Supporting Information

Ab Initio Assessment of the Structural and Optoelectronic Properties of Organic-ZnO Nanoclusters

Pushpendra Kumar, Suman Kalyan Pal*

School of Basic Sciences and Advanced Material Research Center,

Indian Institute of Technology Mandi, Kamand 175005, H.P, India.

*Corresponding Author: Tel.: +91 1905 267040; Fax: +91 1905 237924; E-mail:

suman@iitmandi.ac.in.

Table S1. Summary of major vertical transitions having reasonably high oscillator strengths of the dye obtained from TD-DFT calculations in the vacuum

Basis Set	Energy (eV)	Oscillator Strength (f)	Assignment
STO-3G	3.51	0.24	[a]HOMO->[b]LUMO (80%) H-2->LUMO (14%), H-1->LUMO (2%)
”	4.07	0.04	H-1->LUMO (69%), HOMO->L+1 (20%) H-3->LUMO (3%)
”	4.71	0.18	H-3->LUMO (47%), HOMO->L+1 (19%) H-5->LUMO (9%)
”	5.55	0.17	H-3->L+1 (54%), HOMO->L+4 (22%) H-2->L+1 (3%)
3-21 G	3.30	0.28	HOMO->LUMO (94%) H-1->LUMO (4%)
”	3.83	0.06	H-1->LUMO (68%), HOMO->L+1 (26%) HOMO->LUMO (3%)
”	4.37	0.13	H-5->LUMO (45%), H-1->LUMO (12%), HOMO->L+1 (29%)
”	5.09	0.19	H-1->L+1 (20%), HOMO->L+2 (25%), HOMO->L+3 (29%), HOMO->L+4 (10%)
6-31G	3.21	0.25	HOMO->LUMO (94%) H-1->LUMO (4%)
	3.74	0.08	H-1->LUMO (73%), HOMO->L+1 (20%) HOMO->LUMO (4%)

”	4.30	0.18	H-1->LUMO (18%), HOMO->L+1 (63%) H-5->LUMO (7%), H-1->L+1 (4%)
”	5.11	0.25	H-1->L+1 (15%), HOMO->L+2 (26%), HOMO->L+3 (33%)
6-31G (d)	3.23	0.25	HOMO->LUMO (94%) H-1->LUMO (4%)
”	3.73	0.06	H-1->LUMO (67%), HOMO->L+1 (26%) HOMO->LUMO (4%)
”	4.26	0.20	H-1->LUMO (22%), HOMO->L+1 (61%) H-3->LUMO (4%)
”	5.08	0.30	H-1->L+1 (16%), HOMO->L+2 (18%), HOMO->L+3 (39%) H-4->L+1 (5%)
6-311G	3.23	0.26	HOMO->LUMO (94%) H-1->LUMO (4%)
”	3.75	0.07	H-1->LUMO (72%), HOMO->L+1 (22%) HOMO->LUMO (4%)
”	4.30	0.17	H-5->LUMO (25%), H-1->LUMO (16%), HOMO->L+1 (48%) H-1->L+1 (2%)
”	5.08	0.21	H-1->L+1 (14%), HOMO->L+2 (27%), HOMO->L+3 (28%), HOMO->L+4 (11%)
6-311G (d,p)	3.24	0.25	HOMO->LUMO (94%)

			H-1->LUMO (4%)
”	3.72	0.05	H-1->LUMO (64%), HOMO->L+1 (30%) HOMO->LUMO (3%)
”	4.24	0.23	H-3->LUMO (10%), H-1->LUMO (25%), HOMO->L+1 (55%) H-1->L+1 (3%)
”	4.99	0.15	H-2->L+1 (50%), H-1->L+1 (20%), HOMO->L+3 (11%) H-6->LUMO (3%)
LanL2DZ	3.16	0.25	HOMO->LUMO (94%) H-1->LUMO (4%)
”	3.67	0.08	H-1->LUMO (74%), HOMO->L+1 (19%) HOMO->LUMO (4%)
”	4.23	0.19	H-1->LUMO (17%), HOMO->L+1 (63%) H-5->LUMO (7%), H-1->L+1 (4%)
”	5.07	0.26	H-1->L+1 (12%), HOMO->L+2 (12%), HOMO->L+3 (53%) H-4->L+1 (8%)

[a]Highest occupied molecular orbital (HOMO)
[b]Lowest unoccupied molecular orbital (LUMO)

Table S2. Summary of major vertical transitions having reasonably high oscillator strengths of the dye obtained from TD-DFT calculations (using IEFPCM) in THF

Basis Set	Energy (eV)	Oscillator Strength (f)	Assignment
STO-3G	3.41	0.38	HOMO->LUMO (96%)
”	3.97	0.05	H-1->LUMO (83%), HOMO->L+1 (10%)
”	4.64	0.23	H-3->LUMO (44%), HOMO->L+1 (27%), H-5->LUMO (9%), H-1->L+1 (7%)
”	5.25	0.27	H-3->L+1 (10%), H-1->L+1 (24%), HOMO->L+2 (57%) HOMO->L+5 (3%)
3-21 G	3.17	0.39	HOMO->LUMO (96%), H-1->LUMO (2%)
”	3.73	0.11	H-1->LUMO (82%), HOMO->L+1 (13%), HOMO->LUMO (2%)
”	4.31	0.16	H-1->LUMO (13%), HOMO->L+1 (74%), H-4->LUMO (3%), H-1->L+1 (4%)
”	5.11	0.41	H-1->L+1 (29%), HOMO->L+2 (43%), HOMO->L+4 (10%) HOMO->L+3 (7%)
6-31G	3.07	0.35	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.61	0.16	H-1->LUMO (86%) HOMO->LUMO (3%),

			HOMO->L+1 (9%)
”	4.27	0.18	HOMO->L+1 (80%) H-1->LUMO (9%), H-1->L+1 (4%)
”	5.05	0.21	H-6->LUMO (11%), H-2->L+1 (56%), H-1->L+1 (16%), HOMO->L+2 (11%)
6-31G (d)	3.08	0.35	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.61	0.14	H-1->LUMO (83%), HOMO->L+1 (12%) HOMO->LUMO (3%)
”	4.22	0.23	H-1->LUMO (12%), HOMO->L+1 (80%) H-1->L+1 (2%)
”	5.03	0.48	H-2->L+1 (13%), H-1->L+1 (32%), HOMO->L+2 (32%) H-6->LUMO (5%)
6-311G	3.08	0.36	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.62	0.16	H-1->LUMO (86%) HOMO->LUMO (3%), HOMO->L+1 (9%)
”	4.26	0.21	HOMO->L+1 (80%) H-1->LUMO (9%), H-1->L+1 (3%)
”	5.06	0.32	H-6->LUMO (10%), H-2->L+1 (39%), H-1->L+1 (21%), HOMO->L+2 (21%)
6-311G (d,p)	3.09	0.36	HOMO->LUMO (96%)

