Electronic Supplementary Information (ESI) for

Orbital-dependent redox potential regulation of quinone derivatives for electrical energy storage

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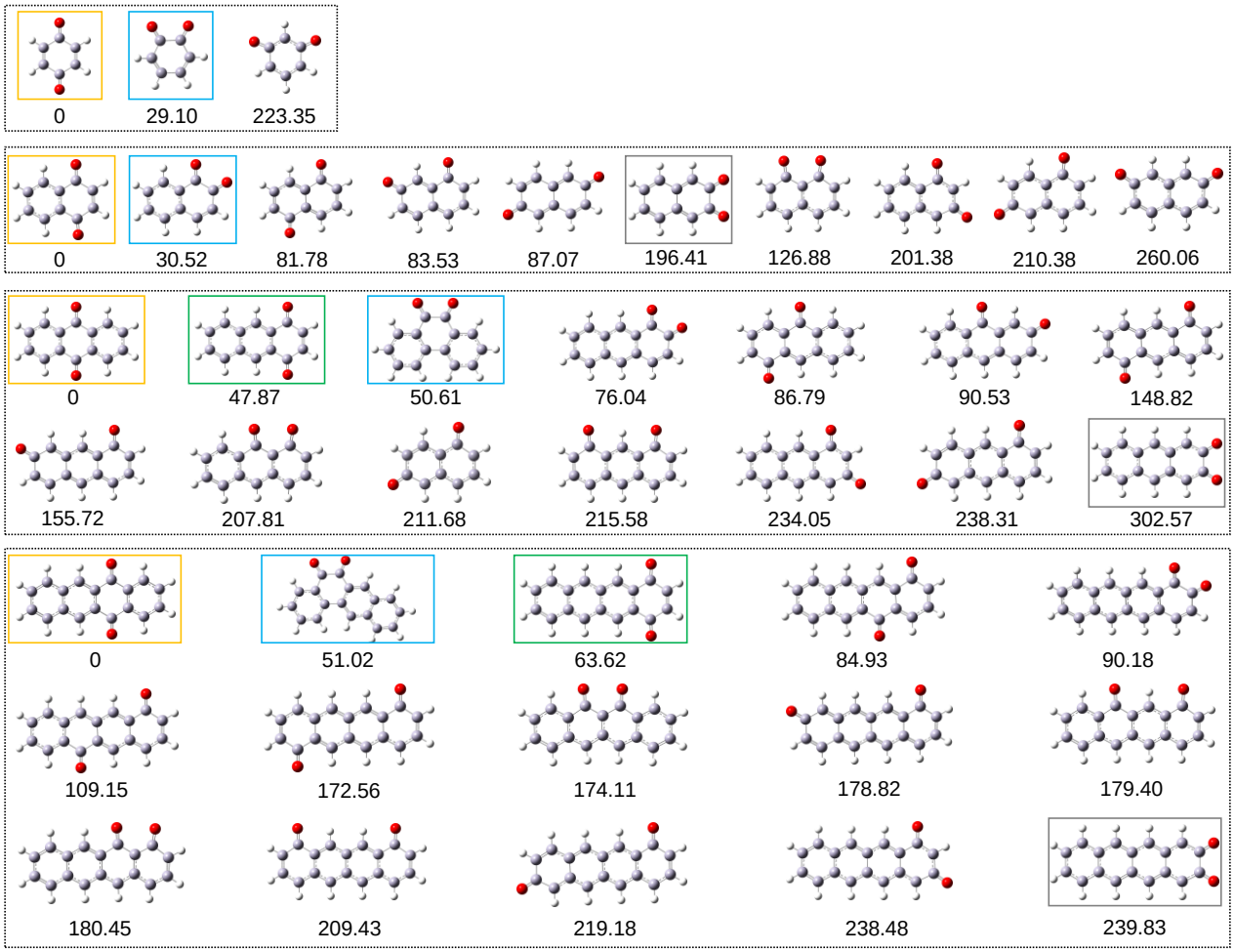


Fig. S1. The total ground state energy of selected quinone derivatives. The values (in kJ·mol^{-1}) stand for the ground state energy difference with respect to the most stable configuration in each panel.

