

Supporting Information

Unexpected Electrochemical Behavior of Crown-Based Organic Compounds for Lithium-Ion Battery Cathodes

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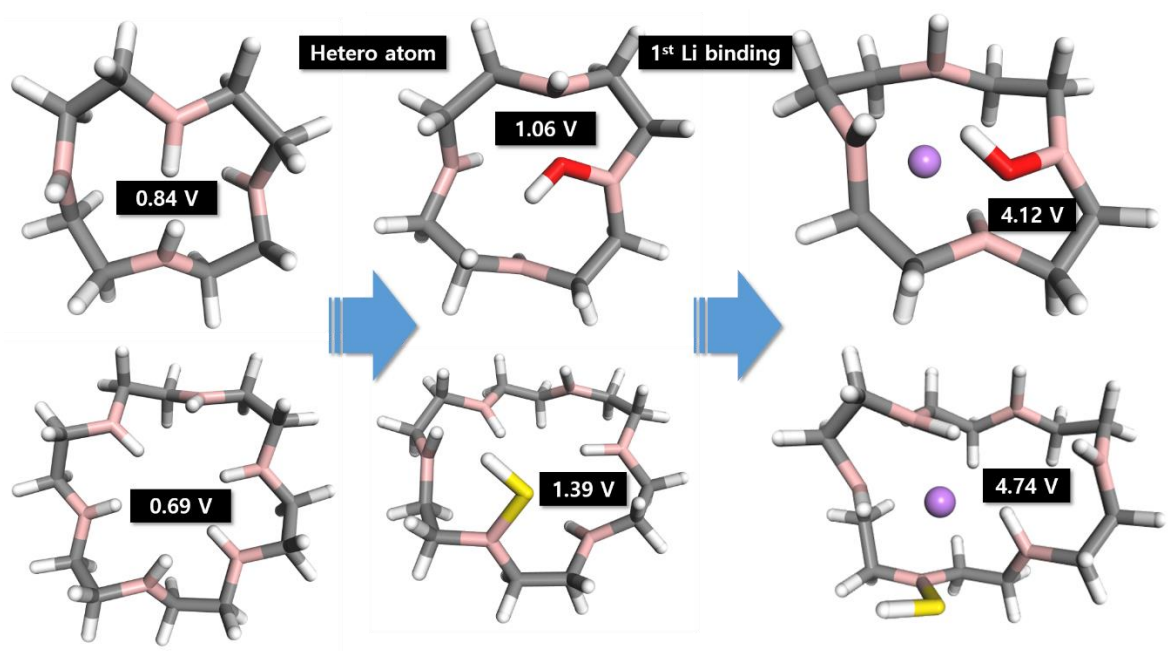


Figure S2. Structural modification of B-crown compounds. Li-induced improvement in the redox potentials of O-incorporated B-crown-4 and S-incorporated B-crown-6 compounds. The atoms in gray, white, red, pink, yellow, and violet depict carbon, hydrogen, oxygen, boron, sulfur, and lithium, respectively.