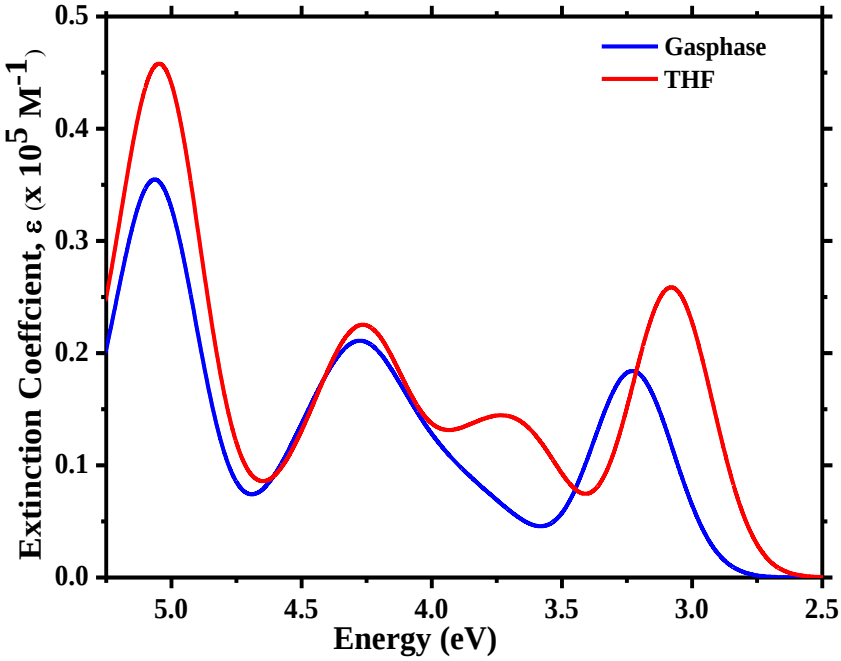
			H-1->LUMO (3%)
”	3.62	0.13	H-1->LUMO (82%), HOMO->L+1 (14%) HOMO->LUMO (3%)
”	4.19	0.26	H-1->LUMO (13%), HOMO->L+1 (78%) H-3->LUMO (2%), H-1->L+1 (2%)
”	4.98	0.46	H-1->L+1 (32%), HOMO->L+2 (39%) HOMO->L+3 (8%), HOMO->L+4 (9%)
LanL2DZ	3.01	0.34	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.54	0.17	H-1->LUMO (87%) HOMO->LUMO (3%), HOMO->L+1 (8%)
”	4.20	0.20	HOMO->L+1 (81%) H-1->LUMO (8%), H-1->L+1 (4%)
”	4.95	0.23	H-6->LUMO (11%), H-2->L+1 (55%), H-1->L+1 (18%), HOMO->L+2 (11%)

Table S3. Summary of major vertical transitions of the dye reasonably have high oscillator strengths obtained by TD-DFT (using CPCM) in THF

Basis Set	Energy (eV)	Oscillator Strength (f)	Assignment
STO-3G	3.40	0.38	HOMO->LUMO (96%)
”	3.97	0.05	H-1->LUMO (83%), HOMO->L+1 (10%)
”	4.63	0.24	H-3->LUMO (46%), HOMO->L+1 (28%) H-5->LUMO (8%), H-4->LUMO (4%), H-1->L+1 (6%)
”	5.25	0.28	H-1->L+1 (23%), HOMO->L+2 (58%) H-3->L+1 (9%), HOMO->L+5 (3%)
3-21 G	3.17	0.40	HOMO->LUMO (96%), H-1->LUMO (2%)
”	3.73	0.12	H-1->LUMO (83%), HOMO->L+1 (13%) HOMO->LUMO (2%)
”	4.29	0.18	H-1->LUMO (13%), HOMO->L+1 (75%) H-4->LUMO (3%), H-1->L+1 (3%)
”	5.09	0.42	H-1->L+1 (29%), HOMO->L+2 (44%), HOMO->L+4 (10%) H-4->L+1 (2%)
6-31G	3.06	0.36	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.61	0.17	H-1->LUMO (87%)

			HOMO->LUMO (3%), HOMO->L+1 (8%)
”	4.26	0.20	HOMO->L+1 (82%) H-1->LUMO (8%), H-1->L+1 (3%)
”	5.06	0.26	H-6->LUMO (12%), H-2->L+1 (50%), H-1->L+1 (18%), HOMO->L+2 (14%)
6-31G (d)	3.07	0.36	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.62	0.14	H-1->LUMO (84%), HOMO->L+1 (11%) HOMO->LUMO (3%)
”	4.22	0.25	H-1->LUMO (11%), HOMO->L+1 (81%) H-1->L+1 (2%)
”	5.03	0.53	H-1->L+1 (33%), HOMO->L+2 (36%) H-6->LUMO (4%), H-2->L+1 (8%)
6-311G	3.08	0.37	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.61	0.16	H-1->LUMO (87%) HOMO->LUMO (2%), HOMO->L+1 (9%)
”	4.25	0.22	HOMO->L+1 (81%) H-1->LUMO (9%), H-1->L+1 (3%)
”	5.05	0.39	H-2->L+1 (29%), H-1->L+1 (24%), HOMO->L+2 (27%) H-6->LUMO (9%)

6-311G (d,p)	3.08	0.38	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.61	0.14	H-1->LUMO (82%), HOMO->L+1 (13%) HOMO->LUMO (2%)
”	4.18	0.27	H-1->LUMO (13%), HOMO->L+1 (78%) H-3->LUMO (2%)
”	4.97	0.48	H-1->L+1 (32%), HOMO->L+2 (41%) HOMO->L+3 (6%), HOMO->L+4 (9%)
LanL2DZ	3.00	0.35	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.53	0.18	H-1->LUMO (87%) HOMO->LUMO (3%), HOMO->L+1 (8%)
”	4.19	0.22	HOMO->L+1 (82%) H-1->LUMO (8%), H-1->L+1 (3%)
”	4.95	0.28	H-6->LUMO (11%), H-2->L+1 (49%), H-1->L+1 (20%), HOMO->L+2 (14%)