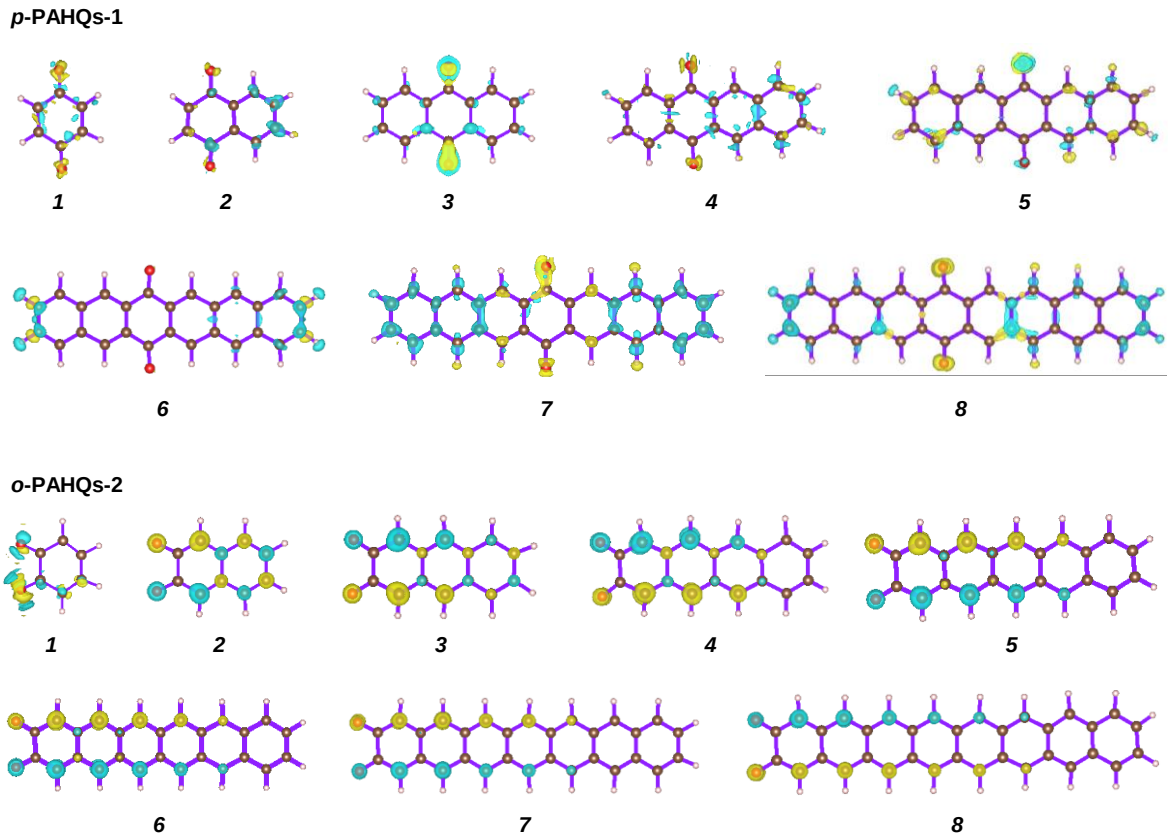


Fig. S2. The spin density isosurface of *p*-PAHQs-1 (isosurface value: 5.05×10^{-8}) and *o*-PAHQs-2 (isosurface value: 2.08×10^{-8} for 1 and 2, 9×10^{-3} for 3–8). For the *p*-PAHQs-1, the distribution of isosurface is not regular and the values can be neglectable, so there are no electron spin of these structures. However, for the *o*-PAHQs-2, the distribution of electron spin density are regular with 10^5 times larger than that of *p*-PAHQs-1, which suggest the *o*-PAHQs-2 exhibit obviously induced magnetism by the strong electron spin.

