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Structure-electrochemical property relationship of quinone electrodes for lithium-ion batteries†

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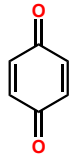
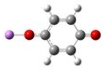
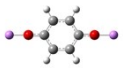
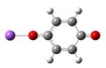
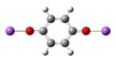
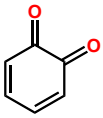
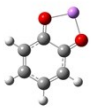
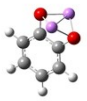
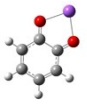
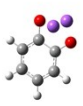
Table S1. The geometries of lithiated, sodiated, and potassiated 20 quinone isomers. The BE (in kcal/mol), and redox potentials (in V) of them. The atoms in gray, white, red, lilac, violet, and modena denote those of carbon, hydrogen, oxygen, lithium, sodium, and potassium, respectively.

	Li		Na		K	
	case 1	**case 2**	**case 1**	**case 2**	**case 1**	**case 2**
 **1,4-BQ** LUMO=**-3.733**						
	BE_1=**-68.6**	BE_2=**-65.3**	BE_1=**-49.6**	BE_2=**-37.1**	BE_1=**-55.5**	BE_2=**-40.1**
	E_1=**2.66**	E_2=**2.45**	E_1=**1.88**	E_2=**1.35**	E_1=**2.17**	E_2=**1.38**
	E=**2.55**		E=**1.61**		E=**1.77**	
 **1,2-BQ** LUMO=**-3.829**						
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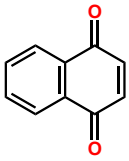
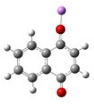
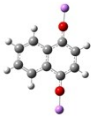
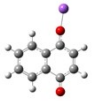
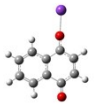
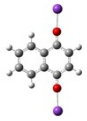
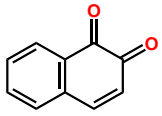
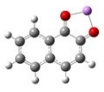
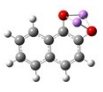
	E_1=**3.67**	E_2=**2.50**	E_1=**2.74**	E_2=**1.58**	E_1=**2.85**	E_2=**1.71**
	E=**3.08**		E=**2.16**		E=**2.28**	
 **1,4-NQ** LUMO=**-3.412**						
	BE_1=**-62.5**	BE_2=**-61.8**	BE_1=**-43.5**	BE_2=**-34.3**	BE_1=**-49.4**	BE_2=**-38.0**
	E_1=**2.38**	E_2=**2.29**	E_1=**1.62**	E_2=**1.22**	E_1=**1.88**	E_2=**1.35**
	E=**2.33**		E=**1.42**		E=**1.61**	
 **1,2-NQ** LUMO=**-3.474**						
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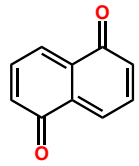
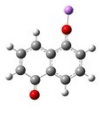
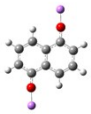
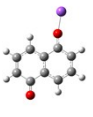
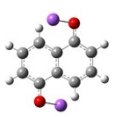
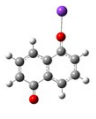
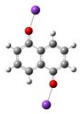
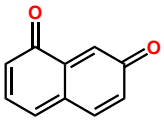
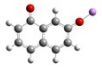
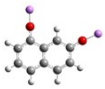
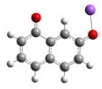
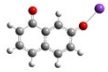
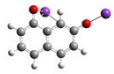
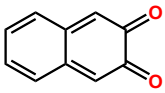
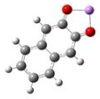
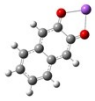
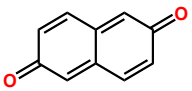
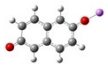
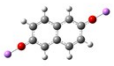
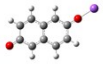
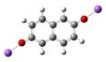
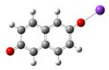
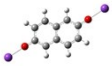
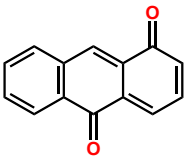
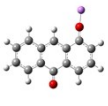
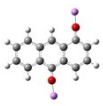
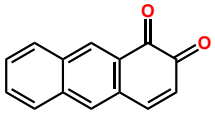
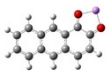
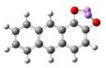
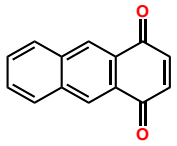
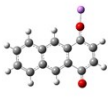
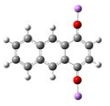
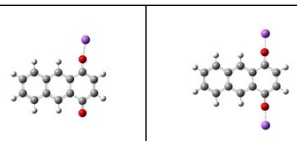
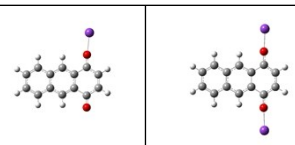
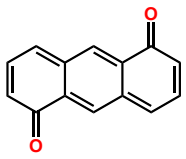
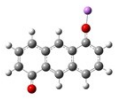
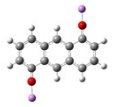
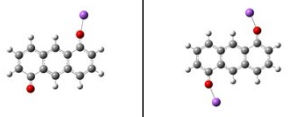
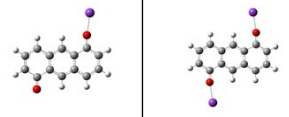
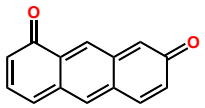
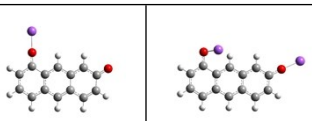
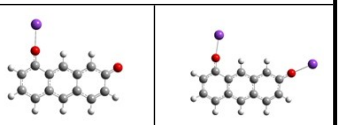
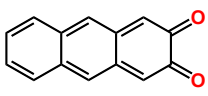
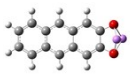
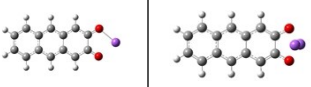
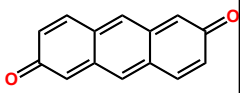
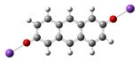
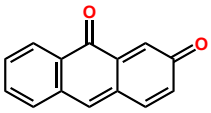
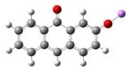
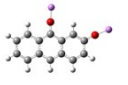
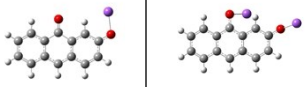
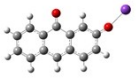
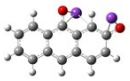
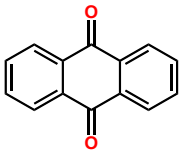
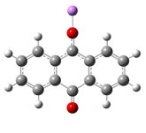
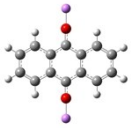
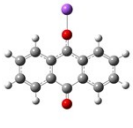
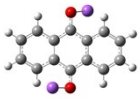
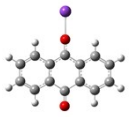
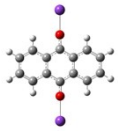
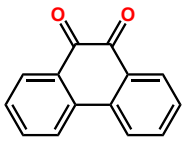
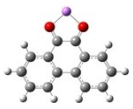
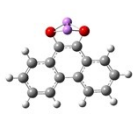
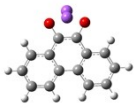
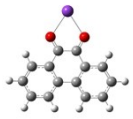
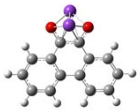
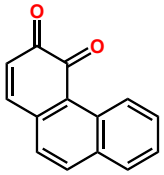
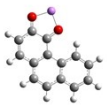
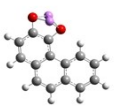
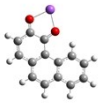
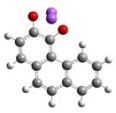
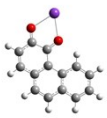
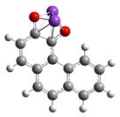
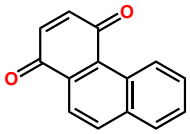
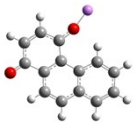
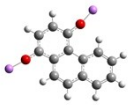
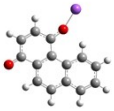
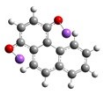
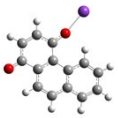
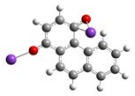
	E_1=**3.39**	E_2=**2.26**	E_1=**2.45**	E_2=**1.39**	E_1=**2.55**	E_2=**1.55**
	E=**2.83**		E=**1.92**		E=**2.05**	

