Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Tuning Optical Properties of Graphene Quantum Dots by Selective Oxidation: A Theoretical Perspective

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Validation of the theoretical method: First, the absorption spectra of circumcoronene (C54, the GQD model used in this study) were simulated using the ωB97XD, M06-2X, and CAM-B3LYP functionals. As shown in Figure S1, the spectra exhibit a very similar profile with a slight difference in their peak intensities and positions. Moreover, these three funcitionals produce very consistent values for the optical gap and emission gap of C54 (Table S1), in good agreement with the previous report. Further, to make a direct comparison with previous experimental and theoretical data, we also calculated the optical gap energy and first ionization potential energy of a smaller-sized polycyclic aromatic hydrocarbon, coronene ($C_{24}H_{12}$). As shown in Table S2, all these three functionals give very close results to the experimental results and to the theoretical results that are calculated using a higher basis set, and the ωB97XD functional best reproduces the first ionization potential measured in the experiment. Thus, through these comprehensive comparisons, a good accuracy from the ωB97XD/6-311G(d,p) level of calculations can be expected.

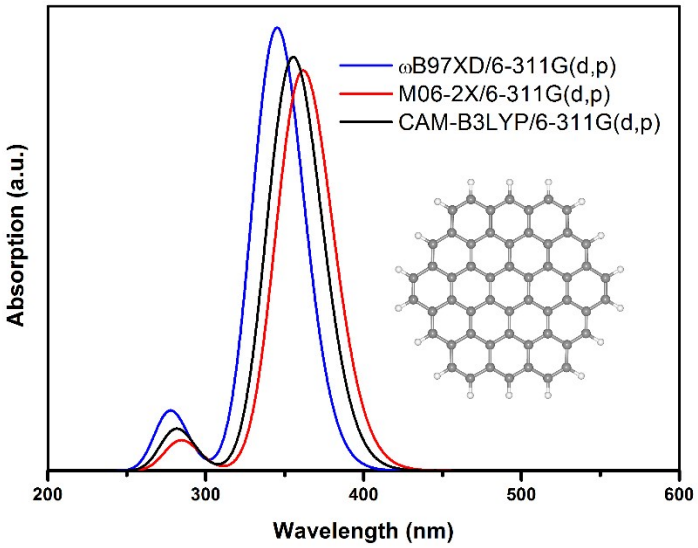
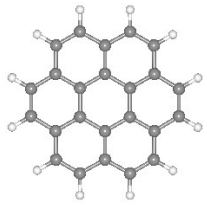


Figure S1. Comparison of the simulated absorption spectrum for C54. The lowest 15 excitations were considered in each calculation.

Table S1. Comparison of the calculated results for the optical gap and emission energy of C54.

Level of theory	Optical gap (eV)	Emission energy (eV)
ωB97XD /6-311G(d,p)	2.68	2.50
M06-2X/6-311G(d,p)	2.61	2.46
CAM-B3LYP/6-311G(d,p)	2.63	2.47
ωB97XD /6-311+G(d)[S3]	2.67	2.50

Table S2. Comparison of the calculated results with experimental results for the lowest excitation energy and first ionization potential (IP) of coronene molecule. The structure was fully optimized by each of these theoretical levels. The IP was taken as the total energy difference between the +1 charged and neutral coronene, i.e., IP=*E*(+1) – *E*(0).

	Method	Optical gap (eV)	First ionization potential (eV)
	Experimental[S1, S2]	3.54	7.29
	ωB97XD /6-311G(d,p)	3.58	7.24
	M06-2X/6-311G(d,p)	3.57	7.41
	CAM-B3LYP/6-311G(d,p)	3.56	7.20
	ωB97XD /6-311+G(d)[S3]	3.57	7.34

References:

S1. Rieger, Ralph, et al. Entry to coronene chemistry-making large electron donors and acceptors. *Chem. Eur. J.* **2008**, *14*, 6322-6325.

S2. Clar, E., et al. Photoelectron spectra of polynuclear aromatics. 6. Applications to structural elucidation:" circumanthracene". *J. Am. Chem. Soc.***1981**, *103,* 1320-1328.

S3. Geethalakshmi, K. R., et al. Tunable optical properties of OH-functionalised graphene quantum dots. *J. Mater. Chem. C* **2016**, *4*, 8429-8438.