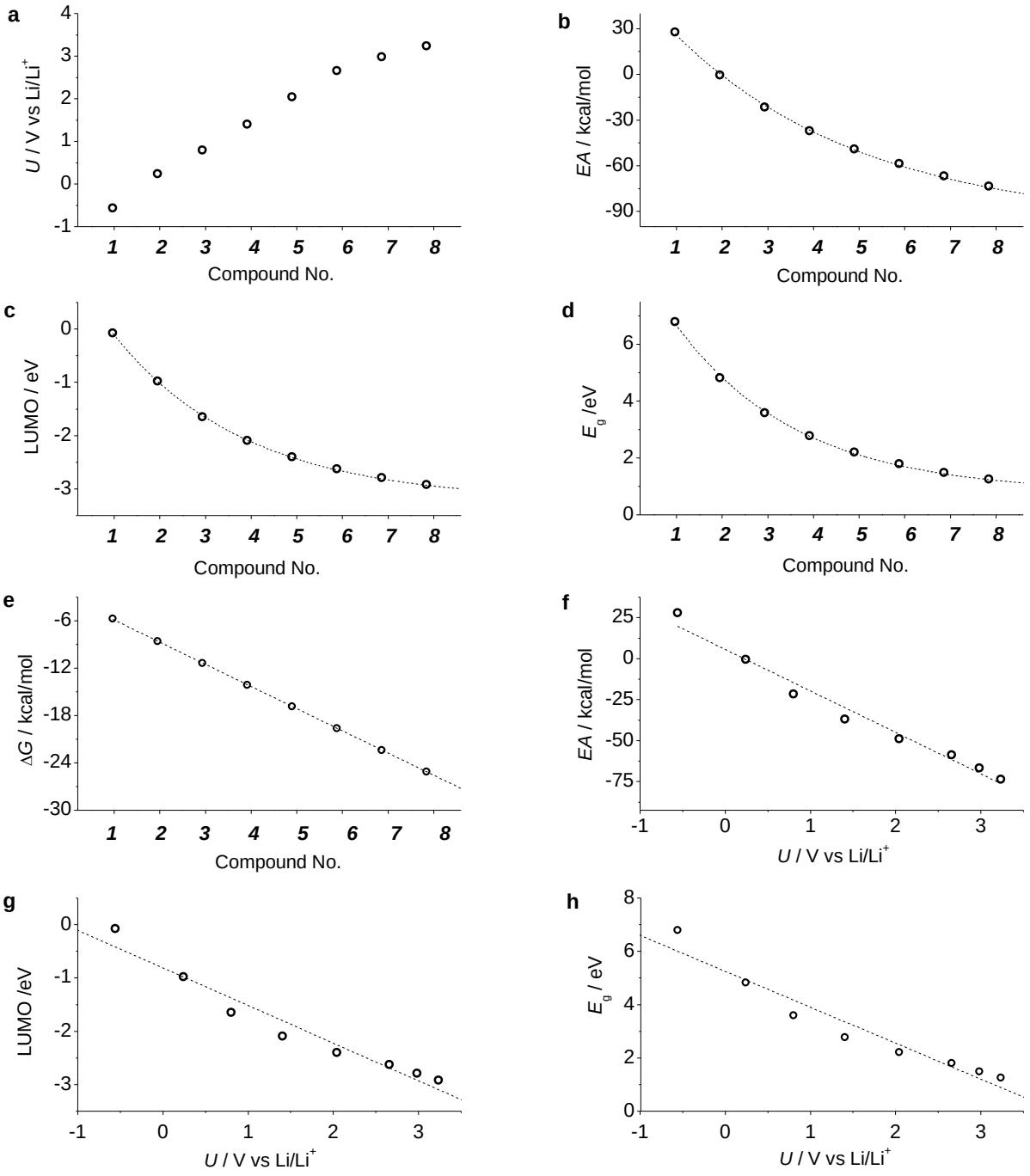


Fig. S3. Selected referential acene derivatives and their electrochemical properties. (a) Calculated redox potential. (b) Electron affinity (*EA*). (c) LUMO energy level. (d) Energy gap (E_g, LUMO-HOMO). (e) Solvation free energy (ΔG). (f) *EA* versus the redox potential. (g) LUMO energy level versus the redox potential. (h) E_g versus the redox potential.