 **1,5-NQ** LUMO=**-4.001**						
	BE_1=**-76.3**	BE_2=**-72.2**	BE_1=**-56.9**	BE_2=**-50.2**	BE_1=**-62.6**	BE_2=**-51.2**
	E_1=**3.00**	E_2=**2.74**	E_1=**2.20**	E_2=**1.74**	E_1=**2.45**	E_2=**1.96**
	E=**2.87**		E=**1.97**		E=**2.20**	
 **1,7-NQ** LUMO=**-3.945**						
	BE_1=**-77.1**	BE_2=**-69.7**	BE_1=**-56.3**	BE_2=**-47.6**	BE_1=**-63.3**	BE_2=**-49.4**
	E_1=**3.01**	E_2=**2.62**	E_1=**2.16**	E_2=**1.68**	E_1=**2.48**	E_2=**1.77**
	E=**2.82**		E=**1.92**		E=**2.12**	
 **2,3-NQ** LUMO=**-4.124**						
	BE_1=**-99.8**	BE_2=**-73.1**	BE_1=**-77.7**	BE_2=**-52.7**	BE_1=**-79.7**	BE_2=**-56.2**
	E_1=**3.94**	E_2=**2.75**	E_1=**3.01**	E_2=**1.87**	E_1=**3.13**	E_2=**2.03**
	E=**3.34**		E=**2.44**		E=**2.58**	
 **2,6-NQ** LUMO=**-3.881**						
	BE_1= **-73.3**	BE_2=**-70.6**	BE_1=**-54.0**	BE_2=**-44.6**	BE_1=**-59.9**	BE_2=**-48.1**
	E_1=**2.86**	E_2=**2.66**	E_1=**2.08**	E_2=**1.62**	E_1=**2.33**	E_2=**1.76**
	E=**2.76**		E=**1.85**		E=**2.05**	
 **1,10-AQ** LUMO=**-3.683**						
	BE_1= **-70.6**	BE_2=**-65.0**	BE_1=**-51.1**	BE_2=**-44.8**	BE_1=**-56.7**	BE_2=**-48.1**
	E_1=**2.73**	E_2=**2.45**	E_1=**1.94**	E_2=**1.51**	E_1=**2.20**	E_2=**1.67**
	E=**2.59**		E=**1.72**		E=**1.94**	

