Supplementary information for A Theoretical Study on the Cyanation Strategy for Modulating Borate Performance in the Design of Electrolytes for High-Voltage Lithium-Ion and Lithium Metal Batteries

Jiahao Zhu[a], Peiyan Li[a], Zixiang Li[a], Guoqiang He[a], Longlong Li[a], Yingen Feng[a], Fredrick Mwange Mulei[c], Alice A. Kasera[c], Ronghua Zeng[b]*, Jianhui Li[a]*

[a] *School of Materials and New Energy, South China Normal University, Shanwei 516600, Guangdong, China*

[b]*Guangdong Provincial International Joint Research Center for Energy Storage Materials, School of Chemistry, South China Normal University, Guangzhou 510006, Guangdong, China*

[c] *School of Engineering, Mount Kenya University, Thika 342-01000, Kenya*

E-mail address: Jianhuili@m.scnu.edu.cn (J Li)

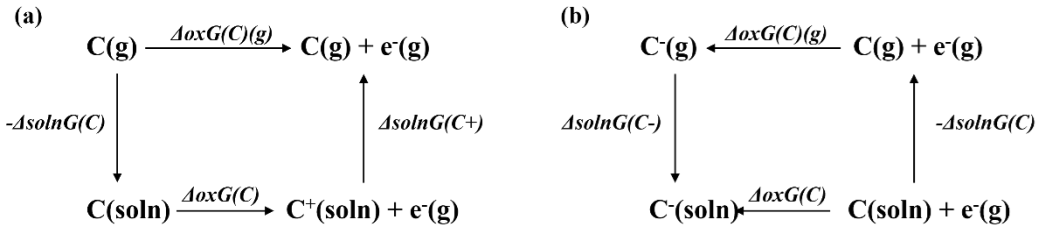


Figure S1. Schematic diagram of the thermodynamic cycle.

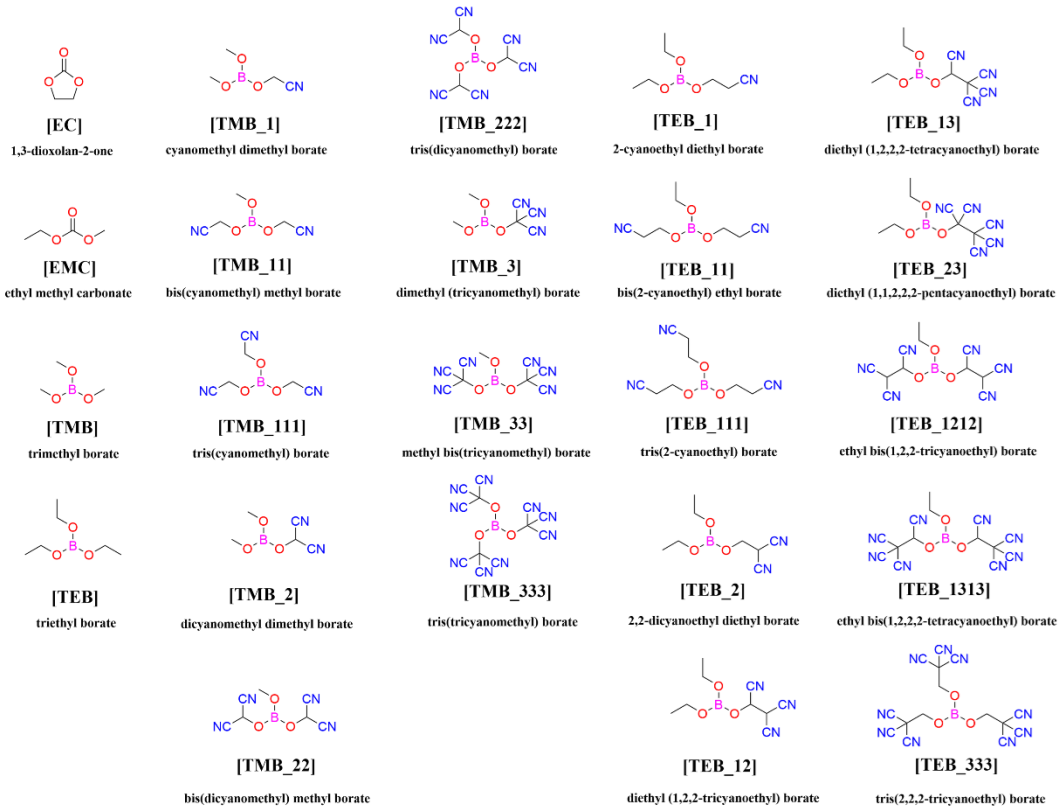
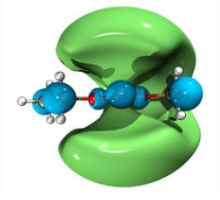
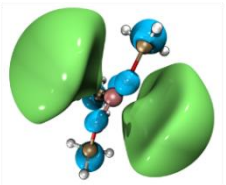


Figure S2. The structure and nomenclature of ethylene carbonate (EC), ethyl methyl carbonate (EMC), trimethyl borate (TMB), triethyl borate (TEB) and cyano-modified borates.