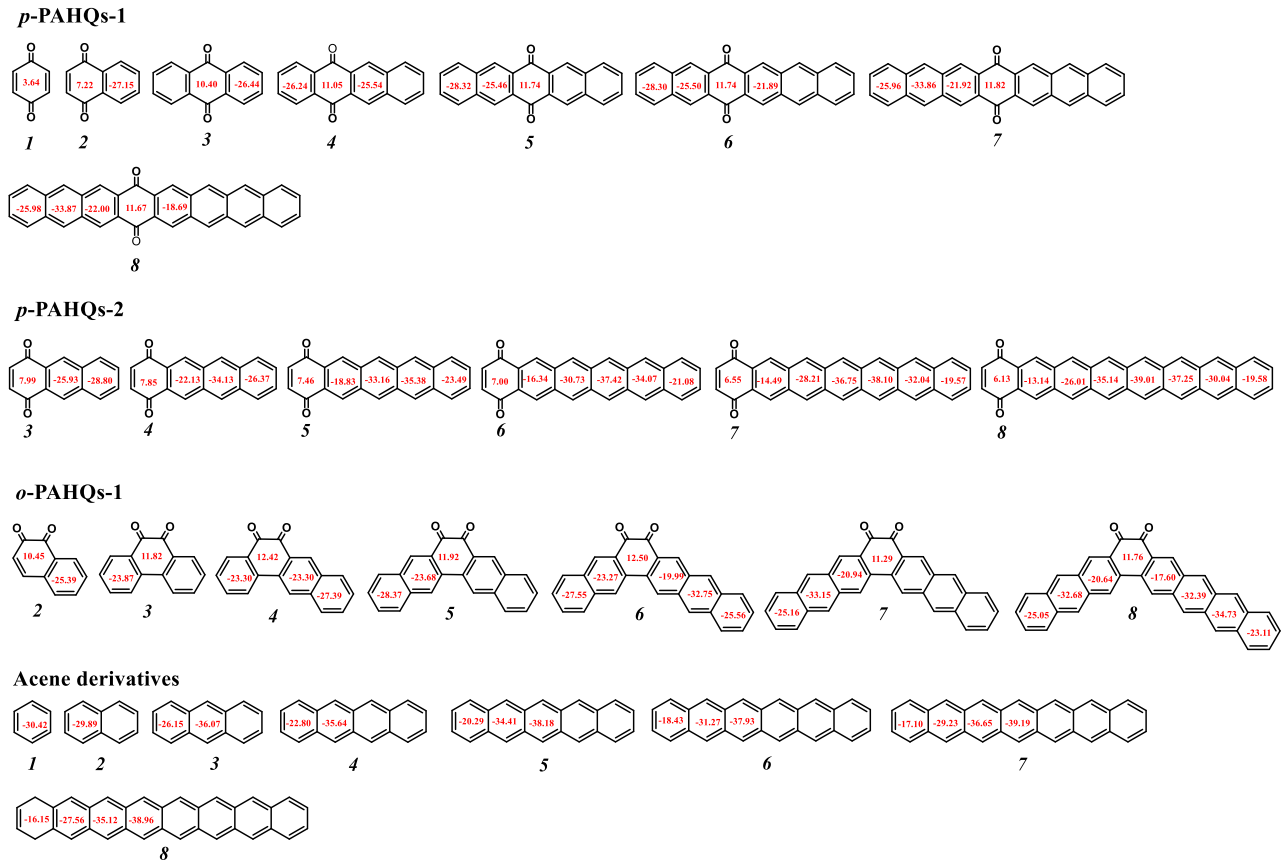


Fig. S4. Selected molecular structures and corresponding NICS values of *p*-PAHQs-1, *p*-PAHQs-2, o-PAHQs-1 and acene derivatives.