 **1,2-AQ** LUMO=**-3.298**						
BE_1=**-85.1**	BE_2=**-59.0**	BE_1=**-62.3**	BE_2=**-39.0**	BE_1=**-64.0**	BE_2=**-42.9**	
E_1=**3.28**	E_2=**2.17**	E_1=**2.33**	E_2=**1.30**	E_1=**2.44**	E_2=**1.47**	
E=**2.73**		E=**1.82**		E=**1.95**		
 **1,4-AQ** LUMO=**-3.257**						
BE_1=**-60.2**	BE_2=**-60.4**	BE_1=**-41.2**	BE_2=**-33.3**	BE_1=**-47.0**	BE_2=**-37.1**	
E_1=**2.31**	E_2=**2.23**	E_1=**1.54**	E_2=**1.17**	E_1=**1.80**	E_2=**1.31**	
E=**2.27**		E=**1.36**		E=**1.56**		
 **1,5-AQ** LUMO=**-3.990**						
BE_1=**-77.4**	BE_2=**-71.9**	BE_1=**-57.8**	BE_2=**-48.3**	BE_1=**-63.4**	BE_2=**-53.4**	
E_1=**3.05**	E_2=**2.71**	E_1=**2.25**	E_2=**1.86**	E_1=**2.50**	E_2=**1.98**	
E=**2.88**		E=**2.05**		E=**2.24**		
 **1,7-AQ** LUMO=**-3.964**						
BE_1=**-78.4**	BE_2=**-70.4**	BE_1=**-58.6**	BE_2=**-46.7**	BE_1=**-64.2**	BE_2=**-50.9**	
E_1=**3.07**	E_2=**2.65**	E_1=**2.27**	E_2=**1.63**	E_1=**2.52**	E_2=**1.87**	
E=**2.86**		E=**1.95**		E=**2.19**		
 **2,3-AQ** LUMO=**-4.274**						
BE_1=**-104.8**	BE_2=**-74.5**	BE_1=**-81.1**	BE_2=**-56.1**	BE_1=**-83.0**	BE_2=**-60.1**	
E_1=**4.17**	E_2=**2.77**	E_1=**3.20**	E_2=**1.98**	E_1=**3.32**	E_2=**2.16**	
E=**3.47**		E=**2.59**		E=**2.74**		

 **2,6-AQ** LUMO=**-3.935**						
	BE_1=**-75.7**	BE_2=**-71.7**	BE_1=**-56.2**	BE_2=**-47.4**	BE_1=**-62.0**	BE_2=**-51.4**
	E_1=**2.97**	E_2=**2.69**	E_1=**2.18**	E_2=**1.71**	E_1=**2.44**	E_2=**1.90**
	E=**2.83**		E=**1.95**		E=**2.17**	
 **2,9-AQ** LUMO=**-3.617**						
	BE_1=**-71.1**	BE_2=**-62.4**	BE_1=**-50.3**	BE_2=**-41.8**	BE_1=**-57.2**	BE_2=**-44.4**
	E_1=**2.76**	E_2=**2.32**	E_1=**1.89**	E_2=**1.44**	E_1=**2.21**	E_2=**1.53**
	E=**2.54**		E=**1.67**		E=**1.87**	
 **9,10-AQ** LUMO=**-3.083**						
	BE_1= **-55.1**	BE_2=**-56.5**	BE_1=**-36.1**	BE_2=**-29.0**	BE_1=**-41.9**	BE_2=**-34.5**
	E_1=**2.08**	E_2=**2.07**	E_1=**1.33**	E_2=**0.84**	E_1=**1.58**	E_2=**1.23**
	E=**2.08**		E=**1.08**		E=**1.41**	
 **9,10-PQ** LUMO=**-3.312**						
	BE_1=**-84.9**	BE_2=**-59.8**	BE_1=**-62.2**	BE_2=**-39.7**	BE_1=**-63.9**	BE_2=**-43.6**
	E_1=**3.28**	E_2=**2.19**	E_1=**2.33**	E_2=**1.33**	E_1=**2.44**	E_2=**1.50**
	E=**2.74**		E=**1.83**		E=**1.97**	
 **3,4-PQ** LUMO=**-3.543**						
	BE_1=**-89.6**	BE_2=**-63.8**	BE_1=**-66.6**	BE_2=**-43.8**	BE_1=**-68.5**	BE_2=**-47.3**
	E_1=**3.45**	E_2=**2.36**	E_1=**2.49**	E_2=**1.50**	E_1=**2.60**	E_2=**1.66**
	E=**2.91**		E=**2.00**		E=**2.13**	

 **1,4-PQ** LUMO=**-3.485**						
	BE_1= **-63.8**	BE_2=**-62.6**	BE_1=**-45.0**	BE_2=**-36.4**	BE_1=**-50.9**	BE_2=**-41.1**
	E_1=**2.43**	E_2=**2.34**	E_1=**1.67**	E_2=**1.17**	E_1=**1.95**	E_2=**1.40**
	E=**2.39**		E=**1.42**		E=**1.67**	