Table S3. Reaction energy (ΔE_B, kcal/mol) for forming of the C54 oxides from the reaction of C54 with the O-containing groups ($\Delta E_B = E_{C54} + nE_{O\text{-}group} - E_{C54\ oxide}$. $E_{C54\ oxide}$ is the total energy of the C54 oxide, E_{C54} is the total energy of a single C54, n is the number of contained O-containing groups, and $E_{O\text{-}group}$ is the total energy of the single O-containing group)

Structure	ΔE_B	Structure	ΔE_B	Structure	ΔE_B
C54-O-P1	38.9	C54-2OH-C1	90.3	C54-2O-C1	80.0
C54-O-P2	25.1	C54-2OH-C2	39.2	C54-2O-C1b	78.2
C54-O-P3	39.1	C54-2OCH_3-C1	76.5	C54-2O-C2	68.5
C54-O-P4	29.2	C54-2OCH_3-C2	25.0	C54-2O-C2b	66.6
C54-O-P5	36.1	C54-2COOH-C1	119.2	C54-3O	114.0
C54-O-P6	55.5	C54-2COOH-C2	65.0	C54-4O	157.7
C54-O-P7	25.7	C54-2COCH_3-C1	88.2	C54-5O	213.0
C54-O-P8	73.7	C54-2COCH_3-C2	33.2	C54-6O	255.8
				C54-6O-C2	234.2

Table S4. Energies and oscillator strengths (OS) of the 15 vertical excitations for C54 and its eight mono-epoxides.

Transition No.	C54		C54-O-P1		C54-O-P2	
	Energy (eV)	OS	Energy (eV)	OS	Energy (eV)	OS
1	2.68	0.0000	2.63	0.1391	2.04	0.0022
2	2.88	0.0000	2.95	0.0013	2.08	0.1448
3	3.59	1.5565	3.36	0.0001	3.00	1.0381
4	3.59	1.5561	3.39	0.4088	3.10	0.5944
5	3.67	0.0000	3.67	0.0631	3.35	0.0056
6	3.67	0.0000	3.68	0.2265	3.49	0.0224
7	3.67	0.0000	3.73	0.4048	3.55	0.4329
8	3.89	0.0000	3.76	0.1603	3.59	0.1641
9	3.89	0.0000	3.86	0.0075	3.73	0.0045
10	4.10	0.0000	3.94	0.2073	3.74	0.1435
11	4.11	0.0000	3.99	0.3710	3.88	0.0052
12	4.38	0.0000	4.21	0.6228	3.93	0.0864
13	4.39	0.0000	4.22	0.4324	3.99	0.0001
14	4.47	0.2141	4.28	0.3046	4.07	0.0965
15	4.47	0.2095	4.35	0.0499	4.19	0.0092
Transition No.	C54-O-P3		C54-O-P4		C54-O-P5	
	Energy (eV)	OS	Energy (eV)	OS	Energy (eV)	OS
1	2.86	0.0184	2.12	0.0006	2.69	0.1355

2	2.94	0.0270	2.21	0.1563	2.77	0.0172
3	3.17	0.0106	3.11	1.1432	3.37	0.4351
4	3.43	0.0517	3.11	0.1731	3.53	0.0650
5	3.58	0.0054	3.33	0.0838	3.65	0.7961
6	3.69	0.2000	3.35	0.8354	3.74	0.1013
7	3.74	1.0355	3.40	0.0601	3.85	0.2606
8	3.82	1.4010	3.75	0.0308	3.87	0.4920
9	3.92	0.2008	3.82	0.0006	3.89	0.1831
10	4.03	0.0460	3.86	0.0581	4.08	0.0531
11	4.12	0.0260	3.87	0.0091	4.12	0.1122
12	4.15	0.3418	4.12	0.1032	4.23	0.0599
13	4.25	0.0303	4.13	0.3503	4.25	0.2424
14	4.37	0.0052	4.24	0.0130	4.32	0.0275
15	4.43	0.2124	4.24	0.1387	4.45	0.1275

Transition No.	**C54-O-P6**		**C54-O-P7**		**C54-O-P8**	
	Energy (eV)	OS	Energy (eV)	OS	Energy (eV)	OS
1	2.55	0.3177	1.93	0.2309	2.77	0.0001
2	2.75	0.0028	2.51	0.0189	2.89	0.1446
3	3.45	0.0098	2.94	0.0604	3.63	0.0113
4	3.52	1.1600	3.07	0.8081	3.65	1.0093
5	3.55	0.1112	3.29	0.0733	3.68	1.4659
6	3.72	0.1502	3.37	0.0319	3.71	0.2656
7	3.80	0.3196	3.54	0.2407	3.83	0.0033
8	3.85	0.1876	3.67	0.0198	3.91	0.0006
9	4.03	0.2879	3.79	0.0368	4.16	0.0098
10	4.07	0.0096	3.80	0.1183	4.23	0.0004
11	4.08	0.0005	3.82	0.3564	4.24	0.0032
12	4.19	0.0185	4.01	0.4049	4.34	0.0129
13	4.26	0.2403	4.09	0.0821	4.40	0.0174
14	4.37	0.0522	4.12	0.1854	4.41	0.0913
15	4.48	0.0788	4.19	0.0084	4.49	0.1397

