266.266	229.457	256.396	228.622	226.779	174.814	189.248	185.605	175.761	164.684	203.944	235.712	223.935	241.187		444
DMAC	245.866	213.198	230.853	234.082	234.92	216.4	230.43	208.549	217.078	173.743	187.222	184.548	174.742	164.382	200.87	197.234	214.686	212.351	249.535	

Table S3. The calculated LiTFSI solubility (M) (upper triangular matrix) and mole fraction of solvent A (lower triangular matrix) for 190 binary mixtures at eutectic composition.

	EC	PC	FEC	VC	DMC	DEC	EMC	FEMC	GBL	MA	EA	MP	DOL	THF	DME	DEE	FDMB	TMS	PES	DMAC
EC		1.939	0.653	1.352	2.25	2.202	2.28	1.294	2.63	2.685	2.518	2.475	2.802	2.784	2.564	2.123	1.398	2.501	1.035	2.871
PC	0.111		1.657	1.89	2.088	2.185	2.124	1.667	2.356	2.581	2.442	2.41	2.66	2.745	2.449	2.173	1.751	2.446	1.934	2.346
FEC	0.471	0.804		0.905	1.723	2.08	1.942	1.232	2.197	2.616	2.452	2.421	2.679	2.715	2.454	2.089	1.343	2.252	0.477	2.441
VC	0.467	0.854	0.518		2.104	2.153	2.156	1.276	2.497	2.667	2.494	2.456	2.771	2.758	2.516	2.109	1.385	2.432	1.195	2.645
DMC	0.287	0.77	0.388	0.361		2.25	2.348	1.571	2.646	2.677	2.515	2.474	2.79	2.779	2.556	2.15	1.602	2.568	2.256	2.792
DEC	0.064	0.534	0.151	0.141	0.251		2.233	1.78	2.494	2.603	2.429	2.397	2.707	2.706	2.421	2.148	1.836	2.539	2.189	2.451
EMC	0.184	0.736	0.309	0.289	0.43	0.68		1.636	2.613	2.663	2.496	2.458	2.774	2.766	2.522	2.151	1.667	2.561	2.269	2.688
FEMC	0.11	0.64	0.092	0.114	0.369	0.586	0.427		2.069	2.443	2.216	2.187	2.518	2.572	2.129	1.897	1.286	2.284	1.238	2.029
GBL	0.139	0.537	0.277	0.226	0.274	0.497	0.318	0.401		2.704	2.595	2.563	2.798	2.805	2.658	2.314	2.129	2.633	2.639	2.83
MA	0.013	0.188	0.052	0.029	0.053	0.164	0.071	0.148	0.17		2.637	2.638	2.757	2.773	2.674	2.604	2.59	2.647	2.689	2.707
EA	0.018	0.258	0.064	0.046	0.088	0.266	0.125	0.221	0.252	0.672		2.501	2.725	2.725	2.537	2.383	2.347	2.611	2.518	2.568
MP	0.015	0.25	0.053	0.037	0.079	0.264	0.115	0.214	0.248	0.744	0.541		2.733	2.737	2.508	2.35	2.328	2.599	2.475	2.522
DOL	0.018	0.202	0.079	0.042	0.058	0.163	0.075	0.163	0.165	0.484	0.318	0.25		2.836	2.78	2.716	2.68	2.685	2.808	2.824
THF	0.009	0.114	0.06	0.036	0.033	0.13	0.049	0.134	0.095	0.423	0.257	0.173	0.441		2.761	2.691	2.72	2.754	2.783	2.791
DME	0.032	0.374	0.111	0.091	0.143	0.39	0.201	0.325	0.36	0.831	0.684	0.678	0.835	0.886		2.32	2.244	2.637	2.564	2.64
DEE	0.014	0.229	0.056	0.051	0.094	0.347	0.151	0.272	0.26	0.85	0.67	0.665	0.855	0.881	0.46		1.998	2.546	2.117	2.215
FDMB	0.071	0.65	0.102	0.104	0.307	0.598	0.381	0.494	0.61	0.941	0.872	0.889	0.928	0.959	0.749	0.824		2.322	1.365	1.966
TMS	0.167	0.308	0.215	0.195	0.216	0.279	0.228	0.232	0.293	0.412	0.349	0.331	0.43	0.424	0.303	0.301	0.221		2.443	2.706
PES	0.714	0.967	0.767	0.789	0.89	0.985	0.944	0.985	0.938	0.997	0.996	0.997	0.995	0.997	0.992	0.987	0.988	0.88		2.869
DMAC	0.214	0.765	0.362	0.36	0.449	0.733	0.529	0.582	0.738	0.966	0.927	0.936	0.969	0.985	0.872	0.91	0.649	0.791	0.113	

Table S4. The z-scores corresponding to the seven σ-descriptors of 20 solvents and three diluents.