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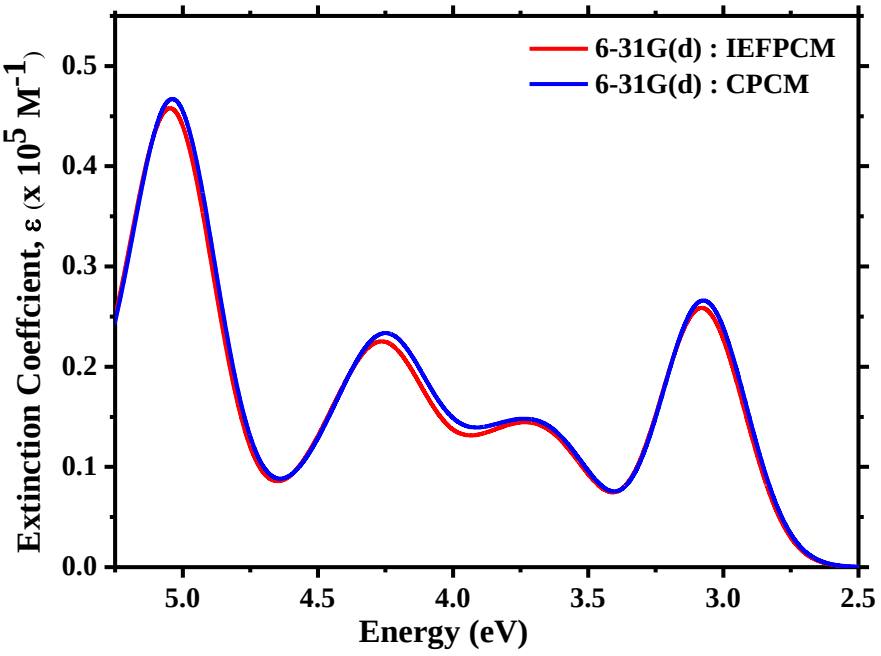


(b)

Figure S1. (a) Comparison of simulated UV-Vis absorption spectra of the dye calculated by TD-DFT in vacuum as well as THF solvent (using IEFPCM) at 6-31G (d) level of basis set. **(b)** Simulated absorption spectra of dye for two different salvation models in THF.

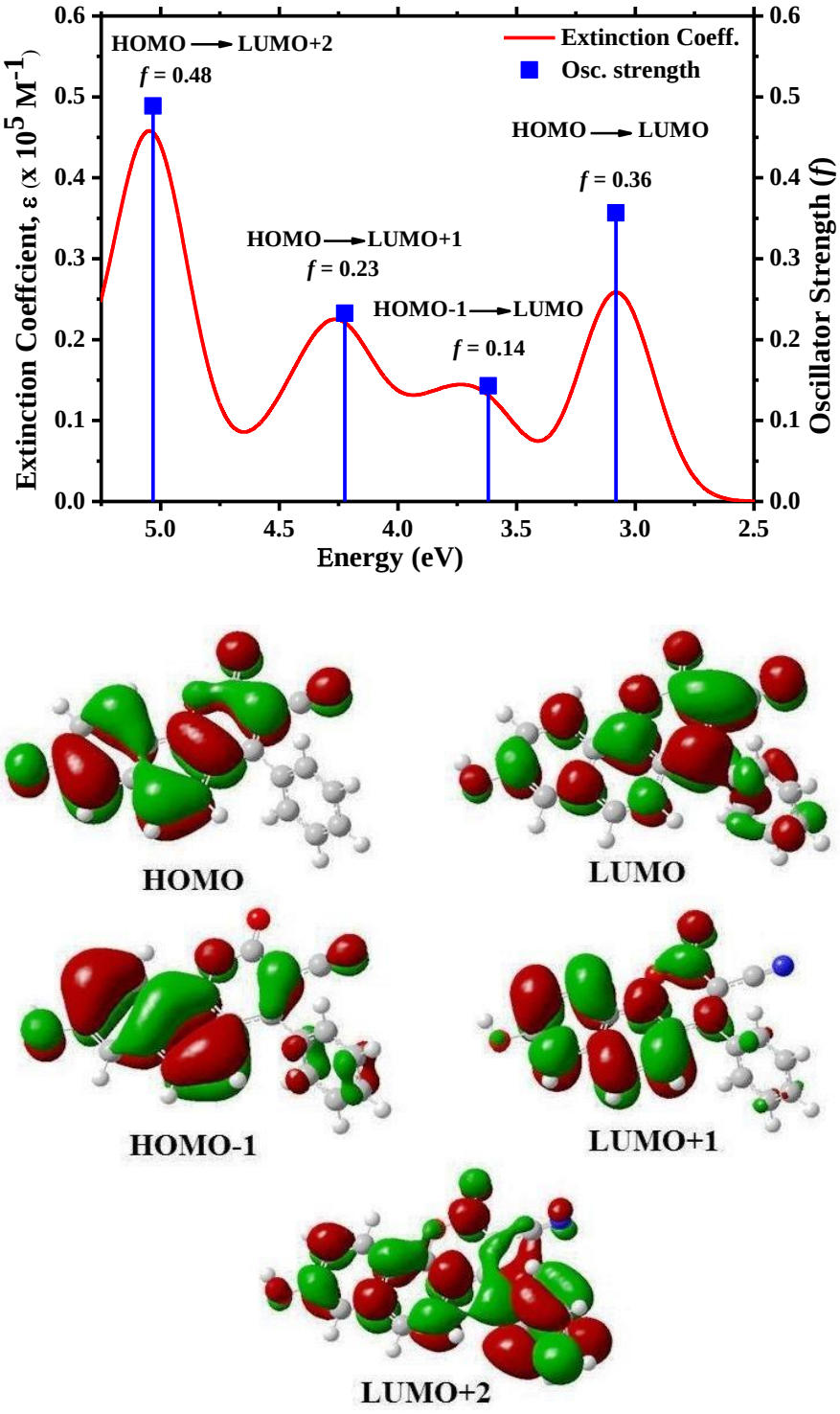


Figure S2. Simulated absorption spectra of BC5 including major electronic transitions with isodensity surfaces of molecular orbitals corresponding major transitions calculated by TD-DFT at 6-31G (d) level of basis set in THF.

Table S4. Summary of the major vertical electronic transitions with reasonably high oscillator strengths (f) including respective orbitals contribution calculated by TD-DFT (using IEFPCM) in THF

Basis set	Energy (eV)	Oscillator strength (f)	Assignment
6-31G (d)	3.08	0.3566	HOMO->LUMO (96%) H-1->LUMO (3%)
”	3.61	0.1428	H-1->LUMO (83%), HOMO->L+1 (12%) HOMO->LUMO (3%)
”	4.22	0.2325	HOMO->L+1 (80%) H-1->LUMO (12%), H-1->L+1 (2%)
”	5.03	0.4887	H-1->L+1 (32%), HOMO->L+2 (32%) H-2->L+1 (13%), H-6->LUMO (5%)