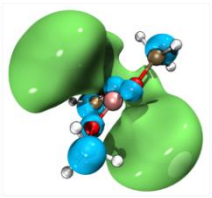
EC LUMO



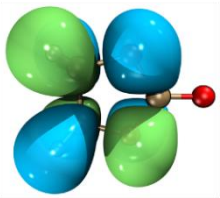
EMC LUMO



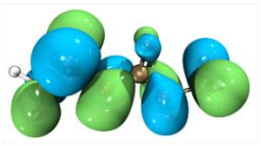
TMB LUMO



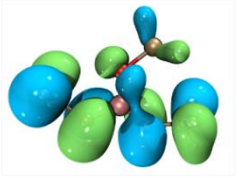
TMB_1 LUMO



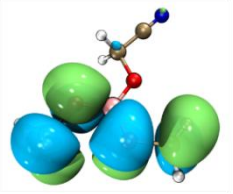
EC HOMO



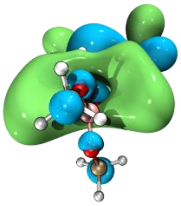
EMC HOMO



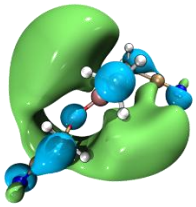
TMB HOMO



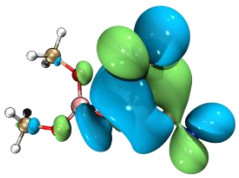
TMB_1 HOMO



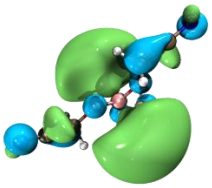
TMB_2 LUMO



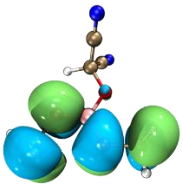
TMB_11 LUMO



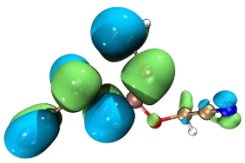
TMB_3 LUMO



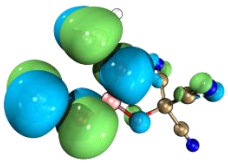
TMB_111 LUMO



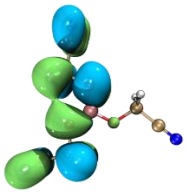
TMB_2 HOMO



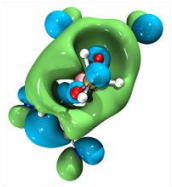
TMB_11 HOMO



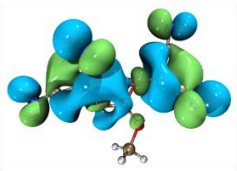
TMB_3 HOMO



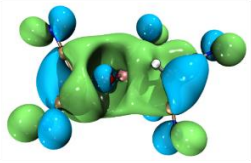
TMB_111 HOMO



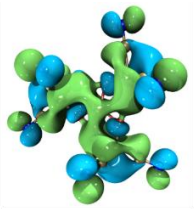
TMB_22 LUMO



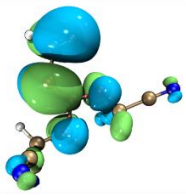
TMB_33 LUMO



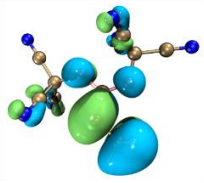
TMB_222 LUMO



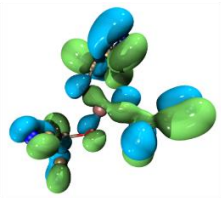
TMB_333 LUMO



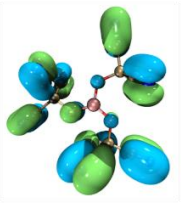
TMB_22 HOMO



TMB_33 HOMO



TMB_222 HOMO



TMB_333 HOMO

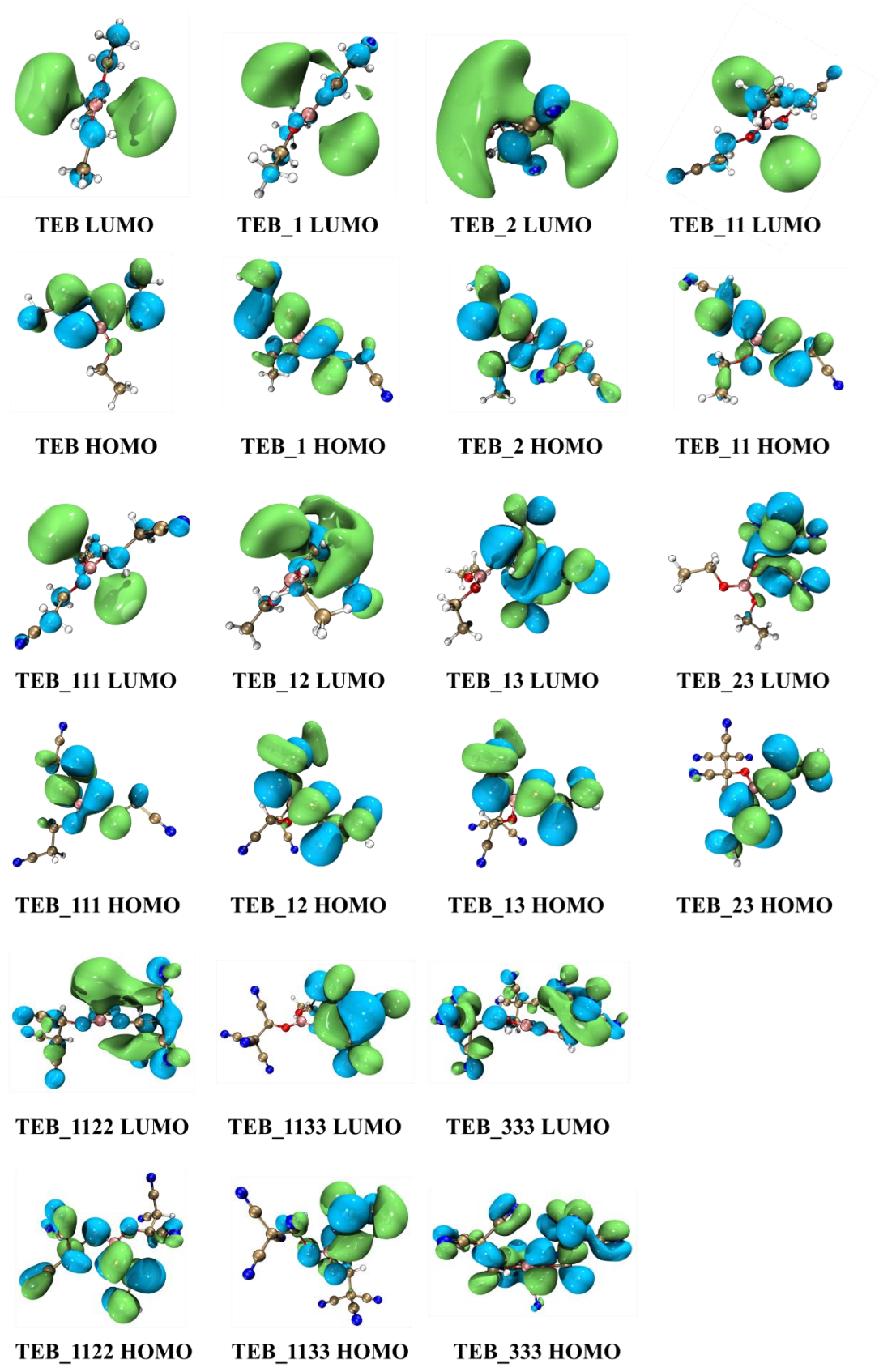


Figure S3. Under the 0.02 isovalue surface, the HOMO and LUMO orbital diagrams of 23 molecules.

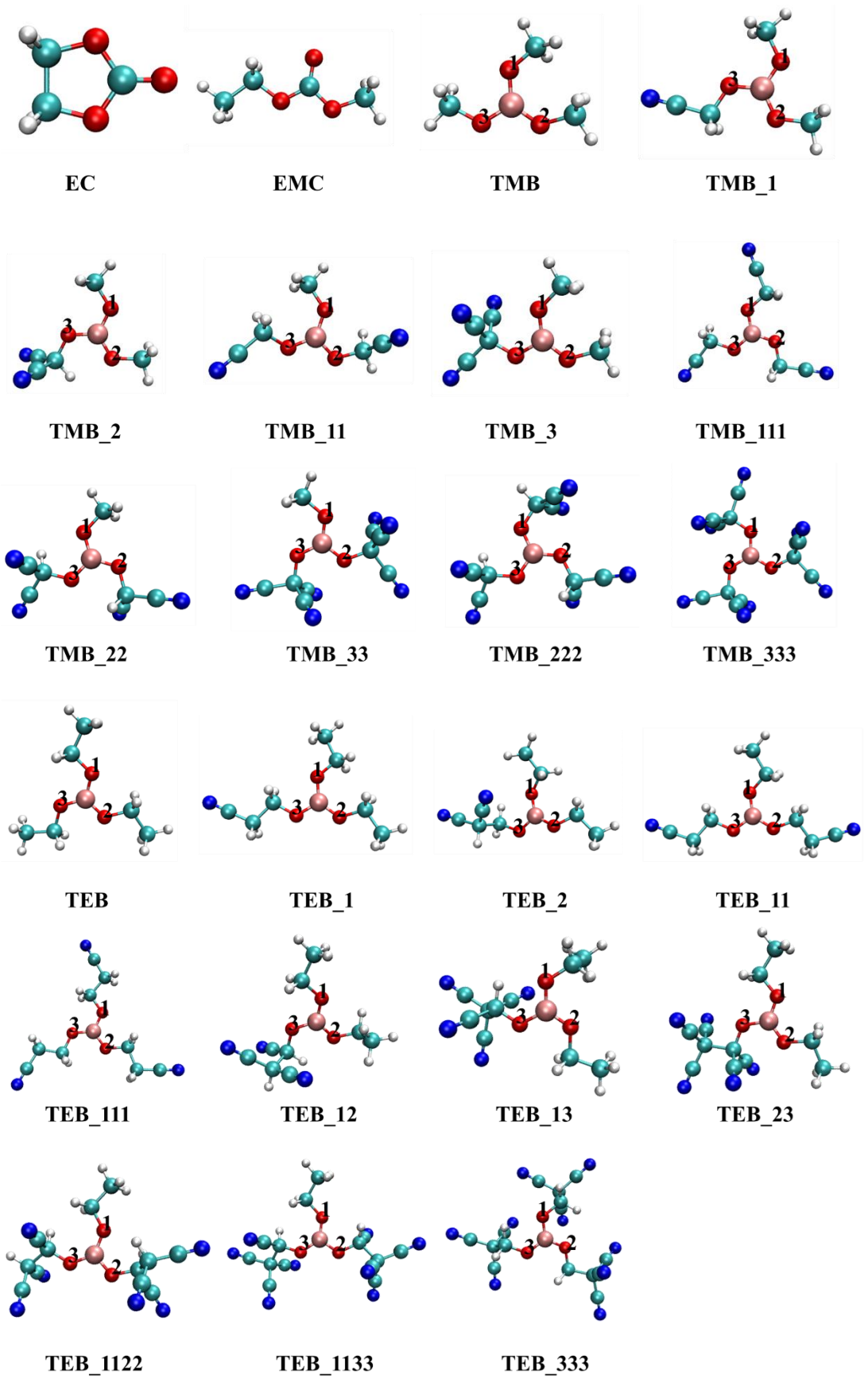


Figure S4. The bond position for each molecule correspond to Table S2.