Compounds	z1	z2	z3	z4	z5	z6	z7
EC	-0.218	-0.506	0.415	-1.731	-0.397	1.020	-0.685
PC	-0.218	-0.582	0.780	-0.885	-0.425	1.068	-0.685
FEC	-0.218	1.694	-1.592	-1.781	0.315	0.038	-0.685
VC	-0.218	0.797	-1.967	-0.828	-0.187	-0.095	-0.685
DMC	-0.218	-0.672	0.350	-0.504	-0.488	0.746	-0.632
DEC	-0.218	-0.672	1.190	1.188	-0.498	0.849	-0.580
EMC	-0.218	-0.672	0.818	0.269	-0.496	0.811	-0.582
FEMC	-0.218	0.521	-0.279	-0.031	0.731	-0.021	-0.685
GBL	-0.218	-0.672	0.684	-0.822	-0.686	0.731	0.006
MA	-0.218	-0.672	-0.072	-0.307	-0.646	0.233	-0.159
EA	-0.218	-0.672	0.237	0.559	-0.590	0.146	-0.076
MP	-0.218	-0.672	0.161	0.386	-0.520	0.069	0.015
DOL	-0.218	-0.672	0.205	-0.922	-0.640	-0.260	0.726
THF	-0.218	-0.672	-1.041	1.051	-0.758	-1.401	1.265
DME	-0.218	-0.672	0.469	0.895	-0.593	-0.691	1.680
DEE	-0.218	-0.672	0.724	3.208	-0.374	-0.866	2.149
FDMB	-0.218	-0.465	2.022	0.292	1.065	-0.321	0.123
TMS	-0.218	-0.602	1.515	-0.667	-0.745	2.076	-0.678
PES	-0.218	1.119	-0.520	-1.239	-0.420	2.083	-0.685
DMAC	-0.218	-0.672	0.278	0.690	-0.713	-1.297	4.200
TTE	0.512	2.520	-2.346	0.122	3.035	-2.155	-0.685
BTFE	-0.218	1.630	-1.609	-0.088	1.821	-1.622	-0.685
TFEO	-0.218	2.717	-0.701	1.526	3.379	-1.137	-0.685

Table S5. The calculated Li^+ binding energy ($E_{B, Li}$ in eV), and $TFSI^-$ binding energy ($E_{B, TFSI}$ in eV) of 20 solvents and 3 diluents.

Compounds	$E_{B, Li}$	$E_{B, TFSI}$
EC	-0.712	-0.259
PC	-0.722	-0.295
FEC	-0.608	-0.289
VC	-0.636	-0.238
DMC	-0.695	-0.140
DEC	-0.715	-0.149
EMC	-0.704	-0.150
FEMC	-0.593	-0.250
GBL	-0.780	-0.186
MA	-0.743	-0.140
EA	-0.756	-0.140
MP	-0.780	-0.131
DOL	-0.713	-0.212
THF	-0.847	-0.146
DME	-0.712	-0.143
DEE	-0.753	-0.148
FDMB	-0.754	-0.213
TMS	-0.779	-0.203
PES	-0.580	-0.248
DMAC	-1.012	-0.135
TTE	-0.460	-0.297
BTFE	-0.582	-0.274
TFEO	-0.724	-0.380

Table S6. The corresponding coefficients of the seven σ-descriptors from 23 CV iterations for Li-ion binding energy prediction.

CV Iteration	C1	C2	C3	C4	C5	C6	C7
1	0.0375	0.1179	0.0520	0.0001	-0.1091	-0.0713	-0.0970
2	0.0372	0.1118	0.0482	-0.0010	-0.1028	-0.0670	-0.0950
3	0.0379	0.1597	0.0827	-0.0069	-0.1616	-0.1125	-0.1158
4	0.0370	0.1125	0.0449	-0.0004	-0.1050	-0.0697	-0.0955
5	0.0378	0.1248	0.0574	-0.0009	-0.1152	-0.0769	-0.0984
6	0.0399	0.1385	0.0680	0.0033	-0.1352	-0.0890	-0.1113
7	0.0372	0.1132	0.0487	-0.0005	-0.1043	-0.0688	-0.0956
8	0.0440	0.1590	0.0852	-0.0034	-0.1572	-0.1074	-0.1124
9	0.0379	0.1159	0.0529	-0.0031	-0.1072	-0.0718	-0.0969
10	0.0369	0.1090	0.0462	-0.0004	-0.1005	-0.0673	-0.0954
11	0.0376	0.1153	0.0512	0.0013	-0.1100	-0.0738	-0.1006
12	0.0368	0.1056	0.0438	0.0014	-0.0999	-0.0665	-0.0966
13	0.0365	0.0963	0.0311	0.0082	-0.0821	-0.0461	-0.0878
14	0.0340	0.0866	0.0237	0.0049	-0.0894	-0.0587	-0.0893
15	0.0340	0.0702	0.0144	0.0013	-0.0561	-0.0327	-0.0801
16	0.0352	0.1078	0.0529	-0.0180	-0.1034	-0.0833	-0.0989
17	0.0382	0.1127	0.0366	0.0037	-0.1050	-0.0628	-0.0949
18	0.0418	0.1299	0.0612	-0.0006	-0.1164	-0.0636	-0.0975
19	0.0370	0.1338	0.1029	-0.0096	-0.1643	-0.1526	-0.1491
20	0.0352	0.0809	0.0174	-0.0143	-0.0420	-0.0172	-0.0149
21	0.0000	0.1012	0.0444	-0.0005	-0.0886	-0.0636	-0.0953
22	0.0436	0.1021	0.0414	0.0029	-0.0920	-0.0492	-0.0855
23	0.0124	0.0714	0.0094	0.0191	-0.0096	-0.0068	-0.0632

Table S7. The corresponding coefficients of the seven σ-descriptors from 23 CV iterations for TFSI-ion binding energy prediction.

