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Fundamental Promises of Anthraquinone Functionalized Graphene Based Next Generation Battery Electrodes: A DFT Study

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Supporting Information

Table S1. Calculated values of the free energy of formation, $\Delta G_{n,}$ for the AQ-coverage of graphene calculated according to equation (1).

n in $(AQ)_nC_{72}$	G_n, eV	ΔG_n, kJ/mol
0	-666.4271	0
1	-831.2541	-35
2	-996.6593	-126
3	-1161.9457	-205
4	-1327.3132	-292
5	-1491.7615	-290
6	-1653.1331	8
7	-1817.6844	0

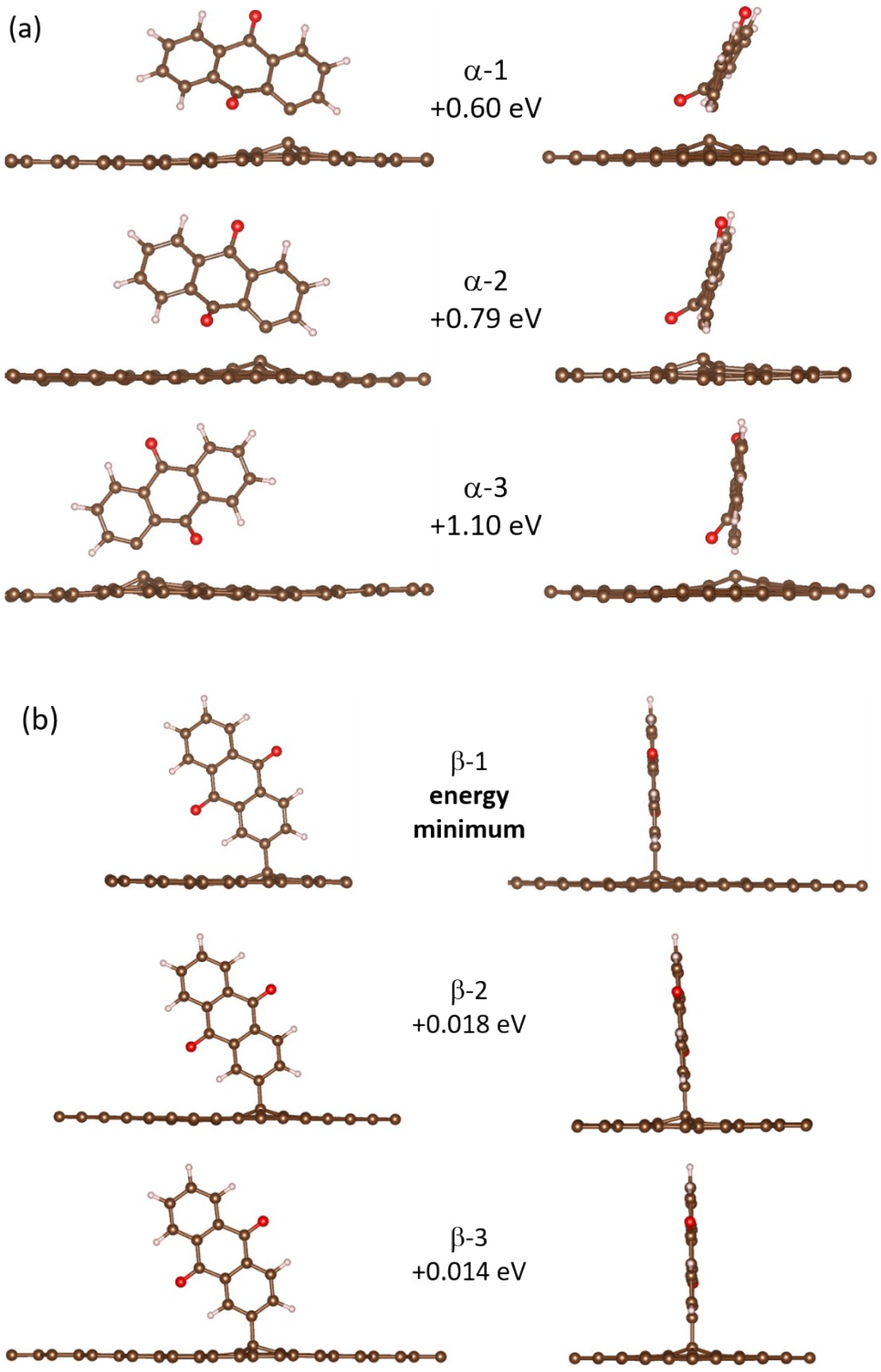
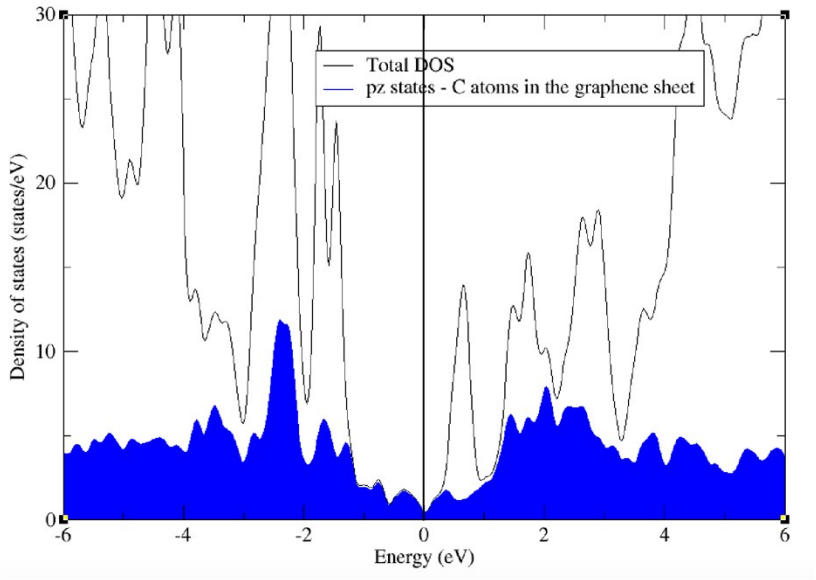


