Supporting Information

Optical and Electronic Properties of Graphene Quantum Dots with Oxygen-Containing Groups: A Density Functional Theory Study

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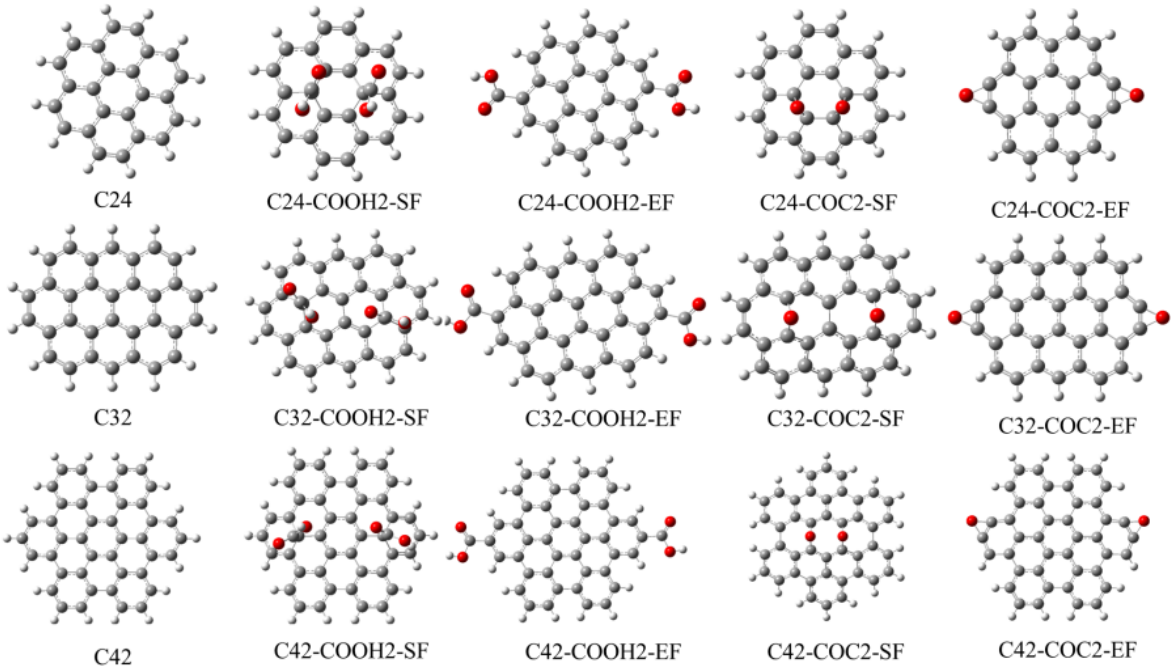


Fig. S1 Structures of C24, C32, and C42 and their functionalized GQDs.

Table S1: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states. The values were obtained using B3LYP/6-31G* for the optimized ground state geometry. Water was taken into account as solvent by using the polarizable continuum model.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
Pristine GQD	1	1.92	645.75	0.0017
	2	1.98	626.58	0.0604
	3	2.22	559.83	3.2236
	4	2.31	537.56	1.3336
	5	2.35	528.55	0.0016
	6	2.46	503.84	0.0085
	7	2.51	494.23	0.0003
	8	2.55	485.79	0.0025
	9	2.65	466.64	0.0001
	10	2.66	466.94	0.0009
	11	2.70	459.25	0.0023
	12	2.77	447.34	0.0064
	13	2.83	438.45	0.0859
	14	2.85	435.23	0.0473
	15	2.88	430.78	0.0003
	16	2.90	427.42	0.0438
	17	2.94	421.05	0.0002
	18	2.96	419.30	0.0004
	19	2.98	415.56	0.0555
	20	3.00	413.80	0.0020

Table S2: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-COOH8-EF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-COOH8-EF	1	1.89	656.69	0.0306
	2	1.95	636.73	0.0339
	3	2.16	573.46	3.3237
	4	2.24	552.76	0.3598
	5	2.25	550.44	1.0524
	6	2.33	532.89	0.0000
	7	2.45	507.06	0.0002
	8	2.51	494.85	0.0013
	9	2.53	490.36	0.0146
	10	2.56	485.73	0.0114
	11	2.67	464.65	0.0327
	12	2.72	455.79	0.0023
	13	2.73	453.79	0.0371
	14	2.80	443.60	0.0311
	15	2.81	440.78	0.1879
	16	2.85	435.10	0.0014
	17	2.85	434.78	0.0701
	18	2.88	429.88	0.0125
	19	2.90	427.87	0.0003
	20	2.91	426.11	0.0456

Table S3: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-COC8-EF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-COC8-EF	1	1.80	687.71	0.0003
	2	1.85	669.13	0.1736
	3	2.06	601.53	2.8095
	4	2.16	572.93	0.8856
	5	2.24	553.94	0.0001
	6	2.30	538.68	0.1991
	7	2.35	527.84	0.0016
	8	2.44	508.02	0.0508
	9	2.47	501.17	0.1794
	10	2.50	496.02	0.0039
	11	2.56	483.82	0.0092
	12	2.58	479.74	0.1394
	13	2.63	471.58	0.0426
	14	2.66	466.34	0.0143
	15	2.71	456.95	0.0001
	16	2.73	454.74	0.0105
	17	2.75	450.85	0.0028
	18	2.77	447.11	0.0097
	19	2.80	442.82	0.0549
	20	2.80	442.64	0.0072

Table S4: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-CHO8-EF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-CHO8-EF	1	1.86	666.28	0.0666
	2	1.92	645.45	0.0106
	3	2.12	585.08	3.0540
	4	2.15	577.03	0.0464
	5	2.20	564.16	1.3135
	6	2.22	558.48	0.0244
	7	2.35	527.94	0.0057
	8	2.42	512.11	0.0029
	9	2.47	502.14	0.0300
	10	2.50	496.58	0.0024
	11	2.56	483.51	0.1313
	12	2.61	474.99	0.0018
	13	2.67	463.61	0.1062
	14	2.69	460.84	0.0439
	15	2.69	460.65	0.0078
	16	2.71	458.08	0.0007
	17	2.72	455.48	0.0760
	18	2.73	454.68	0.2813
	19	2.73	453.83	0.0000
	20	2.75	450.10	0.0001

Table S5: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-$OCH_3$8-EF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-$OCH_3$8-EF	1	1.89	655.88	0.0094
	2	1.95	636.93	0.0591
	3	2.17	572.11	3.2518
	4	2.26	548.75	1.2808
	5	2.30	539.57	0.0482
	6	2.39	519.47	0.0043
	7	2.48	500.18	0.0068
	8	2.52	491.67	0.0044
	9	2.55	485.38	0.0124
	10	2.57	482.05	0.0084
	11	2.67	464.71	0.0005
	12	2.74	452.81	0.0413
	13	2.77	448.11	0.1280
	14	2.79	444.95	0.0650
	15	2.84	436.54	0.0001
	16	2.86	434.20	0.0253
	17	2.87	431.70	0.0018
	18	2.88	430.44	0.0015
	19	2.94	421.70	0.1200
	20	2.95	420.27	0.0001