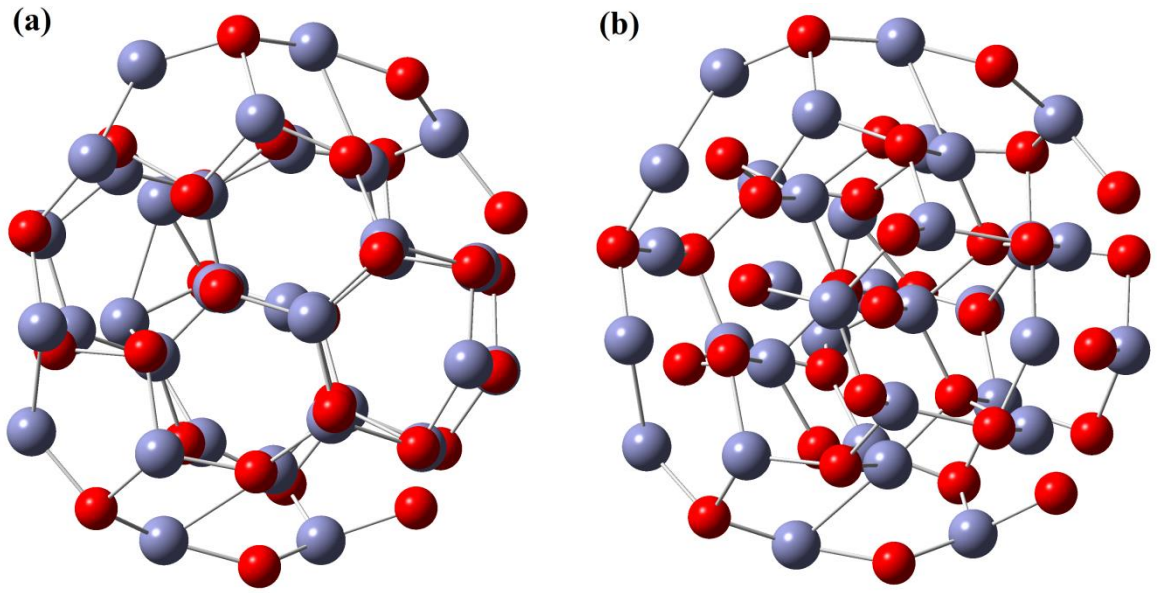


Figure S3. Top and side view of the modelled structure of $(ZnO)_{34}$ cluster without optimization represented by (a) and (b), respectively. Colour code: blue for Zinc atoms and red for Oxygen atoms.

Table S5. Computed HOMO, LUMO and band gap energies of isolated BC5 dye and $(ZnO)_n$ (n = 3, 6, 9, 12, 21 and 34) nanoclusters

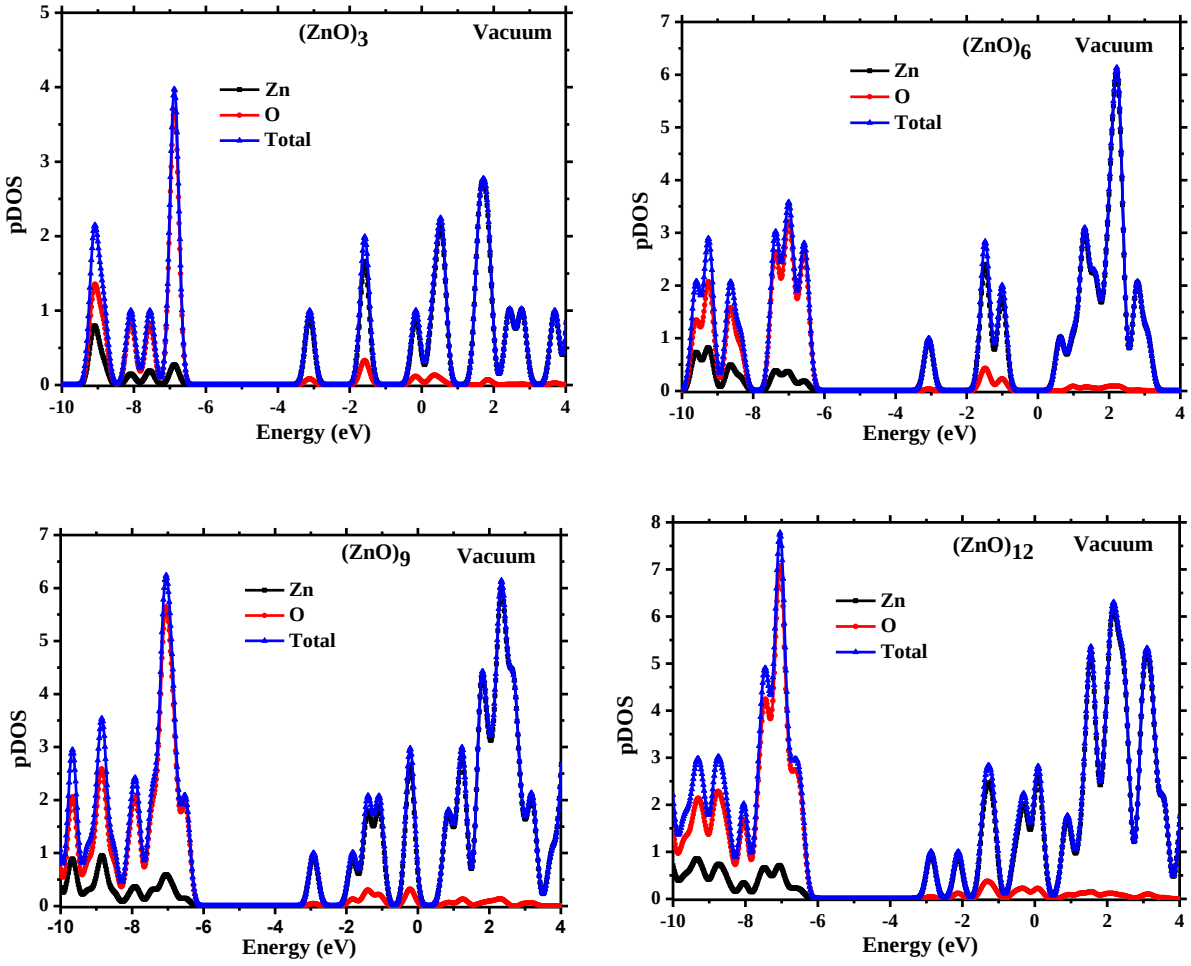
Sample	Environment	HOMO (eV)	LUMO (eV)	Band gap (eV)
BC5	Vacuum	-6.06	-2.48	3.58
’’	THF	-6.03	-2.55	3.48
$(ZnO)_3$	Vacuum	-6.86	-3.11	3.75
$(ZnO)_6$	’’	-6.52	-3.06	3.46
$(ZnO)_9$	’’	-6.50	-2.91	3.59
$(ZnO)_{12}$	’’	-6.47	-2.86	3.61
$(ZnO)_{21}$	’’	-6.08	-3.3	2.78
$(ZnO)_{34}$	’’	-4.90	-3.02	1.88

Table S6. Summary of major vertical transitions of $(ZnO)_n$ clusters (n = 3, 6, 9, 12, 21 and 34) obtained from TD-DFT calculations in vacuum