Figure S1. Optimized geometries and relative energies of the functionalized graphene with the anthraquinone residue attached at alpha (a.) and beta (b.) position. The connecting bond in a. is longer than 1.6 Å and therefore is not visualized. A PAW energy cut-off of 350 eV were used for the optimizations.

Table S2. Charges of: all lithium atoms present – *q(Li)*; the 72 carbon atoms of the graphene sheet – *q(graphene)*; all atoms (carbon, oxygen and hydrogen) of the four AQs – *q(AQ)*; the 8 O-atoms in the AQs – *q(O in AQ)*; the 56 carbon atoms in the AQs – *q(C in AQ)*.

x in $Li_x(AQ)_4C_{72}$	**q(Li)**	**q(Li) per atom**	**q(graphene)**	**q(AQ)**	**q(O in AQ)**	**q(C in AQ)**
0	0.000	-	0.063	-0.063	-8.486	5.630
1	0.883	0.883	-0.076	-0.807	-8.938	5.543
2	1.754	0.877	-0.021	-1.733	-9.183	5.081
4	3.521	0.880	-0.279	-3.242	-9.708	4.601
6	5.236	0.873	-0.339	-4.896	-10.000	3.252
8	7.066	0.883	-0.284	-6.783	-10.189	1.831
12	10.475	0.873	-0.697	-9.777	-10.192	-1.468
14	12.188	0.871	-1.497	-10.690	-10.329	-2.117
16	13.859	0.866	-2.483	-11.377	-10.278	-2.835

(a)



(b)