Table S6: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-OH8-EF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-OH8-EF	1	1.90	652.61	0.0184
	2	1.96	633.10	0.0372
	3	2.18	567.90	3.2101
	4	2.27	547.34	1.1266
	5	2.29	540.37	0.2173
	6	2.39	519.86	0.0002
	7	2.46	503.82	0.0113
	8	2.51	494.43	0.0021
	9	2.59	479.31	0.0197
	10	2.60	476.20	0.0004
	11	2.69	461.41	0.0000
	12	2.71	457.31	0.0250
	13	2.74	452.99	0.1156
	14	2.79	444.90	0.0560
	15	2.83	437.66	0.0406
	16	2.83	437.53	0.0063
	17	2.88	430.01	0.0012
	18	2.89	428.79	0.0074
	19	2.92	423.88	0.0860
	20	2.95	420.72	0.0117

Table S7: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-COOH2-SF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-COOH2-SF	1	0.17	7494.02	0.0251
	2	1.11	1114.07	0.0017
	3	1.18	1047.61	0.3385
	4	1.31	945.73	0.0641
	5	1.44	861.00	0.0416
	6	1.53	812.15	0.5973
	7	1.57	791.34	0.0615
	8	1.60	773.97	0.0582
	9	1.74	712.37	0.2000
	10	1.83	677.86	0.0103
	11	1.89	657.72	0.0900
	12	1.95	635.76	0.0481
	13	1.98	625.79	0.2016
	14	2.05	603.92	0.0583
	15	2.07	598.03	0.0632
	16	2.08	595.81	0.0804
	17	2.13	580.77	0.0115
	18	2.16	573.53	0.0013
	19	2.21	560.86	0.0249
	20	2.26	547.54	0.0186

Table S8: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-CHO2-SF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-CHO2-SF	1	0.09	13648.62	0.0050
	2	1.12	1109.47	0.0147
	3	1.27	974.93	0.2008
	4	1.34	928.17	0.0923
	5	1.42	874.74	0.6971
	6	1.53	812.85	0.1301
	7	1.58	783.46	0.0384
	8	1.72	721.79	0.0034
	9	1.74	711.20	0.0041
	10	1.80	689.68	0.0013
	11	1.84	672.80	0.0699
	12	1.93	641.03	0.0079
	13	1.99	622.92	0.0325
	14	2.02	613.69	0.0715
	15	2.04	607.49	0.0782
	16	2.11	588.30	0.2196
	17	2.14	578.97	0.0844
	18	2.18	567.74	0.0105
	19	2.19	565.78	0.1189
	20	2.26	548.31	0.0452

Table S9: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-COC2-SF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-COC2-SF	1	1.57	789.15	0.3348
	2	1.92	644.85	0.1678
	3	2.04	608.33	0.0000
	4	2.08	596.25	0.0104
	5	2.23	556.63	2.0054
	6	2.32	535.12	0.0008
	7	2.40	516.61	0.0050
	8	2.44	508.67	0.0076
	9	2.49	498.39	0.0014
	10	2.50	495.87	0.0378
	11	2.57	481.96	0.0033
	12	2.64	470.07	0.0384
	13	2.66	466.34	0.1729
	14	2.68	463.05	0.0893
	15	2.71	458.31	0.0193
	16	2.71	458.23	0.2353
	17	2.74	452.59	0.0101
	18	2.78	445.93	0.0546
	19	2.82	440.23	0.0044
	20	2.84	436.86	0.0064

Table S10: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-OH2-SF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-OH2-SF	1	0.13	9747.91	0.0128
	2	1.01	1227.33	0.0037
	3	1.11	1113.25	0.4164
	4	1.33	935.68	0.0187
	5	1.43	868.97	0.0449
	6	1.48	835.59	0.0576
	7	1.59	777.61	0.0137
	8	1.68	736.51	0.8984
	9	1.77	698.76	0.0224
	10	1.77	698.72	0.1997
	11	1.87	662.55	0.3631
	12	1.96	631.21	0.0677
	13	2.01	618.16	0.0048
	14	2.04	606.57	0.0047
	15	2.14	580.19	0.0023
	16	2.14	579.19	0.0300
	17	2.22	558.08	0.1221
	18	2.24	554.47	0.0273
	19	2.31	537.80	0.0436
	20	2.32	534.70	0.0015

Table S11: Absorption energies, wavelengths, and oscillator strengths for the first 20 singlet states of GQD-$OCH_3$2-SF.

	Singlet states	Absorption energy (eV)	Wavelength (nm)	Oscillator strengths
GQD-$OCH_3$2-SF	1	0.12	10642.94	0.0109
	2	1.00	1238.36	0.0055
	3	1.10	1124.28	0.4376
	4	1.33	929.23	0.0181
	5	1.42	870.34	0.0287
	6	1.50	826.81	0.0578
	7	1.59	781.07	0.0263
	8	1.69	734.07	0.9008
	9	1.77	700.32	0.1973
	10	1.79	690.84	0.0050
	11	1.85	668.48	0.3895
	12	1.94	637.65	0.0705
	13	2.00	619.69	0.0078
	14	2.05	604.27	0.0037
	15	2.14	579.45	0.0197
	16	2.15	577.22	0.0009
	17	2.22	557.31	0.1203
	18	2.26	547.89	0.0220
	19	2.30	538.12	0.0462
	20	2.34	530.30	0.0020