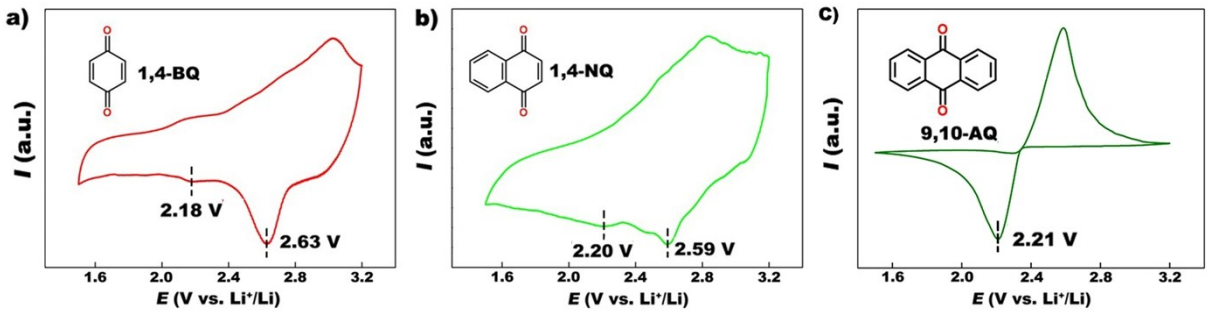


Fig. S1 CV curves of first cycle at 0.1 mV s^{-1} of 1,4-BQ, 1,4-NQ and 9,10-AQ.

Table S2. Comparison between experimental voltages and the theoretical voltages of 1,4-BQ, 1,4-NQ and 9,10-AQ calculated by different levels of theory.

System	Voltage (V vs Li^+/Li)			
	Theo.			Expt.
	lc-wpbe/6-311+g(d,p)	wb97x/6-311+g(d,p)	b3lyp/6-311+g(d,p)	
1,4-BQ	2.59	2.67	2.55	2.41
1,4-NQ	2.35	2.43	2.33	2.40
9,10-AQ	2.05	2.12	2.08	2.21

Table S3. Comparison between the theoretical and experimental voltages.

	Voltage (V vs Li^+/Li)	
System	Theo.	Expt.
1,4-benzoquinone (1,4-BQ)	2.55	2.41
1,4-naphthoquinone (1,4-NQ)	2.33	2.40
9,10-anthraquinone (9,10-AQ)	2.08	2.21
9,10-phenanthraquinone (9,10-PQ)	2.74	2.72[a]
5,7,12,14-pentacenetetrone (PT)	2.00	2.22[b]
2,2′-bi(1,4-naphthoquinone) (BNQ)	2.56	2.45[c]
1,4,5,8-phenanthrenediquinone (PADQ)	2.68	2.63[d]
pyrene-4,5,9,10-tetraone (PTQ)	2.75	2.59[e]
5,12-naph-thacenequinone (NAQ)	1.99	2.20[f]
1,2-benzanthraquinone (BAQ)	2.08	~2.3[g]

[a-j]Experimental data from [1] Yao et al.,[2] Chen et al.,[3] Chen et al.,[4] and Chen et al.,[5] respectively. [i,j]Experimental data from Cho et al.[6]

To examine the reliability of the results, we calculated the energies of the lowest unoccupied molecular orbitals (LUMO) for each neutral molecule and radical anion, which is directly related to the acceptance of electrons.[7] As shown in Figure S1 of Supporting Information, all neutral molecules can obtain electrons from Li^+/Li redox couple (-1.36 eV) because all of LUMO levels are located from -4.27 to -3.08 eV, while radical anions cannot get more electrons because of higher LUMO levels, which are located from 1.10 to 2.90 eV. Therefore, all the parent quinone molecules can only bear two electrons in their structure.