CV Iteration	C1	C2	C3	C4	C5	C6	C7
1	0.0100	-0.0399	-0.0084	0.0189	-0.0404	-0.0117	-0.0083
2	0.0115	-0.0311	0.0015	0.0197	-0.0515	-0.0193	-0.0152
3	0.0112	-0.0251	0.0001	0.0230	-0.0555	-0.0215	-0.0141
4	0.0107	-0.0185	0.0034	0.0234	-0.0650	-0.0279	-0.0179
5	0.0125	0.0060	0.0228	0.0227	-0.0868	-0.0443	-0.0235
6	0.0114	-0.0168	0.0066	0.0230	-0.0655	-0.0286	-0.0180
7	0.0108	-0.0210	0.0027	0.0225	-0.0593	-0.0246	-0.0140
8	0.0116	-0.0163	0.0073	0.0234	-0.0658	-0.0295	-0.0179
9	0.0112	-0.0181	0.0056	0.0234	-0.0636	-0.0276	-0.0174
10	0.0120	-0.0065	0.0145	0.0231	-0.0732	-0.0346	-0.0198
11	0.0112	-0.0186	0.0053	0.0227	-0.0621	-0.0267	-0.0160
12	0.0116	-0.0127	0.0097	0.0221	-0.0671	-0.0303	-0.0173
13	0.0117	-0.0089	0.0157	0.0185	-0.0756	-0.0406	-0.0212
14	0.0098	-0.0305	-0.0058	0.0255	-0.0570	-0.0231	-0.0151
15	0.0112	-0.0197	0.0045	0.0232	-0.0621	-0.0263	-0.0161
16	0.0119	-0.0163	0.0047	0.0247	-0.0647	-0.0234	-0.0127
17	0.0126	-0.0195	-0.0065	0.0290	-0.0665	-0.0190	-0.0157
18	0.0115	-0.0173	0.0062	0.0233	-0.0642	-0.0258	-0.0174
19	0.0113	-0.0093	0.0256	0.0194	-0.0862	-0.0582	-0.0370
20	0.0118	-0.0105	0.0133	0.0264	-0.0780	-0.0386	-0.0263
21	0.0000	-0.0160	0.0054	0.0235	-0.0546	-0.0257	-0.0173
22	0.0149	-0.0205	0.0027	0.0254	-0.0570	-0.0173	-0.0119
23	0.0033	-0.0247	-0.0068	0.0287	-0.0283	-0.0078	-0.0070

Table S8. Mean values and standard deviations of the predicted Li^+ binding energy (eV), and $TFSI^-$ binding energy (eV) of 20 solvents and 3 diluents.

Compounds	$E_{B, Li, Mean}$	$E_{B, Li, STD}$	$E_{B, TFSI, Mean}$	$E_{B, TFSI, STD}$
EC	-0.7279	0.0084	-0.2446	0.0087
PC	-0.7608	0.0077	-0.2358	0.0105
FEC	-0.5634	0.0437	-0.2935	0.0048
VC	-0.6431	0.0082	-0.2095	0.0189
DMC	-0.6435	0.0139	-0.1635	0.0054
DEC	-0.6814	0.0129	-0.1415	0.0045
EMC	-0.6633	0.0071	-0.1536	0.0025
FEMC	-0.6478	0.0097	-0.2469	0.0044
GBL	-0.763	0.004	-0.2138	0.0053
MA	-0.7008	0.0091	-0.1629	0.0046
EA	-0.73	0.0074	-0.1553	0.0045
MP	-0.7961	0.0049	-0.1431	0.0021
DOL	-0.7354	0.0107	-0.1725	0.0036
THF	-0.8212	0.0037	-0.1319	0.0041
DME	-0.7626	0.0058	-0.1401	0.0034
DEE	-0.8385	0.0054	-0.1348	0.0038
FDMB	-0.7708	0.0077	-0.2074	0.0012
TMS	-0.7659	0.0058	-0.2324	0.0051
PES	-0.626	0.0063	-0.2449	0.0053
DMAC	-0.9348	0.0047	-0.1566	0.0032
TTE	-0.4597	0	-0.2971	0
BTFE	-0.648	0.0094	-0.3126	0.0056
TFEO	-0.6468	0.0043	-0.3638	0.0016

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