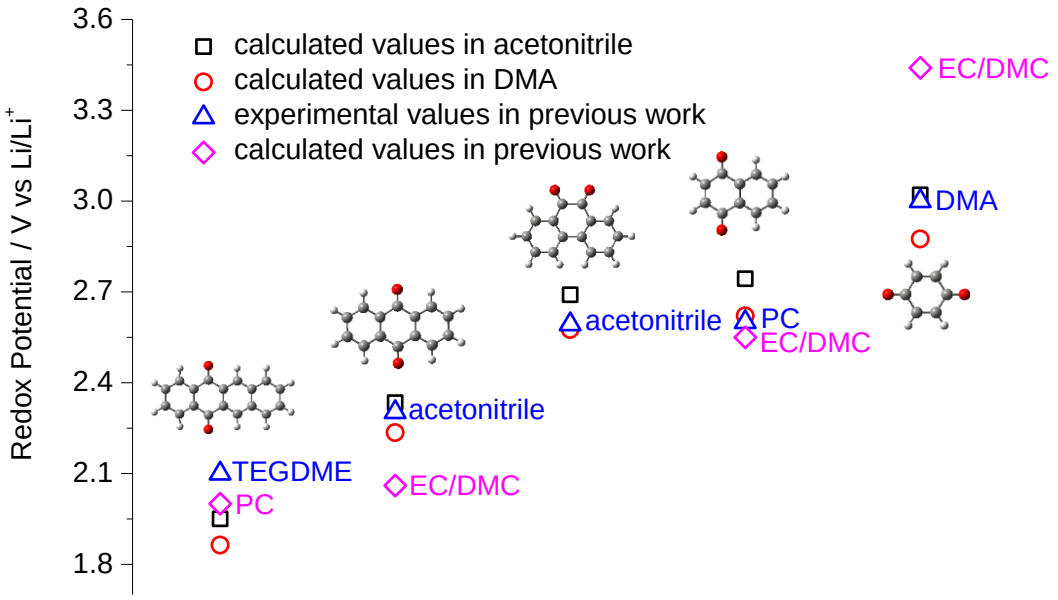


Fig. S5. Comparison of the calculated redox potentials with former calculated and experimental redox potentials of five quinone derivatives. The experimental values and calculated values in previous works are adapted from ref. S1-S3, and ref. S4-S5, respectively.

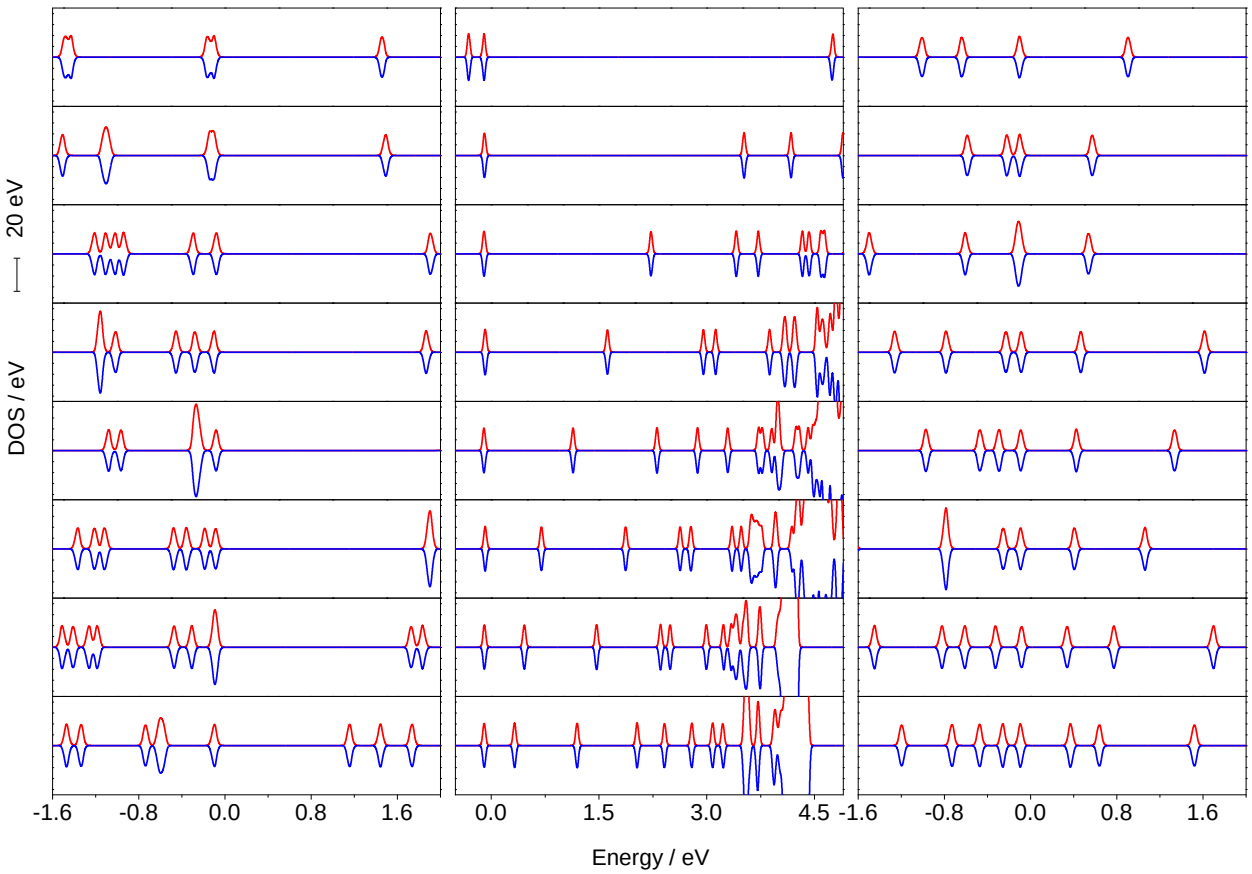


Fig. S6. Calculated total DOS of *p*-PAHQs-1 (left panel), referential benzene derivatives (middle panel), and *o*-PAHQs-2 (right panel).

