Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Nature of photoexcited states in ZnO-embedded graphene quantum dots

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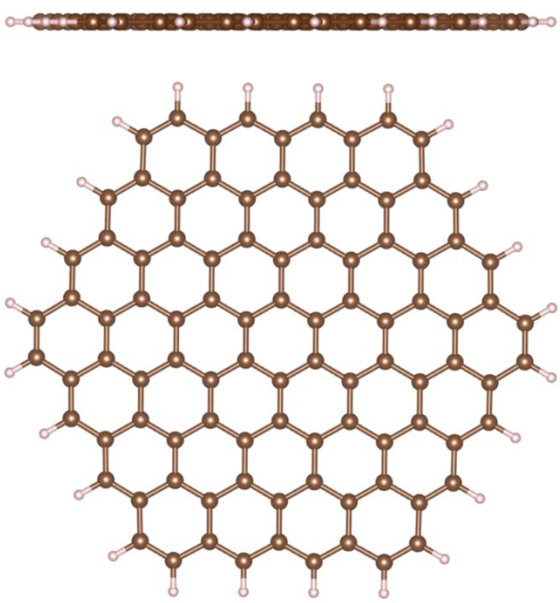


Figure S1. (Side and top views) Optimized structure of $C_{96}H_{24}$ molecule by using PBE0 functional. Brown and whitish balls correspond to carbon and hydrogen atoms, respectively.

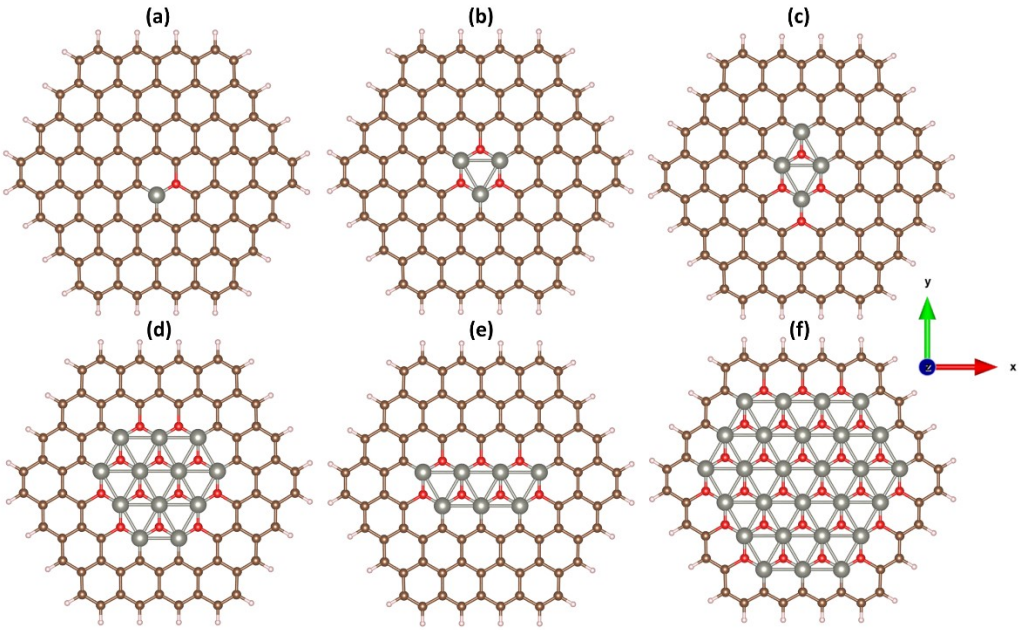


Figure S2. (Top views) Non-relaxed structures of the $(ZnO)_nC_{96-2n}$: (a) n=1, (b) n=3, (c) n=4, (d) n=7, (e) n=12 and (f) n=27, respectively. Brown, whitish, blue, and red balls correspond to carbon, hydrogen, zinc, and oxygen atoms, respectively.

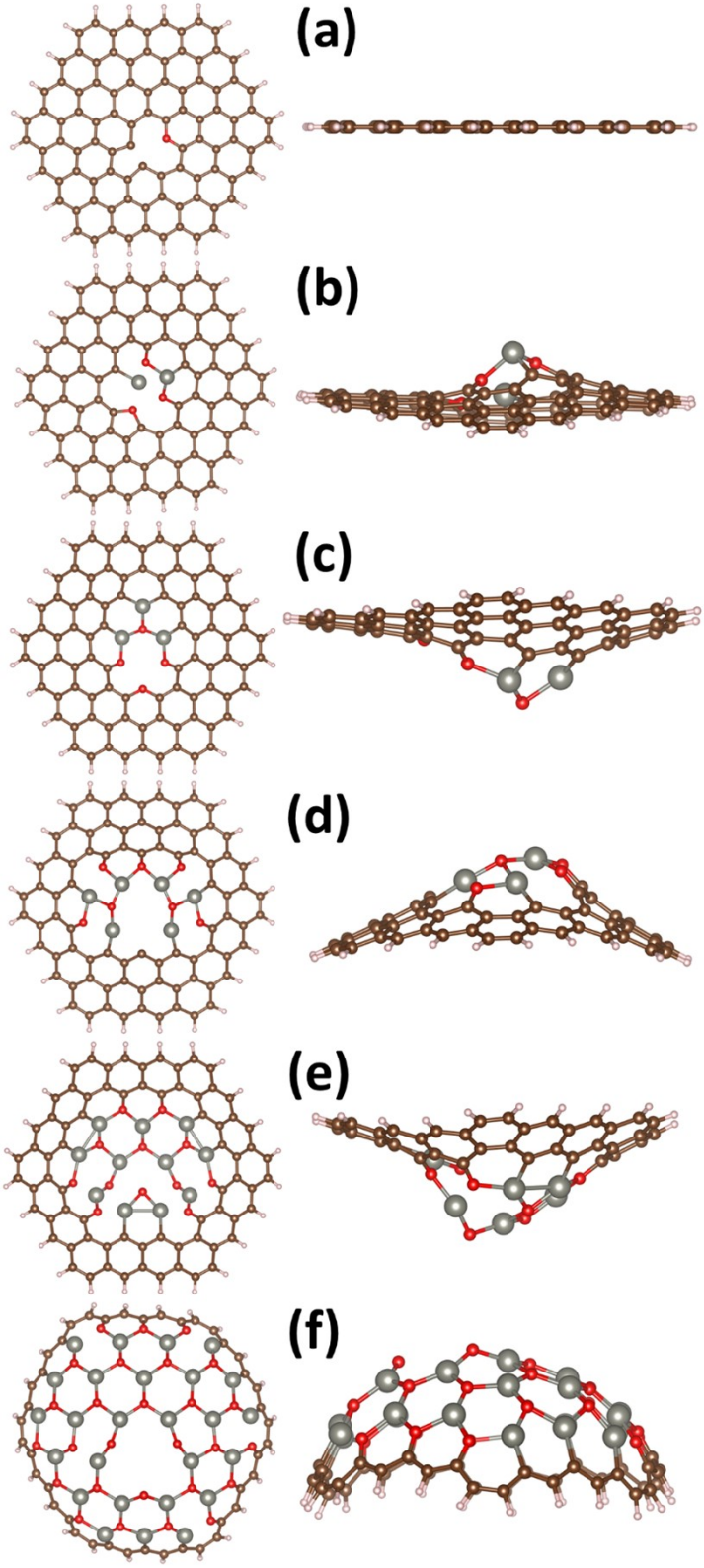


Figure S3. (Top and side views) Optimized structures of $(ZnO)_nC_{96-2n}$ after removal of Zn atom: (a) n=1, (b) n=3, (c) n=4, (d) n=7, (e) n=12 and (f) n=27, respectively. Brown, whitish, blue, and red balls correspond to carbon, hydrogen, zinc, and oxygen atoms, respectively. All calculations are performed using PBE0 functional.

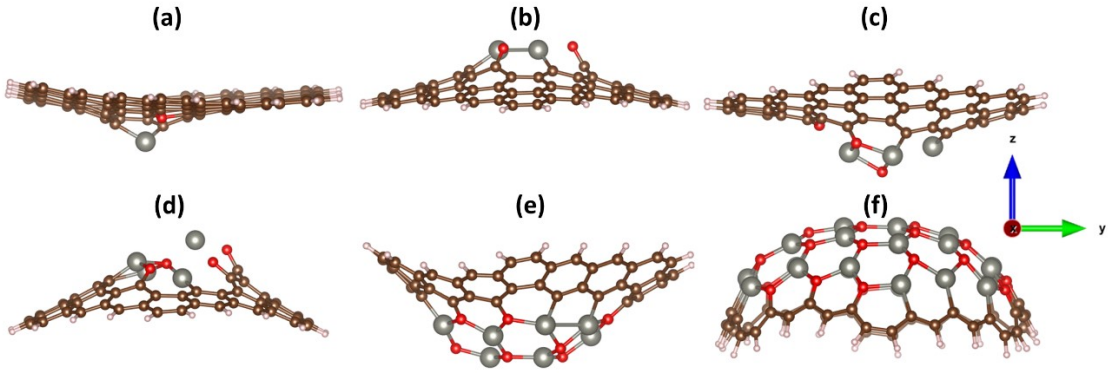


Figure S4. (Side view) Optimized structures of the $(ZnO)_nC_{96-2n}$: (a) n=1, (b) n=3, (c) n=4, (d) n=7, (e) n=12 and (f) n=27, respectively. Brown, whitish, blue, and red balls correspond to carbon, hydrogen, zinc, and oxygen atoms, respectively. All calculations are performed using PBE0 functional.

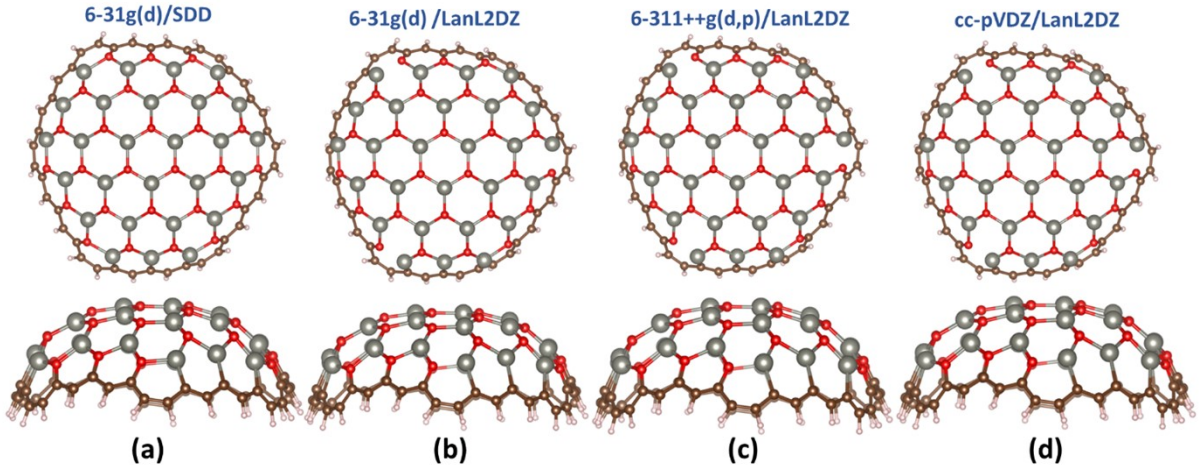


Figure S5. (Top and side views) Optimized structures of the $(ZnO)_{27}C_{42}$ predicted by PBE0 functional using different combination of basis sets: (a) 6-31g(d)/SDD, (b) 6-31g(d)/LanL2DZ, (c) 6-311++g(d, p)/LanL2DZ and (d) cc-PVDZ/LanL2DZ, respectively.

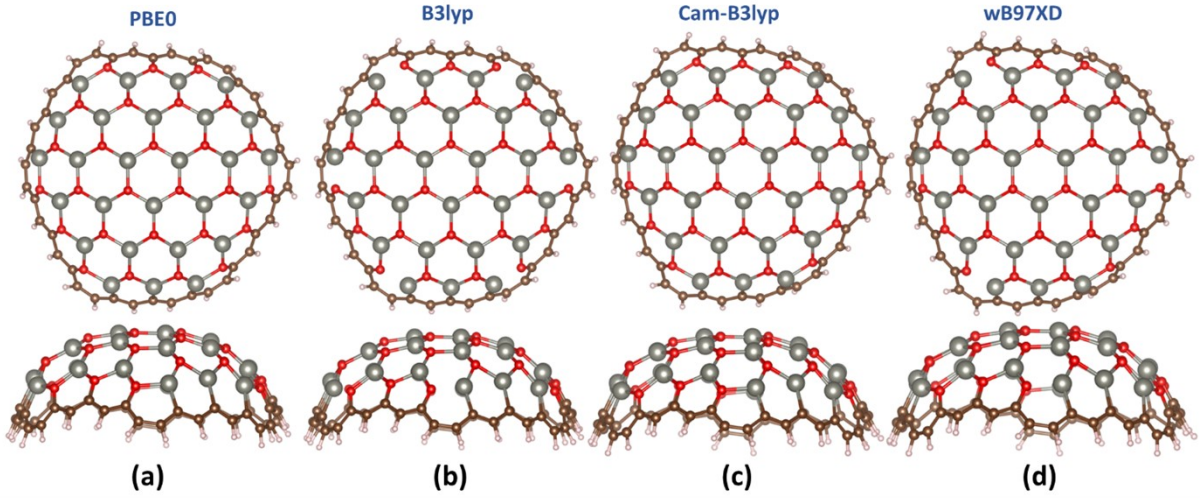


Figure S6. (Top and side views) Optimized structures of the $(ZnO)_{27}C_{42}$ predicted using different functionals: (a) PBE0, (b) B3LYP, (c) CAM-B3LYP and (d) wB97XD, respectively.

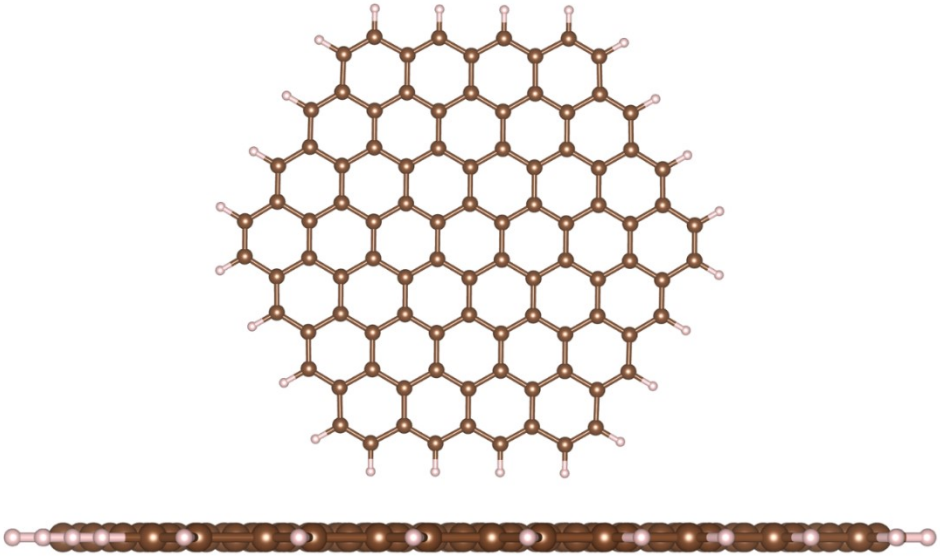


Figure S7. (Top and side views) Optimized structure of $C_{96}H_{24}$ molecule by using CAM-B3LYP functional. Brown and whitish balls correspond to carbon and hydrogen atoms, respectively.