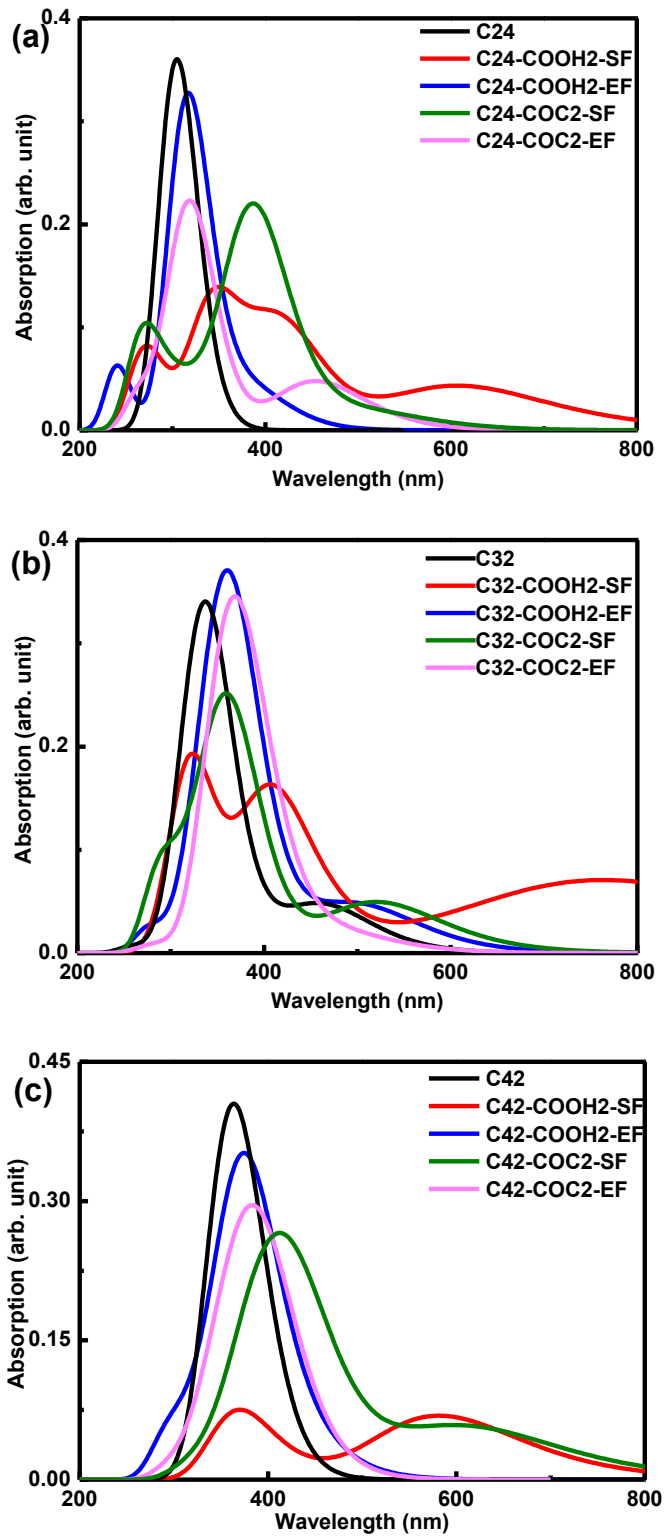
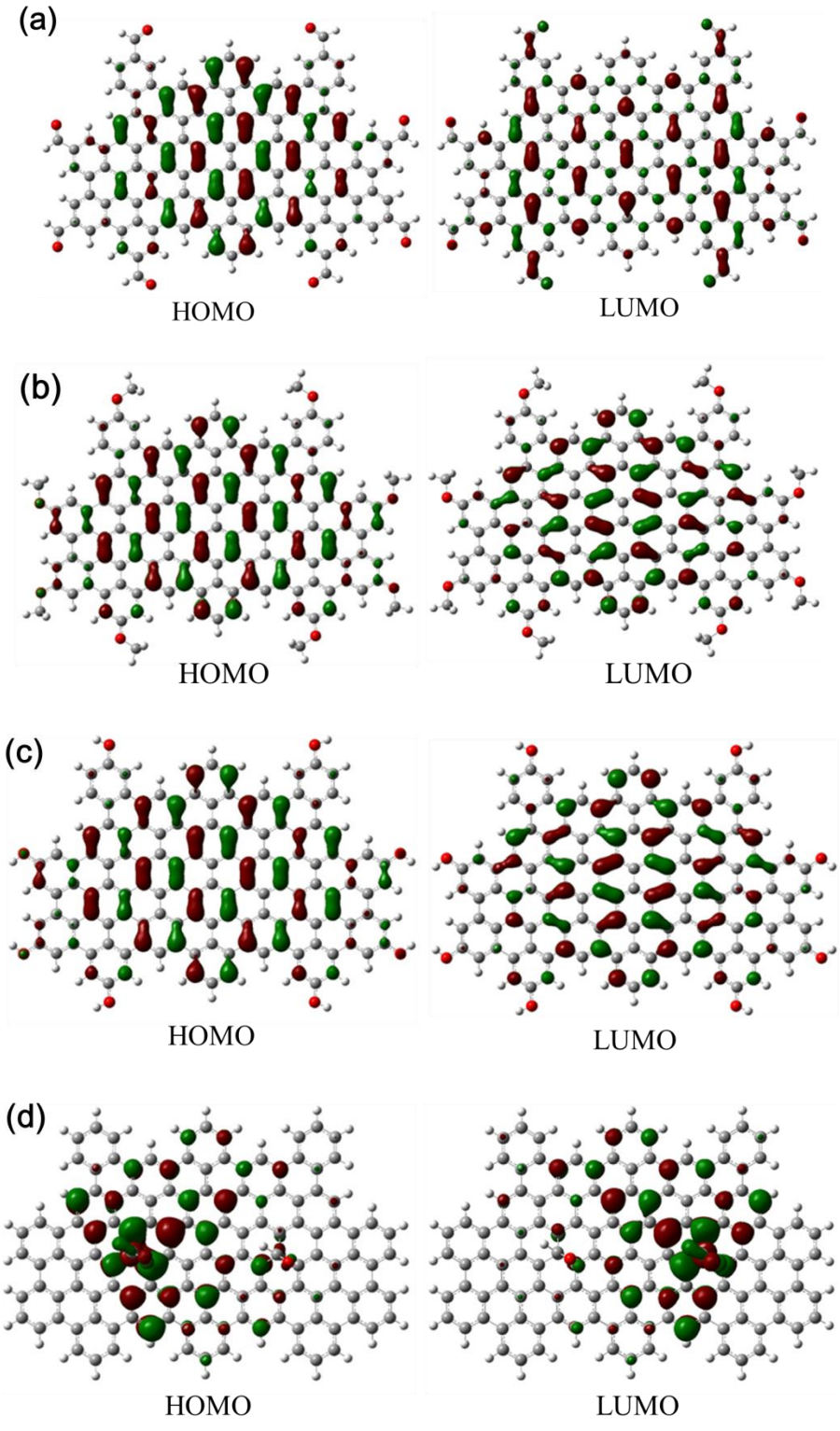


Fig. S2 Calculated absorption spectra of C24-C42 and their functionalized GQDs.


(a)
HOMO
LUMO
(b)
HOMO
LUMO
(c)
HOMO
LUMO
(d)
HOMO
LUMO

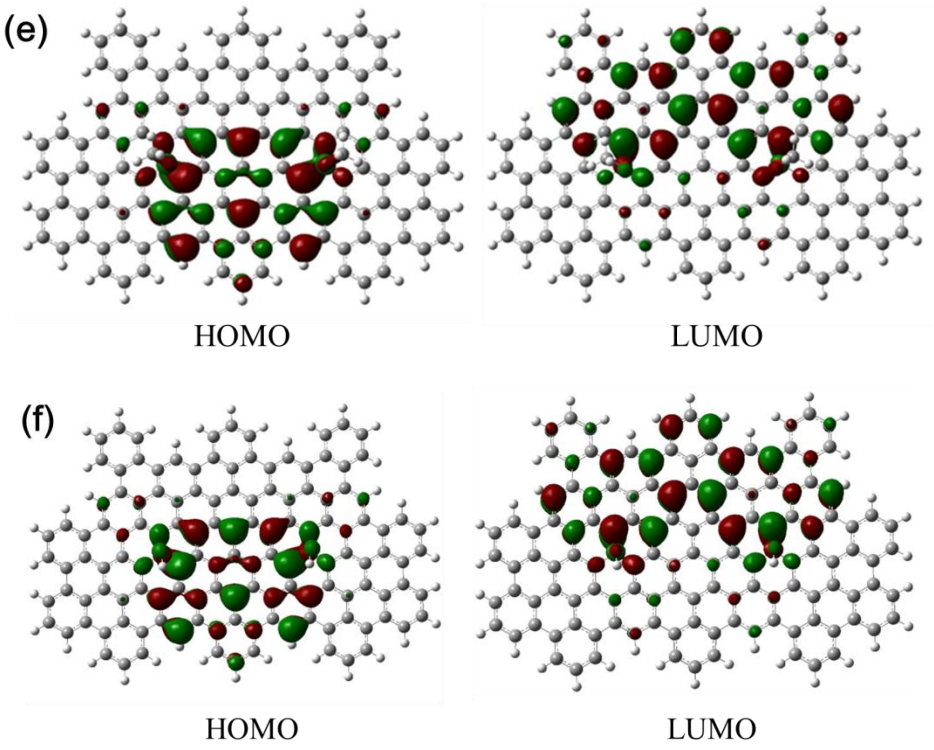


Fig. S3 Isosurfaces of HOMO and LUMO in GQDs with different oxygen-containing groups in ground state. The positive and negative orbital lobes are displayed in red and green, respectively. (a) C132-CHO8-EF, (b) C132-$OCH_3$8-EF, (c) C132-OH8-EF, (d) C132-CHO2-SF, (e) C132-$OCH_3$2-SF, (f) C132-OH2-SF.