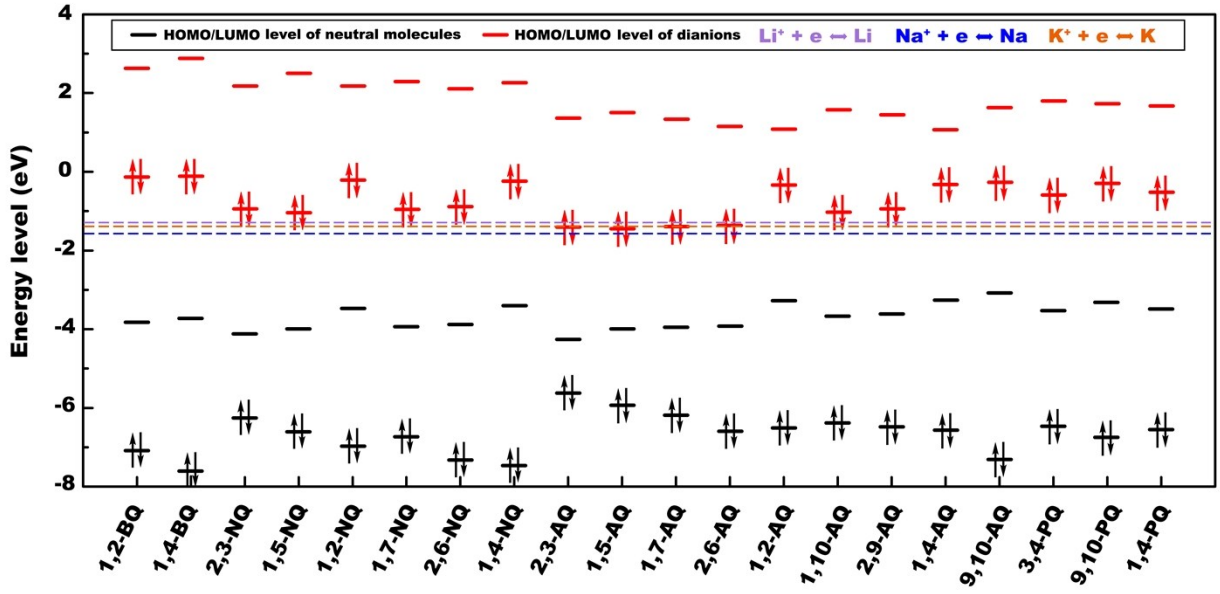


Fig. S2 Calculated HOMO/LUMO level of neutral molecules and dianions (in eV).

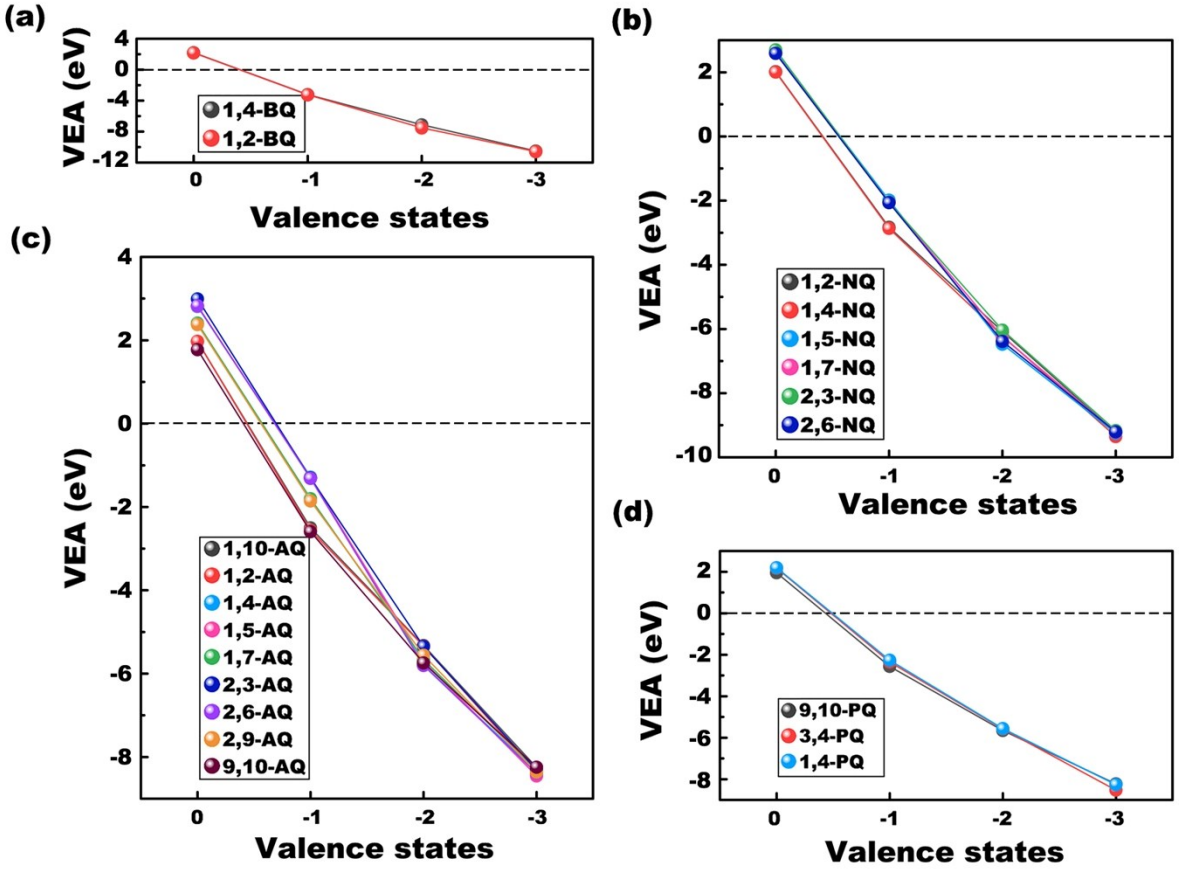


Fig. S3 Calculated VEA under vacuum condition of neutral molecules, radical anions, dianions, and radical trianions of different isomers.