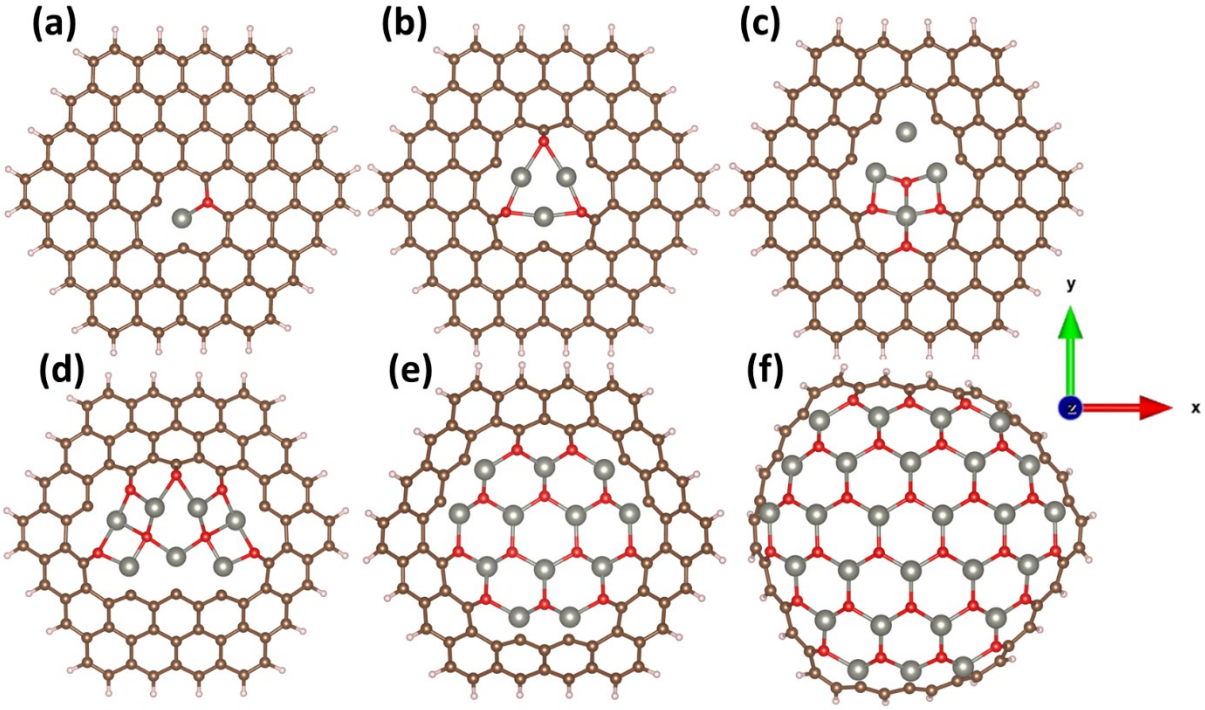


Figure S8. (Top views) Optimized structures of the $(ZnO)_nC_{96-2n}$: (a) n=1, (b) n=3, (c) n=4, (d) n=7, (e) n=12 and (f) n=27, respectively. Brown, whitish, blue, and red balls correspond to carbon, hydrogen, zinc, and oxygen atoms, respectively. All calculations are performed using CAM-B3LYP functional.

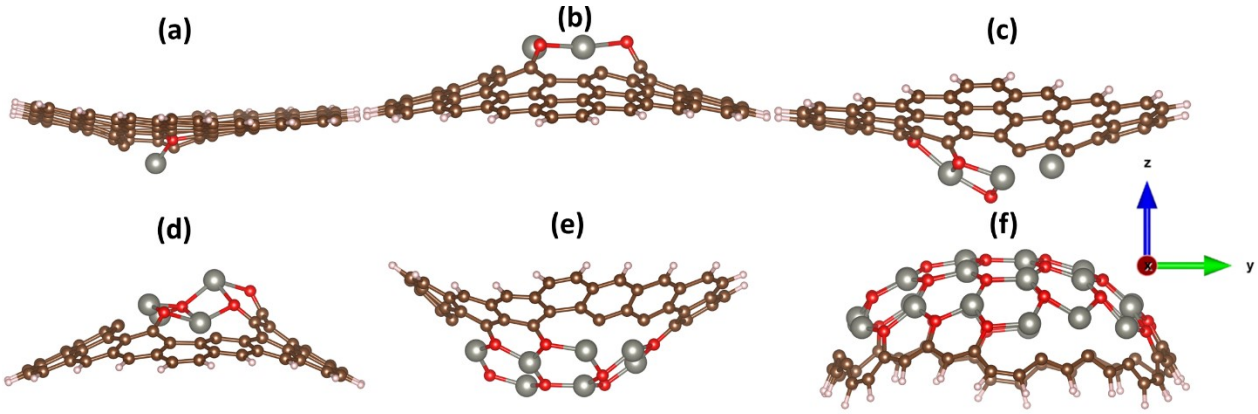


Figure S9. (Side views) Optimized structures of the $(ZnO)_nC_{96-2n}$: (a) n=1, (b) n=3, (c) n=4, (d) n=7, (e) n=12 and (f) n=27, respectively. Brown, whitish, blue, and red balls correspond to carbon, hydrogen, zinc, and oxygen atoms, respectively. All calculations are performed using CAM-B3LYP functional.

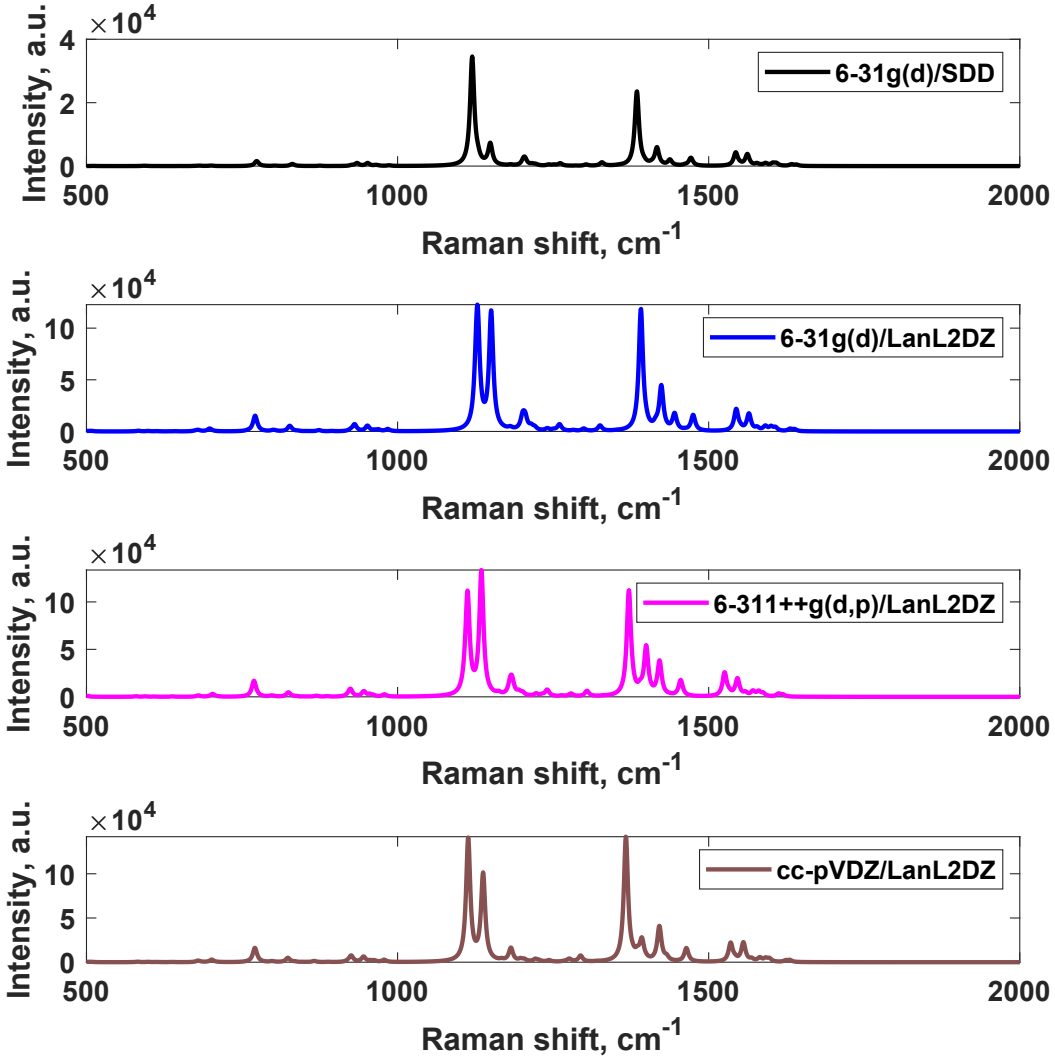


Figure S10. Raman spectra of the $(ZnO)_{27}C_{42}$ predicted by PBE0 functional using different combination of basis sets: 6-31g(d)/SDD, 6-31g(d)/LanL2DZ, 6-311++g(d, p)/LanL2DZ and cc-PVDZ/LanL2DZ, respectively.

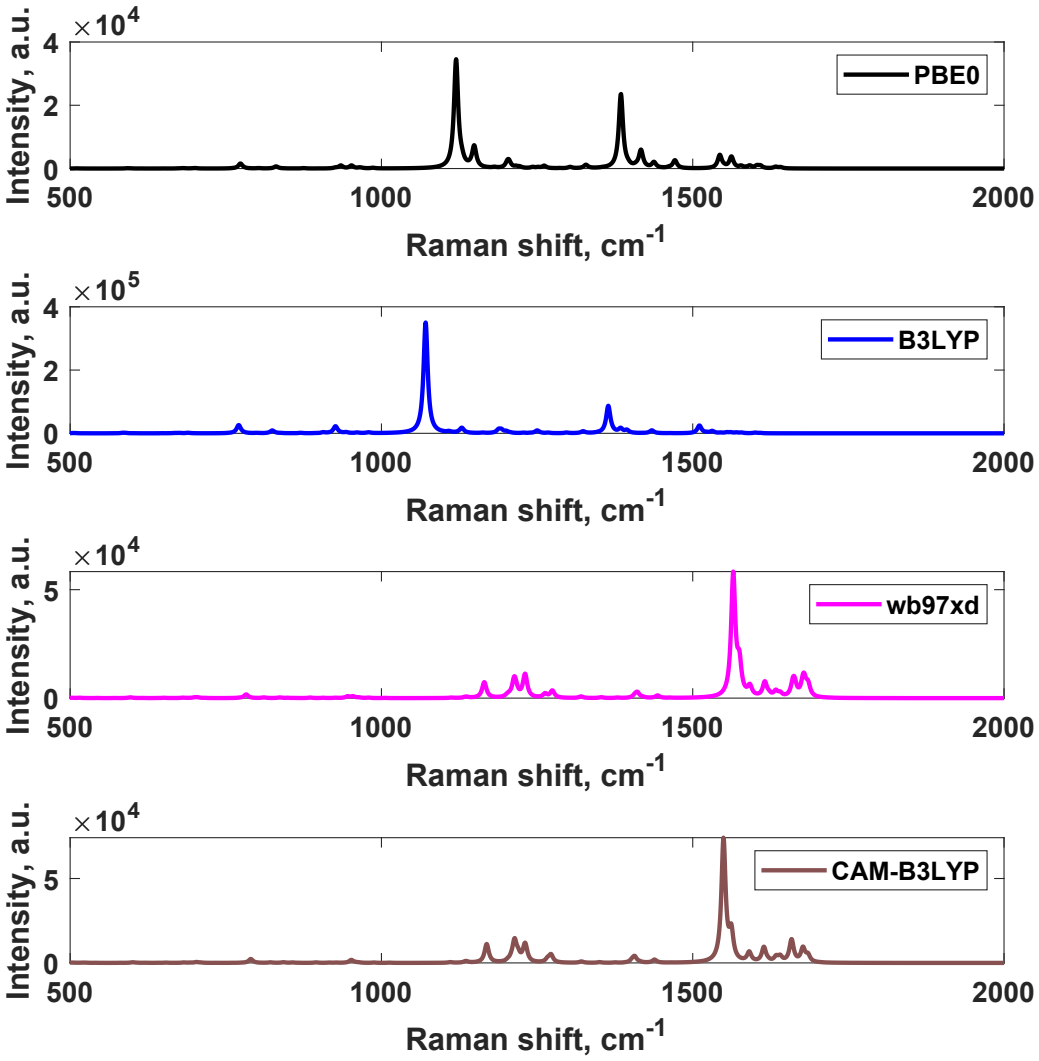
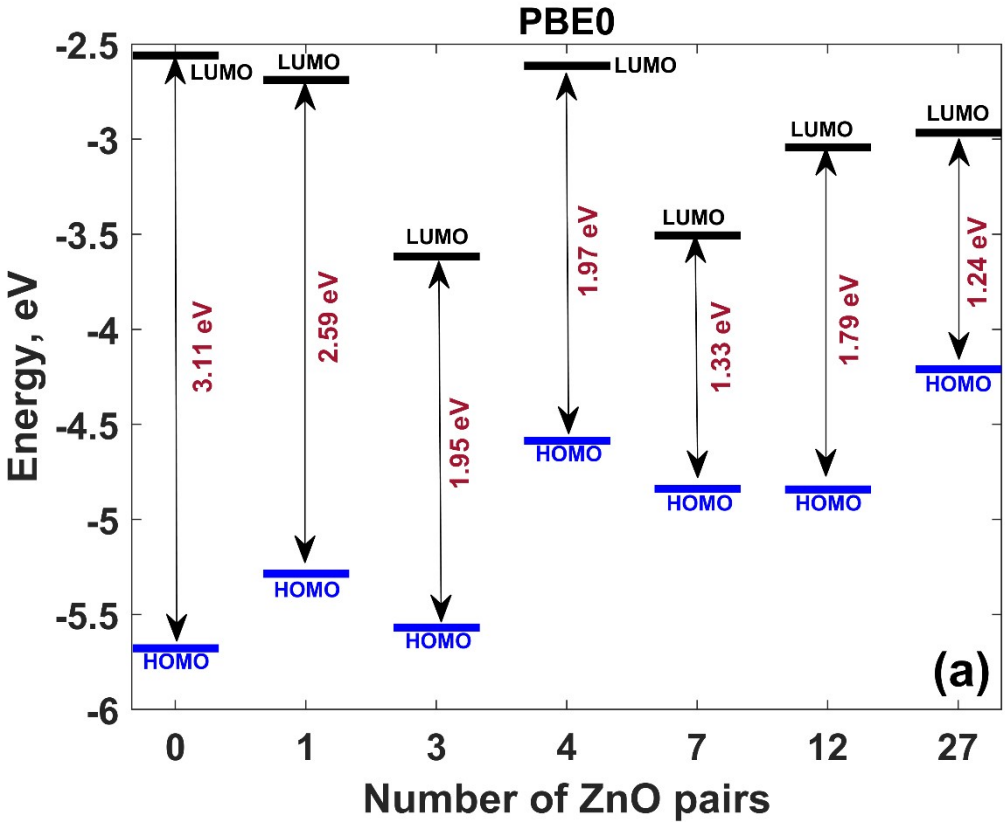
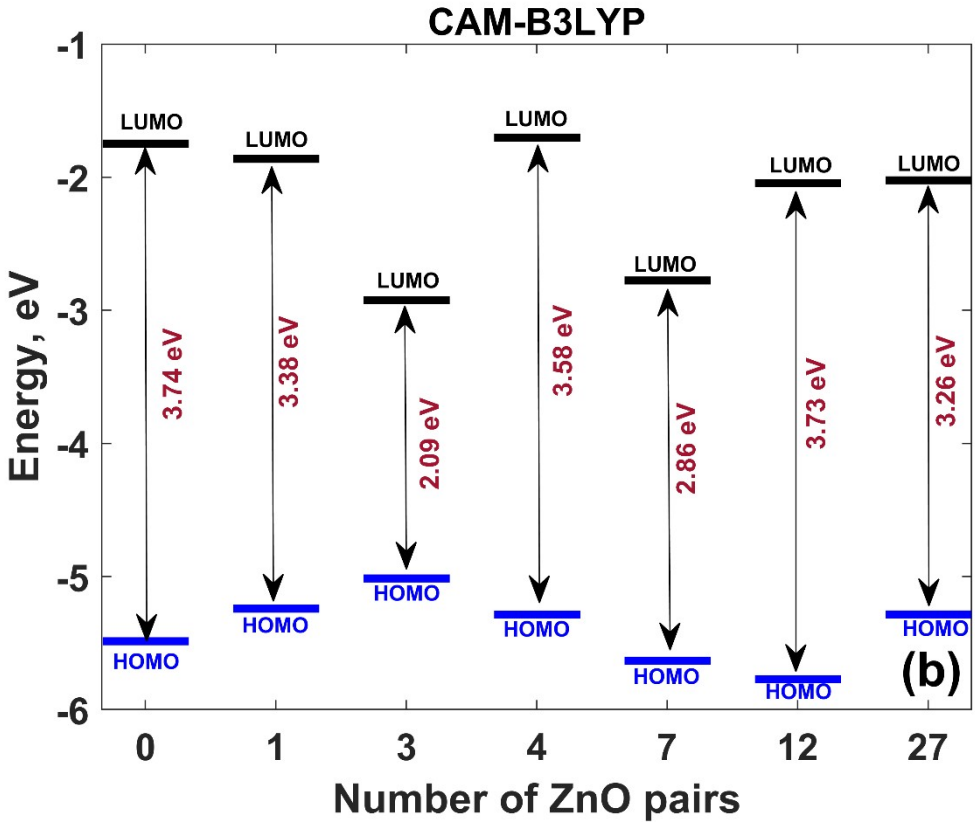