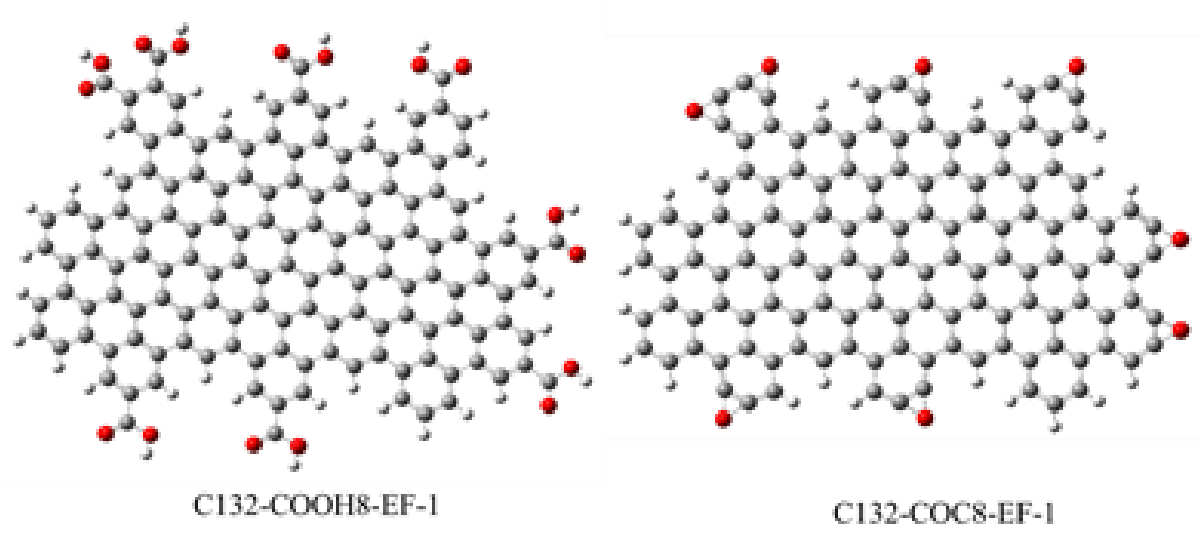


Fig. S4 Structures of edge-functionalized GQDs with carboxyl and epoxy groups.

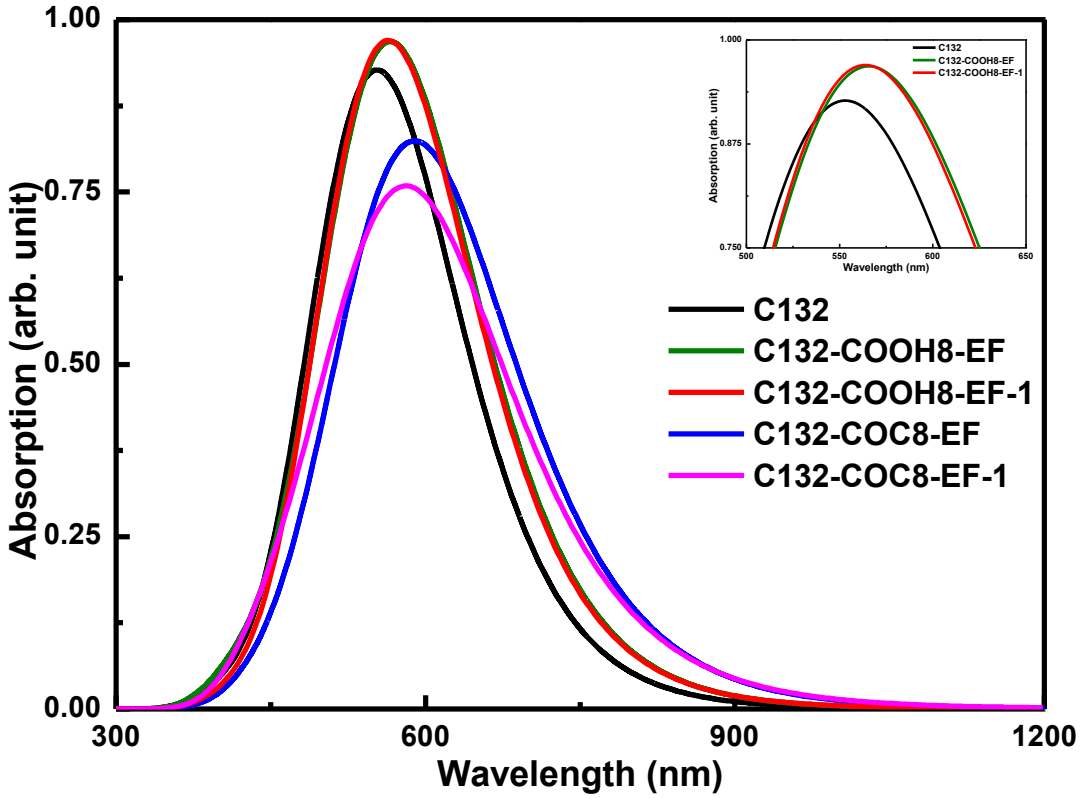


Fig. S5 Calculated absorption spectra of edge-functionalized GQDs with carboxyl and epoxy groups in Fig. S4.