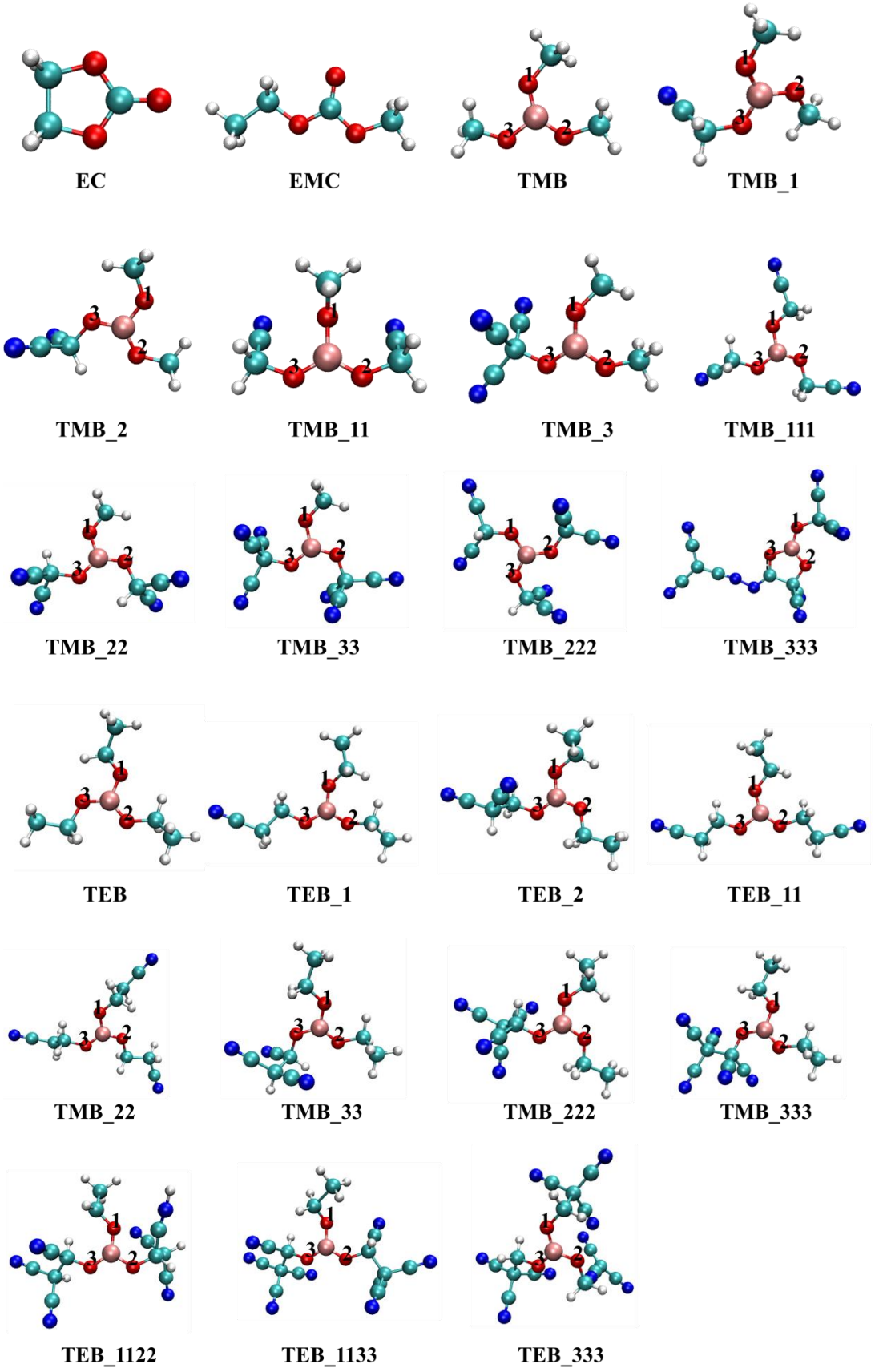


Figure S5. The bond position for each molecule in the oxidation state correspond to Table S2.

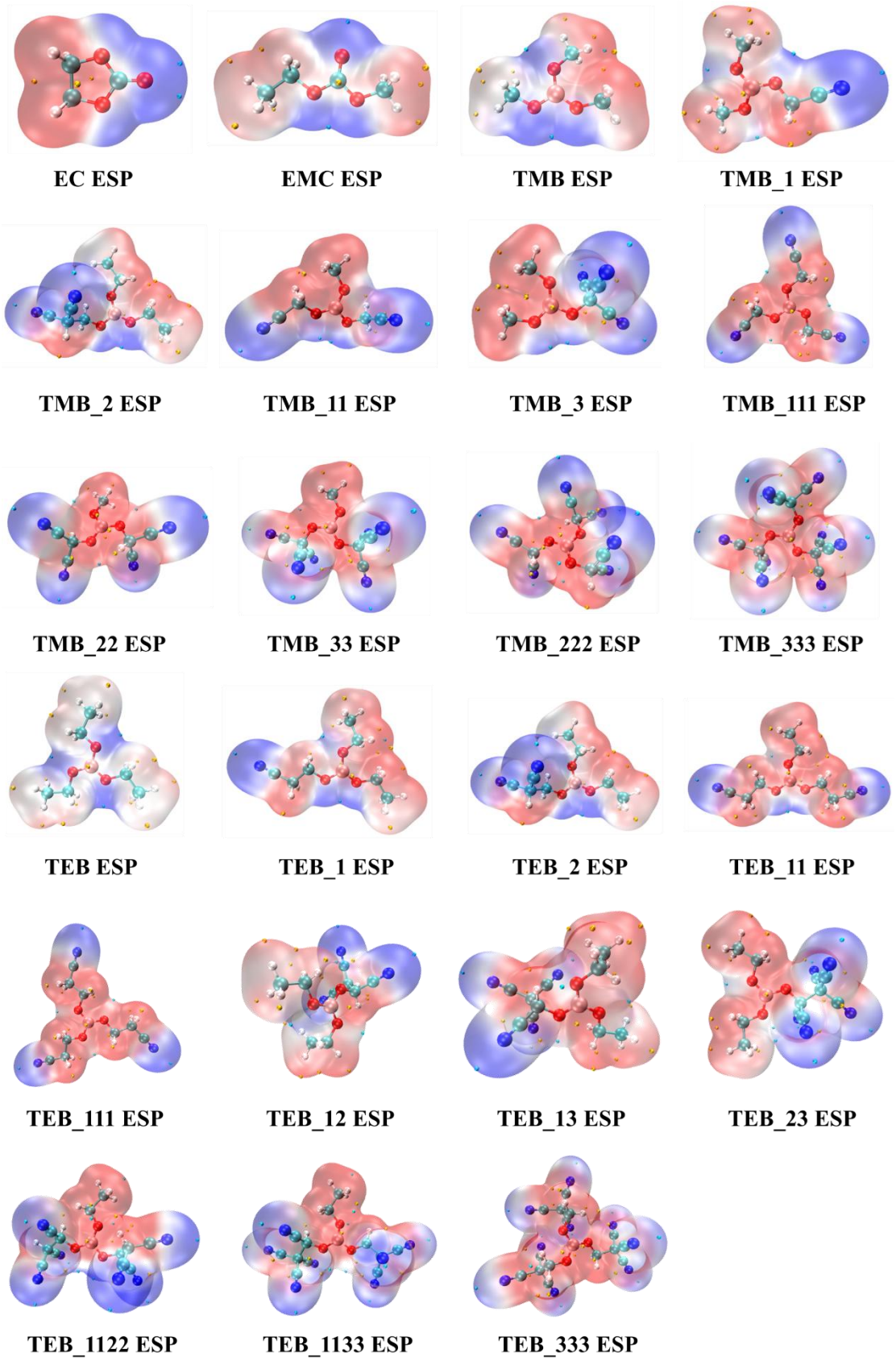


Figure S6. Electrostatic potential mapped van der Waals surface (i.e. ρ = 0.001 a.u. isosurface) of all molecules.

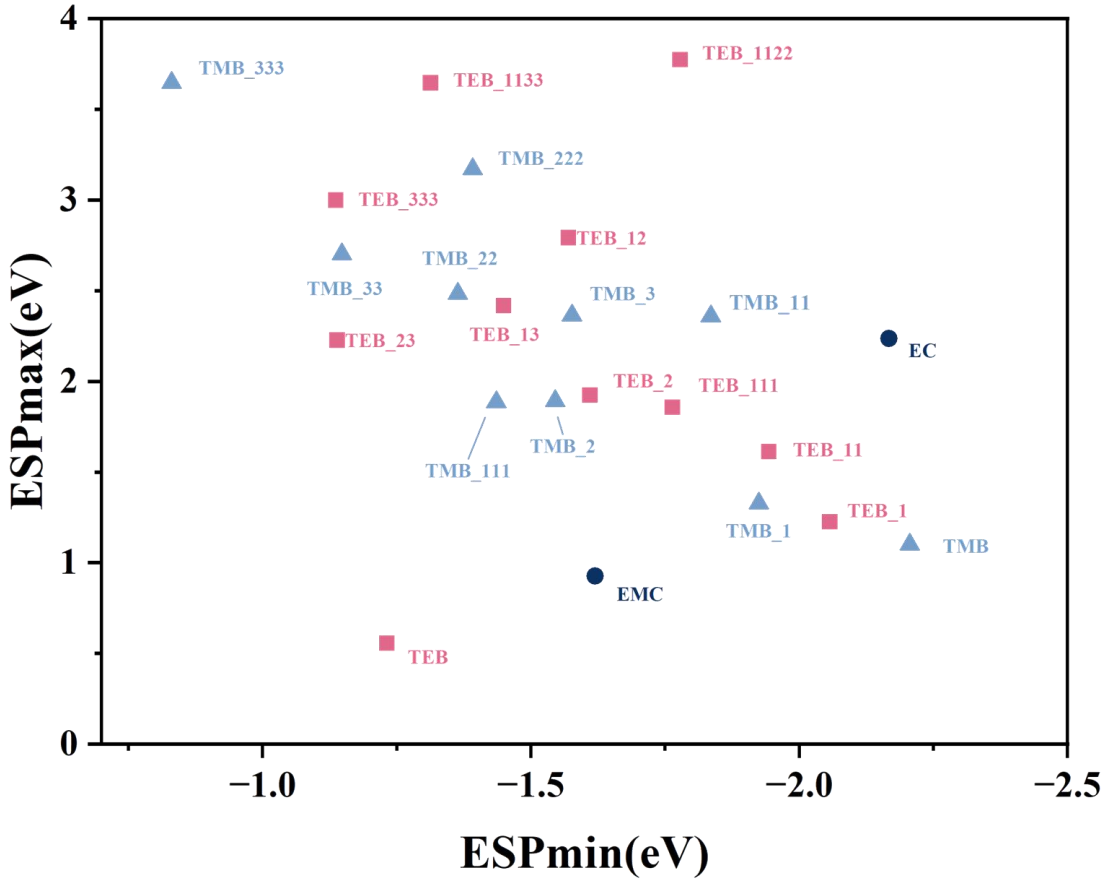


Figure S7. The minimum and maximum electrostatic potential values of all molecules.