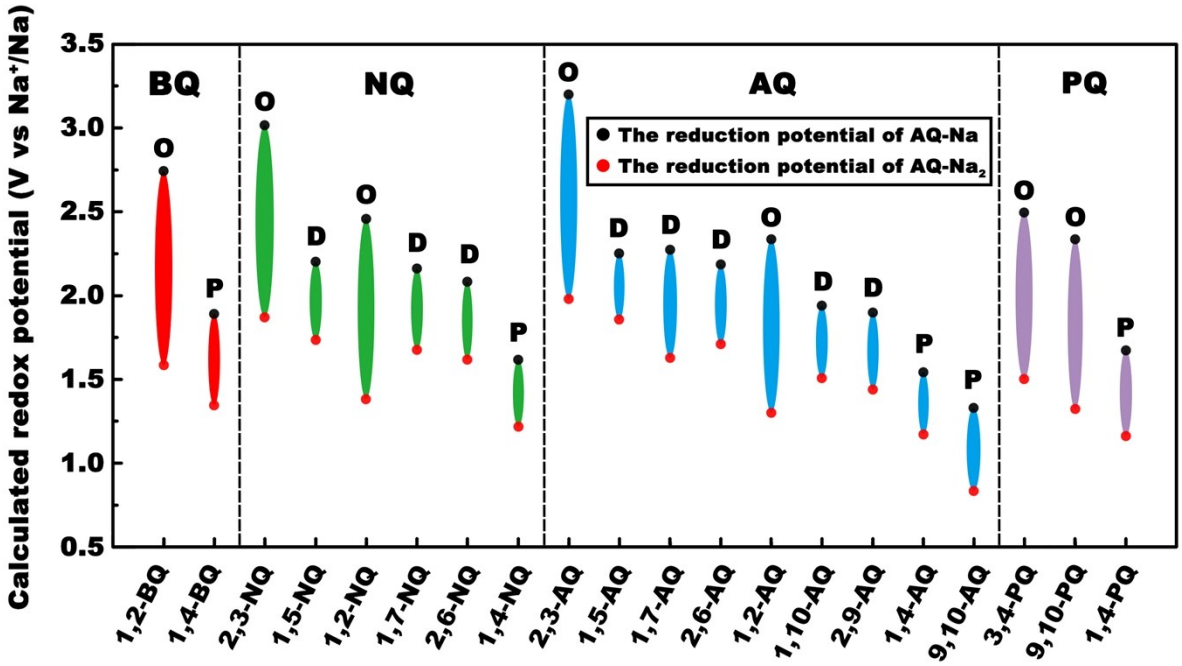


Fig. S4 Calculated the first and second voltage plateau for all the isomers of BQs (red), NQs (green), AQs (blue), and PQs (purple) in sodium-ion batteries. O, P, and D represents the *ortho*-quinones, *para*-quinones, and *discrete*-quinones, respectively.

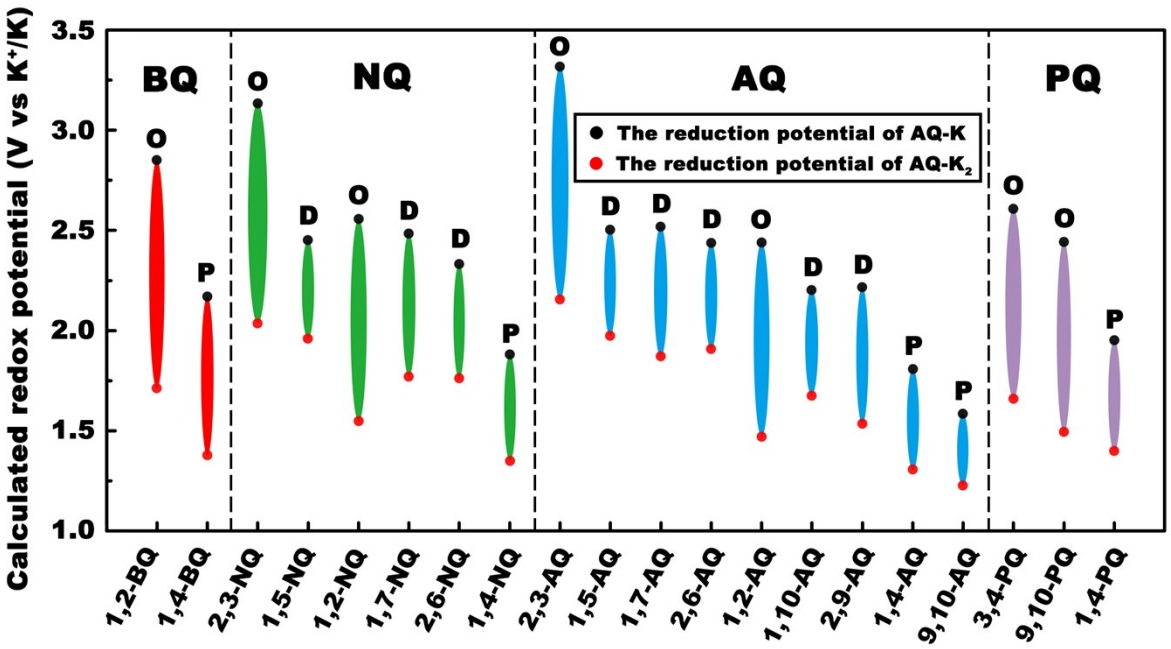


Fig. S5 Calculated the first and second voltage plateau for all the isomers of BQs (red), NQs (green), AQs (blue), and PQs (purple) in potassium-ion batteries. O, P, and D represents the *ortho*-quinones, *para*-quinones, and *discrete*-quinones, respectively.