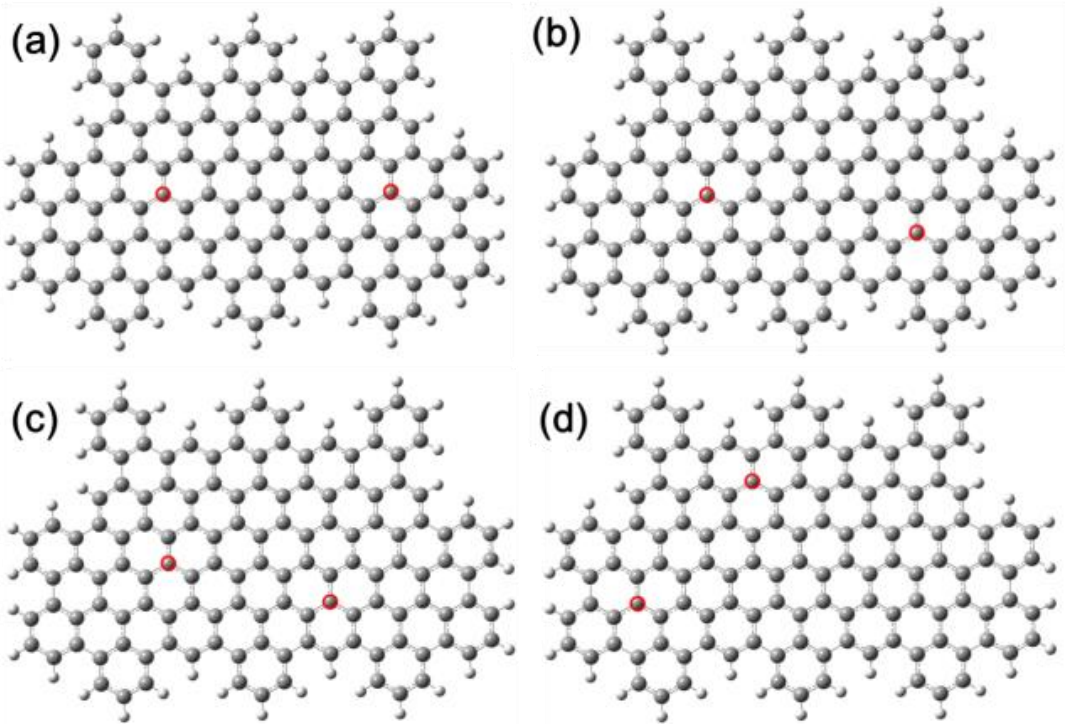


Fig. S6 Schematics of surface functionalization position on C132 GQDs: (a) C132-R2-SF-1, (b) C132-R2-SF-2, (c) C132-R2-SF-3, and (d) C132-R2-SF-4. R indicates the functional group.

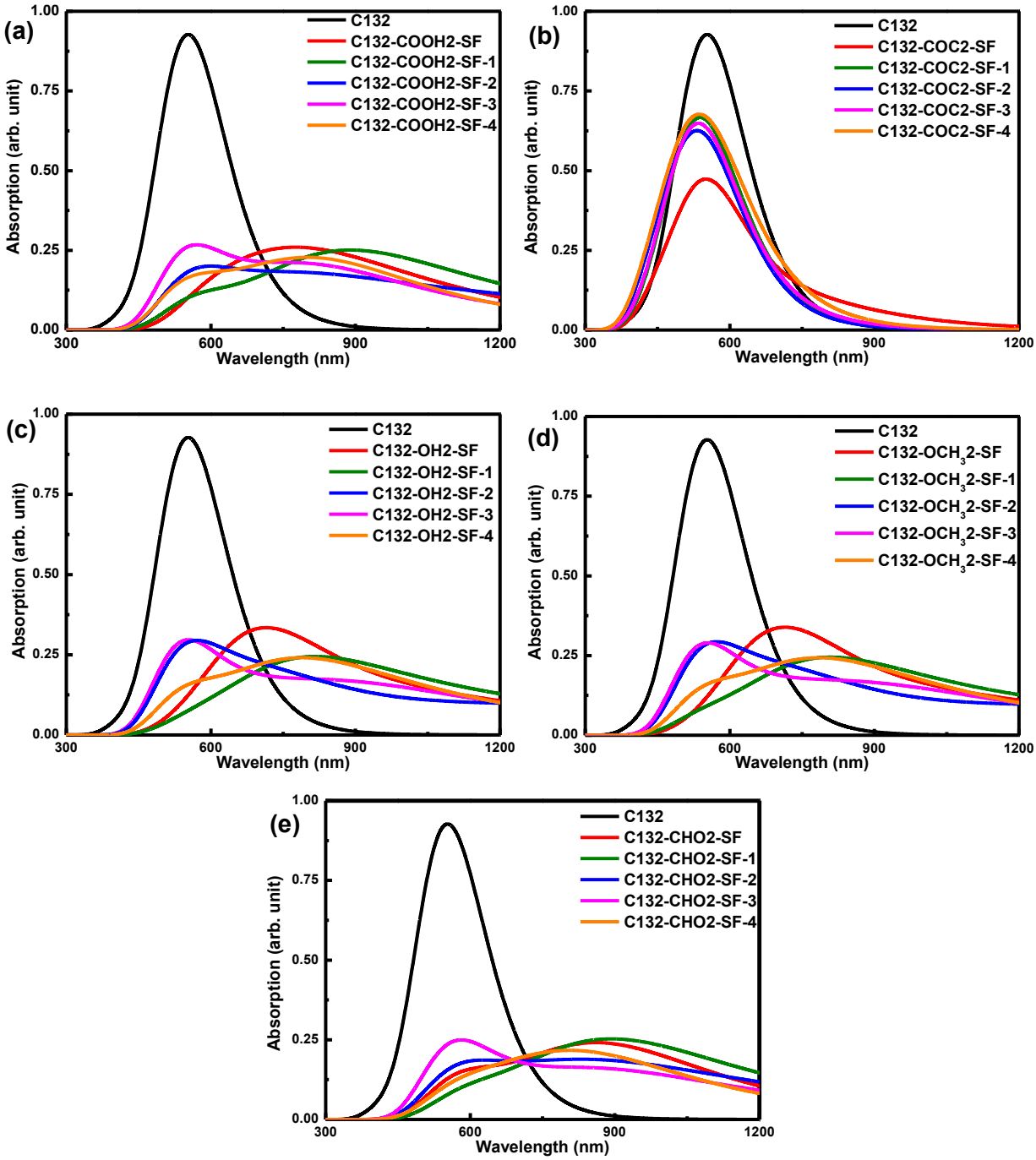


Fig. S7 Calculated absorption spectra of the surface-functionalized GQDs with five oxygen groups in Fig. S6.

Table S12: HOMO energy, LUMO energy, HOMO-LUMO gap, and absorption maximum wavelengths of the surface-functionalized GQDs with different positions.

GQDs	HOMO energy (eV)	LUMO energy (eV)	HOMO-LUMO gap(eV)	λ_{max} (nm)
C132-COOH2-SF	-4.04	-3.73	0.32	812.15
C132-COOH2-SF-1	-4.02	-3.74	0.28	847.90
C132-COOH2-SF-2	-4.04	-3.71	0.33	809.14
C132-COOH2-SF-3	-4.06	-3.75	0.31	854.68
C132-COOH2-SF-4	-4.08	-3.67	0.42	777.45
C132-COC2-SF	-4.84	-2.98	1.86	556.63
C132-COC2-SF-1	-4.95	-2.77	2.18	556.52
C132-COC2-SF-2	-5.01	-2.75	2.26	567.66
C132-COC2-SF-3	-4.95	-2.79	2.16	552.95
C132-COC2-SF-4	-4.89	-2.76	2.13	566.34
C132-CHO2-SF	-4.00	-3.60	0.39	574.74
C132-CHO2-SF-1	-3.94	-3.68	0.27	891.45
C132-CHO2-SF-2	-3.95	-3.66	0.29	1162.59
C132-CHO2-SF-3	-3.98	-3.64	0.33	567.19
C132-CHO2-SF-4	-4.02	-3.62	0.40	778.60
C132-$OCH_3$2-SF	-4.24	-3.87	0.37	734.07
C132-$OCH_3$2-SF-1	-4.21	-3.89	0.32	844.92
C132-$OCH_3$2-SF-2	-4.26	-3.85	0.41	556.08
C132-$OCH_3$2-SF-3	-4.32	-3.84	0.47	538.26
C132-$OCH_3$2-SF-4	-4.27	-3.80	0.47	795.92
C132-OH2-SF	-4.22	-3.86	0.36	736.51
C132-OH2-SF-1	-4.20	-3.88	0.31	850.95
C132-OH2-SF-2	-4.25	-3.84	0.41	535.91
C132-OH2-SF-3	-4.30	-3.84	0.46	544.20
C132-OH2-SF-4	-4.26	-3.79	0.46	800.63