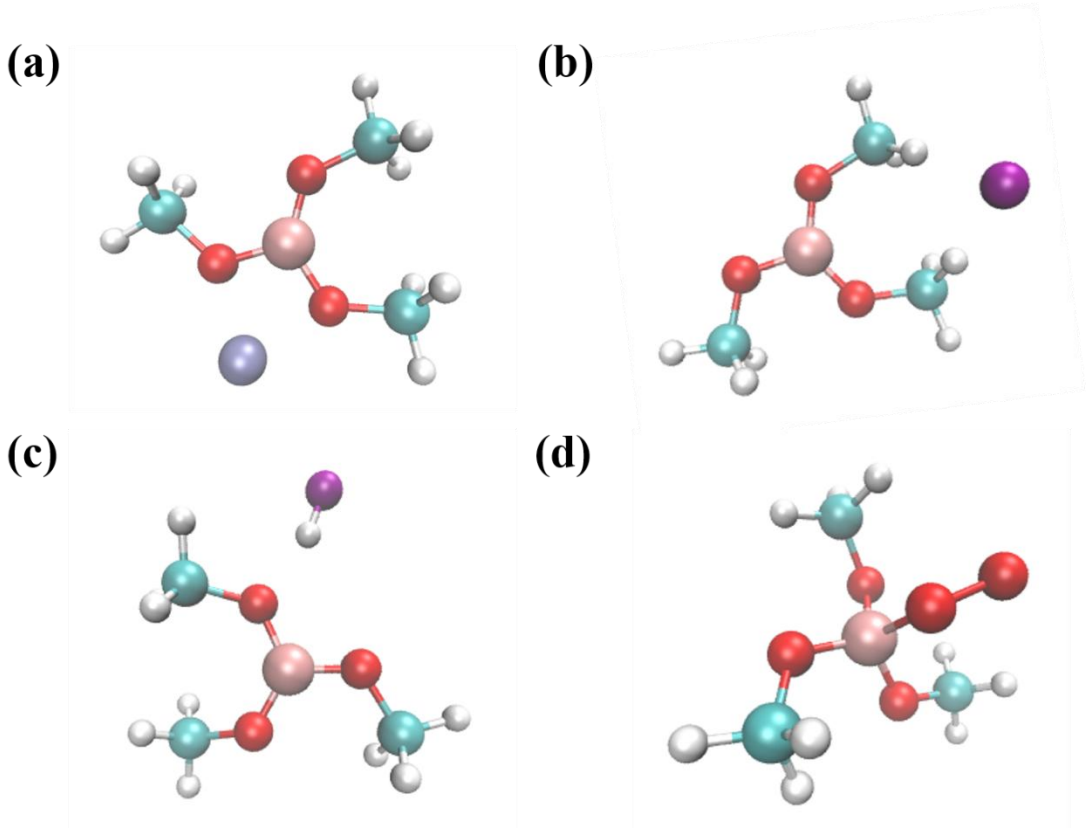


Figure S8. The binding site of each molecule to (a)Li^+ (b)F^- (c) HF (d) O_2^-.

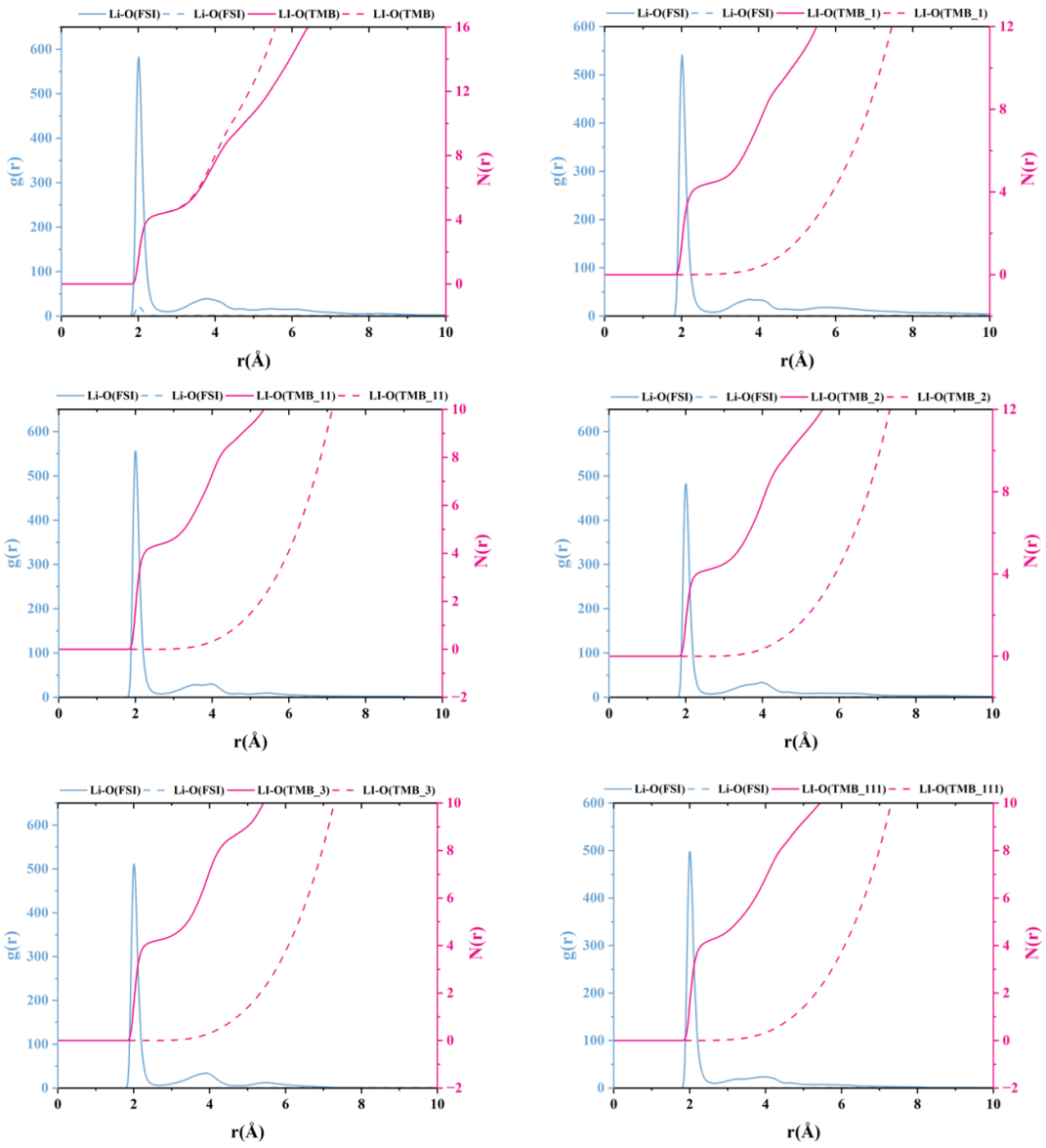


Figure S9. Continued.

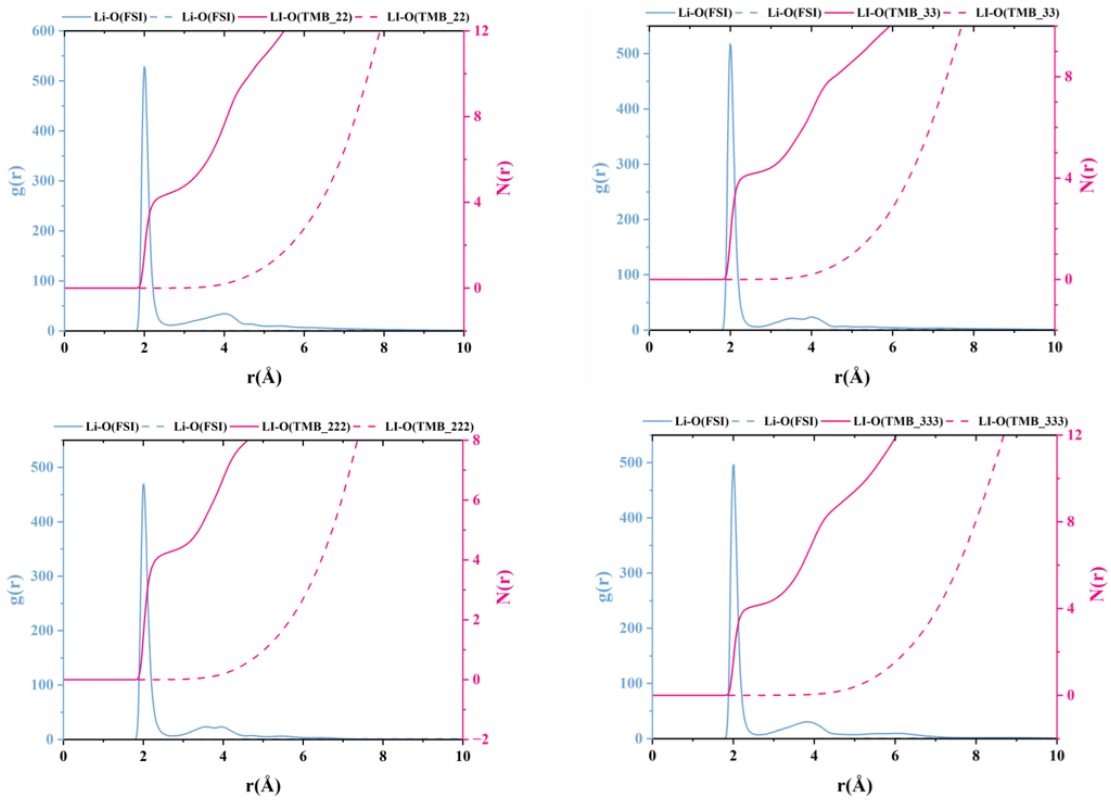


Figure S9. The corresponding coordination number and RDF of LiFSI across the TMB series (from TMB TO TMB_333).