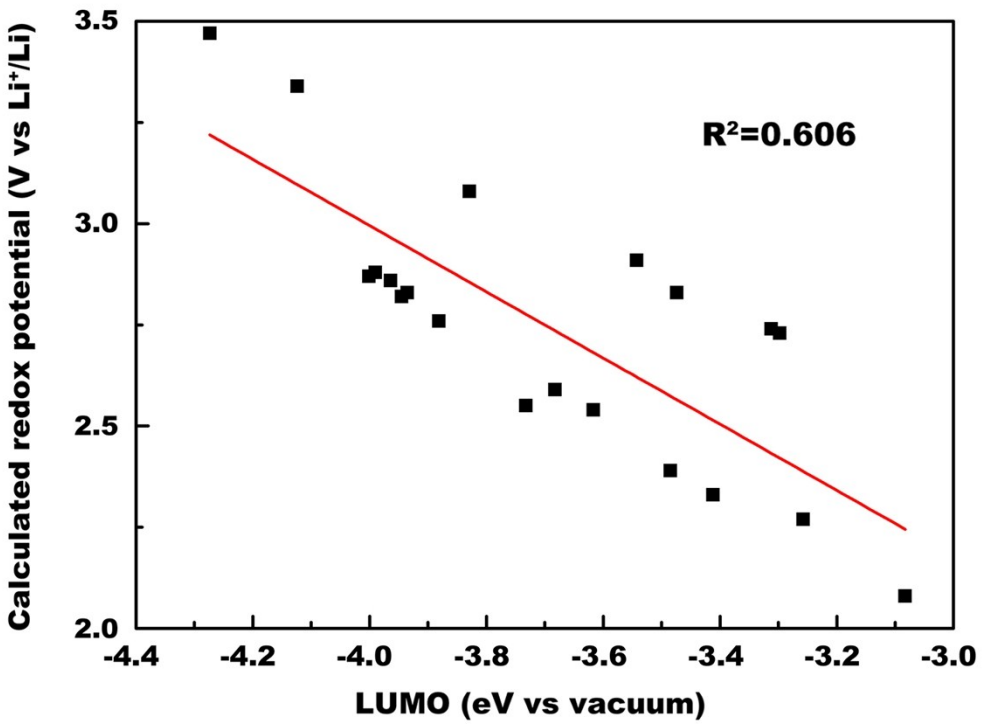


Fig. S6 Calculated redox potentials and LUMO energies of 20 parent quinones.

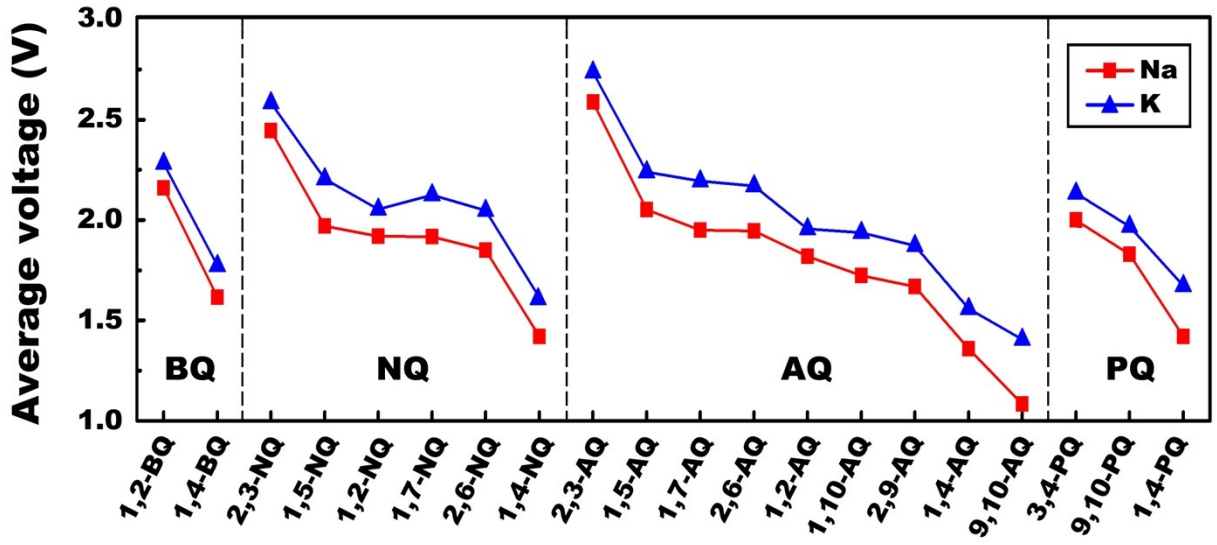


Fig. S7 Calculated average voltages vs Na^+/Na (red), and K^+/K (blue) for all the isomers.

Table S4. Comparison of the calculated electron affinities of 1,4-BQ, 1,4-NQ and 9,10-AQ with those of experimental values.

System	Theo. (eV)	Expt. (eV)
1,4-benzoquinone (1,4-BQ)	2.17	~2.1[8]
1,4-naphthoquinone (1,4-NQ)	2.00	1.81[9]
9,10-anthraquinone (9,10-AQ)	1.77	1.59[9]

Table S5. The LUMO energy and VEAs of 1,2-NQ, 1,2-AQ, 2,3-NQ and 2,3-AQ.