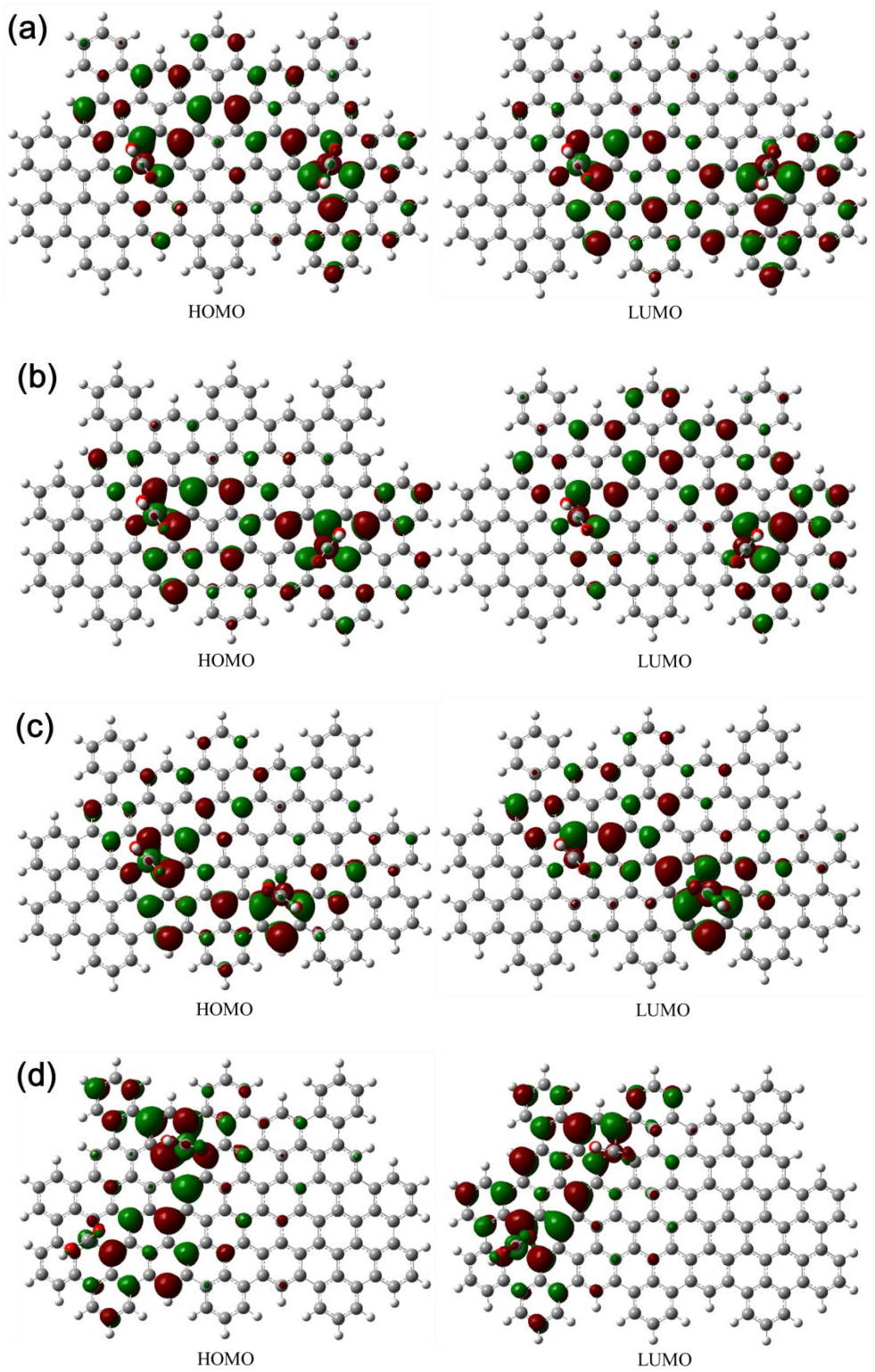
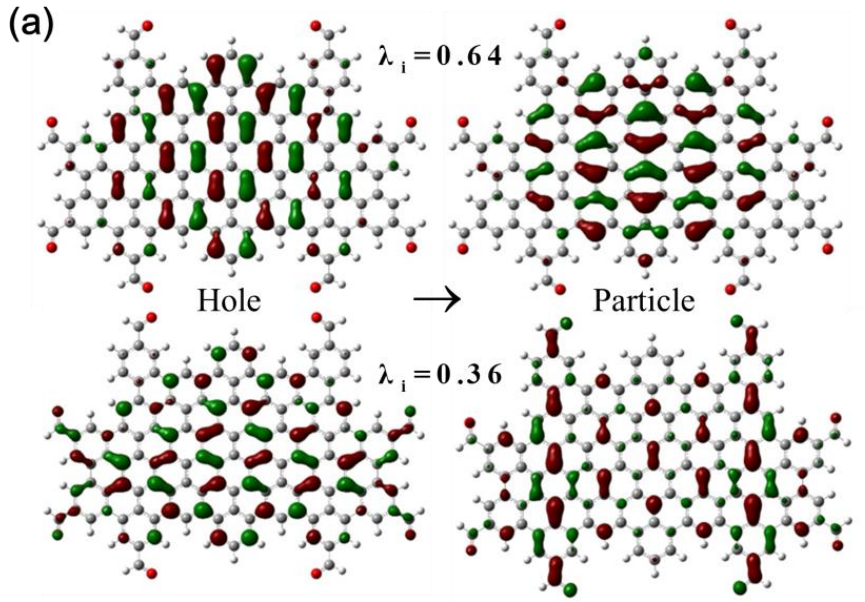
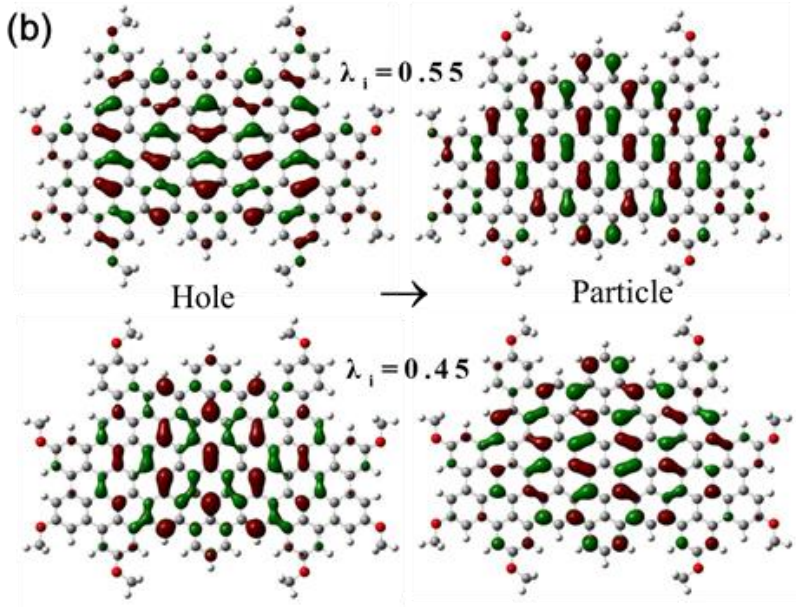