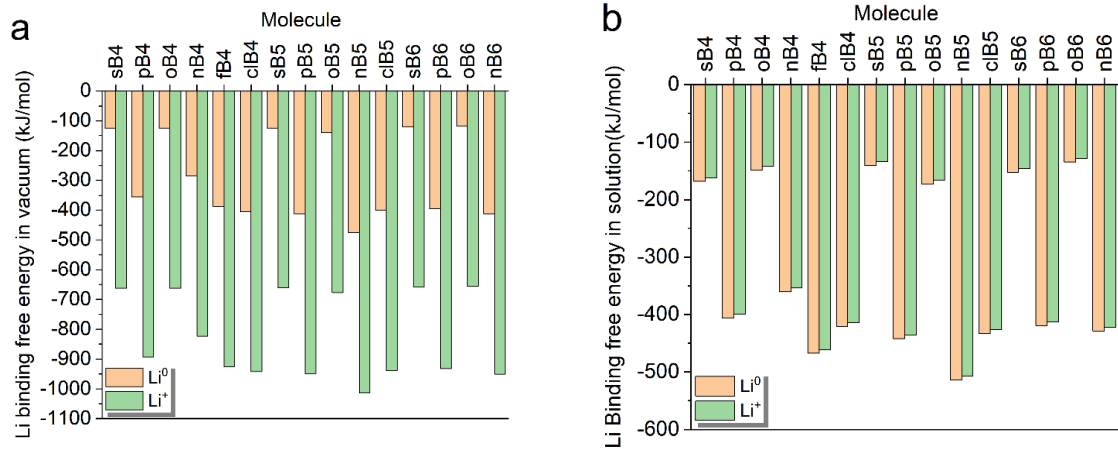


Figure S3. Thermodynamic properties. Binding free energies of *x*-incorporated B-crown-*n* compounds, namely, *x*B*n* (*x*: S, P, O, N, F, Cl; *n*: 4, 5, 6) with the first Li atom in (a) vacuum and (b) solution phase.

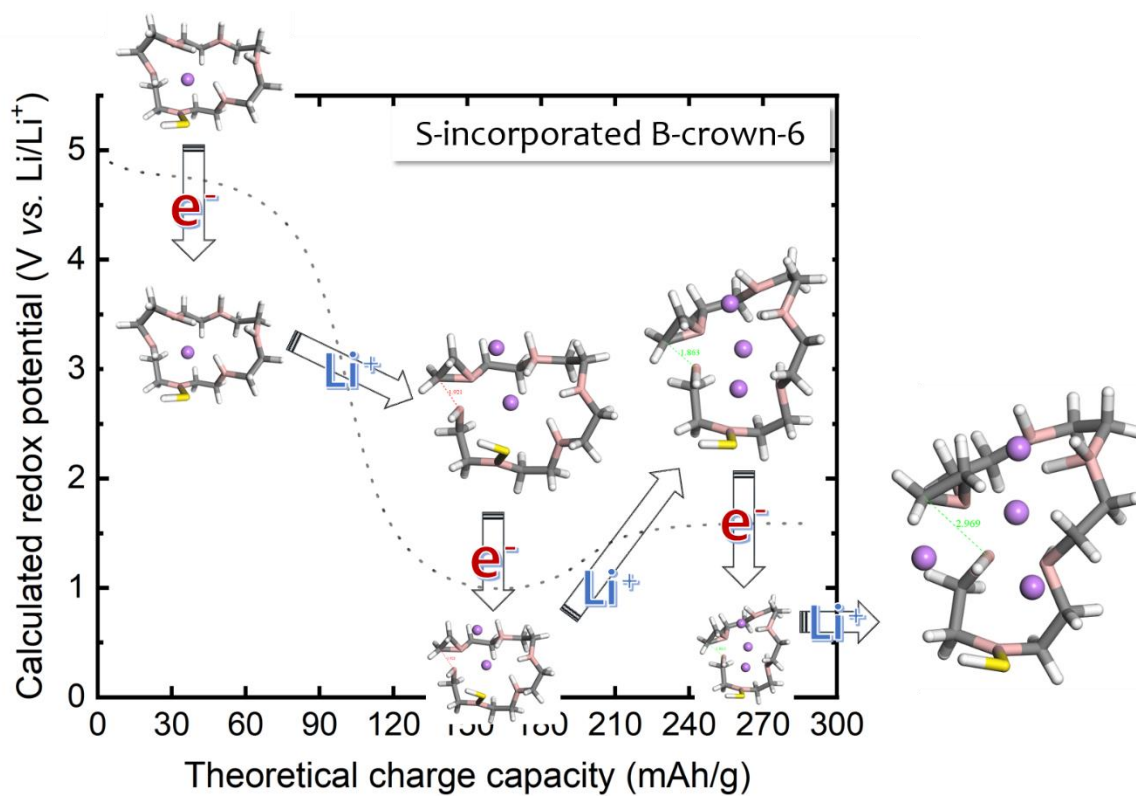


Figure S4. Discharging mechanism. The Li-storage mechanism of *S*-incorporated B-crown-6 during the discharging process.