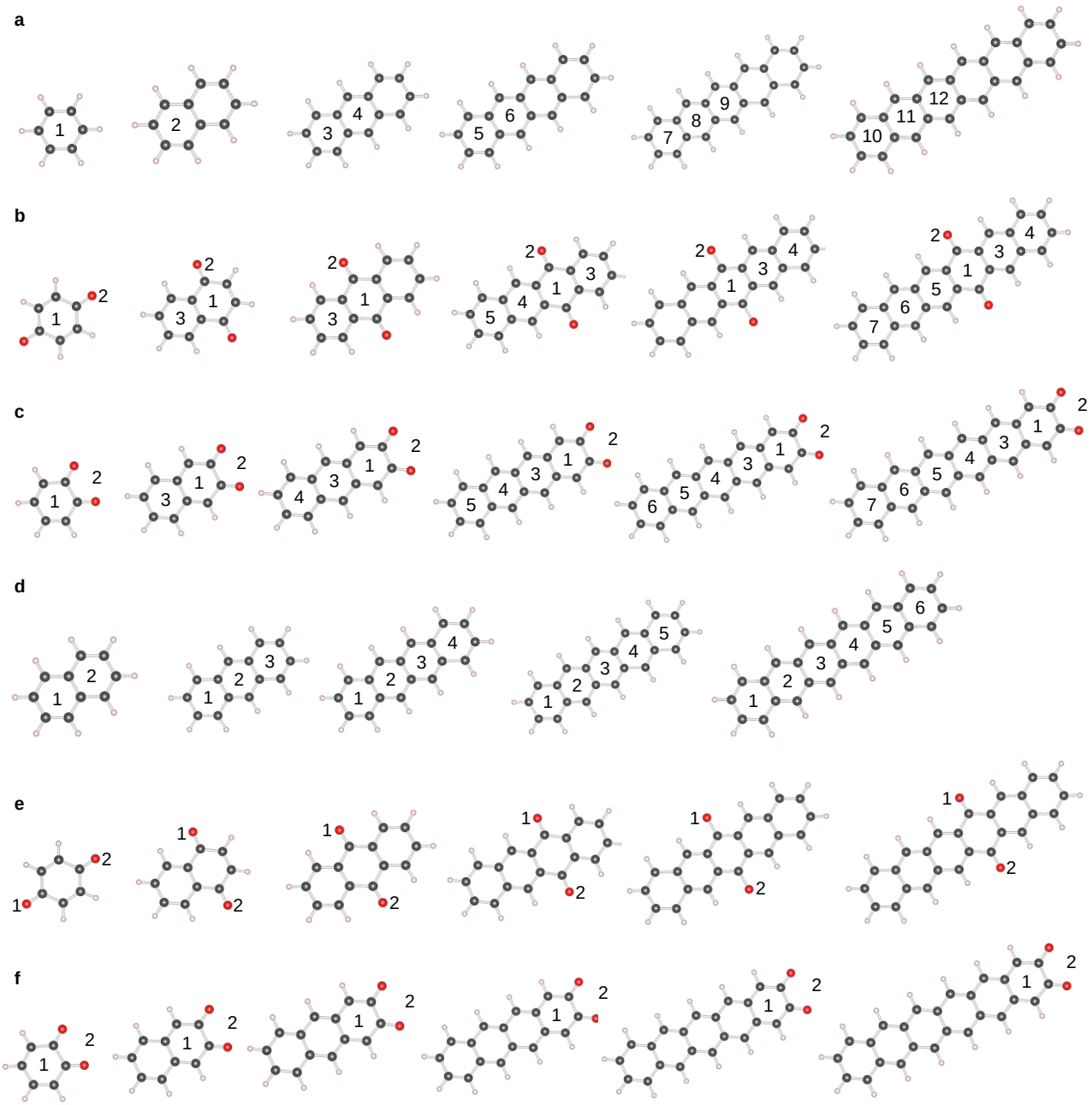


Fig. S7. Possible binding position of Li^+-ion in acene derivatives, *p*-PAHQs-1 and *o*-PAHQs-2. (a–c) one Li^+-ion and (d–f) two Li^+-ions.