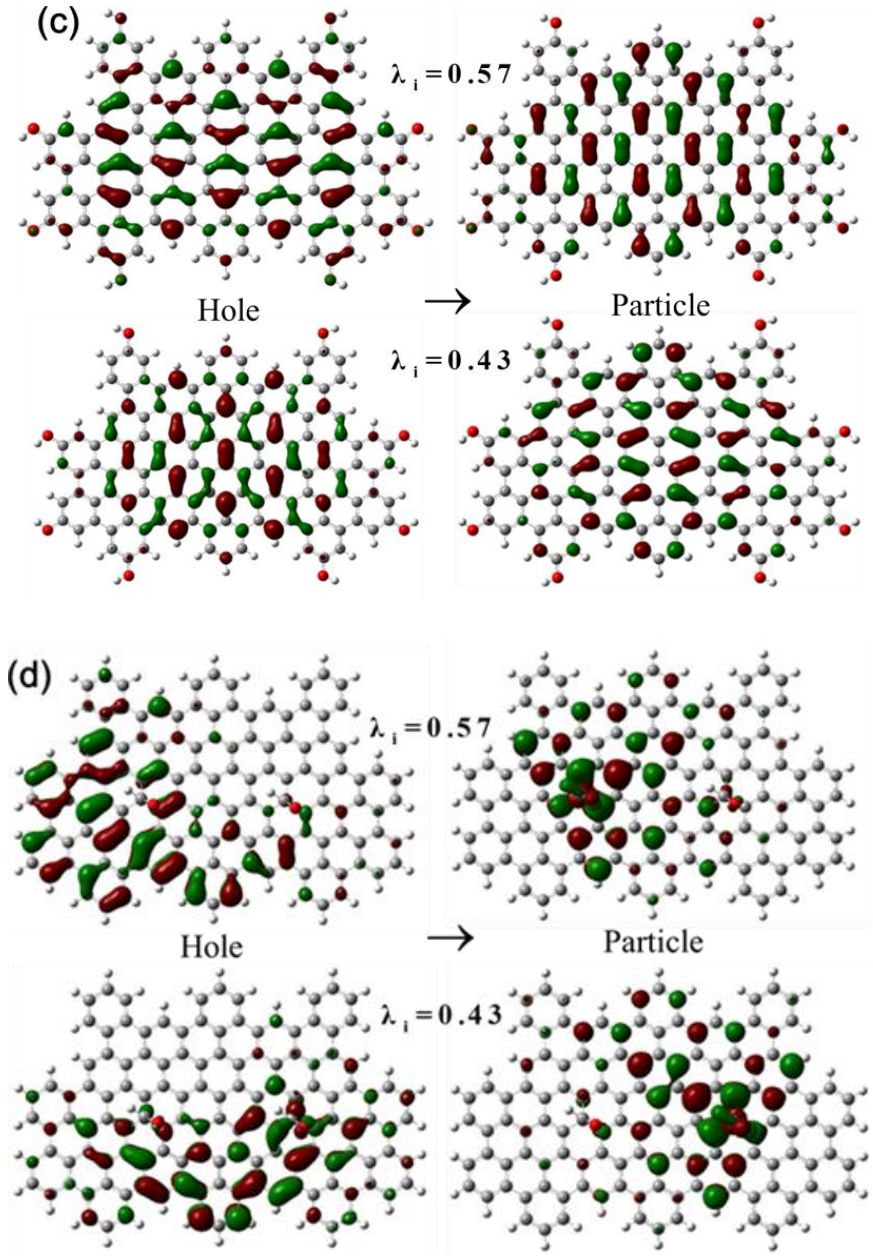
Fig. S8 Isosurfaces of HOMO and LUMO in GQDs with different surface positions in ground state. (a) C132-COOH2-SF-1, (b) C132-COOH2-SF-2, (c) C132-COOH2-SF-3, (d) C132-COOH2-SF-4.

Table S13: Excitation energies, wavelengths, oscillator strengths, transition coefficients, and associated eigenvalues of the dominated excitation in GQDs.

GQDs	Dominated excitation	Excitation energy(eV)	Wavelength(nm)	Oscillator strength(f)	Transition coefficients		Associated eigenvalues(λ_i)
C132-$OCH_3$8-EF	S3	2.17	572.11	3.25	H-1 -> L	0.47	0.55
					H -> L+1	0.5	0.45
C132-CHO8-EF	S3	2.12	585.09	3.05	H-1 -> L	0.56	0.64
					H -> L+1	-0.42	0.36
C132-OH8-EF	S3	2.18	567.89	3.21	H-1 -> L	-0.46	0.57
					H -> L+1	0.53	0.43
C132-$OCH_3$2-SF	S8	1.69	734.08	0.90	H-7 -> L	0.10	
					H-5 -> L	-0.16	0.89
					H-2-> L	0.12	0.11
					H-> L+2	0.65	
C132-CHO2-SF	S5	1.42	874.74	0.70	H-3 -> L	0.12	
					H-2 -> L	0.21	0.57
					H-1 -> L	0.39	0.43
					H-> L+1	-0.32	
					H->L+2	0.40	
					H-> L+3	0.12	
C132-OH2-SF	S8	1.68	736.51	0.90	H-5 -> L	-0.20	
					H-2 -> L	0.12	0.87
					H->L+2	0.64	0.13
					H->L+3	0.12	