Basis Set	Energy (eV)	Oscillator Strength (f)	Assignment
$(ZnO)_3$	2.95	0.049	H-2->LUMO (97%)
”	2.96	0.050	H-3->LUMO (97%)
”	3.49	0.056	H-4->LUMO (97%)
$(ZnO)_6$	2.79	0.047	H-2->LUMO (98%)
”	3.25	0.094	H-5->LUMO (95%)
”	3.25	0.094	H-6->LUMO (95%)
”	4.26	0.003	HOMO->L+3 (70%) H-5->LUMO (2%), H-3->L+3 (3%), H-1->L+2 (8%), HOMO->L+1 (8%)
$(ZnO)_9$	2.84	0.016	HOMO->LUMO (98%)
	2.85	0.016	H-1->LUMO (98%)
”	3.48	0.150	H-7->LUMO (94%) H-4->L+1 (4%)
”	3.81	0.097	H-12->LUMO (94%) H-3->L+1 (2%)
”	4.31	0.010	H-4->L+1 (85%) H-7->LUMO (4%), H-1->L+4 (3%), HOMO->L+5 (3%)
$(ZnO)_{12}$	2.91	0.013	HOMO->LUMO (96%)
”	2.92	0.013	H-1->LUMO (96%)
”	3.34	0.049	H-4->LUMO (94%) H-8->L+1 (3%)

”	3.93	0.217	H-15->LUMO (92%) H-8->L+1 (5%)
$(ZnO)_{21}$	2.33	0.021	HOMO->LUMO (97%)
”	2.94	0.020	H-9->LUMO (25%), HOMO->L+1 (56%)
”	3.11	0.015	H-14->LUMO (11%), H-13->LUMO (46%), H-12->LUMO (15%)
”	3.14	0.027	H-15->LUMO (38%), H-3->L+1 (11%), H-2->L+1 (10%)
$(ZnO)_{34}$	1.55	0.003	HOMO->LUMO (98%)
”	1.93	0.054	H-1->LUMO (71%), H-1->L+3 (21%) HOMO->L+3 (3%)
”	2.11	0.030	H-1->L+2 (82%) H-1->LUMO (3%), H-1->L+3 (3%), HOMO->L+2 (6%), HOMO->L+3 (4%)
”	2.34	0.114	H-1->L+3 (44%), HOMO->L+5 (34%) H-1->LUMO (9%), H-1->L+2 (4%), HOMO->L+4 (3%)
”	3.08	0.067	H-1->L+8 (71%) H-8->L+1 (6%), H-2->L+2 (7%)
”	3.23	0.022	H-2->L+3 (24%), H-1->L+9 (23%) H-19->L+2 (3%), H-12->LUMO (4%), H-10->LUMO (9%),

			H-9->LUMO (3%), H-9->L+1 (3%), H-1->L+8 (3%)
”	3.26	0.018	H-10->L+1 (37%), H-4->L+2 (25%) H-17->L+1 (5%), H-16->L+1 (9%), H-13->L+1 (2%)



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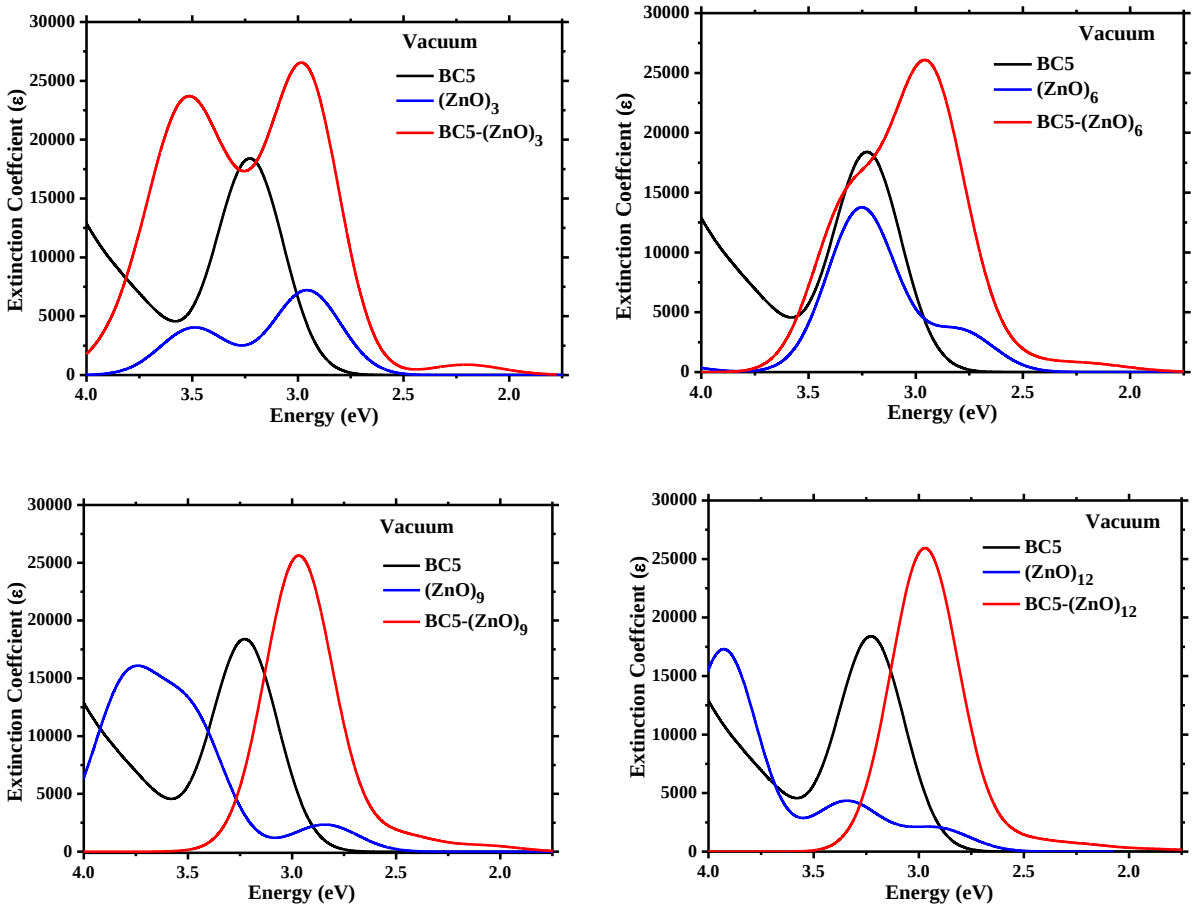
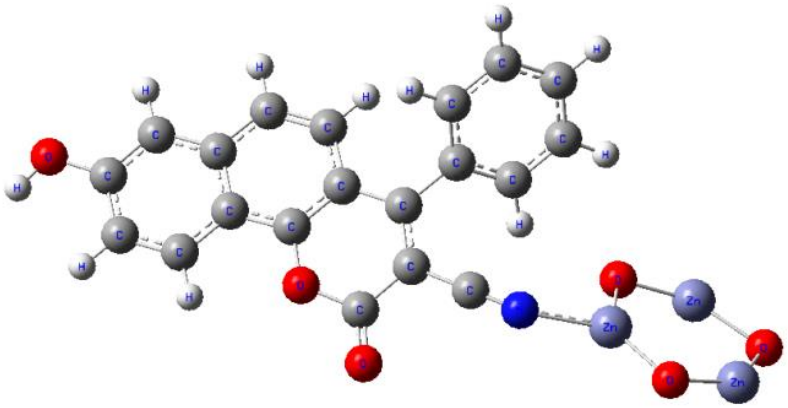
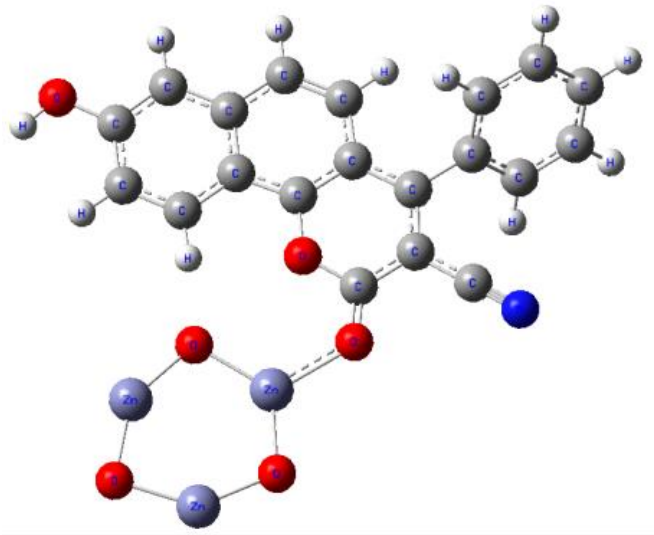
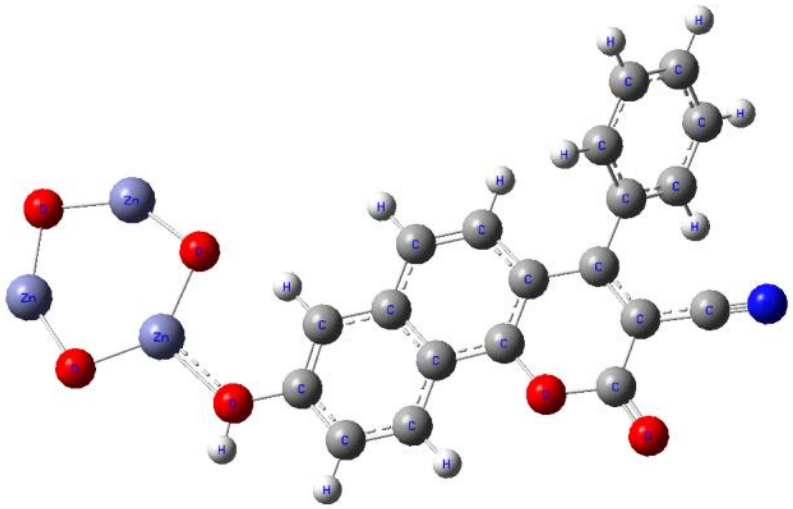