Figure S11. Raman spectra of the $(ZnO)_{27}C_{42}$ predicted using different functionals: PBE0, B3LYP, CAM-B3LYP, and wB97XD, respectively.


PBE0
Energy, eV
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
LUMO
HOMO
3.11 eV
2.59 eV
1.95 eV
1.97 eV
1.33 eV
1.79 eV
1.24 eV
(a)
0
1
3
4
7
12
27
Number of ZnO pairs


CAM-B3LYP
Energy, eV
-1
-2
-3
-4
-5
-6
LUMO
HOMO
3.74 eV
3.38 eV
2.09 eV
3.58 eV
2.86 eV
3.73 eV
3.26 eV
(b)
0
1
3
4
7
12
27
Number of ZnO pairs

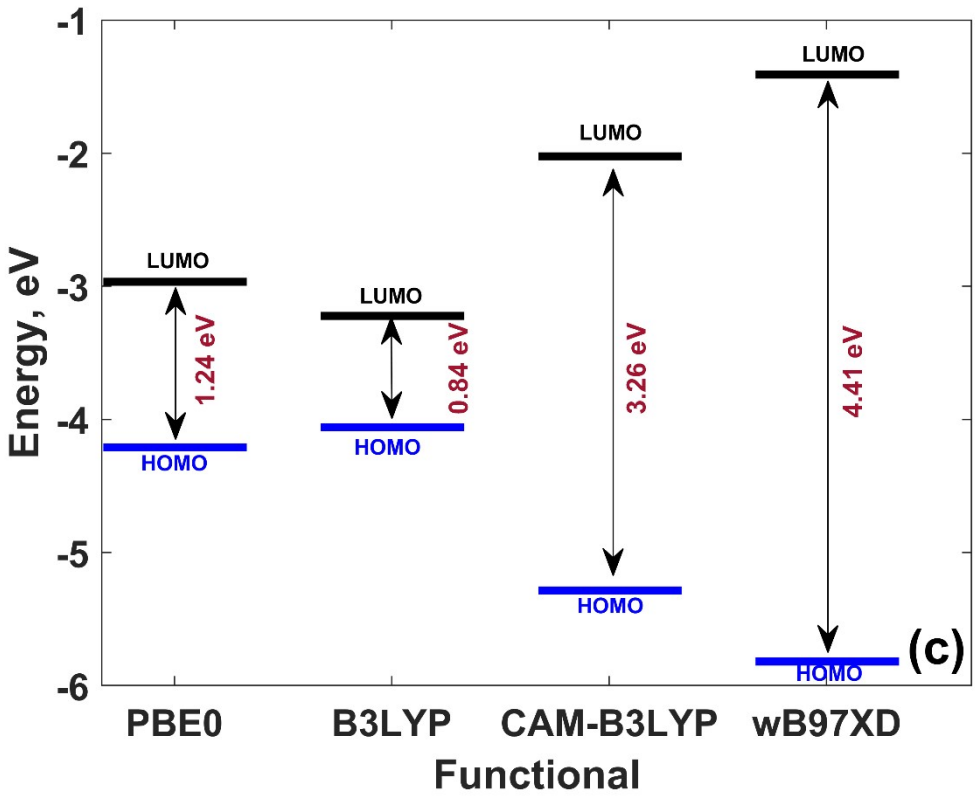


Figure S12. Molecular orbital diagram summarising all considered systems predicted by using different functionals: (a) PBE0 and (b) CAM-B3LYP. (c) A comparison of HOMO–LUMO gaps of $(ZnO)_{27}C_{42}$ system predicted by using different functionals. The arrows designate HOMO–LUMO gaps.

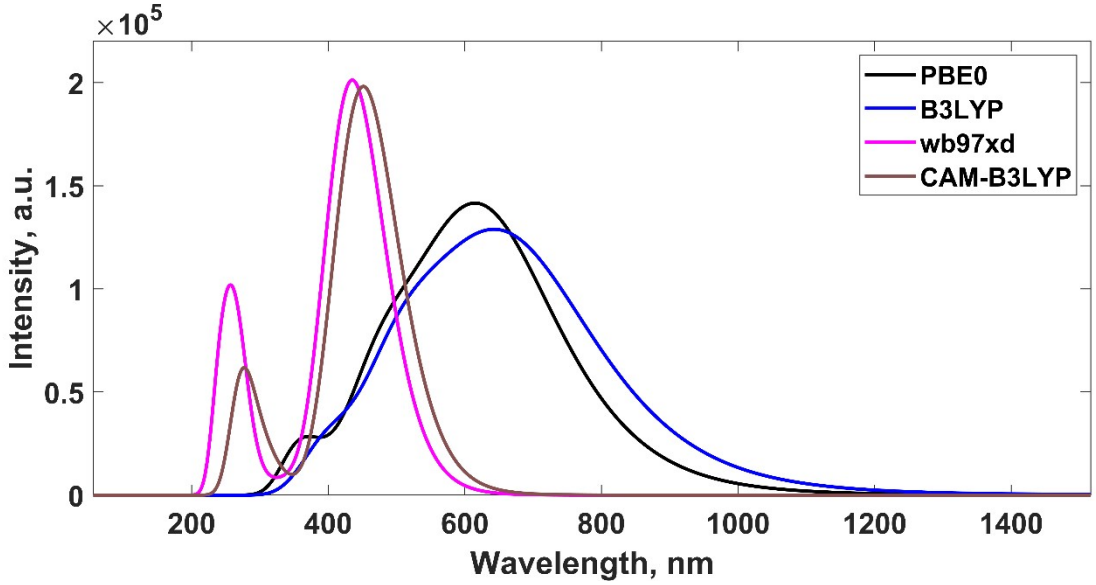


Figure S13. UV-vis absorption spectra of the $(ZnO)_{27}C_{42}$ system predicted by different functionals.

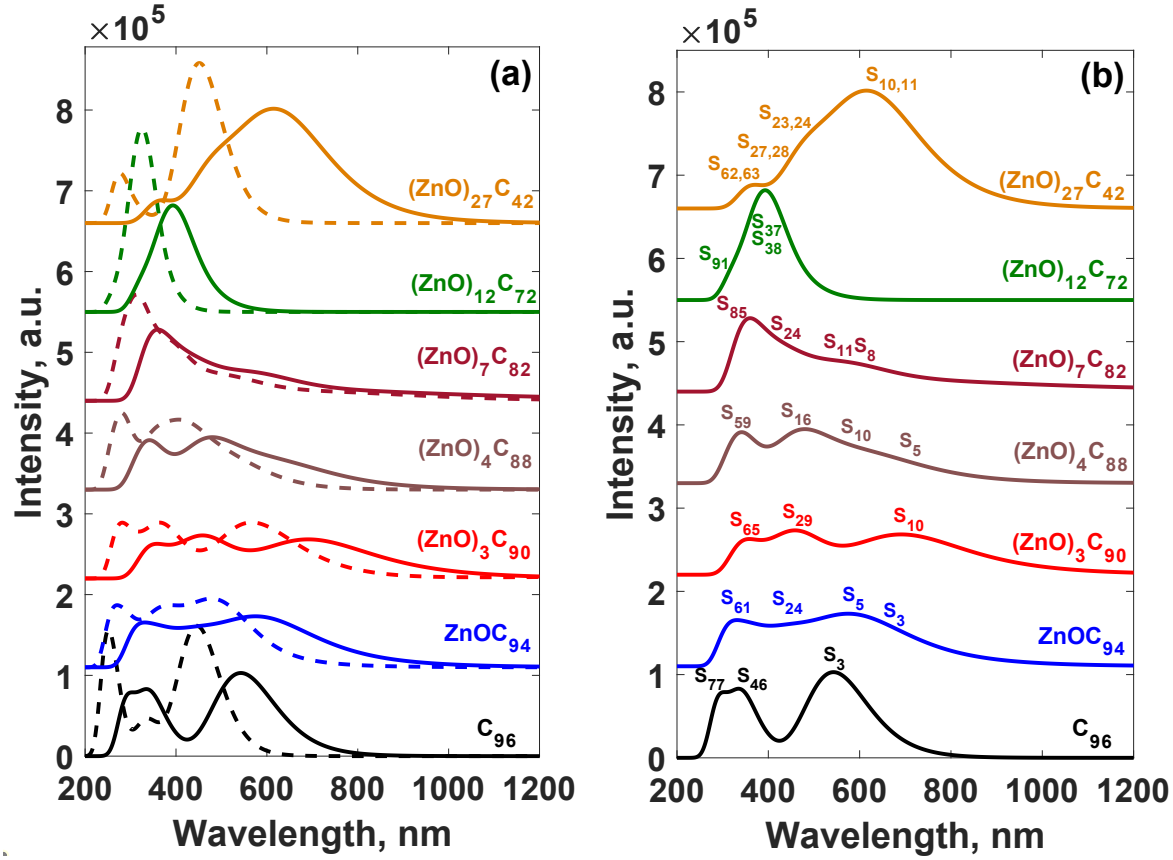


Figure S14. (a) A comparison of ultraviolet-visible (UV-vis) absorption spectra of the $(ZnO)_nC_{96-2n}$ structures predicted by using PBE0/6-31G*/SDD and CAM-B3LYP/6-31G*/SDD methods. (b) Assignment of absorption bands of $(ZnO)_nC_{96-2n}$ structures predicted by using PBE0/6-31G*/SDD method.

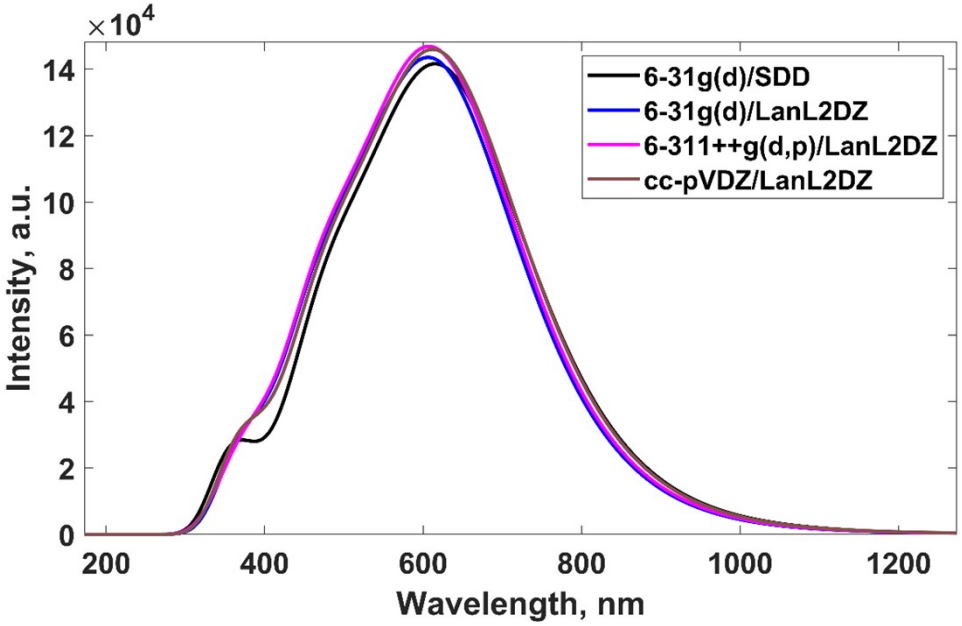


Figure S15. UV-vis absorption spectra of the $(ZnO)_{27}C_{42}$ system predicted by PBE0 functional using different combination of basis sets.

Table S1. Properties of S_1 excited states in $(ZnO)_nC_{96-2n}$: (a) n=1, (b) n=3, (c) n=4, (d) n=7, (e) n=12 and (f) n=27, respectively. All calculations are performed using CAM-B3LYP functional.

Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
0	592.74	0	0.000	0.96	-1.195	LE	H-1->LUMO (47%), HOMO->L+1 (47%)
1	672.54	0.08	0.666	0.92	-3.507	LE	H-1->L+1 (17%), HOMO->LUMO (72%)
3	2295.57	0.03	0.719	0.69	-3.360	LE	HOMO->LUMO (95%)
4	670.65	0	0.900	0.87	-3.521	LE	H-1->L+1 (31%), HOMO->LUMO (62%)
7	810.61	0.19	2.561	0.61	-1.273	LE-CT	H-2->LUMO (18%), HOMO->LUMO (73%)
12	532.92	0	3.866	0.21	1.663	CT	H-1->LUMO (86%)
27	613.44	0.002	4.087	0.20	1.882	CT	HOMO->LUMO (80%)

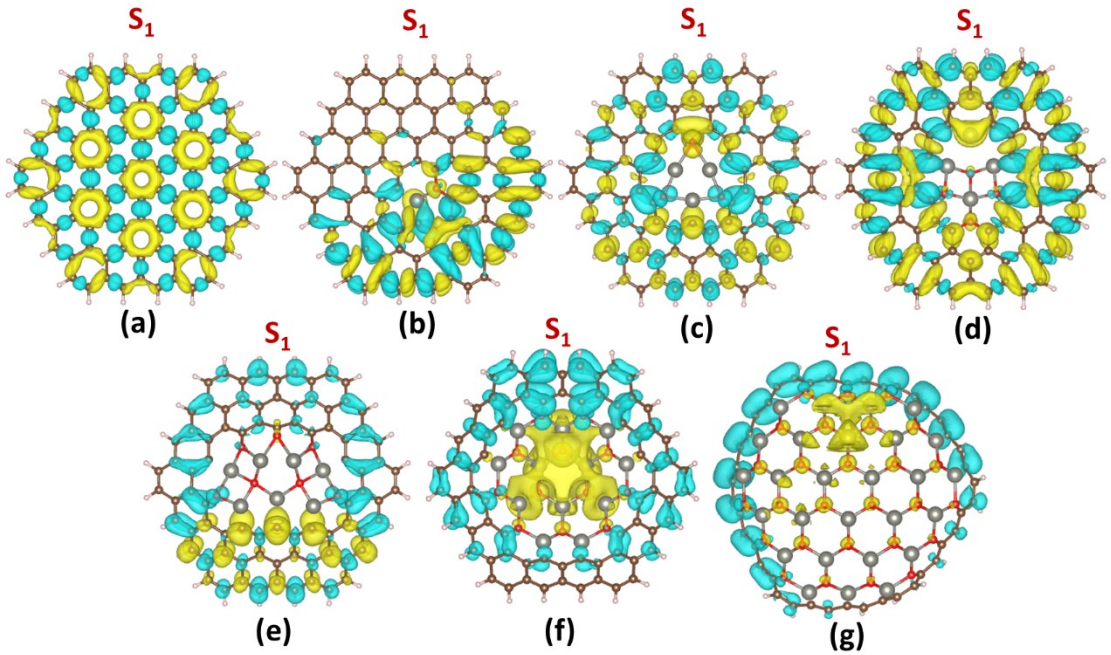


Figure S16. CDD for S_1 excited states in $(ZnO)_nC_{96-2n}$: (a) n=1, (b) n=3, (c) n=4, (d) n=7, (e) n=12 and (f) n=27, respectively. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using CAM-B3LYP functional.

Table S2. Properties of dominant excited states (with oscillator strength f >0.1) in C_{96} system. All calculations are performed using CAM-B3LYP functional.

Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
S1	592.74	0	0.000	0.96	-1.195	LE	H-1->LUMO (47%), HOMO->L+1 (47%)
S3	446.01	1.98	0.000	0.96	-1.900	LE	H-1->LUMO (23%), H-1->L+1 (25%), HOMO->LUMO (25%), HOMO->L+1 (23%)
S4	446.01	1.98	0.000	0.96	-1.098	LE	H-1->LUMO (25%), H-1->L+1 (23%), HOMO->LUMO (23%), HOMO->L+1 (25%)
S18	338.93	0.39	0.000	0.87	-4.939	LE	H-2->L+3 (23%), H-1->L+7 (13%), HOMO->L+6 (13%), HOMO->L+9 (16%)
S19	338.93	0.39	0.000	0.87	-4.645	LE	H-2->L+4 (23%), H-1->L+6 (13%), H-1->L+9 (16%), HOMO->L+7 (13%)
S21	333.31	0.15	0.000	0.89	-4.707	LE	H-6->LUMO (25%), H-3->L+2 (21%), H-1->L+8 (14%)
S22	333.31	0.15	0.000	0.89	-4.539	LE	H-6->L+1 (25%), H-4->L+2 (21%), HOMO->L+8 (14%)
S48	270.54	0.47	0.000	0.95	-3.107	LE	H-4->L+4 (21%), H-3->L+3 (21%)
S49	270.54	0.47	0.000	0.95	-2.116	LE	H-4->L+3 (21%), H-3->L+4 (21%)
S51	266.00	0.16	0.000	0.93	-3.899	LE	H-5->L+4 (11%), H-2->L+3 (36%)
S52	266.00	0.16	0.000	0.93	-3.315	LE	H-5->L+3 (11%), H-2->L+4 (36%)
S58	262.47	0.21	0.000	0.87	-4.674	LE	H-6->LUMO (11%), H-3->L+2 (47%)
S59	262.47	0.21	0.000	0.87	-3.593	LE	H-6->L+1 (11%), H-4->L+2 (47%)
S69	249.98	0.75	0.000	0.91	-3.957	LE	H-3->L+5 (21%), H-3->L+12 (18%)
S70	249.98	0.75	0.000	0.91	-4.144	LE	H-4->L+5 (21%), H-4->L+12 (18%)
S81	243.83	0.70	0.000	0.95	-3.466	LE	H-3->L+12 (23%), H-1->L+13 (12%), HOMO->L+14 (12%)
S82	243.83	0.70	0.000	0.95	-2.821	LE	H-4->L+12 (23%), H-1->L+14 (12%), HOMO->L+13 (12%)
S92	235.04	0.11	0.000	0.95	-3.932	LE	H-18->LUMO (8%), H-4->L+5 (7%), H-4->L+11 (7%), H-3->L+10 (7%)
S93	235.04	0.11	0.000	0.95	-2.623	LE	H-18->L+1 (8%), H-4->L+10 (7%), H-3->L+5 (7%)

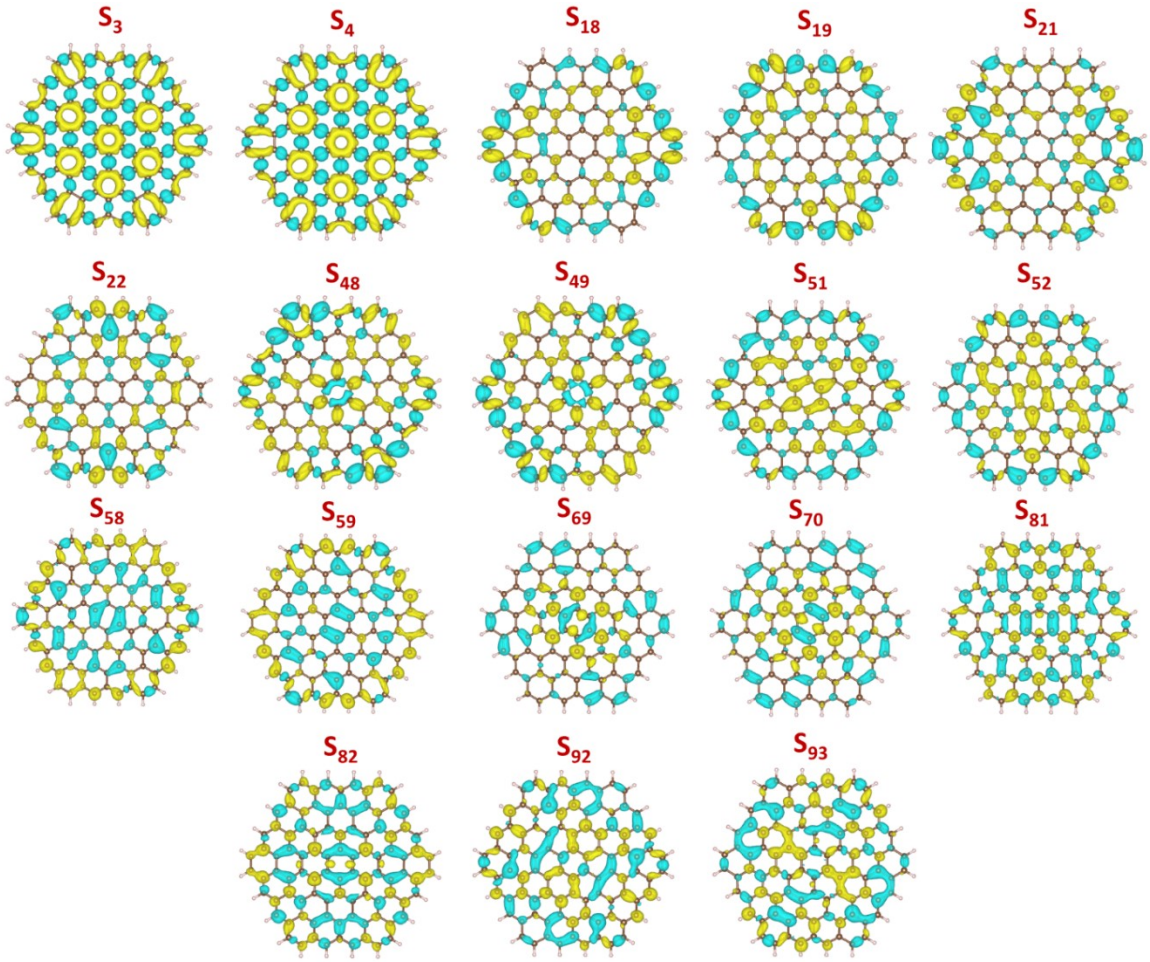


Figure S17. CDD for selected excited states (with the largest oscillator strength) in ZnO-free GQDs. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using CAM-B3LYP functional.

Table S3. Properties of dominant excited states (with oscillator strength f >0.1) in $ZnOC_{94}$ hybrid system. All calculations are performed using CAM-B3LYP functional.

Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
S1	672.54	0.08	0.666	0.92	-3.507	LE	H-1->L+1 (17%), HOMO->LUMO (72%)
S3	535.70	0.51	1.433	0.85	-2.391	LE-CT	H-1->LUMO (26%), HOMO->L+1 (35%)
S4	513.68	0.43	0.873	0.84	-2.290	LE-CT	H-1->L+1 (41%), HOMO->L+2 (22%)
S5	489.26	0.32	1.409	0.86	-2.498	LE-CT	H-2->L+1 (20%), H-1->L+1 (11%), H-1->L+2 (28%)
S6	482.16	0.36	1.851	0.76	-1.757	LE-CT	H-1->L+1 (12%), HOMO->L+2 (44%)
S7	471.88	0.23	0.914	0.83	-2.964	LE-CT	-2->LUMO (38%), H-2->L+1 (12%), H-1->L+2 (10%)
S9	439.90	0.13	1.439	0.79	-2.231	LE-CT	H-2->LUMO (11%), HOMO->L+2 (13%), HOMO->L+3 (32%)
S10	431.97	0.19	1.601	0.85	-2.315	LE-CT	H-4->LUMO (29%), H-2->LUMO (14%), HOMO->L+5 (13%)
S11	412.31	0.38	1.070	0.89	-3.130	LE-CT	H-2->L+1 (22%), H-1->L+2 (13%), H-1->L+3 (14%), HOMO->L+5 (16%)
S13	395.08	0.20	0.477	0.87	-2.610	LE	H-4->L+1 (10%), H-1->L+3 (16%), HOMO->L+6 (10%)
S17	378.90	0.26	0.516	0.92	-3.981	LE	H-3->LUMO (26%), HOMO->L+4 (20%)
S18	376.50	0.15	1.414	0.86	-2.728	LE-CT	H-2->L+2 (15%), HOMO->L+4 (23%)
S22	359.31	0.23	0.401	0.87	-3.867	LE	H-6->LUMO (26%)
S23	353.02	0.16	0.738	0.87	-3.086	LE-CT	H-3->L+1 (12%), H-1->L+5 (11%), HOMO->L+9 (10%)
S24	349.38	0.15	0.447	0.87	-3.287	LE	H-2->L+3 (15%)
S36	317.52	0.10	0.856	0.91	-3.299	LE	H-7->LUMO (20%), HOMO->L+8 (16%)
S50	291.48	0.15	0.552	0.88	-3.634	LE	H-8->LUMO (20%), H-2->L+4 (17%)
S51	290.03	0.18	0.274	0.92	-4.103	LE	H-10->L+1 (12%), HOMO->L+12 (17%)
S73	265.37	0.18	0.815	0.91	-3.576	LE	H-2->L+6 (9%), H-2->L+9 (5%)
S75	263.45	0.11	0.574	0.91	-3.736	LE	H-10->L+2 H-5->L+5 (6%)
S80	259.77	0.21	1.053	0.91	-3.101	LE	H-16->LUMO (7%), H-15->LUMO (5%), H-5->L+5 (5%)
S98	247.77	0.11	0.470	0.92	-3.556	LE	H-8->L+2 (7%), H-2->L+12 (6%), HOMO->L+14 (7%), HOMO->L+17 (8%)

Table S4. Properties of dominant excited states (with oscillator strength f >0.1) in $(ZnO)_3C_{90}$ hybrid system. All calculations are performed using CAM-B3LYP functional.

Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
S1	2295.57	0.03	0.719	0.69	-3.360	LE	HOMO->LUMO (95%)
S5	641.34	0.45	0.817	0.71	-3.321	LE	HOMO->L+1 (90%)
S8	560.20	0.52	1.032	0.82	-2.393	LE-CT	H-5->LUMO (12%), H-1->L+1 (15%), HOMO->L+2 (52%)
S9	554.26	0.69	0.469	0.82	-3.289	LE	H-3->LUMO (75%), H-1->L+2 (13%)
S10	537.35	0.13	1.200	0.74	-2.284	LE-CT	H-7->LUMO (30%), H-5->LUMO (46%)
S17	442.04	0.18	0.795	0.80	-3.583	LE	H-9->LUMO (38%), H-8->LUMO (20%)
S19	413.92	0.15	0.641	0.84	-2.861	LE	H-2->L+1 (11%), HOMO->L+4 (45%)
S25	385.73	0.32	0.353	0.88	-1.864	LE	H-2->L+2 (18%), H-1->L+3 (18%), HOMO->L+7 (23%)
S29	371.26	0.18	0.277	0.86	-3.879	LE	H-4->L+1 (12%), H-3->L+1 (51%)
S30	365.29	0.10	1.249	0.78	-1.874	LE-CT	H-2->L+2 (19%), H-1->L+3 (35%)
S31	363.75	0.19	1.194	0.84	-2.464	LE-CT	H-1->L+5 (28%), HOMO->L+8 (11%)
S33	355.27	0.19	0.274	0.92	-4.307	LE	H-3->L+2 (48%)
S35	352.64	0.10	0.501	0.87	-3.081	LE	H-1->L+7 (17%), HOMO->L+8 (29%)
S47	324.71	0.11	1.209	0.84	-3.053	LE-CT	HOMO->L+9 (32%), HOMO->L+11 (12%)
S58	304.45	0.13	0.631	0.85	-3.031	LE	H-2->L+5 (23%)
S67	290.17	0.10	0.390	0.89	-2.803	LE	H-22->LUMO (10%), H-9->L+1 (13%)
S70	286.99	0.13	0.185	0.87	-3.842	LE	H-4->L+4 (13%), H-2->L+6 (10%)
S87	271.35	0.18	0.185	0.88	-2.095	LE	HOMO->L+15 (24%)
S88	270.97	0.15	0.176	0.91	-3.828	LE	H-12->L+1 (5%), H-11->L+2 (6%),H-2->L+7 (7%), HOMO->L+19 (8%)
S98	263.39	0.21	0.725	0.87	-3.500	LE	H-3->L+6 (19%)

Table S5. Properties of dominant excited states (with oscillator strength f >0.1) in $(ZnO)_4C_{88}$ hybrid system. All calculations are performed using CAM-B3LYP functional.

Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
S1	670.65	0	0.900	0.87	-3.521	LE	H-1->L+1 (31%), HOMO->LUMO (62%)
S2	568.91	0.29	0.594	0.86	-3.486	LE	H-1->LUMO (84%)
S4	508.34	0.32	1.441	0.79	-2.604	LE-CT	H-1->L+2 (24%), H-1->L+3 (13%), HOMO->L+1 (54%)
S6	490.89	0.14	1.563	0.79	-2.321	LE-CT	H-1->L+2 (28%), H-1->L+3 (19%), HOMO->L+1 (32%)
S10	428.72	1.25	0.850	0.87	-3.463	LE	H-3->LUMO (12%), H-2->L+1 (30%), HOMO->L+2 (16%), HOMO->L+3 (15%)
S12	404.33	0.13	1.055	0.83	-2.162	LE-CT	H-2->L+2 (19%), H-1->L+6 (37%)
S14	390.08	0.22	0.814	0.86	-3.167	LE	H-4->LUMO (12%), H-2->L+1 (12%), H-1->L+8 (17%), HOMO->L+6 (22%)
S18	372.33	0.22	0.122	0.84	-4.389	LE	H-6->LUMO (17%), H-4->LUMO (13%), H-1->L+4 (19%)
S22	362.57	0.24	0.989	0.87	-3.014	LE	H-4->L+1 (11%), H-2->L+2 (14%), H-1->L+9 (17%), HOMO->L+5 (13%)
S23	360.35	0.13	0.139	0.87	-1.215	LE	HOMO->L+5 (13%), HOMO->L+8 (11%)
S26	351.83	0.49	0.602	0.90	-3.570	LE	H-5->LUMO (20%), H-2->L+2 (27%)
S30	337.67	0.12	1.091	0.91	-3.687	LE	H-3->L+1 (46%), HOMO->L+4 (13%)
S34	322.90	0.15	0.912	0.90	-3.509	LE	H-6->L+1 (10%), H-5->LUMO (10%), HOMO->L+8 (15%)
S53	291.72	0.17	1.125	0.91	-3.074	LE	H-11->LUMO (10%), H-7->LUMO (10%)
S57	285.88	0.30	1.067	0.83	-2.624	LE	H-1->L+11 (13%), HOMO->L+13 (14%)
S59	284.93	0.33	0.584	0.87	-3.256	LE	H-14->LUMO (9%), H-12->LUMO (6%), H-9->LUMO (8%), H-7->L+1 (7%), H-5->L+1 (6%)
S61	283.54	0.19	0.971	0.75	-1.470	LE-CT	H-1->L+15 (20%)
S63	282.48	0.20	0.506	0.90	-3.420	LE	H-4->L+5 (11%), H-1->L+12 (10%)
S73	270.24	0.14	0.574	0.85	-2.895	LE	H-9->L+2 (13%), HOMO->L+14 (10%)
S90	258.22	0.19	0.218	0.90	-3.507	LE	H-1->L+19 (16%)
S99	252.93	0.15	0.380	0.89	-1.912	LE	H-19->LUMO (8%), H-15->LUMO (9%), H-11->L+2 (3%), H-5->L+7 (6%)

Table S6. Properties of dominant excited states (with oscillator strength f >0.1) in $(ZnO)_7C_{82}$ hybrid system. All calculations are performed using CAM-B3LYP functional.

Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
S1	810.61	0.19	2.561	0.61	-1.273	LE-CT	H-2->LUMO (18%), HOMO->LUMO (73%)
S5	559.69	0.21	6.079	0.50	2.578	CT	H-5->LUMO (15%), H-2->LUMO (54%), HOMO->LUMO (18%)
S7	499.91	0.32	1.375	0.74	-1.965	LE-CT	HOMO->L+1 (74%)
S8	478.61	0.16	3.937	0.57	0.564	CT	H-6->LUMO (52%), H-5->LUMO (36%)
S11	412.56	0.19	1.116	0.73	-1.276	LE-CT	H-4->L+1 (28%), H-3->L+1 (32%), HOMO->L+2 (13%)
S13	404.68	0.20	0.481	0.78	-3.463	LE	H-6->L+1 (10%), H-5->L+1 (10%), H-2->L+1 (24%)
S14	403.41	0.11	3.054	0.57	-0.207	LE-CT	H-12->LUMO (23%), H-8->LUMO (14%), H-7->LUMO (27%)
S16	396.11	0.52	1.887	0.83	-2.727	LE-CT	H-4->L+1 (13%), HOMO->L+2 (43%)
S19	376.33	0.18	1.052	0.83	-2.774	LE-CT	H-18->LUMO (11%), H-4->L+2 (13%), H-3->L+2 (25%)
S29	344.65	0.10	2.830	0.81	-1.232	LE-CT	H-1->L+2 (31%)
S31	341.45	0.12	0.837	0.79	-1.058	LE-CT	H-4->L+1 (15%), HOMO->L+5 (13%)
S32	341.25	0.19	1.557	0.86	-2.375	LE-CT	HOMO->L+6 (14%)
S39	325.40	0.12	2.372	0.80	-1.877	LE-CT	H-23->LUMO (11%)
S40	323.52	0.92	0.907	0.85	-2.464	LE	H-5->L+2 (10%), H-2->L+3 (13%)
S44	317.38	0.22	2.668	0.77	-1.644	LE-CT	H-11->LUMO (10%), H-10->LUMO (18%)
S46	313.24	0.11	1.600	0.72	-0.293	LE-CT	H-2->L+3 (19%)
S49	308.90	0.13	2.084	0.78	-1.691	LE-CT	H-19->LUMO (12%), H-12->LUMO (10%), H-2->L+3 (11%)
S51	307.92	0.18	2.782	0.60	0.095	CT	H-4->L+10 (10%), H-3->L+10 (11%), H-1->L+8 (13%), H-1->L+10 (12%)
S60	295.58	0.11	2.770	0.78	-1.253	LE-CT	H-16->LUMO (18%), H-14->LUMO (13%)
S65	292.04	0.33	1.116	0.84	-2.992	LE-CT	H-3->L+5 (16%), HOMO->L+8 (10%)
S67	289.11	0.11	1.013	0.81	-1.376	LE-CT	H-4->L+5 (15%), H-3->L+5 (13%)
S71	285.09	0.10	0.574	0.81	-3.000	LE	H-6->L+3 (11%)
S89	270.34	0.15	0.881	0.80	-2.535	LE	HOMO->L+12 (11%)

Table S7. Properties of dominant excited states (with oscillator strength f >0.1) in $(ZnO)_{12}C_{72}$ hybrid system. All calculations are performed using CAM-B3LYP functional.

Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
S1	532.92	0	3.866	0.21	1.663	CT	H-1->LUMO (86%)
S10	388.14	0.10	0.220	0.90	-3.632	LE	H-1->L+3 (20%), HOMO->L+4 (20%)
S11	388.14	0.10	0.223	0.90	-4.638	LE	H-1->L+4 (20%), HOMO->L+3 (20%)
S21	341.35	0.78	0.553	0.84	-2.199	LE	H-5->L+3 (13%)
S22	341.35	0.78	0.552	0.84	-2.394	LE	H-5->L+4 (13%)
S24	327.05	1.18	0.379	0.82	-2.468	LE	H-3->L+6 (8%), H-3->L+9 (9%), H-2->L+5 (8%), H-1->L+3 (5%), H-1->L+8 (4%), H-1->L+9 (9%), HOMO->L+4 (5%)
S25	327.05	1.18	0.373	0.83	-2.783	LE	H-3->L+5 (8%), H-2->L+9 (9%), H-1->L+4 (5%), H-1->L+5 (2%), HOMO->L+3 (5%), HOMO->L+9 (9%)
S26	325.68	0.21	2.970	0.46	0.963	CT	H-4->L+1 (25%)
S27	325.66	0.21	2.980	0.46	0.820	CT	H-4->L+2 (25%)
S30	316.42	0.17	2.564	0.55	0.916	CT	H-8->LUMO (12%), H-3->L+2 (12%), H-2->L+1 (12%)
S31	316.42	0.17	2.566	0.55	0.920	CT	H-9->LUMO (12%), H-3->L+1 (12%), H-2->L+2 (12%)
S33	308.94	0.18	2.101	0.64	0.394	CT	H-3->L+2 (14%), H-2->L+1 (14%)
S34	308.94	0.18	2.109	0.64	0.399	CT	H-3->L+1 (14%), H-2->L+2 (14%)
S36	303.55	0.38	1.074	0.77	-0.887	LE-CT	H-3->L+7 (14%)
S37	303.55	0.38	1.061	0.77	-0.765	LE-CT	H-2->L+7 (14%)
S43	295.27	0.15	1.660	0.71	-0.460	LE-CT	HOMO->L+7 (19%)
S44	295.26	0.15	1.650	0.71	-0.495	LE-CT	H-1->L+7 (19%)
S52	287.37	0.18	1.923	0.68	0.127	CT	H-13->LUMO (10%), H-9->LUMO (11%)
S53	287.37	0.18	1.923	0.68	0.130	CT	H-12->LUMO (10%), H-8->LUMO (11%)

Table S8. Properties of dominant excited states (with oscillator strength f >0.1) in $(ZnO)_{27}C_{42}$ hybrid system. All calculations are performed using CAM-B3LYP functional.

Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
S_1	613.44	0.002	4.087	0.20	1.882	CT	HOMO->LUMO (80%)
S_6	453.52	1.73	1.220	0.75	-1.274	LE-CT	H-1->L+1 (13%), H-1->L+3 (12%), HOMO->L+2 (13%), HOMO->L+4 (12%)
S_7	453.52	1.73	1.216	0.75	-1.540	LE-CT	H-1->L+2 (13%), H-1->L+4 (12%), HOMO->L+1 (13%), HOMO->L+3 (12%)
S_8	446.87	0.72	2.795	0.54	0.057	CT	H-1->L+1 (14%), H-1->L+3 (12%), HOMO->L+2 (14%), HOMO->L+4 (12%)
S_9	446.85	0.72	2.791	0.54	0.113	CT	H-1->L+2 (14%), H-1->L+4 (12%), HOMO->L+1 (14%), HOMO->L+3 (12%)
S_{66}	277.94	0.25	1.650	0.61	-0.870	LE-CT	H-12->LUMO (16%)
S_{67}	277.94	0.25	1.676	0.61	-0.919	LE-CT	H-11->LUMO (16%)
S_{72}	273.98	0.17	2.183	0.56	-0.562	LE-CT	H-11->LUMO (25%)
S_{73}	273.96	0.17	2.148	0.56	-0.625	LE-CT	H-12->LUMO (25%)

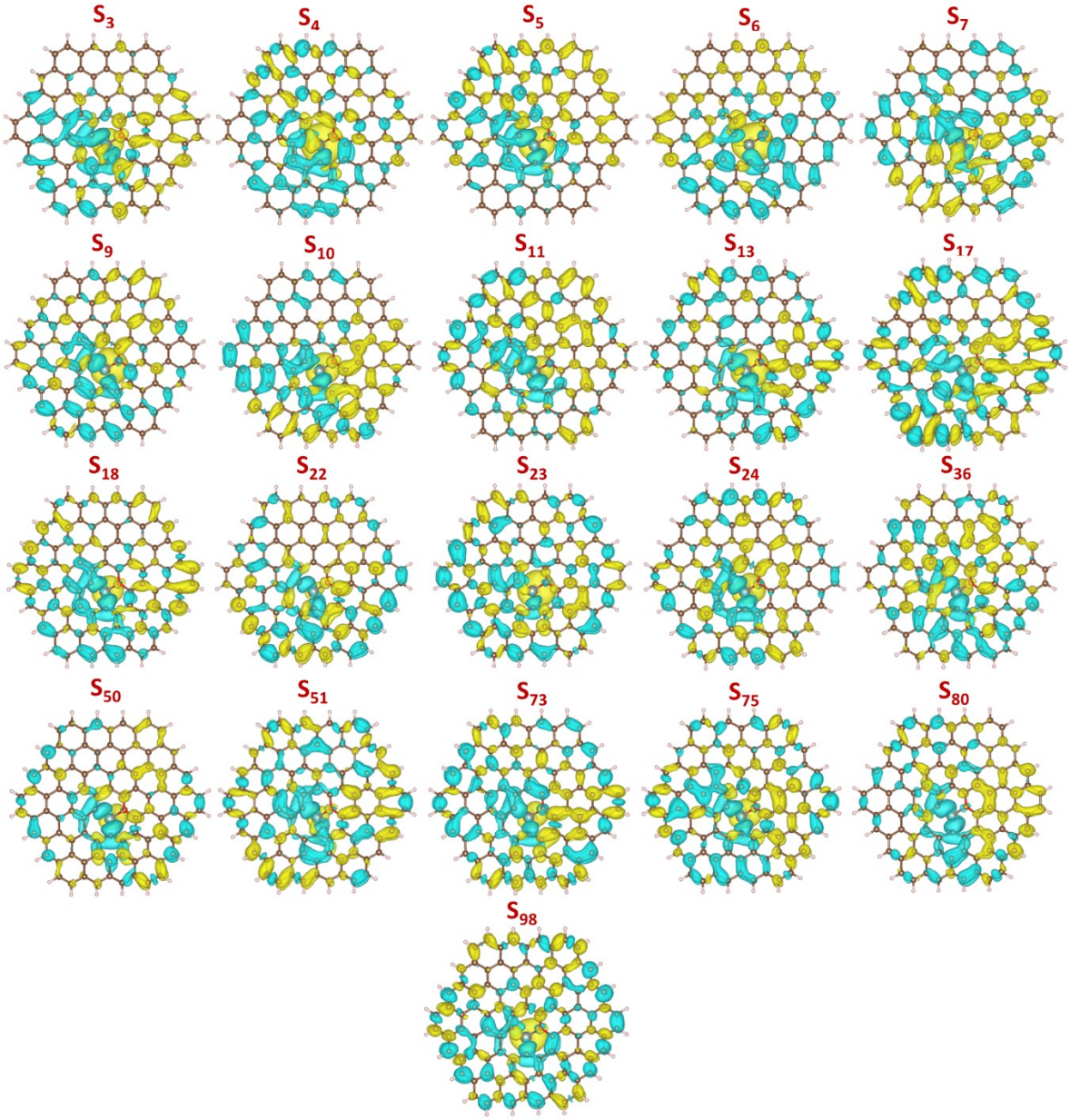


Figure S18. CDD for selected excited states (with the largest oscillator strength) in $ZnOC_{94}$. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using CAM-B3LYP functional.