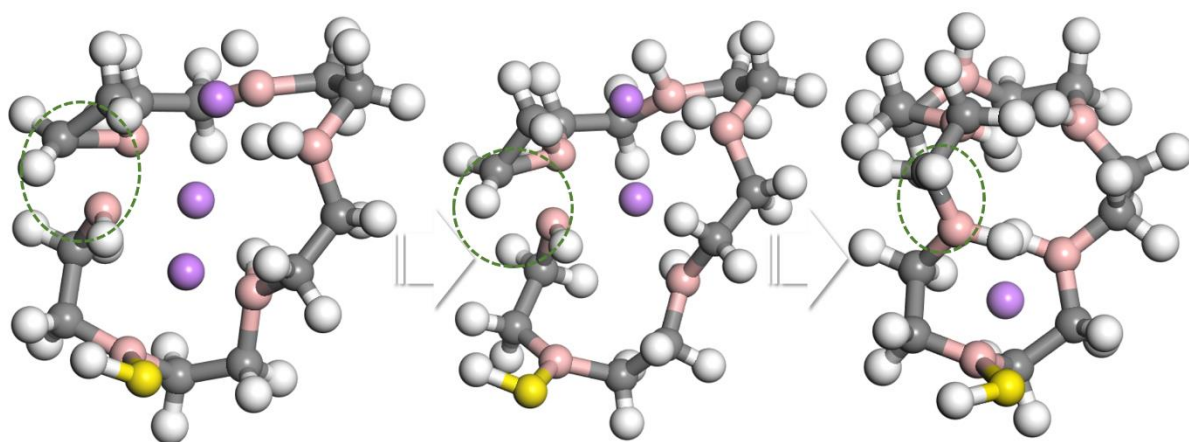


Figure S5. Recharging mechanism. The self-healing mechanism of *S*-incorporated B-crown-6 during the recharging process. The dotted green circle shows a C-B bond broken during the discharging process.

