Electronic Supplementary Information for

A Density Functional Theory Study on the Thermodynamic and Dynamic Properties of Anthraquinone Analogues Cathode Materials for Rechargeable Lithium Ion Batteries

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Fig. S1. Comparison of reduction potential of AQ calculated by implicit solvent model (PCM + SMD) and explicit solvent model (PCM or SMD + propylene carbonate molecule).

As shown in Fig. S1, the influence of explicit solvent molecule on the calculated reduction potential is very slight. By adding a propylene carbonate molecule in the reaction complex, the calculated reduction potentials decrease about 0.1 V by PCM model and 0.25 V by SMD model. Among all the solvation models, reduction potentials of AQ calculated by implicit PCM model matches best with experimental results.



Fig. S2. Potential and Li⁺ concentration dependent equilibrium diagram for the charge and discharge processes in the electrochemical reaction of PPD.



Fig. S3. Comparison of electrostatic potential (ESP) plots of AQ-Li and its derivatives.



Fig. S4. Comparison of electrostatic potential (ESP) plots of AQ-Li $_2$ and its derivatives.



Fig. S5. The natural bond orbital (NBO) charges on lithium atom in three isomer pairs (PQD/PID, PCD/PPD, and BDOZD/BDIOZD).



Fig. S6. The electrostatic potential (ESP) charges on lithium atom in three isomer pairs (PQD/PID, PCD/PPD, and BDOZD/BDIOZD).

No.	Full Name	Abbreviation	Chemical Formula
1	9,10-anthraquinone	AQ	$C_{14}H_8O_2$
2	pyrido[3,4-g]isoquinoline-5,10-dione	PID	$C_{12}H_6N_2O_2$
3	pyrido[2,3-g]quinoline-5,10-dione	PQD	$C_{12}H_6N_2O_2$
4	benzo[1,2-b:4,5-b']dipyrrole-4,8-dione	BDPD	$C_{10}H_6N_2O_2$
5	benzo[1,2-b:4,5-b']difuran-4,8-dione	BDFD	$C_{10}H_4O_4$
6	benzo[1,2-b:4,5-b']dithiophene-4,8-dione	BDTD	$C_{10}H_4O_2S_2$
7	pyridazino[3,4-g]cinnoline-5,10-dione	PCD	$C_{10}H_4N_4O_2$
8	pyridazino[4,5-g]phthalazine-5,10-dione	PPD	$C_{10}H_4N_4O_2$
9	pyrazino[2,3-g]quinoxaline-5,10-dione	PQOD	$C_{10}H_4N_4O_2$
10	pyrimido[4,5-g]quinazoline-5,10-dione	PQZD	$C_{10}H_4N_4O_2$
11	benzo[1,2-d:4,5-d']diimidazole-4,8-dione	BDIZD	$C_8H_4N_4O_2$
12	benzo[1,2-d:4,5-d']dioxazole-4,8-dione	BDOZD	$C_8H_2N_2O_4$
13	benzo[1,2-d:4,5-d']dithiazole-4,8-dione	BDTZD	$C_8H_2N_2O_2S_2$
14	benzo[1,2-d:4,5-d']dipyrazole-4,8-dione	BDPZD	$C_8H_4N_4O_2$
15	benzo[1,2-d:4,5-d']diisoxazole-4,8-dione	BDIOZD	$C_8H_2N_2O_4$
16	benzo[1,2-d:4,5-d']diisothiazole-4,8-dione	BDIOZD	$C_8H_2N_2O_2S_2$

Table S1. Full Name, abbreviation, and chemical formula of the studied molecules

	Experiment ^{S1}	6-31G	6-31+G	6-31++G	6-31+G*	6-31+G**
С9-О	1.220	1.254	1.255	1.255	1.228	1.228
C9-C11	1.499	1.485	1.486	1.486	1.493	1.493
C11-C12	1.400	1.413	1.414	1.414	1.410	1.410
C11-C1	1.400	1.403	1.404	1.404	1.401	1.401
C1-C2	1.400	1.396	1.397	1.397	1.394	1.394
C2-C3	1.400	1.403	1.404	1.404	1.401	1.401
С1-Н	1.087	1.084	1.084	1.084	1.085	1.085
С2-Н	1.087	1.085	1.085	1.085	1.087	1.086
O-C9-C11	121.3	121.0	121.0	121.0	121.2	121.2
C11-C9-C14	117.4	118.0	118.1	118.1	117.6	117.6
C9-C11-C12	121.3	121.0	121.0	121.0	121.2	121.2
C1-C11-C12	120.1	119.7	119.7	119.7	119.7	119.7
C11-C1-C2	119.8	120.2	120.3	120.3	120.2	120.2
C1-C2-C3	119.8	120.1	120.1	120.1	120.1	120.1
С11-С1-Н	120.1	118.3	118.5	118.5	118.6	118.5
С1-С2-Н	120.1	119.1	119.9	119.9	119.9	119.9