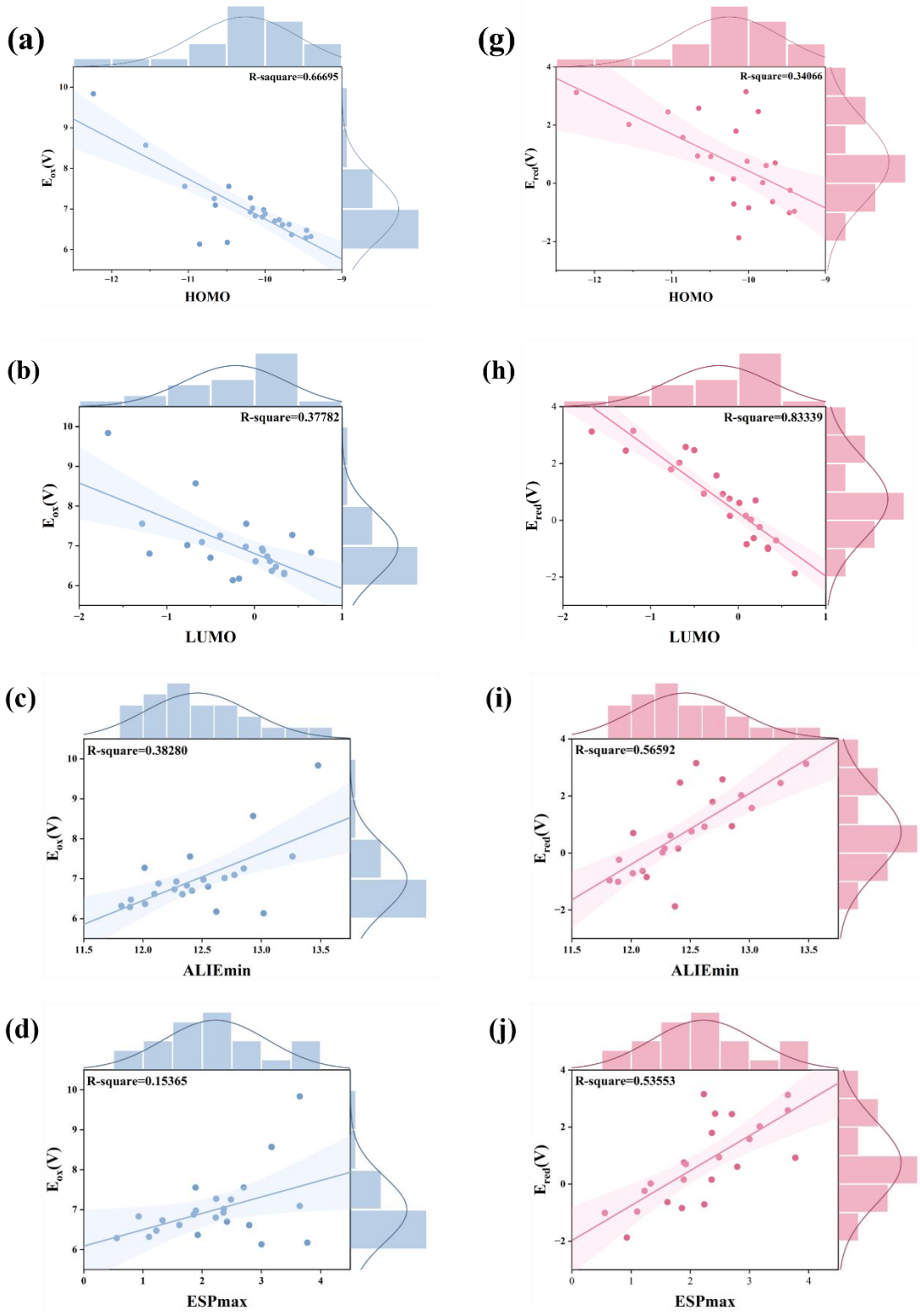


Figure S10. Continued.

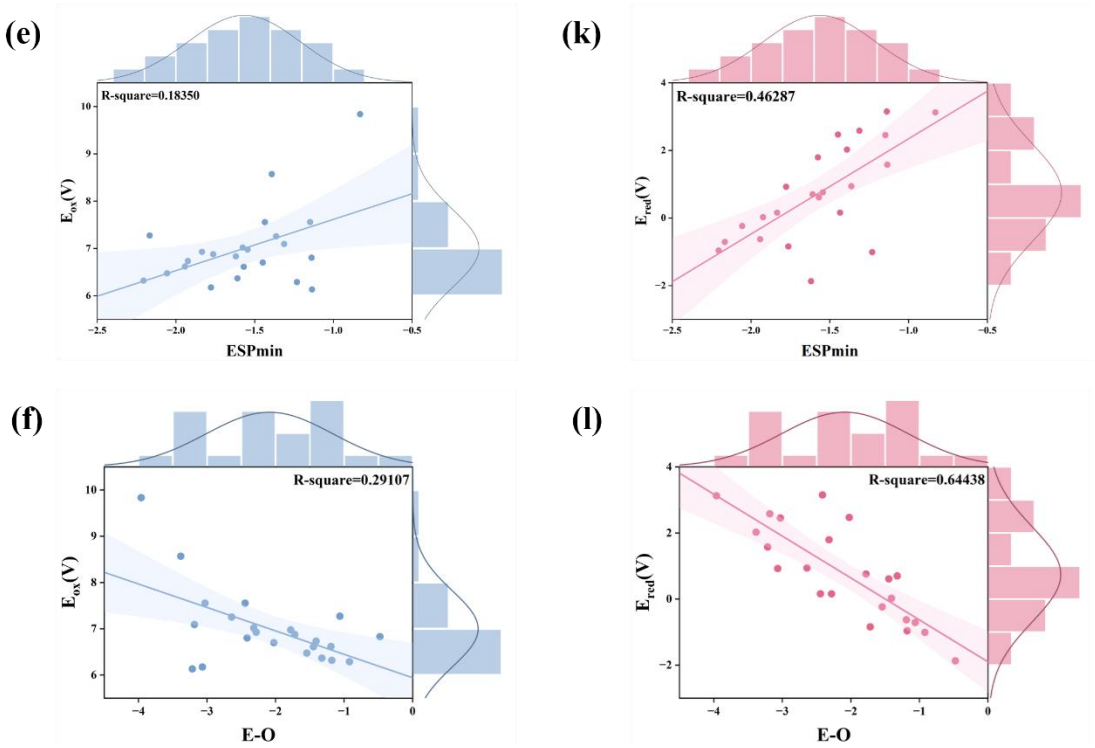


Figure S10. Scatter plots with linear regression of (a) HOMO, (b) LUMO, (c) ALIEmin, (d) ESPmax, (e) ESPmin, and (e) E-O to the oxidation potentials. Panels (g)−(l) show scatter plots with linear regression of them to reduction potentials.