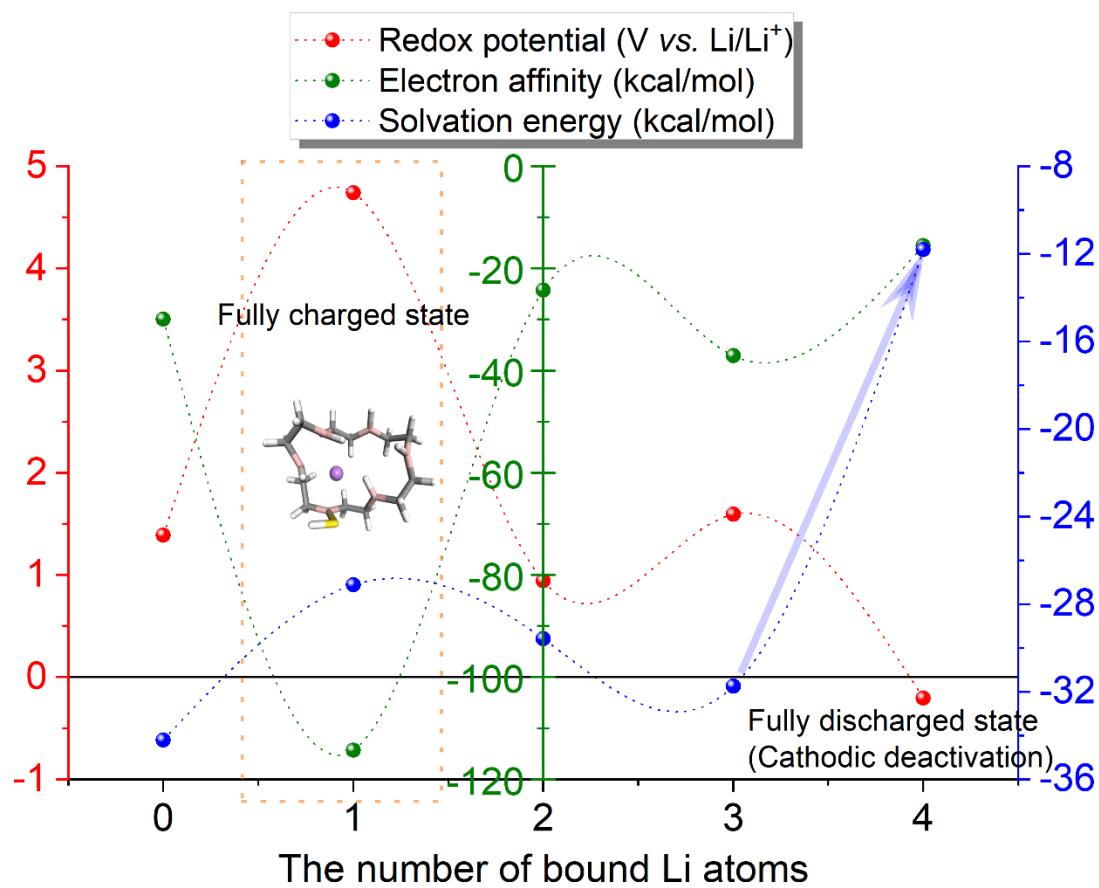


Figure S6. Correlations. Changes in the redox potential, electron affinity, and solvation energy for S-incorporated B-crown-6 during the Li-involved discharging process.