Table S2. Experimental and Calculated Bond Distances (Å) and Bond Angles (deg) of 9,10-Anthraquinone with Different Basis Sets

	Experiment ^{S1}	6-311G	6-311+G	6-311++G	6-311+G*	6-311+G**
С9-О	1.220	1.252	1.252	1.252	1.220	1.220
C9-C11	1.499	1.484	1.485	1.485	1.492	1.492
C11-C12	1.400	1.411	1.412	1.412	1.407	1.407
C11-C1	1.400	1.401	1.402	1.402	1.398	1.398
C1-C2	1.400	1.394	1.394	1.394	1.390	1.390
C2-C3	1.400	1.401	1.401	1.401	1.398	1.398
С1-Н	1.087	1.080	1.081	1.081	1.084	1.083
С2-Н	1.087	1.081	1.082	1.082	1.085	1.084
O-C9-C11	121.3	121.0	121.0	121.0	121.3	121.3
C11-C9-C14	117.4	118.1	118.1	118.1	117.5	117.5
C9-C11-C12	121.3	121.0	121.0	121.0	121.3	121.3
C1-C11-C12	120.1	119.7	119.7	119.7	119.7	119.7
C11-C1-C2	119.8	120.2	120.2	120.2	120.2	120.2
C1-C2-C3	119.8	120.1	120.1	120.1	120.1	120.1
С11-С1-Н	120.1	118.3	118.4	118.4	118.5	118.5
С1-С2-Н	120.1	119.9	119.9	119.9	119.9	119.9

Table S2 tests the influence of basis sets on the molecular structure of 9,10-Anthraquinone in gas phase using the same correlation exchange functional B3LYP. By comparing with experimental results from gas phase electron diffraction,¹ it is found that adding polarization function and diffuse function is necessary to well predict the molecular structure of AQ. 6-311+G(d,p) basis set, including a polarization function to all the atoms and a diffuse function to C, N, O and S atoms, gives the most approximate values to experimental results. The calculated C=O bond length is exactly the same as gas phase electron diffraction value. However, basis sets that without containing additional polarization functions usually underestimate C=O bond strength. All the calculated results given in the main test are computed using 6-311+G(d,p) level.

	AQ-Li/	AQ	AQ-Li ₂ /AQ-Li		AQ-Li ₂ /AQ		ΔΕ	
	PCM	SMD	PCM	SMD	PCM	SMD	PCM	SMD
B3LYP	2.41	2.92	1.92	2.76	2.17	2.84	0.49	0.16
BP86	2.48	2.93	1.91	2.72	2.19	2.82	0.57	0.21
PW91PW91	2.51	2.99	1.98	2.81	2.24	2.90	0.53	0.18
B3P86	2.96	3.46	2.42	3.25	2.69	3.36	0.54	0.21
B3PW91	2.39	2.87	1.84	2.69	2.12	2.78	0.55	0.18
PBEh1PBE	2.40	2.90	1.87	2.71	2.13	2.80	0.53	0.19
M06L	2.23	2.70	1.63	2.45	1.93	2.58	0.60	0.25
B97D	2.33	2.79	1.83	2.57	2.08	2.68	0.50	0.22
CAM-B3LYP	2.39	2.92	1.95	2.78	2.17	2.85	0.44	0.14
wB97XD	2.22	2.71	1.76	2.50	1.99	2.60	0.46	0.21
Exp.	2.63		2.07		2.33		0.46	

Table S3. Experimental and Calculated Reduction Potentials (V vs. Li/Li⁺) of 9,10-Anthraquinone with Different Functionals

Table S3 shows the influence of DFT method and solvation model on the calculated first and second one-electron-one-ion transfer reduction potential of AQ. PCM and SMD are two common solvation models in DFT calculations. As seen, the reduction potentials computed by SMD model are higher than those by PCM model and the separations between the first and second reduction potential calculated by SMD model are smaller than those by PCM model. Zhao et al. studied the cyclic voltammetry (CV) of AQ electrode.² Two redox peaks were observed near 2.63 and 2.07 V vs. Li/Li⁺. Similarly, Song et al. measured a pair of redox peaks centering at 2.33 V vs. Li/Li⁺ in the CV of AQ.³ By comparing our computed reduction potentials with experimental results, we found that PCM model can predict the electrochemical properties of AQ better than SMD model. Table S4 also compares the calculated reduction potentials by different correlation exchange functionals. It is shown that the calculated potentials by B3P86 functional are obviously higher and the calculated potentials by M06L and wB97XD functionals are slightly lower than experimental results. The other functionals give relative approximate values to experimental results. In the main text, all the reduction potentials are given by using hybrid B3LYP functional combined with PCM model.