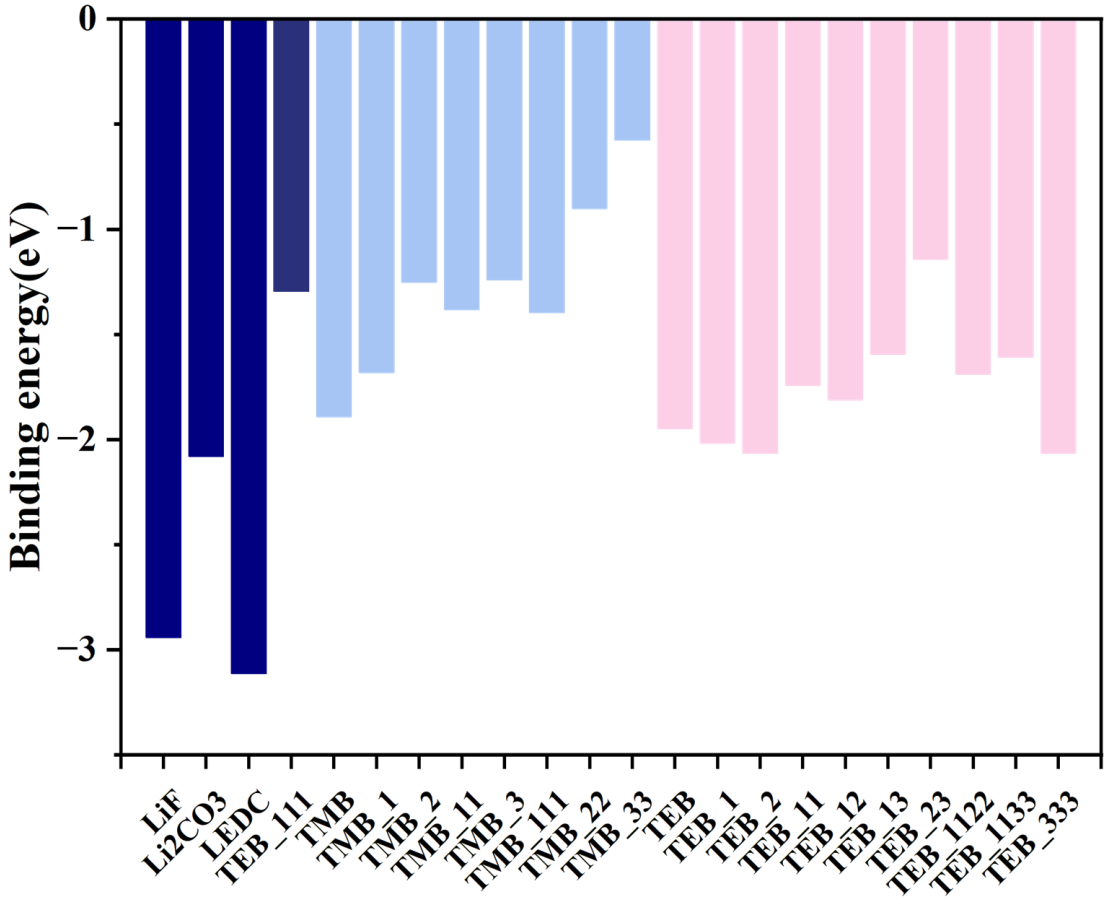


Figure S11. The binding energy of the oxidation decomposition products of each molecule to Li^+ after binding to F.

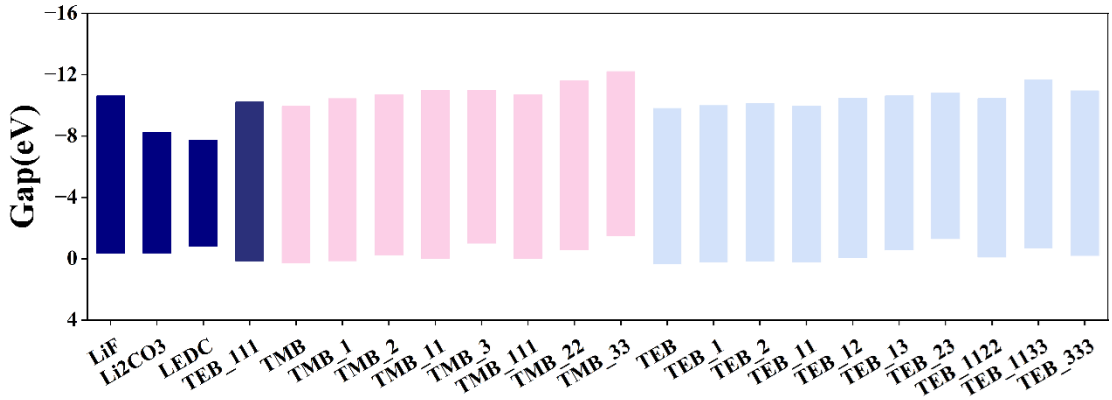


Figure S12. The energy gap of the oxidation decomposition products of each molecule to Li^+ after binding to F.

Table S1. The oxidation and reduction potentials, as well as the frontier molecular orbital energies, of ethylene carbonate (EC), ethyl methyl carbonate (EMC), trimethyl borate (TMB), triethyl borate(TEB), and cyano-modified borate.

Molecule	Number of CN	E^0_{ox}(v) [vs Li/Li$^+$]	E^0_{red}(v) [vs Li/Li$^+$]	ΔE^0_{ox}(v)	ΔE^0_{red}(v)	HUMO (eV)	LUMO (eV)
EC	0	7.27	-0.71	0	0	-10.19	0.43
EMC	0	6.83	-1.87	-0.44	-1.16	-10.13	0.65
TMB	0	6.32	-0.96	-0.95	-0.25	-9.40	0.34
TMB_1	1	6.73	0.02	-0.54	0.73	-9.81	0.14
TMB_2	2	6.98	0.76	-0.29	1.47	-10.02	-0.10
TMB_11	2	6.93	0.16	-0.34	0.87	-10.19	0.09
TMB_3	3	7.02	1.79	-0.25	2.50	-10.16	-0.77
TMB_111	3	7.56	0.16	0.29	0.87	-10.47	-0.10
TMB_22	4	7.26	0.94	-0.01	1.65	-10.66	-0.39
TMB_33	6	7.56	2.45	0.29	3.16	-11.05	-1.28
TMB_222	6	8.57	2.02	1.30	2.73	-11.55	-0.67
TMB_333	9	9.84	3.13	2.57	3.84	-12.24	-1.67
TEB	0	6.29	-1.01	-0.98	-0.30	-9.47	0.34
TEB_1	1	6.47	-0.24	-0.80	0.47	-9.46	0.24
TEB_2	2	6.37	0.70	-0.90	1.41	-9.65	0.20
TEB_11	2	6.62	-0.63	-0.65	0.08	-9.69	0.18
TEB_111	3	6.88	-0.84	-0.39	-0.13	-10.00	0.09
TEB_12	3	6.61	0.61	-0.66	1.32	-9.77	0.01
TEB_13	4	6.70	2.47	-0.57	3.18	-9.87	-0.50
TEB_23	5	6.80	3.15	-0.47	3.86	-10.03	-1.20
TEB_1122	6	6.17	0.92	-1.10	1.63	-10.49	-0.18
TEB_1133	8	7.09	2.58	-0.18	3.29	-10.65	-0.60
TEB_333	9	6.13	1.58	-1.14	2.29	-10.85	-0.25

Table S2. The length of the B-O bond and the O-C bond of each molecule.

Molecule	Number of CN	B-O(1)	O-C(1)	B-O(2)	O-C(2)	B-O(3)	O-C(3)
TMB	0	1.369	1.428	1.369	1.427	1.372	1.427
TMB_1	1	1.360	1.432	1.361	1.432	1.379	1.416
TMB_2	2	1.351	1.434	1.355	1.434	1.396	1.407
TMB_11	2	1.354	1.431	1.380	1.416	1.373	1.414
TMB_3	3	1.349	1.434	1.344	1.433	1.418	1.394
TMB_111	3	1.365	1.422	1.366	1.423	1.365	1.422
TMB_22	4	1.339	1.440	1.378	1.413	1.382	1.413
TMB_33	6	1.328	1.445	1.388	1.409	1.384	1.409
TMB_222	6	1.367	1.419	1.364	1.419	1.365	1.419
TMB_333	9	1.364	1.419	1.365	1.419	1.365	1.419
TEB	0	1.369	1.437	1.368	1.436	1.367	1.437
TEB_1	1	1.364	1.437	1.365	1.436	1.380	1.420
TEB_2	2	1.361	1.439	1.360	1.438	1.390	1.405
TEB_11	2	1.361	1.439	1.372	1.420	1.375	1.421
TEB_111	3	1.367	1.425	1.366	1.425	1.365	1.425
TEB_12	3	1.352	1.444	1.355	1.443	1.396	1.400
TEB_13	4	1.352	1.444	1.347	1.446	1.406	1.387
TEB_23	5	1.340	1.449	1.347	1.447	1.416	1.383
TEB_1122	6	1.344	1.447	1.386	1.402	1.377	1.401
TEB_1133	8	1.336	1.449	1.387	1.396	1.382	1.390
TEB_333	9	1.367	1.404	1.362	1.406	1.365	1.405

Table S3. The length of the B-O bond or the O-C bond of each molecule in the oxidation state

Molecule	Number of CN	B-O(1)	O-C(1)	B-O(2)	O-C(2)	B-O(3)	O-C(3)
TMB	0	1.326	1.441	1.342	1.433	1.454	1.379
TMB_1	1	1.348	1.428	1.419	1.382	1.341	1.432
TMB_2	2	1.413	1.381	1.342	1.429	1.352	1.423
TMB_11	2	1.434	1.388	1.339	1.428	1.337	1.428
TMB_3	3	1.334	1.429	1.407	1.383	1.357	1.422
TMB_111	3	1.433	1.369	1.336	1.432	1.341	1.427
TMB_22	4	1.447	1.349	1.340	1.433	1.338	1.430
TMB_33	6	1.434	1.344	1.344	1.433	1.343	1.434
TMB_222	6	1.417	1.368	1.340	1.429	1.348	1.432
TMB_333	9	1.339	1.427	1.364	1.428	1.420	1.307
TEB	0	1.439	1.378	1.331	1.452	1.346	1.445
TEB_1	1	1.371	1.409	1.395	1.395	1.329	1.441
TEB_2	2	1.345	1.440	1.417	1.381	1.345	1.425
TEB_11	2	1.323	1.458	1.343	1.431	1.464	1.371
TEB_111	3	1.440	1.346	1.341	1.438	1.334	1.435
TEB_12	3	1.418	1.373	1.332	1.447	1.357	1.418
TEB_13	4	1.330	1.449	1.413	1.372	1.365	1.406
TEB_23	5	1.409	1.371	1.323	1.454	1.375	1.402
TEB_1122	6	1.353	1.390	1.385	1.385	1.360	1.410
TEB_1133	8	1.418	1.333	1.345	1.408	1.351	1.406
TEB_333	9	1.359	1.406	1.381	1.383	1.357	1.411

Table S4. The electrostatic potential maximum and minimum values, as well as the Alie maximum and minimum values, of ethylene carbonate (EC), ethyl methyl carbonate (EMC), trimethyl borate (TMB), triethyl borate(TEB), and cyano-modified borate.