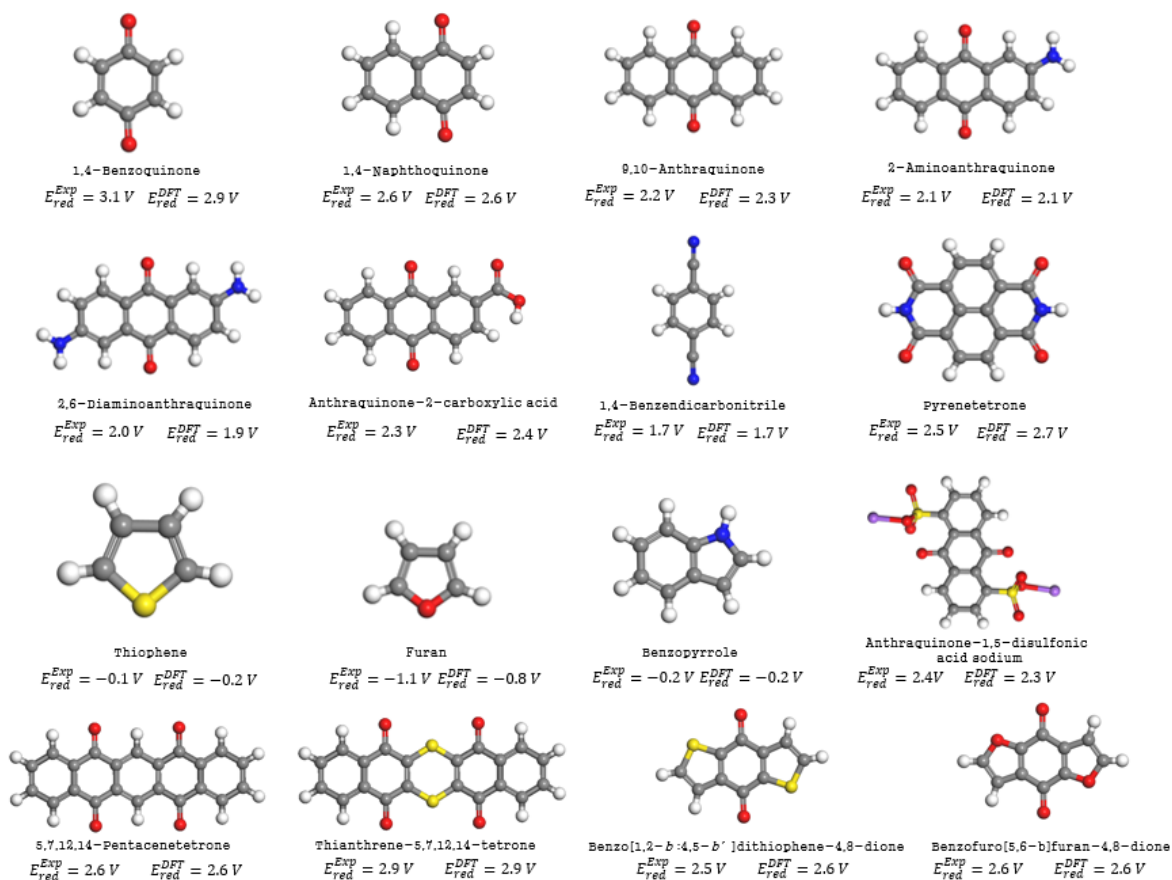


Figure S7. Validation of computational protocol. The chemical structures for eleven organic compounds employed to validate the reliability of the computational protocol. The atoms with gray, white, red, blue, yellow, and purple in color depict carbon, hydrogen, oxygen, nitrogen, sulfur, and sodium, respectively.

Table S1. Redox potentials of designed crown-based compounds (Figure 1) and selected compounds with one bound Li atom.

Molecule (no Li binding)	Redox potential (V vs. Li/Li ⁺)	Molecule (no Li binding)	Redox potential (V vs. Li/Li ⁺)
O-crown-4	-0.78	N-incorporated B-crown-4	3.36
O-crown-5	-0.88	N-incorporated B-crown-5	4.21
O-crown-6	-1.05	N-incorporated B-crown-6	2.98
B-crown-4	0.84	P-incorporated B-crown-4	3.74
B-crown-5	0.57	P-incorporated B-crown-5	3.87
B-crown-6	0.69	P-incorporated B-crown-6	3.33
N-crown-4	-0.63	O-incorporated B-crown-4	1.06
N-crown-5	-0.79	O-incorporated B-crown-5	1.20
N-crown-6	-0.74	O-incorporated B-crown-6	0.85
P-crown-4	-0.50	S-incorporated B-crown-4	1.13
P-crown-5	-0.53	S-incorporated B-crown-5	1.30
P-crown-6	-0.44	S-incorporated B-crown-6	1.39
S-crown-4	-0.67	F-incorporated B-crown-4	3.97
S-crown-5	-0.53	F-incorporated B-crown-5	5.13
S-crown-6	-0.55	F-incorporated B-crown-6	5.18
paired O-crown-4	-0.65	Cl-incorporated B-crown-4	4.35
paired O-crown-5	-0.76	Cl-incorporated B-crown-5	3.87
paired O-crown-6	-0.38	Cl-incorporated B-crown-6	5.04
1Li-involved molecule (promising candidacy)	Redox potential (V vs. Li/Li ⁺)	1Li-involved molecule (non-promising candidacy)	Redox potential (V vs. Li/Li ⁺)
O-incorporated B-crown-4	4.12	N-incorporated B-crown-4	-0.41
S-incorporated B-crown-6	4.74	N-incorporated B-crown-5	1.22
		N-incorporated B-crown-6	1.65
		P-incorporated B-crown-4	1.17
		P-incorporated B-crown-5	0.37
		P-incorporated B-crown-6	0.76
		O-incorporated B-crown-5	1.58
		O-incorporated B-crown-6	2.38
		S-incorporated B-crown-4	1.89
		S-incorporated B-crown-5	1.30
		F-incorporated B-crown-4	-0.50
		Cl-incorporated B-crown-4	-0.57
		Cl-incorporated B-crown-5	0.15