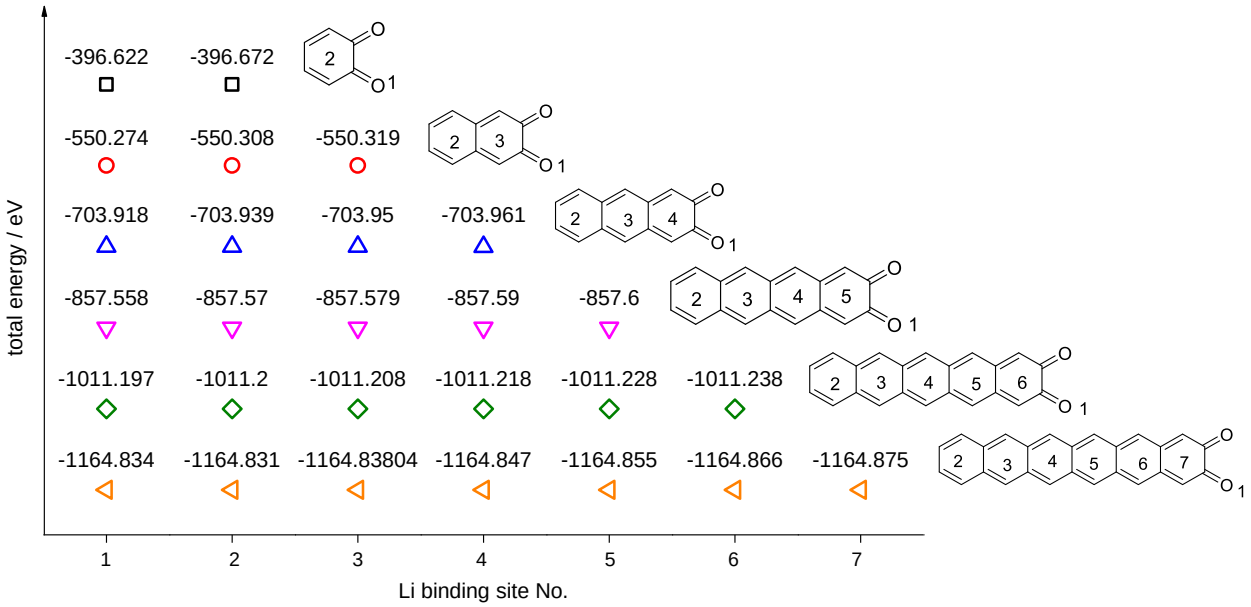


Fig. S8. The total energy of the second Li binding site of *o*-PAHQs-2.

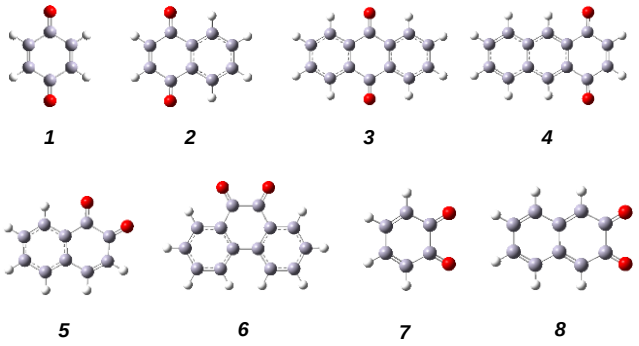
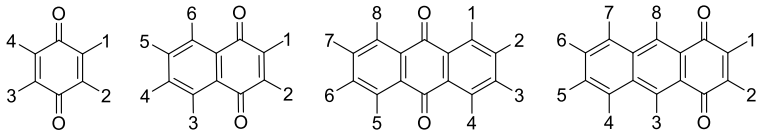


Fig. S9. Selected quinone derivatives used for solvation free energy calculation.

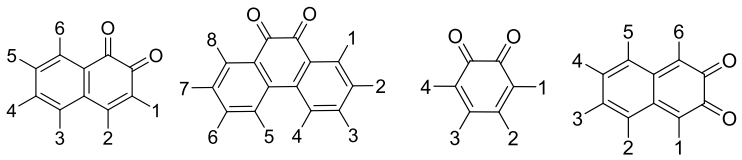
Table S1. Calculated solvation free energy of selected quinone derivatives in acetonitrile and N,N-dimethylacetamide.