Molecule	Number of CN	ESP(min\eV)	ESP(max\eV)	Alie(min\eV)	Alie(max\eV)
EC	0	-2.17	2.24	12.01	18.46
EMC	0	-1.62	0.93	12.37	17.28
TMB	0	-2.21	1.10	11.82	17.11
TMB_1	1	-1.92	1.33	12.26	17.35
TMB_2	2	-1.55	1.89	12.51	17.46
TMB_11	2	-1.84	2.36	12.28	17.53
TMB_3	3	-1.58	2.36	12.69	17.56
TMB_111	3	-1.44	1.89	12.40	17.59
TMB_22	4	-1.36	2.48	12.85	17.88
TMB_33	6	-1.15	2.70	13.26	17.74
TMB_222	6	-1.39	3.17	12.93	18.23
TMB_333	9	-0.83	3.65	13.48	17.27
TEB	0	-1.23	0.56	11.89	15.89
TEB_1	1	-2.06	1.23	11.90	16.15
TEB_2	2	-1.61	1.92	12.02	17.21
TEB_11	2	-1.94	1.61	12.10	16.36
TEB_111	3	-1.76	1.86	12.13	16.31
TEB_12	3	-1.57	2.79	12.33	17.52
TEB_13	4	-1.45	2.42	12.41	17.15
TEB_23	5	-1.14	2.23	12.55	17.32
TEB_1122	6	-1.78	3.77	12.62	17.66
TEB_1133	8	-1.31	3.65	12.77	17.25
TEB_333	9	-1.14	3.00	13.02	17.28

Table S5. The binding energies of ethylene carbonate (EC), ethyl methyl carbonate (EMC), trimethyl borate (TMB), triethyl borate (TEB), and cyano-modified borate with Li^+, F^-, HF, O_2^-.

Molecule	Number of CN	Binding energy of Li^+ (eV)	Binding energy of F^- (eV)	Binding energy of HF (eV)	Binding energy of O_2^- (eV)
LIDFOB	0	-5.96	/	-0.54	/
TMSB	0	-2.21	-1.87	-0.36	-1.40
ADN	2	-1.88	-1.20	-0.36	-1.08
EC	0	-2.21	-1.03	-0.23	-1.06
EMC	0	-2.01	-0.55	-0.37	-0.48
TMB	0	-2.53	-0.71	-0.36	-1.18
TMB_1	0	-1.71	-1.89	-0.27	-1.41
TMB_2	1	-1.20	-2.31	-0.25	-1.78
TMB_11	1	-3.20	-1.52	-0.34	-2.28
TMB_3	2	-1.30	-1.27	-0.47	-2.32
TMB_111	2	-1.06	-2.16	-0.40	-2.45
TMB_22	2	-1.46	-3.25	-0.27	-2.64
TMB_33	2	-0.57	-3.74	-0.20	-3.03
TMB_222	3	-2.46	-4.13	-0.26	-3.38
TMB_333	3	-1.63	-1.89	-0.21	-3.96
TEB	3	-1.95	-1.30	-0.36	-0.92
TEB_1	3	-2.27	-0.90	-0.34	-1.55
TEB_2	4	-2.45	-0.96	-0.33	-1.33
TEB_11	4	-1.87	-2.56	-0.30	-1.19
TEB_111	5	-0.95	-2.60	-0.20	-1.72
TEB_12	6	-1.98	-2.26	-0.28	-1.45
TEB_13	6	-1.77	-2.51	-0.22	-2.03
TEB_23	6	-1.23	-2.85	-0.22	-2.42
TEB_1122	8	-2.74	-3.86	-0.58	-3.07
TEB_1133	9	-2.62	-2.49	-0.35	-3.18
TEB_333	9	-0.99	-3.78	-0.47	-3.22

Table S6. The contributions of cyano group and atom B, O, C, and H to the HOMO orbitals.

Molecule	Number of CN	B(HOMO\%)	O(HOMO\%)	C(HOMO\%)	-CN(HOMO\%)	H(HOMO\%)
TMB	0	5.333	62.247	15.109	/	17.311
TMB_1	1	5.587	60.868	15.496	0.262	17.787
TMB_2	2	5.613	59.953	16.041	0.097	18.296
TMB_11	2	5.036	52.275	16.460	8.760	17.469
TMB_3	3	5.516	56.645	17.454	1.820	18.565
TMB_111	3	4.069	45.148	19.664	14.799	16.320
TMB_22	4	6.085	55.566	17.129	3.087	18.133
TMB_33	6	6.357	51.321	18.720	4.230	19.372
TMB_222	6	1.126	11.359	9.856	69.429	8.230
TMB_333	9	0.264	3.050	1.801	94.885	/
TEB	0	4.979	54.781	18.770	/	21.470
TEB_1	1	4.812	55.055	19.844	0.213	20.076
TEB_2	2	4.863	51.500	22.366	2.155	19.116
TEB_11	2	4.854	57.271	18.529	1.140	18.206
TEB_111	3	5.019	55.566	18.413	0.667	20.335
TEB_12	3	4.829	52.209	24.204	0.234	18.524
TEB_13	4	4.808	51.318	24.675	0.204	18.995
TEB_23	5	4.606	48.311	21.824	1.053	24.206
TEB_1122	6	4.186	40.331	24.681	6.945	23.857
TEB_1133	8	4.710	38.775	27.607	2.338	26.570
TEB_333	9	3.763	42.119	21.783	24.809	7.526

Table S7. The contributions of cyano group and atom B, O, C, and H to the LUMO orbitals.

Molecule	Number of CN	B(LUMO\%)	O(LUMO\%)	C(LUMO\%)	-CN(LUMO\%)	H(LUMO\%)
TMB	0	27.215	9.276	15.799	/	47.710
TMB_1	1	18.222	7.856	13.883	17.057	42.982
TMB_2	2	10.541	9.101	13.154	52.851	14.353
TMB_11	2	21.618	9.105	12.960	26.769	29.548
TMB_3	3	3.426	10.962	13.133	71.923	0.556
TMB_111	3	16.611	7.489	12.849	28.695	34.356
TMB_22	4	8.077	10.800	14.117	57.616	9.390
TMB_33	6	3.100	11.578	14.451	70.296	0.575
TMB_222	6	6.490	11.850	14.974	59.362	7.324
TMB_333	9	3.473	12.310	69.063	15.154	/
TEB	0	20.285	5.164	15.793	/	58.758
TEB_1	1	18.088	5.207	14.248	12.648	49.773
TEB_2	2	9.187	4.042	12.431	38.140	36.200
TEB_11	2	17.792	5.232	14.144	14.025	48.807
TEB_111	3	14.292	4.063	14.048	15.821	51.785
TEB_12	3	6.028	3.667	13.751	55.273	21.281
TEB_13	4	1.162	2.073	22.556	71.972	2.237
TEB_23	5	0.600	3.278	25.570	70.154	0.398
TEB_1122	6	9.704	5.149	12.062	51.265	21.820
TEB_1133	8	0.688	2.099	23.452	71.839	1.922
TEB_333	9	3.808	2.795	13.557	62.076	17.764

Table S8. The symmetry-adapted perturbation theory (SAPT) energy decomposition results of the binding energies of F^- and all molecules.

Molecule	Number of CN	Electrostatics (eV)	Exchange (eV)	Induction (eV)	Dispersion (eV)	Electrostatics (eV)
TMB	0	-1.294	1.176	-0.809	-0.177	-1.294
TMB_1	1	-6.933	6.142	-4.054	-0.614	-6.933
TMB_2	2	-7.424	6.379	-4.302	-0.635	-7.424
TMB_11	2	-2.446	1.821	-1.177	-0.238	-2.446
TMB_3	3	-2.009	1.473	-0.963	-0.204	-2.009
TMB_111	3	-9.987	12.585	-9.198	-0.957	-9.987
TMB_22	4	-8.458	6.650	-4.627	-0.663	-8.458
TMB_33	6	-8.750	6.920	-5.405	-0.659	-8.750
TMB_222	6	-9.426	6.870	-4.906	-0.693	-9.426
TMB_333	9	-7.271	10.071	-6.024	-0.784	-7.271
TEB	0	-6.271	6.115	-4.008	-0.628	-6.271
TEB_1	1	-1.551	1.370	-0.963	-0.286	-1.551
TEB_2	2	-1.696	1.339	-0.956	-0.203	-1.696
TEB_11	2	-7.290	6.349	-4.350	-0.636	-7.290
TEB_111	3	-7.764	6.343	-4.099	-0.665	-7.764
TEB_12	3	-7.555	6.440	-4.364	-0.664	-7.555
TEB_13	4	-7.734	6.527	-4.439	-0.680	-7.734
TEB_23	5	-7.883	6.749	-5.123	-0.634	-7.883
TEB_1122	6	-8.550	6.884	-5.364	-0.838	-8.550
TEB_1133	8	-3.827	2.816	-1.951	-0.347	-3.827
TEB_333	9	-9.059	6.926	-4.848	-0.742	-9.059

Table S9. The symmetry-adapted perturbation theory (SAPT) energy decomposition results of the binding energies of HF and all molecules.