	Eps	AQ-Li/AQ	AQ-Li ₂ /AQ-Li	AQ-Li ₂ /AQ
Ethylene Carbonate	89.78	2.40	1.91	2.15
Propylene Carbonate	64.90	2.41	1.92	2.17
Water	78.36	2.41	1.99	2.24
Dimethylsulfoxide	46.83	2.43	1.94	2.19
n,n-Dimethylformamide	37.78	2.44	1.96	2.20
Acetonitrile	35.69	2.55	2.08	2.32
Benzonitrile	25.59	2.46	2.02	2.24
Acetone	20.49	2.47	2.07	2.27
Tetrahydrofuran	7.43	2.71	2.39	2.55
Toluene	2.37	3.67	3.55	3.61
Gas	1.00	5.91	6.06	5.98

Table S4. Experimental and Calculated Reduction Potentials (V vs. Li/Li^+) of AQ at B3LYP/6-311+G(d,p) level with PCM Model Using Different Solvents

Table S4 shows the on influence of solvent on the calculated reduction potential of AQ. Default parameters were used for all solvents except propylene carbonate (PC) and ethylene carbonate (EC). The static and optical dielectric constants of PC ($\epsilon = 64.90$, $\epsilon_{\infty} = 2.02$) and EC ($\epsilon = 89.78$, $\epsilon_{\infty} = 2.01$) are referred to previous theoretical studies. Organic carbonate and their mixtures are often used as the electrolyte solution for lithium ion batteries. It is found that the calculated reduction potentials by using PC and EC as solvent match well with experimental results. As presented in Table S4, the calculated reduction potentials increase as the decreasing of solvent's dielectric constant. The average reduction potential of AQ in toluene solution is about 1.45 V higher than that in EC and PC solutions. The reduction potential difference between different solvents mainly arises from solvation energy of lithium ion. The Solvation energy of lithium ion in EC solution (5.28 eV) is 2.19 eV higher than that in toluene solution (3.09 eV). It can be concluded from Table S4 that the dielectric property of electrolyte solution can strongly influence the electrochemical property of AQ.

	$\lambda_{\mathrm{R1}} (\mathrm{eV})$	$\lambda_{\rm P1}({\rm eV})$	λ_{i1} (eV)	$\lambda_{\mathrm{R2}}(\mathrm{eV})$	$\lambda_{\mathrm{P2}}\left(\mathrm{eV} ight)$	$\lambda_{i2} (eV)$
AQ	0.20	0.20	0.20	0.19	0.21	0.20
PID	0.21	0.22	0.21	0.21	0.21	0.21
PQD	0.23	0.23	0.23	0.21	0.22	0.22
BDPD	0.19	0.19	0.19	0.20	0.21	0.21
BDFD	0.25	0.20	0.22	0.23	0.23	0.23
BDTD	0.19	0.19	0.19	0.20	0.21	0.20
PCD	0.24	0.24	0.24	0.20	0.21	0.21
PPD	0.23	0.23	0.23	0.20	0.20	0.20
PQOD	0.25	0.24	0.24	0.22	0.22	0.22
PQZD	0.25	0.24	0.25	0.22	0.22	0.22
BDIZD	0.26	0.27	0.26	0.25	0.25	0.25
BDOZD	0.29	0.29	0.29	0.26	0.26	0.26
BDTZD	0.22	0.23	0.23	0.22	0.22	0.22
BDPZD	0.21	0.21	0.21	0.22	0.22	0.22
BDIOZD	0.25	0.25	0.25	0.25	0.25	0.25
BDIOZD	0.20	0.20	0.20	0.21	0.21	0.21

Table S5. Calculated inner reorganization energies λ_i for the first and second concerted one-electron-one-ion transfer reaction

	λ_o^{ET1} (eV)	$\lambda_o^{\mathrm{IT1}} (\mathrm{eV})$	λ_o^{ET2} (eV)	$\lambda_o^{\mathrm{IT2}} (\mathrm{eV})$
AQ	0.72	0.59	0.71	0.57
PID	0.73	0.63	0.72	0.59
PQD	0.73	0.42	0.72	0.37
BDPD	0.76	0.75	0.75	0.73
BDFD	0.77	0.65	0.76	0.64
BDTD	0.74	0.65	0.73	0.63
PCD	0.74	0.45	0.73	0.38
PPD	0.74	0.67	0.73	0.65
PQOD	0.74	0.45	0.74	0.39
PQZD	0.74	0.45	0.73	0.38
BDIZD	0.77	0.64	0.77	0.64
BDOZD	0.79	0.55	0.77	0.53
BDTZD	0.75	0.59	0.74	0.57
BDPZD	0.77	0.78	0.76	0.73
BDIOZD	0.78	0.78	0.77	0.74
BDIOZD	0.75	0.69	0.74	0.66

Table S6. Calculated solvent reorganization energies of electron transfer λ_o^{ET} and ion transfer λ_o^{IT} for the first and second concerted one-electron-one-ion transfer reaction

References

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