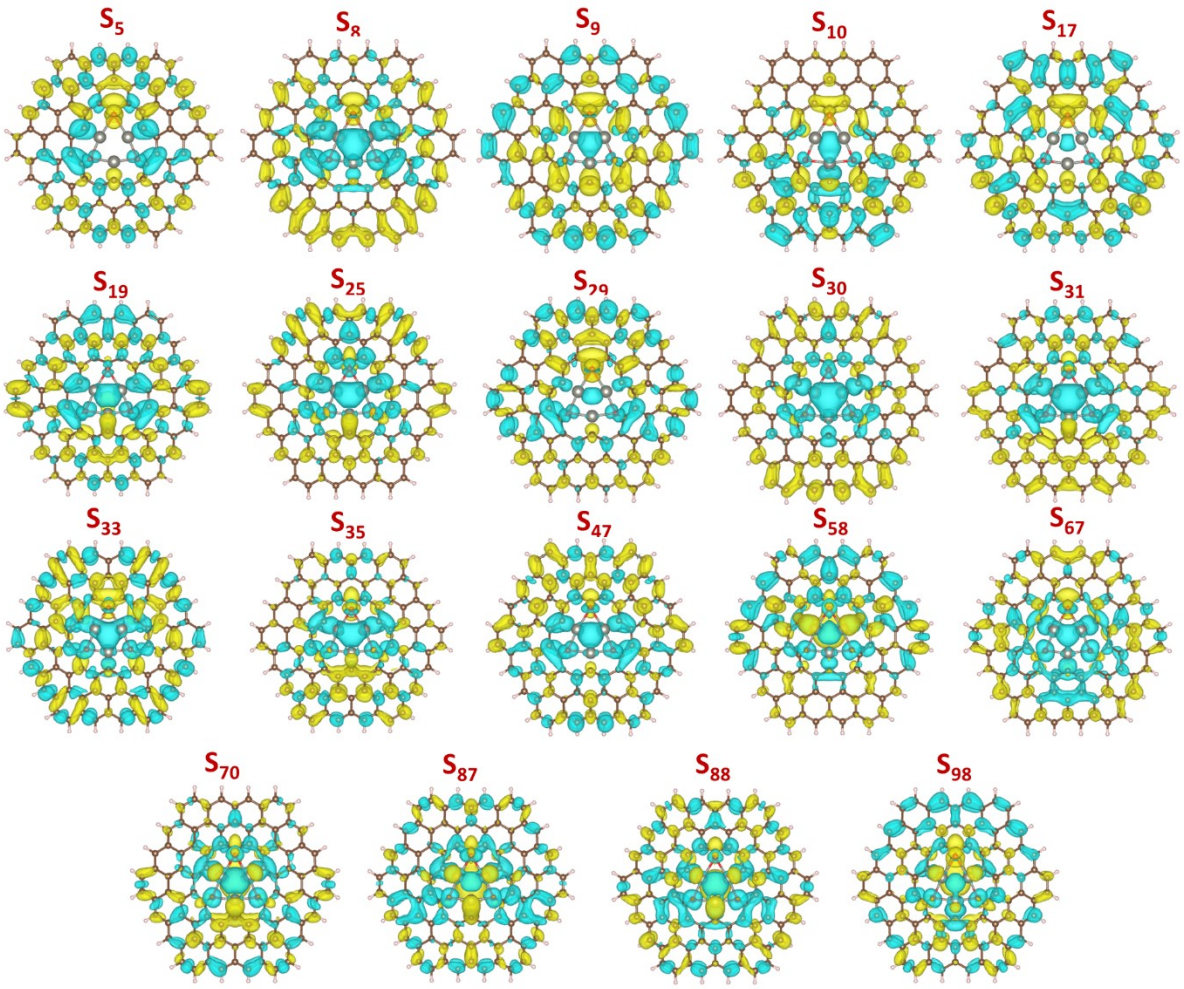


Figure S19. CDD for selected excited states (with the largest oscillator strength) in $(ZnO)_3C_{90}$. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using CAM-B3LYP functional.

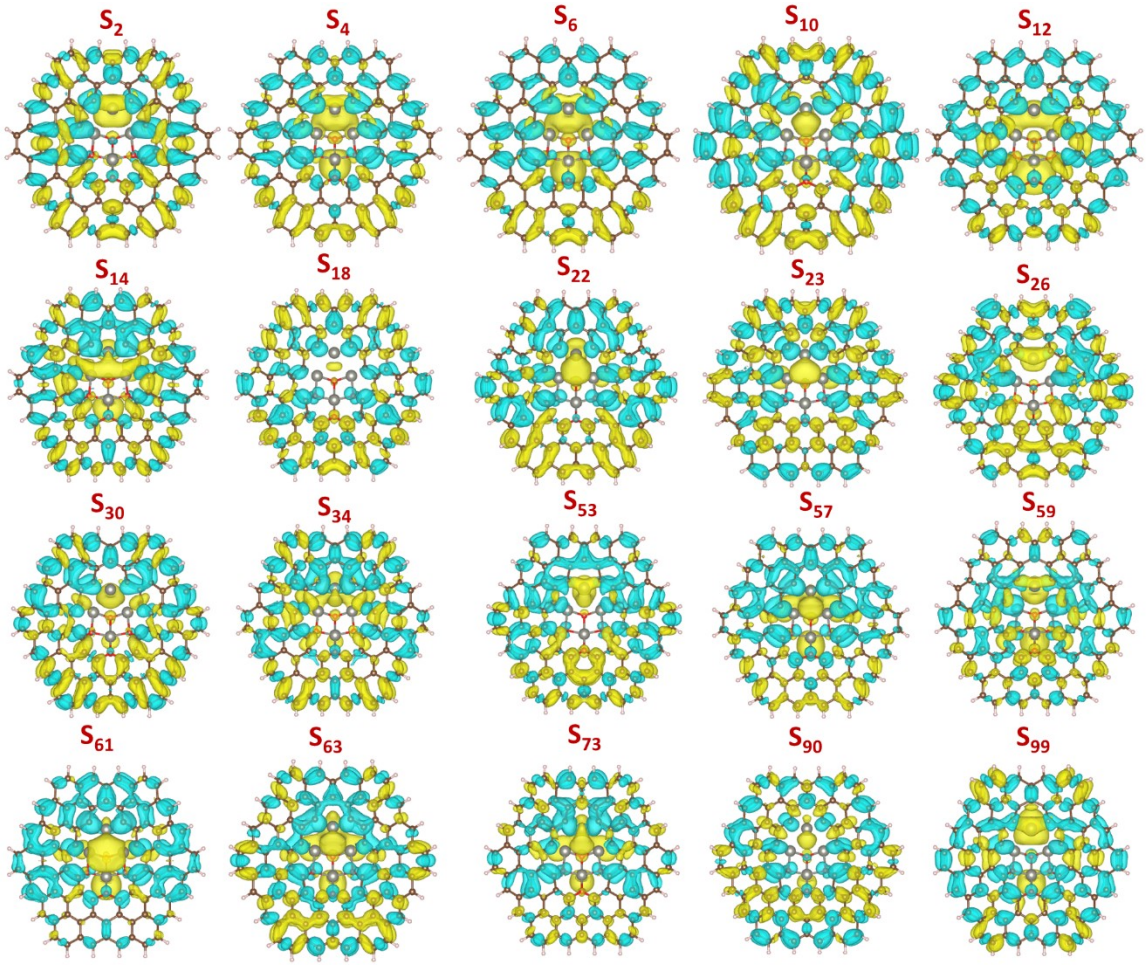


Figure S20. CDD for selected excited states (with the largest oscillator strength) in $(ZnO)_4C_{88}$. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using CAM-B3LYP functional.

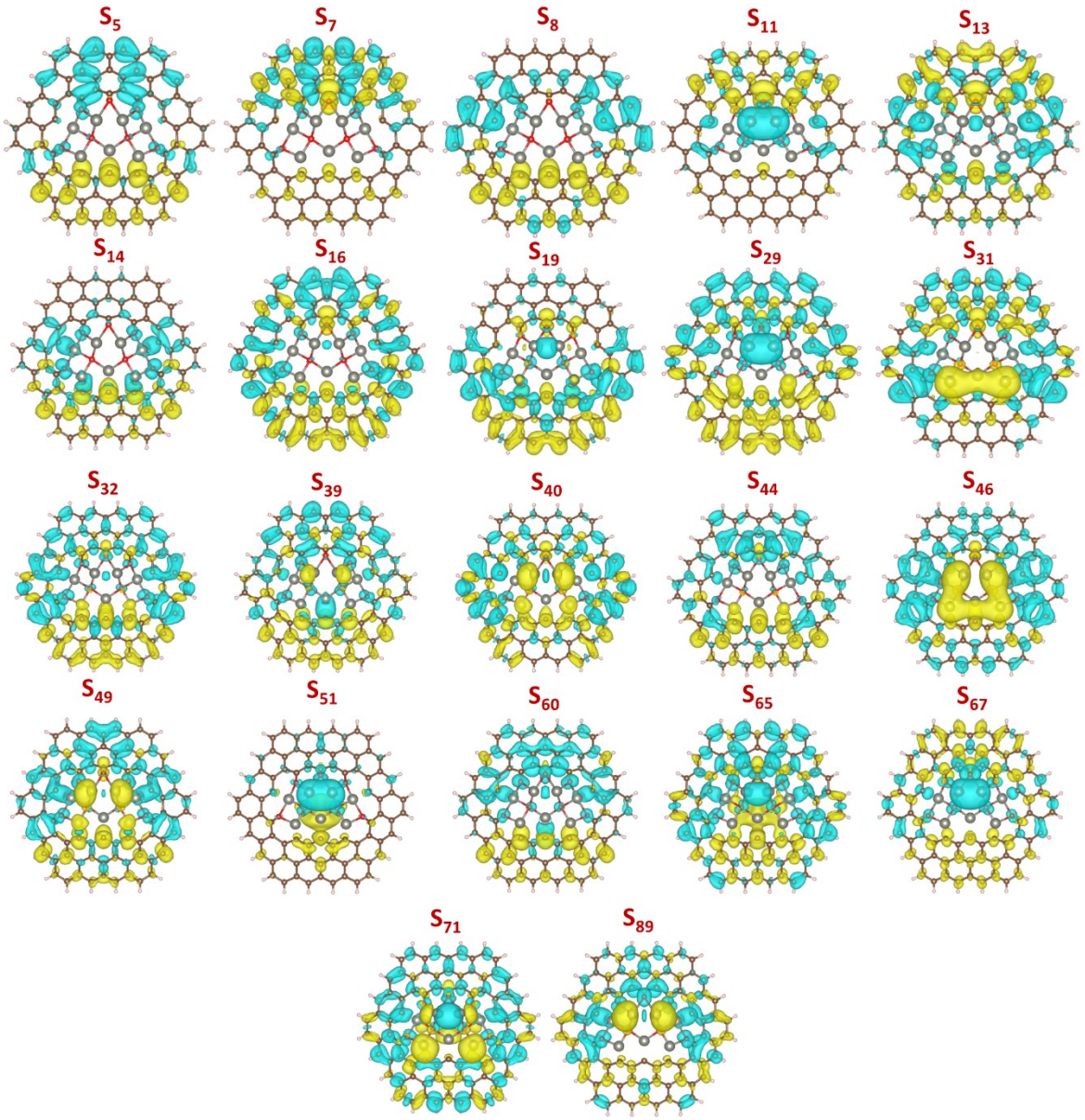


Figure S21. CDD for selected excited states (with the largest oscillator strength) in $(ZnO)_7C_{82}$. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using CAM-B3LYP functional.

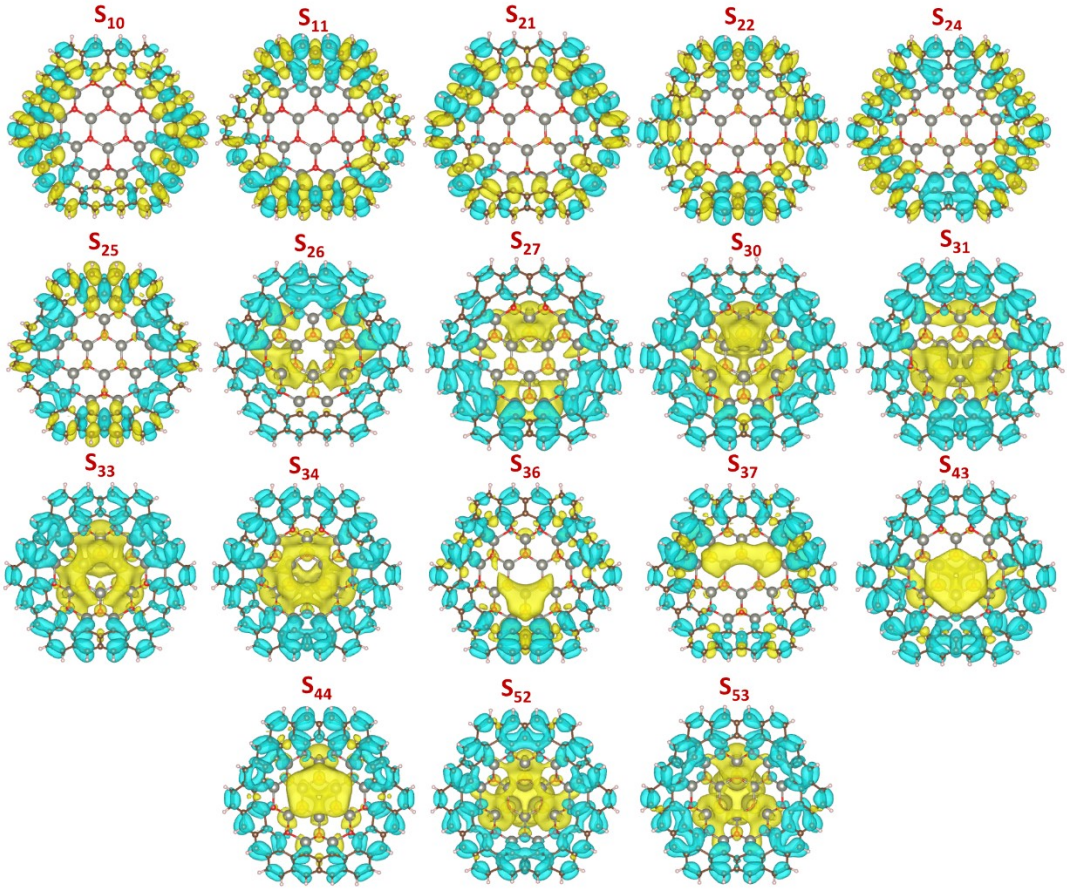


Figure S22. CDD for selected excited states (with the largest oscillator strength) in $(ZnO)_{12}C_{72}$. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003.