(b)

Figure S4. (a) Total and partial density of states (pDOS) of $(ZnO)_n$ (n= 3, 6, 9 and 12) clusters, **(b)** simulated absorption spectra in vacuum of isolated dye (black), $(ZnO)_n$ clusters (blue) and BC5-$(ZnO)_n$ complexes (red) (n= 3, 6, 9 and 12) with cyano anchoring.







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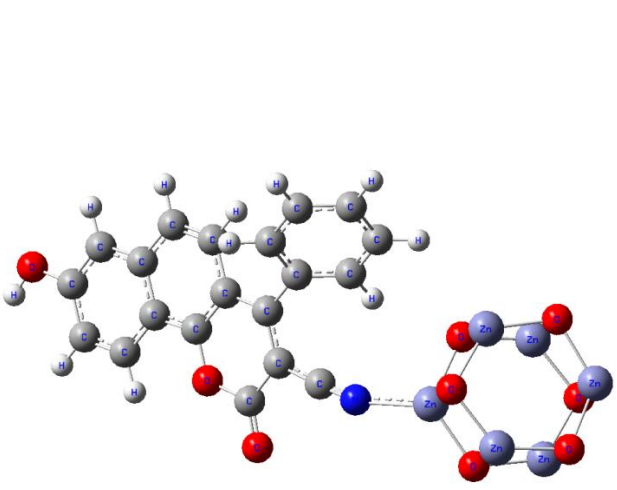