	Solvation free energy (G_{solv}, kcal/mol)	
No.	Acetonitrile	N,N-dimethylacetamide
1	-8.57	-9.46
2	-10.24	-10.61
3	-11.89	-11.80
4	-13.00	-13.05
5	-12.56	-12.92
6	-14.49	-15.53
7	-10.32	-11.00
8	-12.99	-13.34

Table. S2. Calculated solvation free energy of molecules modified by functional groups in N,N-dimethylacetamide.



a ***b*** ***c*** ***d***



e ***f*** ***g*** ***h***

R_1 = -OCH2CH2O-, R_2 = -OH, R_3 = -SO3H, R_4 = -COOCH2CH2O-

a									
No	1	2	3	4					G_{solv} (kcal/mol)
1	R_1								**-15.07**
2	R_1		R_1						-16.26
3	R_2								-12.70
4	R_3								**-17.41**
5	R_4								**-15.58**
6	R_4		R_4						**-19.90**

b									
No	1	2	3	4	5	6			G_{solv} (kcal/mol)
1	R_1								-13.87
2			R_1						**-14.00**
3				R_1					-13.62
4	R_1	R_1							-15.81
5			R_1			R_1			**-17.88**
6				R_1	R_1				-15.99
7	R_2								-14.05
8	R_3								**-18.14**
9	R_4								-16.21
10			R_4						**-17.18**
11					R_4				-14.51
12	R_4	R_4							-21.19
13			R_4			R_4			**-21.47**
14				R_4	R_4				-19.74

c									
No.	1	2	3	4	5	6	7	8	G_{solv} (kcal/mol)
1	R_1								**-15.07**
2		R_1							-14.87
3	R_1			R_1					-18.42
4		R_1	R_1						-17.31
5	R_1				R_1				**-19.23**
6		R_1				R_1			-18.03
7	R_2								-15.51
8	R_3								**-19.18**

9	R_4								-16.29
10		R_4							**-16.68**
11	R_4			R_4					**-22.56**
12	R_4				R_4				-21.83
13		R_4	R_4						-20.88
14		R_4				R_4			-19.45

d

No.	1	2	3	4	5	6	7	8	G_{solv} (kcal/mol)
1	R_1								**-16.38**
2								R_1	-14.66
3							R_1		-15.34
4						R_1			-16.08
5	R_1	R_1							-18.06
6			R_1					R_1	-15.97
7				R_1			R_1		**-18.45**
8					R_1	R_1			-18.31
9	R_4								**-18.22**
10								R_4	-17.82
11							R_4		-15.81
12						R_4			-17.31
13	R_4	R_4							-22.49
14			R_4					R_4	-22.11
15				R_4			R_4		-21.30
16					R_4	R_4			**-23.44**

e

No.	1	2	3	4	5	6			G_{solv} (kcal/mol)
1		R_1							-15.41
2						R_1			**-16.27**
3					R_1				-15.78
4			R_1						-15.93
5				R_1	R_1				-18.99
6			R_1			R_1			**-19.24**
7		R_4							-15.69
8						R_4			**-18.22**
9					R_4				-16.37
10			R_4						-16.05
11				R_4	R_4				**-22.45**
12			R_4			R_4			-21.44

f

No.	1	2	3	4	5	6	7	8	G_{solv} (kcal/mol)
1	R_1								-17.54
2		R_1							**-17.91**
3			R_1						-17.13
4	R_1							R_1	-20.64
5		R_1					R_1		-20.44
6			R_1			R_1			**-22.23**
7	R_4								-16.29
8		R_4							**-18.07**
9			R_4						-17.85
10	R_4							R_4	**-26.21**

11		R_4				R_4	-23.50
12			R_4			R_4	-23.64

g

No.	1	2	3	4	G_{solv} (kcal/mol)
1	R_1				-13.95
2		R_1			**-15.98**
3	R_1			R_1	-17.34
4		R_1	R_1		**-18.26**
5	R_4				**-16.18**
6		R_4			-14.94
7	R_4			R_4	**-21.68**
8		R_4	R_4		-19.12

h

No.	1	2	3	4	5	6	G_{solv} (kcal/mol)
1	R_1						-14.62
2		R_1					-15.91
3			R_1				**-18.24**
4	R_1					R_1	-18.37
5		R_1			R_1		-18.32
6			R_1	R_1			**-18.48**
7	R_4						**-19.10**
8		R_4					-17.48
9			R_4				-17.10
10	R_4					R_4	-20.57
11		R_4			R_4		-21.05
12			R_4	R_4			**-23.58**

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