Molecule	Number of CN	Electrostatics (eV)	Exchange (eV)	Induction (eV)	Dispersion (eV)	Electrostatics (eV)
TMB	0	-0.671	0.569	-0.287	-0.126	-0.671
TMB_1	1	-0.584	0.619	-0.299	-0.148	-0.584
TMB_2	2	-0.447	0.421	-0.224	-0.120	-0.447
TMB_11	2	-0.541	0.508	-0.246	-0.118	-0.541
TMB_3	3	-0.401	0.398	-0.207	-0.118	-0.401
TMB_111	3	-0.553	0.500	-0.264	-0.141	-0.553
TMB_22	4	-0.486	0.414	-0.208	-0.159	-0.486
TMB_33	6	-0.406	0.345	-0.145	-0.171	-0.406
TMB_222	6	-0.549	0.378	-0.167	-0.187	-0.549
TMB_333	9	-0.456	0.382	-0.141	-0.200	-0.456
TEB	0	-0.763	0.739	-0.373	-0.169	-0.763
TEB_1	1	-0.673	0.608	-0.307	-0.142	-0.673
TEB_2	2	-0.630	0.572	-0.278	-0.165	-0.630
TEB_11	2	-0.625	0.601	-0.287	-0.147	-0.625
TEB_111	3	-0.575	0.691	-0.296	-0.196	-0.575
TEB_12	3	-0.667	0.701	-0.341	-0.170	-0.667
TEB_13	4	-0.356	0.350	-0.166	-0.126	-0.356
TEB_23	5	-0.370	0.384	-0.172	-0.134	-0.370
TEB_1122	6	-0.821	0.795	-0.411	-0.224	-0.821
TEB_1133	8	-0.616	0.639	-0.287	-0.190	-0.616
TEB_333	9	-0.567	0.557	-0.270	-0.152	-0.567

Table S10. The binding energies of TEB_1122, TEB_333, TMB_33, and TMB_22 with F^-, and the activation energy barriers of their side reactions with F^-.

Molecule	Number of CN	Binding energy of F^- (eV)	activation energy barrier (kcal/mol)
TEB_1122	6	-3.86	0.8422
TEB_333	9	-3.78	0.0015
TMB_33	6	-3.74	0.5594
TMB_22	4	-3.25	42.0266

Table S11. The binding energies of TMB_333, TMB_222, and TEB_333 with O_2^-, and the activation energy barriers of their side reactions with O_2^-.

Molecule	Number of CN	Binding energy of O_2^- (eV)	activation energy barrier (kcal/mol)
TMB_333	9	-3.96	0.0006
TMB_222	6	-3.38	0.6804
TEB_333	9	-3.22	60.1432

Table S12. The number of lithium salts and solvents used in molecular dynamics calculations.

Molecule	Number of CN	Li	FSI	number
TMB	0	15	15	507
TMB_1	1	15	15	409
TMB_2	2	15	15	342
TMB_11	2	15	15	342
TMB_3	3	15	15	294
TMB_111	3	15	15	294
TMB_22	4	15	15	258
TMB_222	6	15	15	207
TMB_33	6	15	15	207
TMB_333	9	15	15	160

Table S13. Table of the coordination number of lithium ions and FSI^- as well as the Li^+ transference number.

Molecule	Number of CN	Li-O_FSI	t_{Li}
TMB	0	4.48	0.486
TMB_1	1	4.45	0.428
TMB_2	2	4.25	0.489
TMB_11	2	4.38	0.496
TMB_3	3	4.23	0.483
TMB_111	3	4.31	0.493
TMB_22	4	4.42	0.482
TMB_222	6	4.3	0.517
TMB_33	6	4.22	0.496
TMB_333	9	4.16	0.437

Table S14. Table of the coordination number of lithium ions and PF_6^- as well as the Li^+ transference number.

Molecule	Number of CN	Li-F_ PF_6^-	t_{Li}
TMB	0	0.143	1.13
TMB_1	1	0.149	0.728
TMB_3	3	0.153	0.771
TMB_22	4	0.272	0.996
TMB_333	9	0.15	0.686

Table S15. List of the descriptors.

Descriptor	Name	unit
NCN	Number of nitrile groups	
Eox	Oxidation potential	V
Ered	Reduction potential	V
HOMO	Highest occupied orbital energy	eV
LUMO	Lowest of unoccupied orbital energy	eV
ESPmax	Maximum electrostatic potential	eV
ESPmin	Minimum electrostatic potential	eV
ALIEmax	Maximum average local ionization energy	eV
ALIEmin	Minimum average local ionization energy	eV
MPI	Molecular polarity index	eV
DM	Dipole moment	Debye
E-Li	Binding energy of Li^+	eV
E-O	Binding energy of O_2^-	eV
E-HF	Binding energy of HF	eV
E-F	Binding energy of F^-	eV

Table S16. The HOMO, LUMO, energy gap size, and binging energy of Li^+ of the B-F products after oxidative decomposition.

Molecule	Number of CN	HOMO(eV)	LUMO(eV)	Gap(eV)	Binding energy of Li^+ (eV)
LiF	0	-10.61	-0.33	10.28	-2.942
Li_2CO_3	0	-8.22	-0.37	7.85	-2.081
LEDC	0	-7.73	-0.78	6.94	-3.113
TEB_111	3	-10.21	0.16	10.37	-1.294
TMB	0	-9.94	0.30	10.24	-1.891
TMB_1	1	-10.43	0.14	10.58	-1.681
TMB_2	2	-10.68	-0.22	10.45	-1.252
TMB_11	2	-10.96	0.00	10.96	-1.381
TMB_3	3	-10.96	-1.00	9.96	-1.241
TMB_111	3	-10.71	-0.02	10.69	-1.396
TMB_22	4	-11.61	-0.56	11.05	-0.903
TMB_33	6	-12.19	-1.49	10.71	-0.575
TEB	0	-9.80	0.35	10.15	-1.947
TEB_1	1	-9.98	0.22	10.19	-2.019
TEB_2	2	-10.12	0.18	10.30	-2.064
TEB_11	2	-9.94	0.25	10.19	-1.742
TEB_12	3	-10.21	0.16	10.37	-1.294
TEB_13	4	-10.47	-0.06	10.40	-1.811
TEB_23	5	-10.61	-0.56	10.04	-1.593
TEB_1122	6	-10.82	-1.28	9.53	-1.144
TEB_1133	8	-10.45	-0.09	10.36	-1.689
TEB_333	9	-11.66	-0.66	11.00	-1.608

Table S17. The dipole moments and molecular polarity index of all molecules at the liquid-phase computational level.

Molecule	Number of CN	Molecular polarity index(eV)	Dipole Moment (Debye)
EC	0	1.27	7.476
EMC	0	0.59	0.563
TMB	0	0.64	3.829
TMB_1	1	0.68	5.225
TMB_2	2	0.74	6.082
TMB_11	2	1.12	7.551
TMB_3	3	0.82	8.479
TMB_111	3	1.08	0.358
TMB_22	4	0.94	5.701
TMB_33	6	0.78	5.626
TMB_222	6	1.04	6.495
TMB_333	9	0.80	0.069
TEB	0	0.29	0.004
TEB_1	1	0.70	7.316
TEB_2	2	0.68	5.162
TEB_11	2	0.88	2.351
TEB_111	3	1.06	0.003
TEB_12	3	0.69	4.922
TEB_13	4	0.65	6.543
TEB_23	5	0.60	6.174
TEB_1122	6	1.23	15.847
TEB_1133	8	0.93	9.248
TEB_333	9	0.95	6.642

Table S18. The energy gap, minimum electrostatic potential, binding energy of Li^+, molecular polarity index of ethylene carbonate (EC), propylene carbonate (PC), ethyl methyl carbonate (EMC), diethyl carbonate (DC), ethyl acetate (EA) and candidate solvent molecules.

Molecule	Number of CN	Energy Gap(eV)	ESP(min\eV)	Binding energy of Li^+ (eV)	Molecular polarity index(eV)
EC	0	10.62	-2.17	-2.21	1.27
PC	0	10.72	-2.19	-2.25	1.15
EMC	0	10.77	-1.62	-2.01	0.59
DEC	0	10.69	-1.65	-2.06	0.54
EA	0	10.33	-1.84	-2.08	0.56
TMB_11	2	10.28	-1.84	-3.20	1.12
TMB_111	3	10.38	-1.44	-1.06	1.08
TMB_222	6	10.88	-1.39	-2.46	1.04
TMB_333	9	10.56	-0.83	-1.63	0.80
TEB_111	3	10.09	-1.76	-0.95	1.06