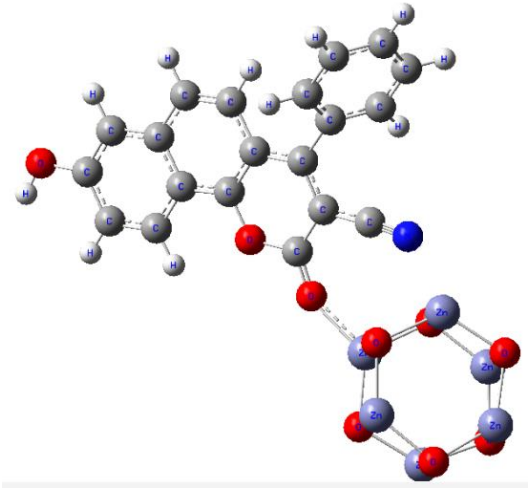

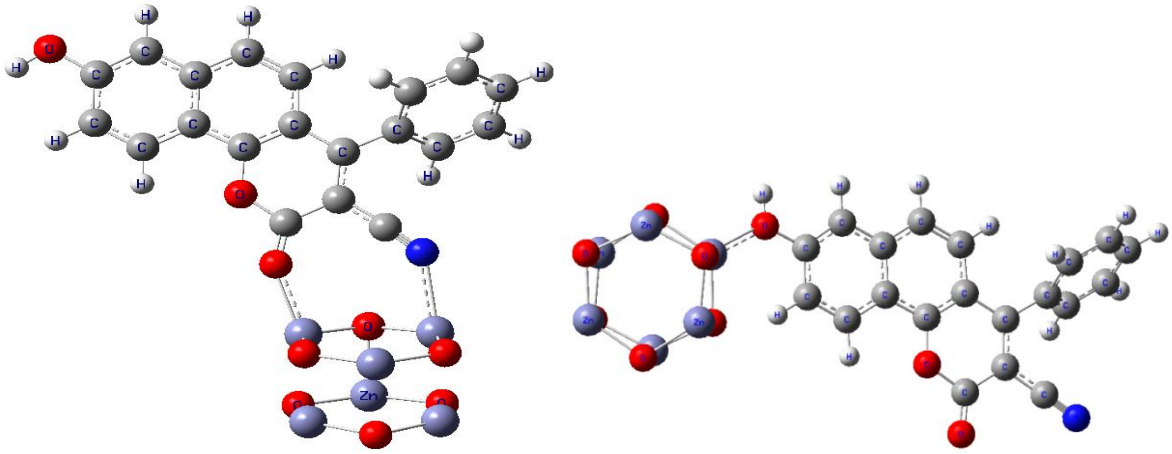

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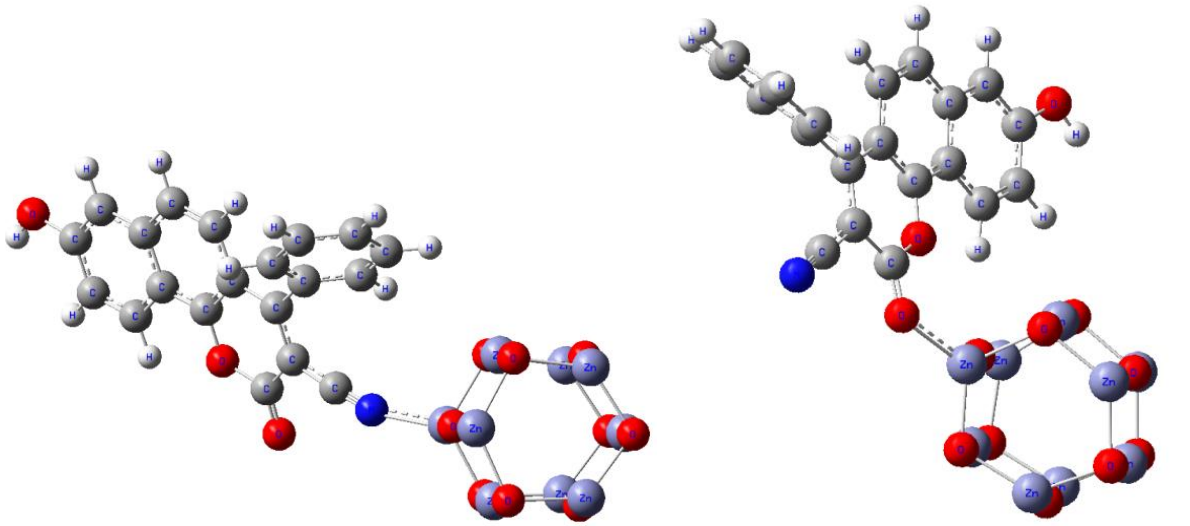