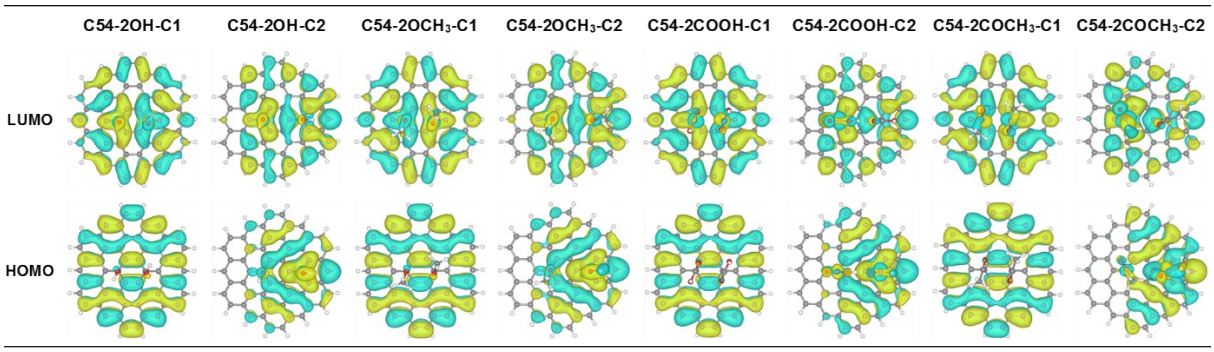


Figure S2. Spatial distributions of HOMO and LUMO orbitals of the ground-state C54 oxides functionalized with two -OH, $-OCH_3$, -COOH, or $-COCH_3$ groups.

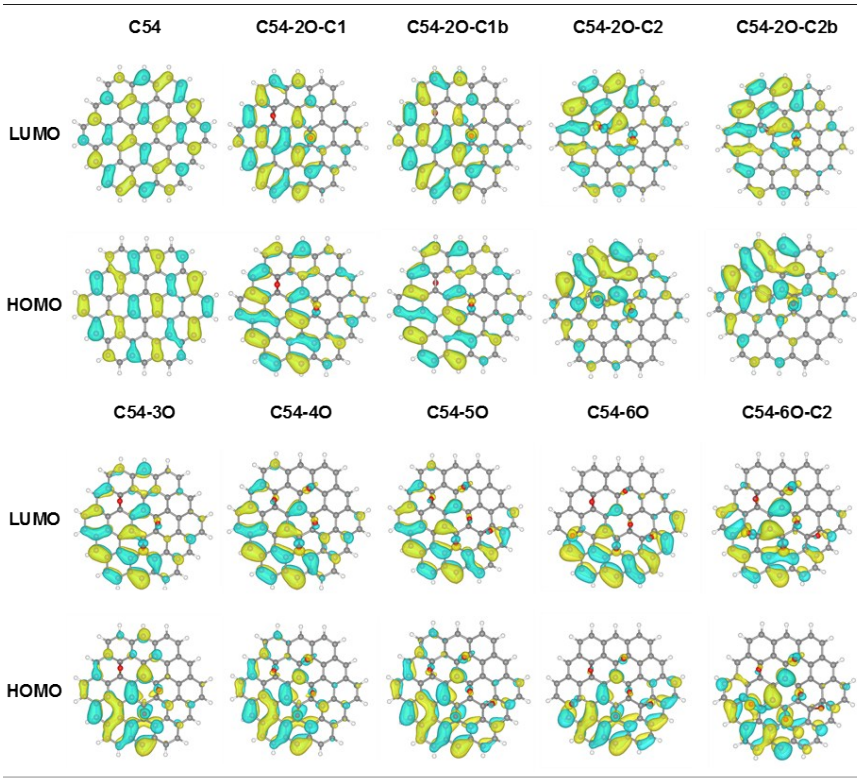


Figure S3. Spatial distributions of HOMO and LUMO orbitals of the ground-state C54 oxides functionalized with 2-6 epoxy (C-O-C) groups. For the convenience of comparison, the HOMO and LUMO orbitals of the ground-state C54 are also provided.