(a)
λ i = 0.64
Hole
Particle
λ i = 0.36


(b)
λ i = 0.55
Hole
Particle
λ i = 0.45


(c)
λ i = 0.57
Hole
Particle
λ i = 0.43
(d)
λ i = 0.57
Hole
Particle
λ i = 0.43

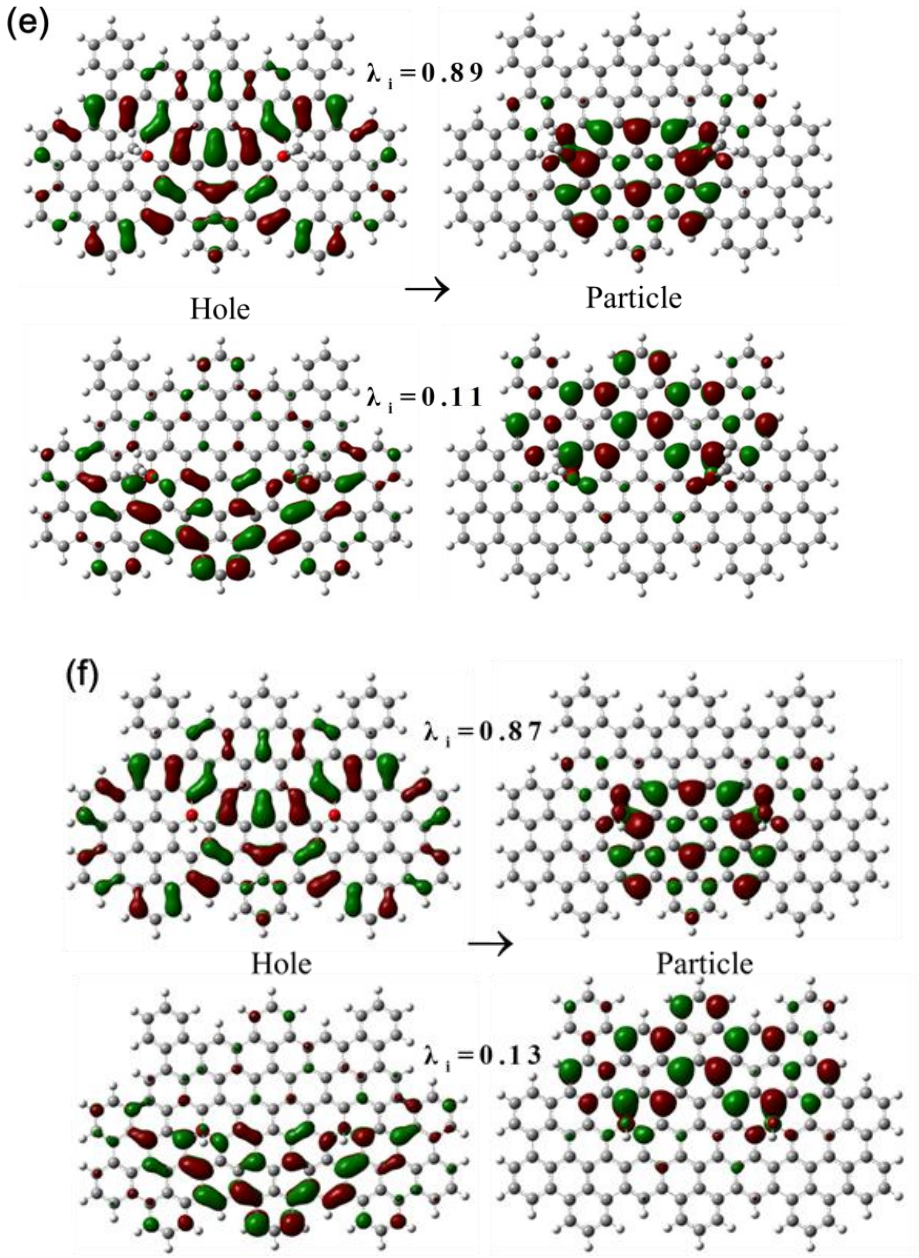


Fig. S9 Natural transition orbital pairs for the dominant excited state of GQDs. (a) C132-CHO8-EF, (b) C132-$OCH_3$8-EF, (c) C132-OH8-EF, (d) C132-CHO2-SF, (e) C132-$OCH_3$2-SF, (f) C132-OH2-SF. For this state the "hole" is on the left, the "particle" is on the right; The values represent the associated eigenvalue (λ_i) of respective NTOs.

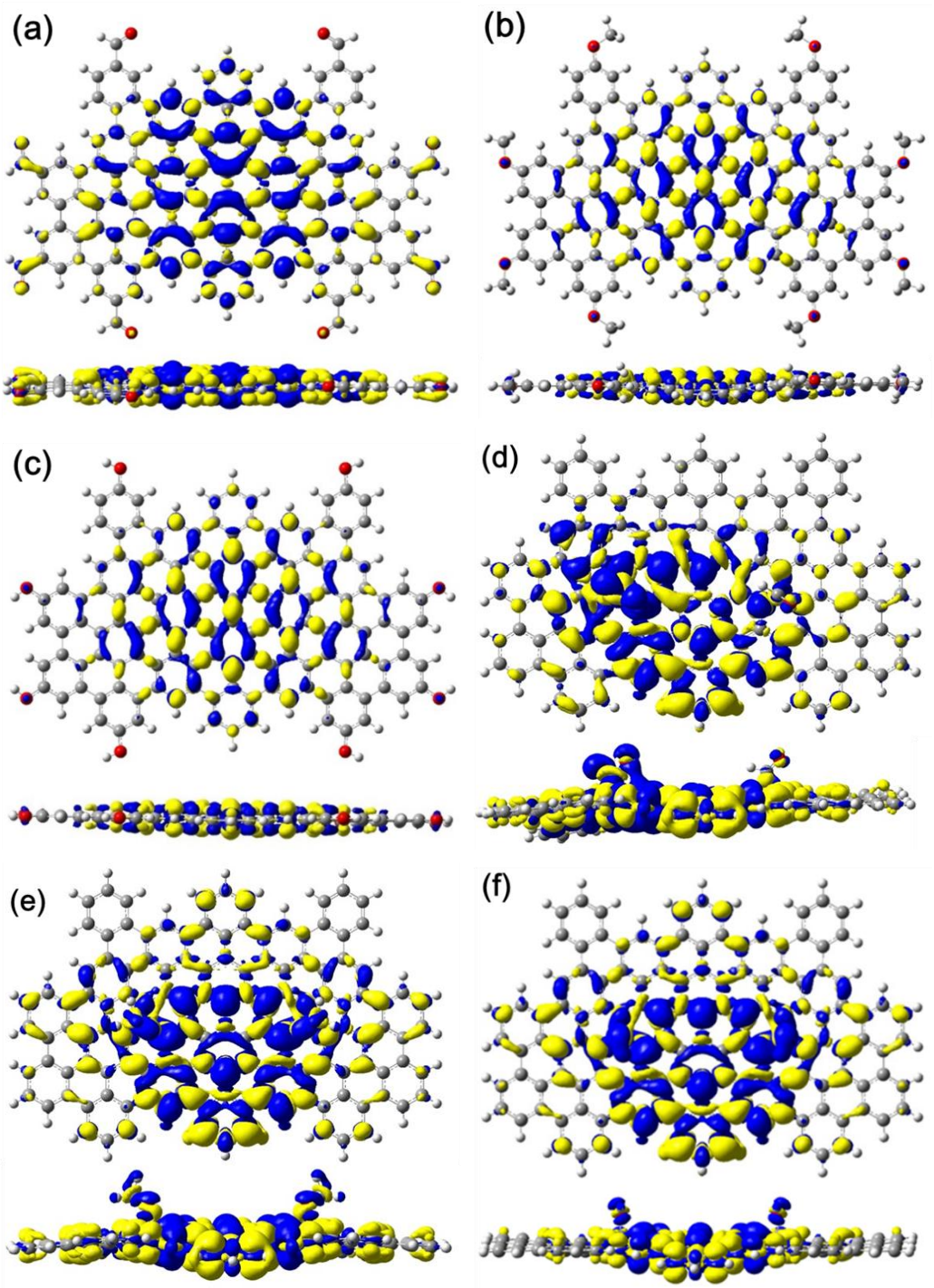


Fig. S10 Representation of the electron difference density between the dominated excited state minus ground state for GQDs. (a) C132-CHO8-EF, (b) C132-$OCH_3$8-EF, (c) C132-OH8-EF, (d) C132-CHO2-SF, (e) C132-$OCH_3$2-SF, (f) C132-OH2-SF. At the bottom, the lateral views are shown. The blue area plots the surface where the value of the difference density is -0.0002 and the yellow area plots the surface where the value of the difference density is +0.0002.