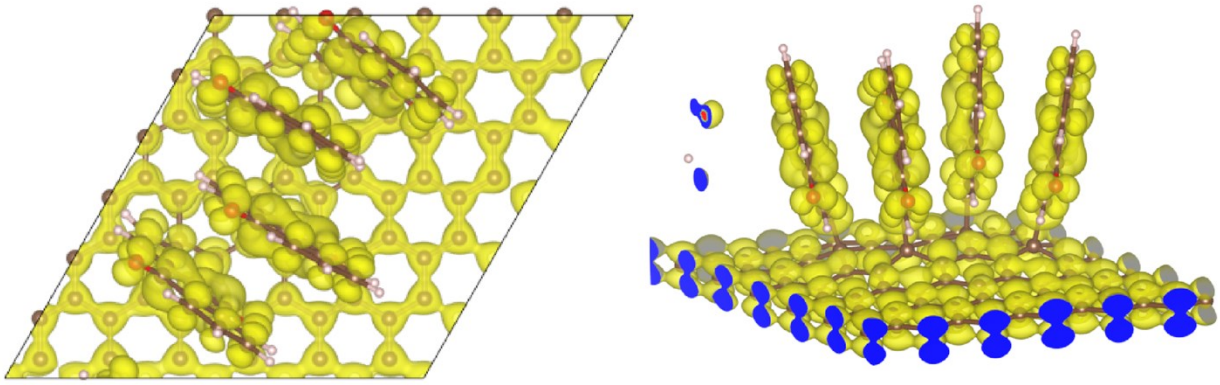


Figure S2: (a) Total and partial density of states (DOS and pDOS) of AQ_4C_{72}. Field colored blue is the summed density of states of the $2p_z$ AOs of the carbons in the sheet (Fermi energy was set to zero). (b) Top and side view of the partial charge density for states close to the Fermi level (isosurface value is 0.008 e/Å^3).

Mass of AQ-only: 828.78 g/mol per periodic box;
Mass of the whole material – AQ_4C_{72} – 1693.5 g/mol per periodic box.

Table S3. Free energies of formation, calculated ΔG, according to equation (3), and potentials for the lithium complexes.

x in $Li_x(AQ)_4C_{72}$	Δx	ΔG, eV	Potential, V
0	–	–	–
1	1	-2.302	2.302
2	1	-2.299	2.299
4	2	-3.511	1.756
6	2	-3.048	1.524
8	2	-3.105	1.553
10	2	-1.593	0.797
14	4	-1.717	0.429
16	2	0.809	-0.405

Table S4. Free energies of formation, calculated ΔG, according to equation (3), and potentials for the calcium complexes.

x in $Ca_x(AQ)_4C_{72}$	Δx	ΔG, eV	Potential, V
0	–	–	–
1	1	-3.115	1.557
2	1	-3.431	1.716
4	2	-4.814	1.203
6	2	-2.276	0.569
7	1	-1.174	0.587
8	1	-0.651	0.325
9	1	0.352	-0.176

Table S5. Sums of the charges of different groups of atoms in the systems with intercalated Ca.

x in $Ca_x(AQ)_4C_{72}$	q(Ca)	q(Ca) per atom	q(graphene)	q(AQ)	q(O in AQ)	q(C in AQ)
0	0.000	-	0.063	-0.063	-8.486	5.630
1	1.612	1.612	-0.319	-1.293	-9.832	5.885
2	3.183	1.592	-0.248	-2.934	-9.298	4.191
4	6.258	1.565	-0.782	-5.475	-9.708	2.661
6	9.204	1.534	-1.735	-7.469	-10.254	1.320
7	10.616	1.517	-1.785	-8.832	-10.046	-0.016
8	11.458	1.432	-1.723	-9.734	-10.687	-0.659
9	12.786	1.421	-2.002	-10.784	-9.962	-2.005

Table S6. Free energies of formation, calculated ΔG, according to equation (3), and potentials for the aluminium complexes.

x in $Al_x(AQ)_4C_{72}$	Δx	ΔG, eV	Potential, V
0	–	–	–
1	1	-0.943	–
2	1	-2.058	0.686
3	1	0.183	-0.061
4	1	0.538	-0.179

Table S7. Sums of the charges of different groups of atoms in the systems with intercalated Al.

x in $Al_x(AQ)_4C_{72}$	q(Al)	q(Al) per atom	q(graphene)	q(AQ)	q(O in AQ)	q(C in AQ)
0	0.000	-	0.063	-0.063	-8.486	5.630
1	2.389	2.389	-0.005	-2.383	-9.315	4.461
2	5.196	2.598	-0.018	-5.177	-11.966	4.889
3	6.432	2.144	-0.076	-6.355	-10.888	2.563
4	6.973	1.743	-0.021	-6.951	-11.457	2.425

Table S8. Calculated electrode capacities and gravimetric energy densities.