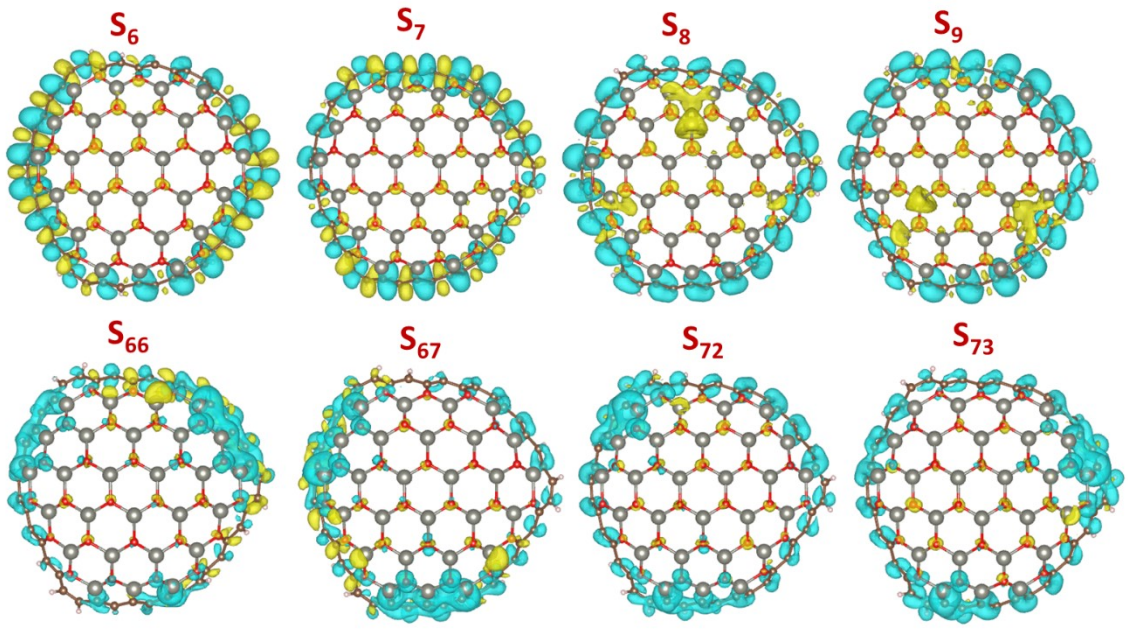


Figure S23. CDD for selected excited states (with the largest oscillator strength) in $(ZnO)_{27}C_{42}$. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using CAM-B3LYP functional.

Table S9. Properties of dominant excited states in $(ZnO)_nC_{96-2n}$ hybrid systems. For doubly degenerate excite states, the properties of second sate adjacent to first state are included in square brackets. All calculations are performed using PBE0 functional.

System	Excited state	Wavelength, nm	Oscillator strength, *f*	*D*, Å	S_r	*t*, Å	Type	Major contribution
C_{96}	$S_{3, 4}$	542.86	1.27	0	0.96	-1.94	LE	H-1->LUMO (43%), HOMO->L+1(43%) [H-1->L+1 (43%), HOMO->LUMO (43%)]
	$S_{48, 49}$	335.47	0.45	0	0.95	-2.61	LE	H-8->LUMO (11%), H-7->L+1(11%), H-4->L+3 (22%), H-3->L+4 (22%) [H-8->L+1(11%), H-7->LUMO (11%), H-4->L+4 (22%), H-3->L+3 (22%)]
	$S_{76, 77}$	290.95	0.46	0	0.91	-3.81	LE	H-5->L+3 (58%) [H-5->L+4 (58%)]
$ZnOC_{94}$	S_3	675.22	0.28	1.97	0.84	-1.97	LE-CT	H-2->LUMO (18%), H-1->LUMO (26%), HOMO->L+1 (38%)
	S_4	628.63	0.26	1.06	0.85	-2.82	LE-CT	H-1->L+1 (49%), HOMO->L+2 (34%)
	S_5	605.3	0.26	2.03	0.83	-1.98	LE-CT	H-1->L+1 (21%), HOMO->L+2 (55%)
$(ZnO)_3C_{90}$	S_{10}	696.97	0.71	0.52	0.86	-3.63	LE	H-4->LUMO (49%), H-3->LUMO (13%), H-1->L+2 (10%), HOMO->L+1 (21%)
	S_{28}	474.2	0.27	0.47	0.89	-4.16	LE	H-4->L+1 (20%), H-2->L+2 (46%)
	S_{29}	472.66	0.32	0.69	0.86	-3.58	LE	H-12->LUMO (51%), H-2->L+1 (11%), H-1->L+6 (12%)
$(ZnO)_4C_{88}$	S_5	658.09	0.41	3.78	0.80	-0.53	LE-CT	H-1->LUMO (17%), H-1->L+2 (18%), HOMO->L+1 (57%)
	S_{10}	532.56	0.44	1.67	0.91	-2.95	LE-CT	H-4->LUMO (10%), H-2->L+1 (54%), HOMO->L+2 (16%)
	S_{16}	480.26	0.36	1.47	0.87	-3.05	LE	H-5->LUMO (11%), H-3->LUMO (31%), H-1->L+4 (26%), H-1->L+5 (21%)
$(ZnO)_7C_{82}$	S_8	612.42	0.39	0.61	0.75	-1.57	LE	HOMO->L+1 (84%)
	S_{11}	555.71	0.27	5.97	0.65	1.58	CT	HOMO->L+2 (85%)
	S_{85}	341.34	0.28	0.52	0.85	-3.36	LE	H-5->L+7 (15%), H-4->L+8 (38%)
$(ZnO)_{12}C_{72}$	$S_{37,38}$	407.09	0.60	1.53	0.81	-2.47	LE-CT	H-9->LUMO (16%), H-4->L+3 (18%), H-3->L+6 (13%), H-2->L+5 (13%) [H-8->LUMO (16%), H-4->L+4 (18%), H-3->L+5 (13%), H-2->L+6 (13%)]
	$S_{43,44}$	388.26	0.38	1.30	0.85	-2.69	LE-CT	H-11->LUMO (12%), H-4->L+3 (16%), HOMO->L+7 (38%) [H-10->LUMO (12%), H-4->L+4 (16%), H-1->L+7 (38%)]
	$S_{52,53}$	375.48	0.21	2.35	0.82	-2.68	LE-CT	H-4->L+6 (13%), HOMO->L+8 (61%) [H-4->L+5 (13%), H-1->L+8 (61%)]
$(ZnO)_{27}C_{42}$	$S_{10,11}$	635.52	1.55	0.24	0.89	-5.25	LE	H-1->L+4 (46%), HOMO->L+3 (46%) [H-1->L+3 (46%), HOMO->L+4 (46%)]
	$S_{23,24}$	496.79	0.51	1.06	0.88	-4.41	LE-CT	H-2->L+4 (15%), H-1->L+9 (11%), HOMO->L+8 (40%), HOMO->L+9 (19%) [H-2->L+3 (15%), H-1->L+8 (40%), H-1->L+9 (19%), HOMO->L+9 (11%)]
	$S_{27,28}$	466.6	0.27	1.33	0.86	-3.63	LE-CT	H-3->L+3 (19%), H-3->L+4 (10%), H-1->L+8 (12%), HOMO->L+9 (32%) [H-3->L+3 (10%), H-3->L+4 (19%), H-1->L+9 (32%), HOMO->L+8 (12%)]

Table S10. Properties of excited states (with oscillator strength f >0.1) in $(ZnO)_nC_{96-2n}$ hybrid systems. For doubly degenerate excite states, the properties of second sate adjacent to first state are included in square brackets. All calculations are performed using PBE0 functional.

System	Excited state	Wavelength, nm	f	D, Å	S_r	t, Å	Type	Major contribution
C_{96}	$S_{21, 22}$	381.22	0.16	0	0.83	-3.92	LE	H-6->LUMO (26%), H-3->L+2 (20%), H-1->L+5 (12%), H-1->L+8 (11%), HOMO->L+6 (12%) [H-6->L+1 (26%), H-4->L+2 (20%), H-1->L+6 (12%), HOMO->L+5 (12%), HOMO->L+8 (11%)]
	$S_{41, 42}$	345.27	0.1	0	0.88	-2.87	LE	H-6->LUMO (16%), H-3->L+2 (10%), H-2->L+3 (14%), HOMO->L+9 (50%) [H-6->L+1 (16%), H-4->L+2 (10%), H-2->L+4 (14%), H-1->L+9 (50%)]
	$S_{46, 47}$	341.27	0.24	0	0.80	-1.26	LE	H-9->LUMO (61%), H-4->L+4 (11%), H-3->L+3 (11%) [H-9->L+1 (61%), H-4->L+3 (11%), H-3->L+4 (11%)]
	$S_{72,73}$	296.42	0.24	0	0.77	-4.50	LE	H-13->L+1(21%),H-12->LUMO(21%),H-3->L+7 (42%) [H-13->LUMO(21%),H-12->L+1(21%),H-4->L+7 (42%)]
$ZnOC_{94}$	S_6	590.45	0.23	1.75	0.73	-2.50	LE-CT	H-2->LUMO (58%), H-1->L+2 (13%)
	S_7	584.08	0.16	1.03	0.81	-3.30	LE-CT	H-2->L+1 (25%), H-1->L+2 (44%)
	S_9	543.52	0.20	3.36	0.67	-0.86	LE-CT	H-3->LUMO (62%)
	S_{10}	533.93	0.15	1.01	0.70	-2.19	LE-CT	H-2->L+1 (28%), H-1->L+2 (12%), H-1->L+3 (22%)
	S_{13}	494.15	0.14	2.33	0.70	-1.91	LE-CT	H-3->L+1 (41%), HOMO->L+5 (27%)
	S_{17}	467.15	0.12	0.47	0.77	-3.24	LE	H-4->LUMO(23%),H-2->L+2(16%),HOMO->L+4(19%)
	S_{24}	437.99	0.20	1.90	0.68	-1.95	LE-CT	H-3->L+2 (29%), H-2->L+2 (18%)
	S_{44}	369.50	0.15	1.41	0.63	-3.03	LE-CT	H-8->L+1(12%), H-3->L+4 (26%), HOMO->L+10 (13%)
	S_{61}	341.36	0.17	2.55	0.60	-1.53	LE-CT	H-5->L+3 (16%), H-3->L+6 (26%)
	S_{100}	298.22	0.12	0.28	0.63	-4.01	LE	H-15->L+1 (16%)
$(ZnO)_3C_{90}$	S_8	747.47	0.19	0.56	0.83	-2.16	LE	H-7->LUMO (16%), HOMO->L+2 (69%)
	S_{12}	671.20	0.15	1.16	0.60	-2.65	LE-CT	H-8->LUMO(17%),H-7->LUMO(54%),H-5->LUMO (13%)
	S_{30}	466.26	0.12	0.52	0.77	-3.64	LE	H-4->L+1 (42%), H-3->L+1 (32%)
	S_{35}	450.57	0.10	0.39	0.81	-4.71	LE	H-4->L+2 (70%)
	S_{65}	356.62	0.18	0.87	0.64	-1.99	LE	H-3->L+4 (19%), H-2->L+5 (59%)
$(ZnO)_4C_{88}$	S_8	603.21	0.14	0.70	0.82	-3.14	LE	H-2->LUMO (26%), H-1->L+2 (14%), H-1->L+3 (44%)
	S_{15}	492.31	0.10	1.84	0.62	-0.31	LE-CT	H-2->L+2 (38%), H-2->L+3 (16%), H-1->L+6 (20%), HOMO->L+4 (13%)
	S_{20}	464.44	0.10	0.82	0.73	-2.86	LE	H-2->L+3 (12%), H-1->L+6 (19%), H-1->L+7 (42%), HOMO->L+8 (10%)
	S_{23}	453.30	0.29	1.32	0.72	-2.87	LE-CT	H-5->LUMO (62%)
	S_{32}	420.62	0.10	0.10	0.72	-1.22	LE	H-5->L+1 (57%), HOMO->L+8 (16%)
	S_{43}	386.54	0.18	0.84	0.63	-3.67	LE	H-5->L+2 (61%)
	S_{59}	353.30	0.18	1.88	0.74	-2.88	LE-CT	H-7->L+2 (17%), H-4->L+4 (34%), H-3->L+5 (12%)
	S_{60}	349.29	0.15	0.44	0.73	-0.91	LE	H-7->L+2 (13%), H-2->L+9 (15%), H-1->L+13 (31%)
	S_{65}	343.38	0.15	1.97	0.66	-2.57	LE-CT	H-10->L+1 (46%), H-4->L+4 (12%), H-3->L+4 (13%)
	S_{81}	324.03	0.11	2.79	0.54	-0.64	LE-CT	H-6->L+5 (14%), H-4->L+7 (36%)
$(ZnO)_7C_{82}$	S_{24}	464.04	0.23	4.57	0.61	0.37	CT	H-9->LUMO (10%), H-3->L+2 (73%)
	S_{30}	437.17	0.10	2.63	0.59	-0.90	LE-CT	H-15->LUMO (28%), H-14->LUMO (20%), H-1->L+3 (10%), HOMO->L+6 (15%)
	S_{31}	435.36	0.12	0.83	0.62	-2.60	LE	H-1->L+3 (73%)
	S_{48}	392.34	0.13	3.17	0.64	-0.52	LE-CT	H-2->L+4 (23%), H-2->L+6 (15%), H-1->L+8 (28%)
	S_{57}	377.02	0.13	1.92	0.69	-2.34	LE-CT	H-4->L+4 (40%), HOMO->L+9 (11%)
	S_{65}	366.27	0.19	0.83	0.67	-2.98	LE	H-5->L+4 (30%), H-4->L+5 (15%)
	S_{66}	365.20	0.13	1.68	0.56	-0.36	LE-CT	H-5->L+3 (41%), H-4->L+6 (29%)
	S_{88}	338.03	0.11	0.53	0.69	-3.32	LE	H-10->L+1 (11%), H-8->L+2 (14%), H-5->L+7 (10%), H-3->L+9 (32%)
	S_{93}	334.17	0.12	0.45	0.64	-3.04	LE	H-5->L+7 (43%), H-2->L+10 (20%)
$(ZnO)_{12}C_{72}$	$S_{32,33}$	414.94	0.12	2.56	0.42	0.52	CT	H-10->LUMO (11%), H-8->LUMO (21%) [H-11->LUMO (11%), H-9->LUMO (21%)]
	$S_{61,62}$	362.51	0.20	1.94	0.66	-1.91	LE-CT	H-17->LUMO(15%), H-5->L+5 (23%), H-2->L+7 (38%) [H-16->LUMO (15%),H-5->L+6(23%),H-3->L+7 (38%)]
	$S_{90,91}$	323.30	0.16	2.34	0.53	-1.68	LE-CT	H-6->L+1 (32%), HOMO->L+16 (23%) [H-6->L+2 (32%), H-1->L+16 (23%)]
$(ZnO)_{27}C_{42}$	$S_{19,20}$	535.45	0.10	1.52	0.79	-3.86	LE-CT	H-2->L+3 (68%) [H-2->L+4 (68%)]

Table S11. A comparison of the properties of dominant excited states (with oscillator strength f>0.1) in $(ZnO)_{27}C_{42}$ predicted by using different functionals: PBE0, B3LYP, CAM-B3LYP and wB97XD, respectively.