System	E_{LUMO} (eV)	VEA (eV)
1,2-NQ	-3.41	-3.19
2,3-NQ	-4.12	-3.74
1,2-AQ	-3.30	-2.99
2,3-AQ	-4.27	-3.95

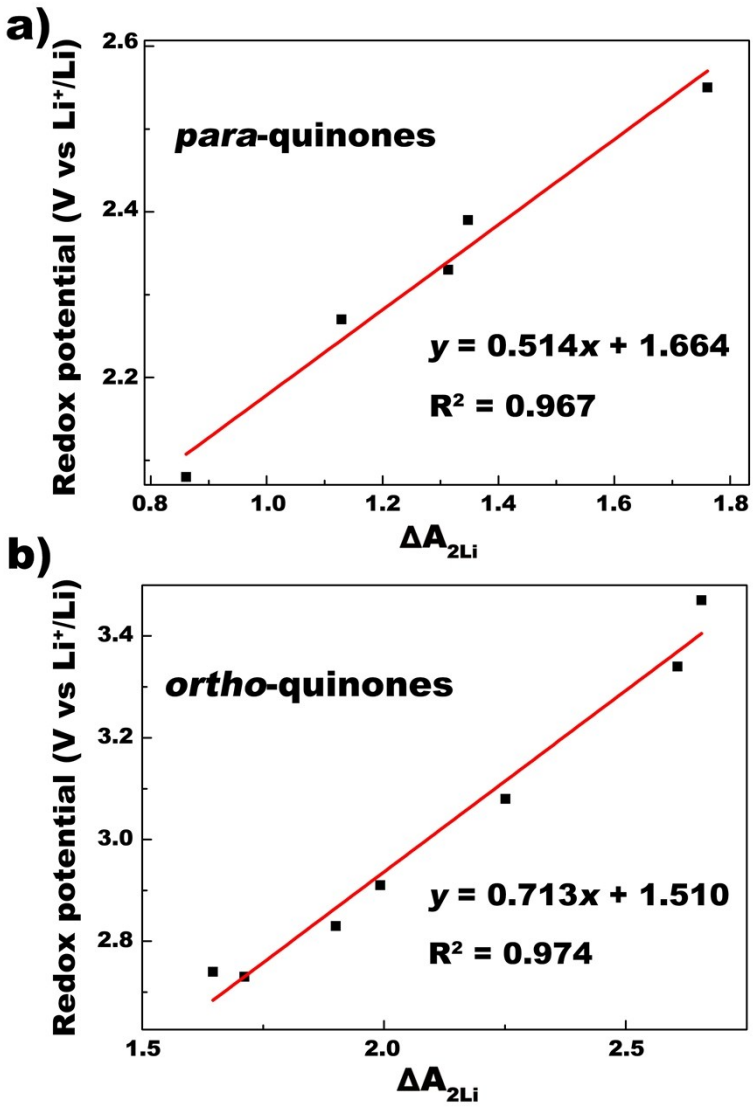


Fig. S8 Plots of calculated voltages against ΔA_{2Li} for a) *para*- and b) *ortho*-quinones.

ΔA_{4Li} values for quinones with four carbonyls were also calculated that can go through four-electron reduction reactions, including 5,7,12,14-pentacenetetrone (PT), 2,2'-bi(1,4-naphthoquinone) (BNQ), 1,4,5,8-phenanthrenediquinone (PADQ), and pyrene-4,5,9,10-tetraone (PTQ). Though four data points are not sufficient for a linear fitting, it is clearly seen in Figure S9 that the voltages of these quinones are in positive correlation with their corresponding ΔA_{4Li}.

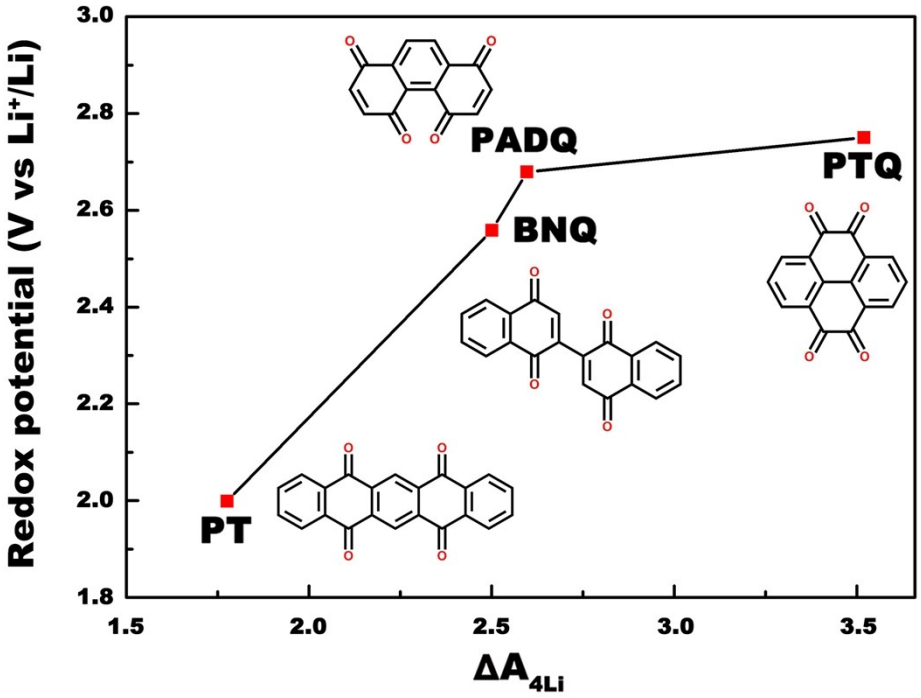


Fig. S9 Calculated voltages variation with ΔA_{4Li}.

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