Metal	Capacity (AQ_4C_{72}), mAh/g	Capacity (AQ_4-only), mAh/g
Li	222	453
Ca	253	517
Al	95	194
	Energy density (AQ_4C_{72}), Wh/kg	**Energy density (AQ_4-only), Wh/kg**
Li	279	570
Ca	251	512
Al	65	133

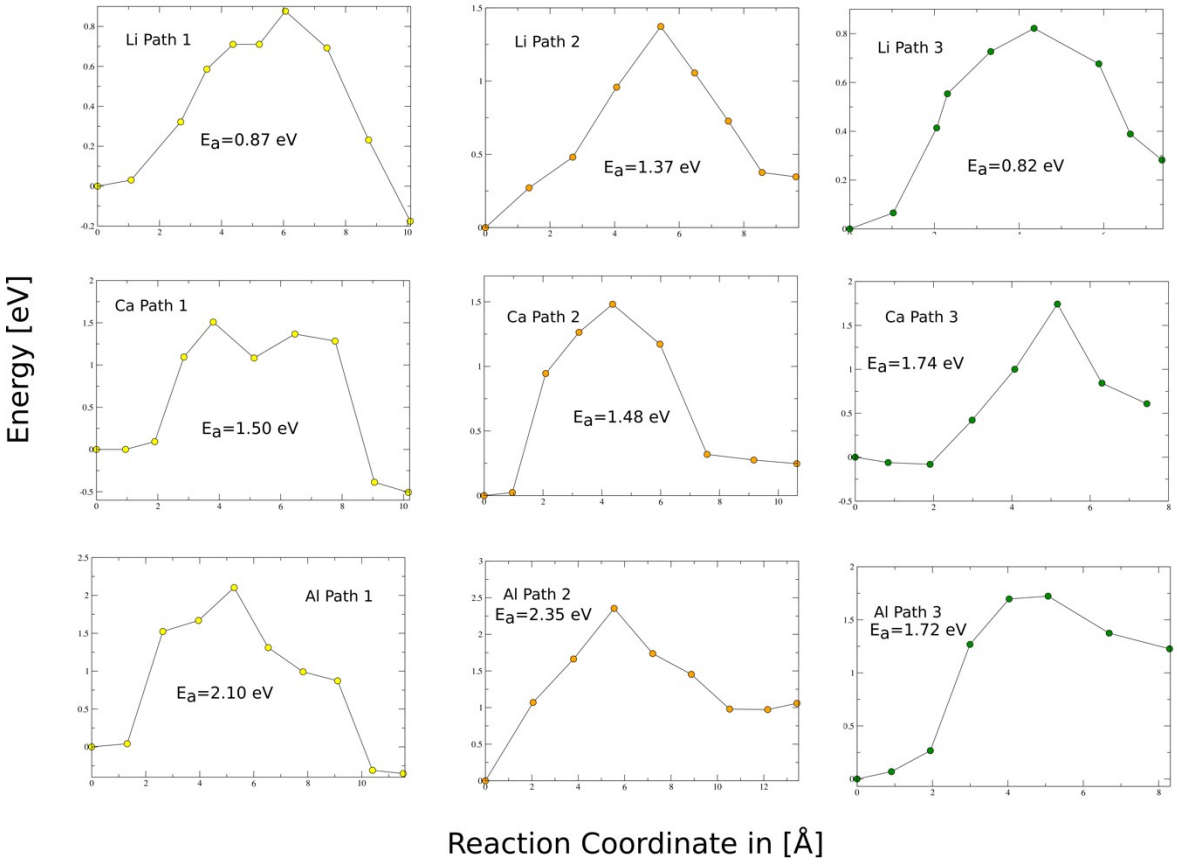


Figure S3: Minimum energy paths (MEP) demonstrating activation barriers for Li, Ca and Al migrating along pathways 1, 2 and 3, yellow, orange and green colours, respectively. Activation barriers are displayed for each case as E_a in eV.