System	Excited state	Wavelength, nm	Oscillator strength, f	D, Å	S_r	t, Å	Type	Major contribution
wB97XD	S_5, S_6	435.32	2.48	0.363	0.85	-4.90	LE	H-2->L+4 (11%), H-1->L+4 (26%), HOMO->L+3 (26%) [H-2->L+3 (11%), H-1->L+3 (26%), HOMO->L+4 (26%)]
	S_{91}, S_{92}	243.13	0.31	0.668	0.58	-1.629	LE-CT	H-27->LUMO (10%) [H-28->LUMO (10%)]
	S_{99}, S_{100}	239.71	0.20	1.350	0.55	-0.794	LE-CT	H-22->LUMO (14%) [H-23->LUMO (14%)]
B3LYP	S_{13},S_{14}	680.74	1.27	0.639	0.89	-4.97	LE	H-1->L+3 (25%), H-1->L+4 (22%), HOMO->L+3 (22%), HOMO->L+4 (25%)
	S_{27},S_{28}	535.66	0.45	0.95	0.85	-3.96	LE	HOMO->L+8 (39%), HOMO->L+9 (23%)
	S_{31},S_{32}	503.59	0.40	1.27	0.86	-3.84	LE	H-3->L+3 (39%), HOMO->L+8 (12%), HOMO->L+9 (28%)
CAM-B3LYP	S_6, S_7	453.52	1.73	1.220	0.75	-1.274	LE-CT	H-1->L+1 (13%), H-1->L+3 (12%), HOMO->L+2 (13%), HOMO->L+4 (12%) [H-1->L+2 (13%), H-1->L+4 (12%), HOMO->L+1 (13%), HOMO->L+3 (12%)]
	S_8, S_9	446.87	0.72	2.795	0.54	0.057	CT	H-1->L+1 (14%), H-1->L+3 (12%), HOMO->L+2 (14%), HOMO->L+4 (12%) [H-1->L+2 (14%), H-1->L+4 (12%), HOMO->L+1 (14%), HOMO->L+3 (12%)]
	S_{66}, S_{67}	277.94	0.25	1.650	0.61	-0.870	LE-CT	H-12->LUMO (16%) [H-11->LUMO (16%)]
PBE0	$S_{10,11}$	635.52	1.55	0.24	0.89	-5.25	LE	H-1->L+4 (46%), HOMO->L+3 (46%) [H-1->L+3 (46%), HOMO->L+4 (46%)]
	$S_{23,24}$	496.79	0.51	1.06	0.88	-4.41	LE-CT	H-2->L+4 (15%), H-1->L+9 (11%), HOMO->L+8 (40%), HOMO->L+9 (19%) [H-2->L+3 (15%), H-1->L+8 (40%), H-1->L+9 (19%), HOMO->L+9 (11%)]
	$S_{27,28}$	466.6	0.27	1.33	0.86	-3.63	LE-CT	H-3->L+3 (19%), H-3->L+4 (10%), H-1->L+8 (12%), HOMO->L+9 (32%) [H-3->L+3 (10%), H-3->L+4 (19%), H-1->L+9 (32%), HOMO->L+8 (12%)]

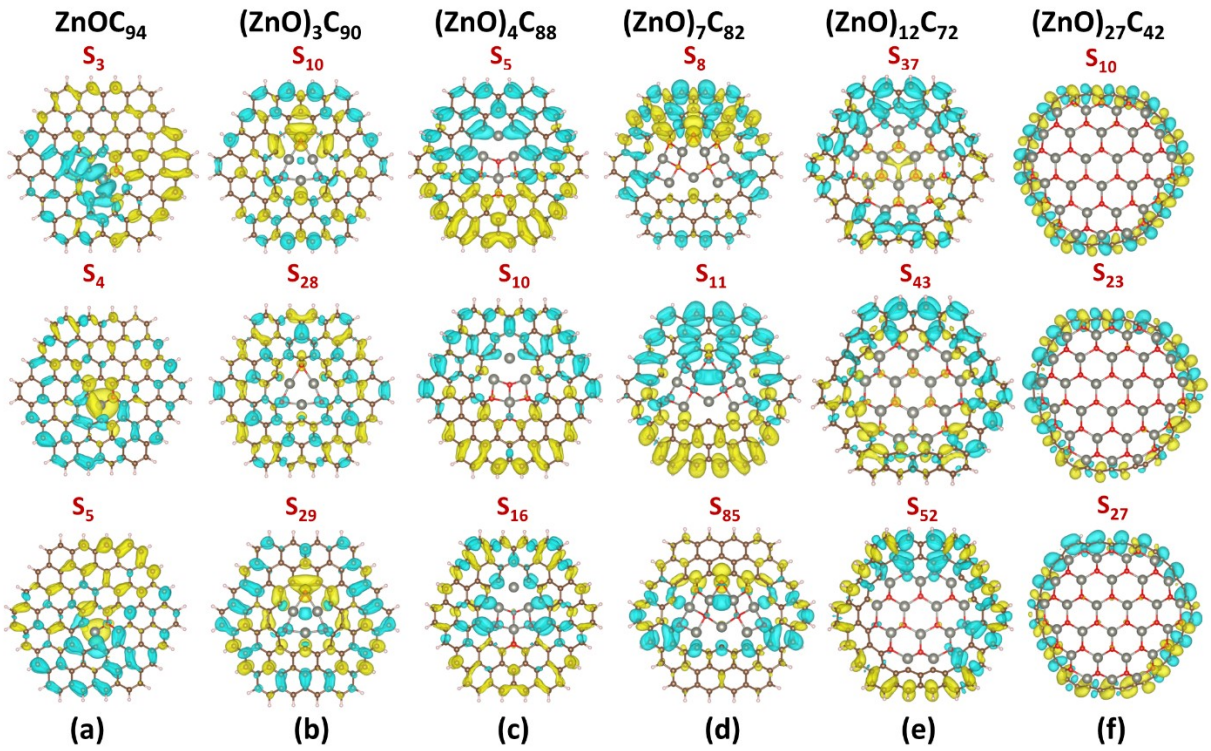


Figure S24. CDD for selected excited states (with the largest oscillator strength) in (a) $ZnOC_{94}$, (b) $(ZnO)_3C_{90}$, (c) $(ZnO)_4C_{88}$, (d) $(ZnO)_7C_{82}$, (e) $(ZnO)_{12}C_{72}$, and (f) $(ZnO)_{27}C_{42}$, respectively. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. All calculations are performed using PBE0 functional.

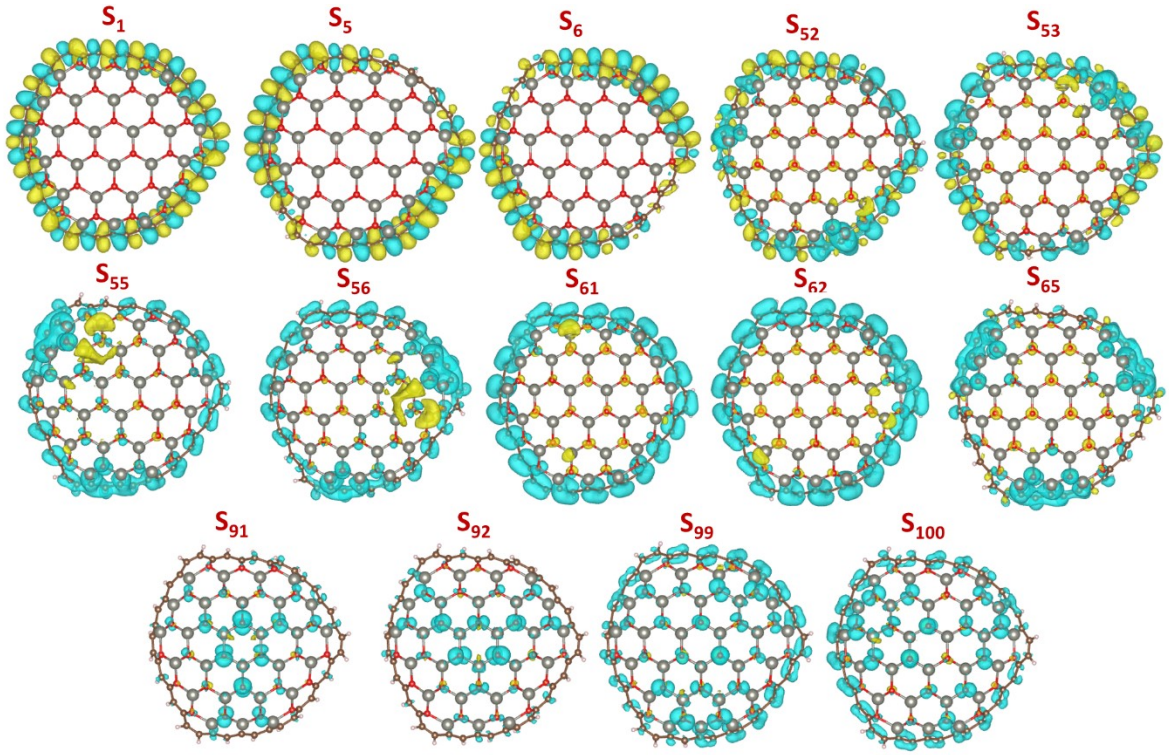


Figure S25. CDD for selected excited states (with the largest oscillator strength) in $(ZnO)_{27}C_{42}$. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using wB97XD functional.

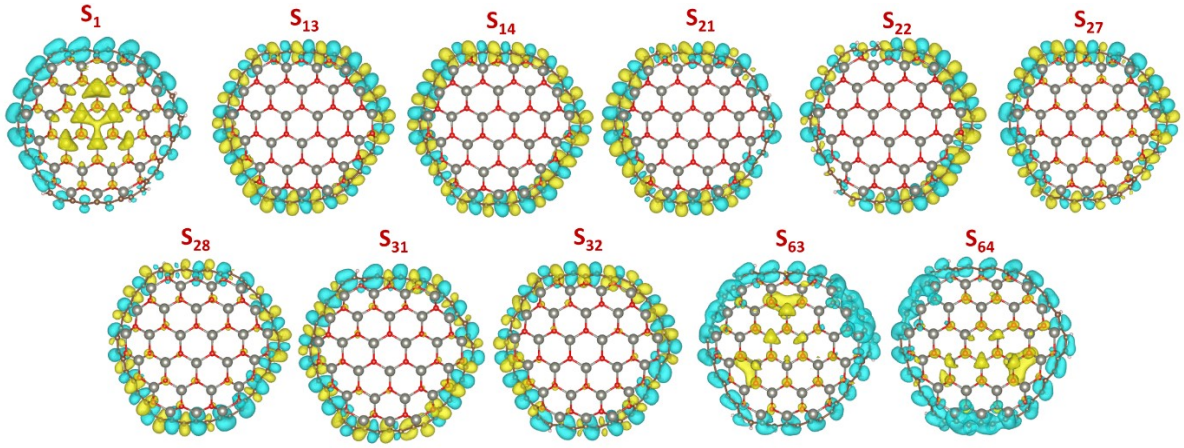


Figure S26. CDD for selected excited states (with the largest oscillator strength) in $(ZnO)_{27}C_{42}$. Herein, yellow denotes positive charge distribution and cyan means negative charge distribution. Isosurface level is set to be 0.0003. All calculations are performed using B3LYP functional.

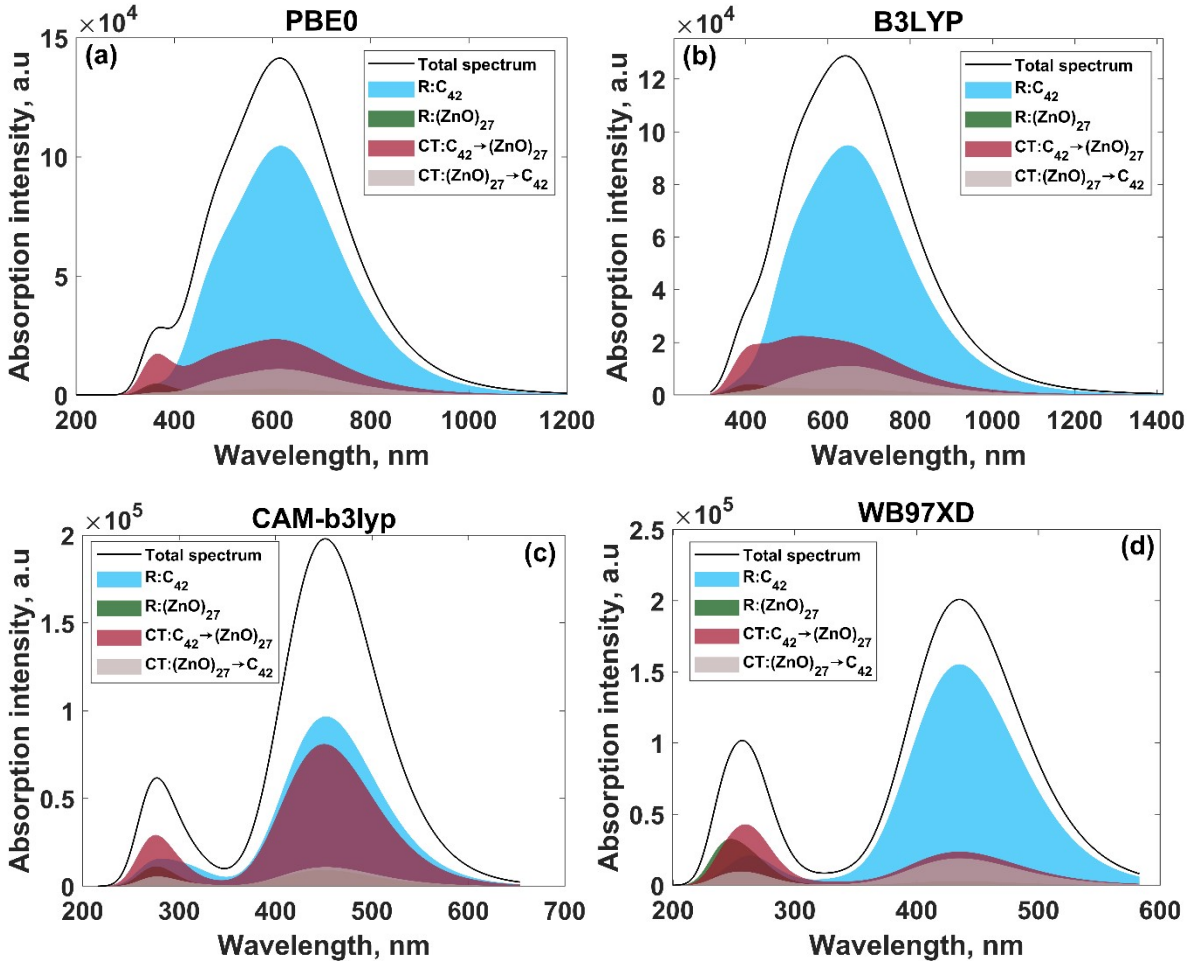


Figure S27. Charge-transfer spectra (CTS) of the $(ZnO)_{27}C_{42}$ predicted using different functionals: (a) PBE0, (b) B3LYP, (c) CAM-B3LYP, and (d) wB97XD, respectively. CTS spectra include intrafragment electron redistribution (R) and interfragment charge transfer (CT) components, respectively.