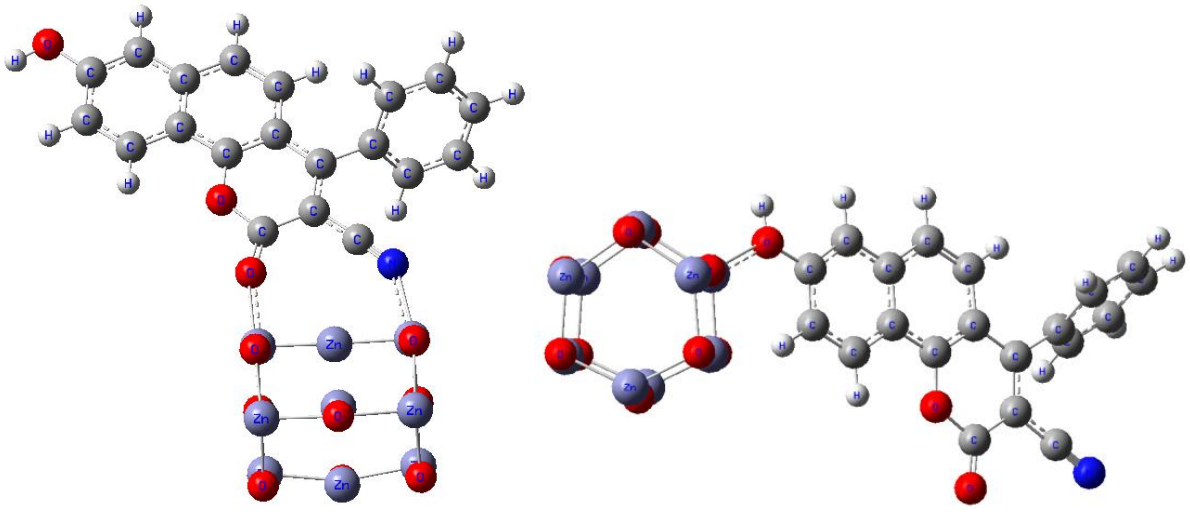

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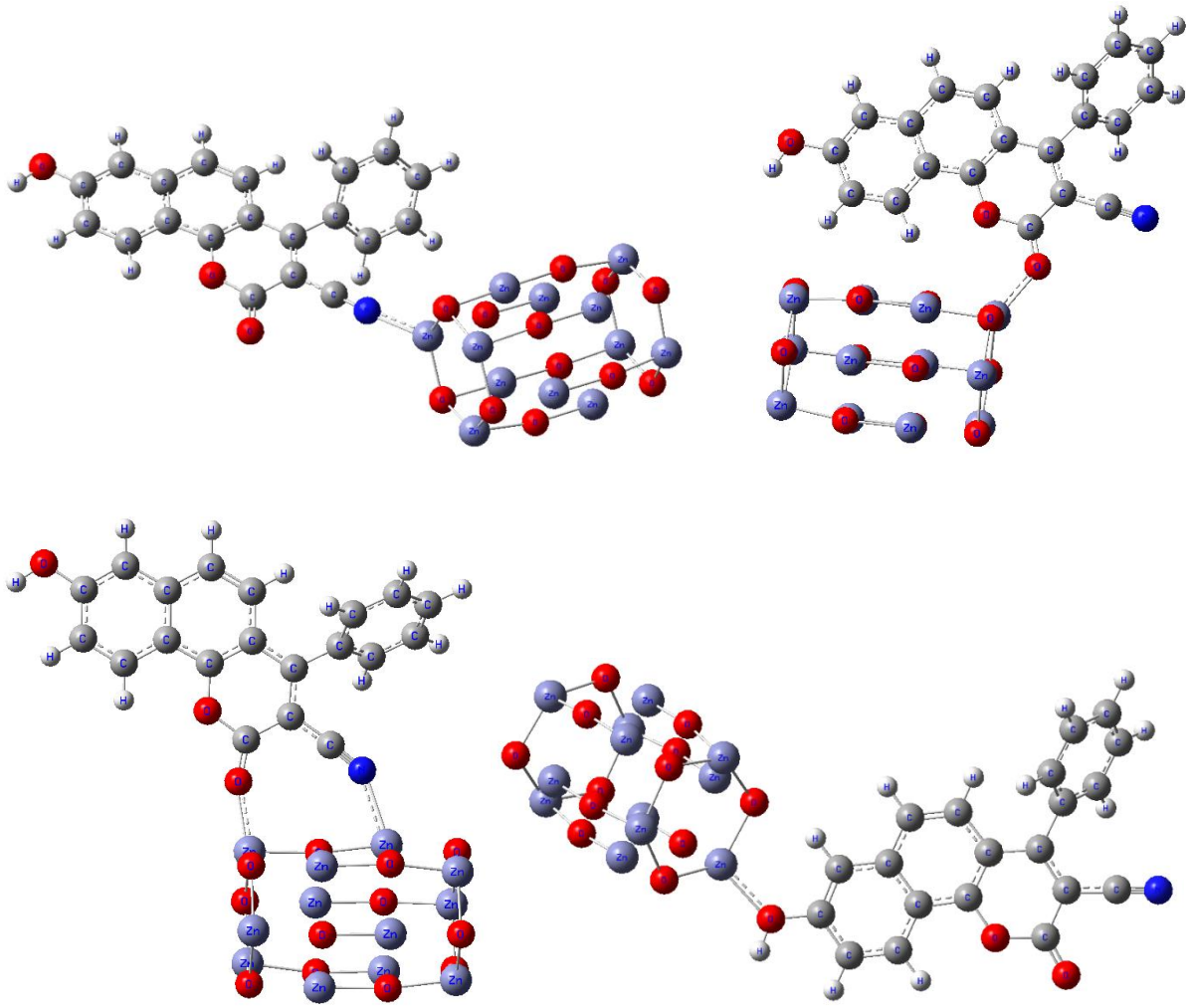
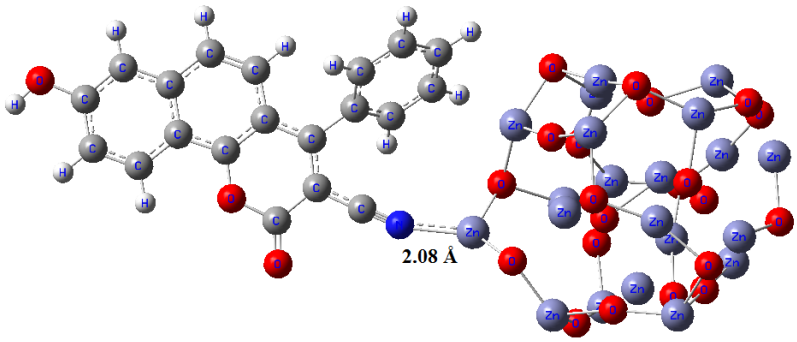
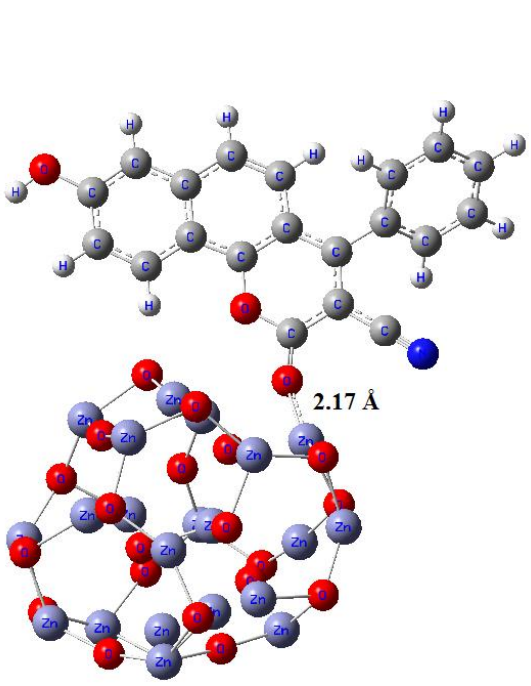
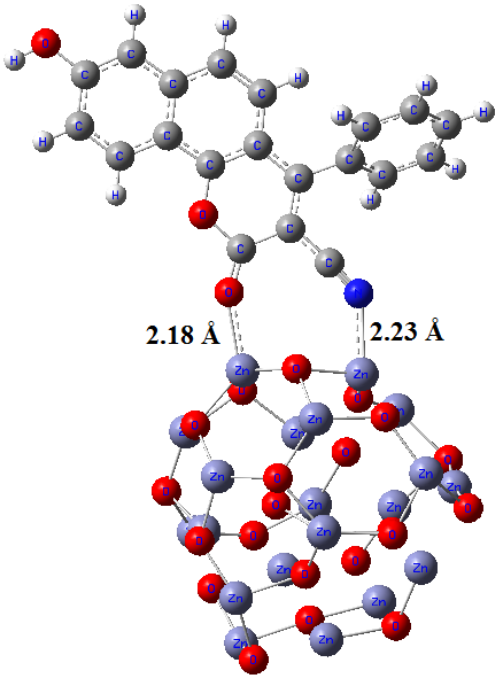
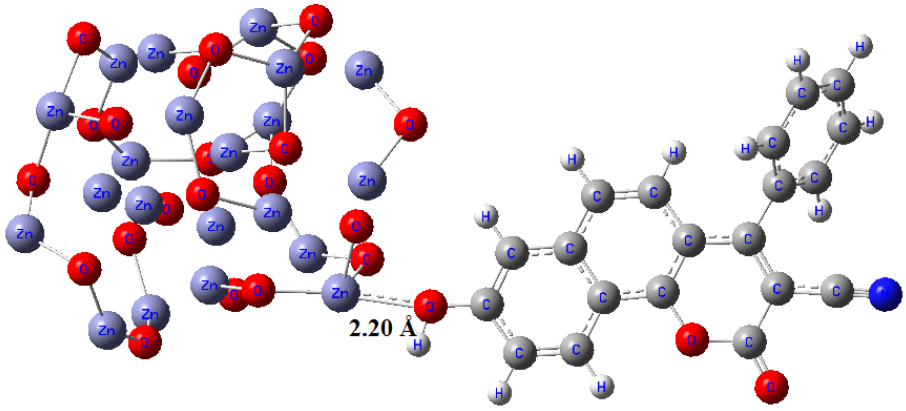


(d)

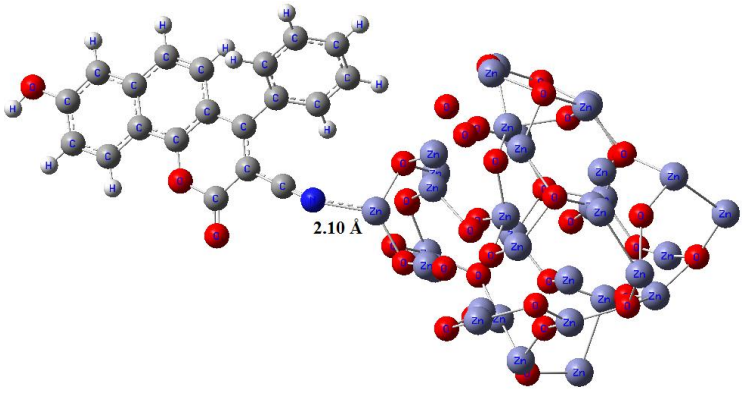


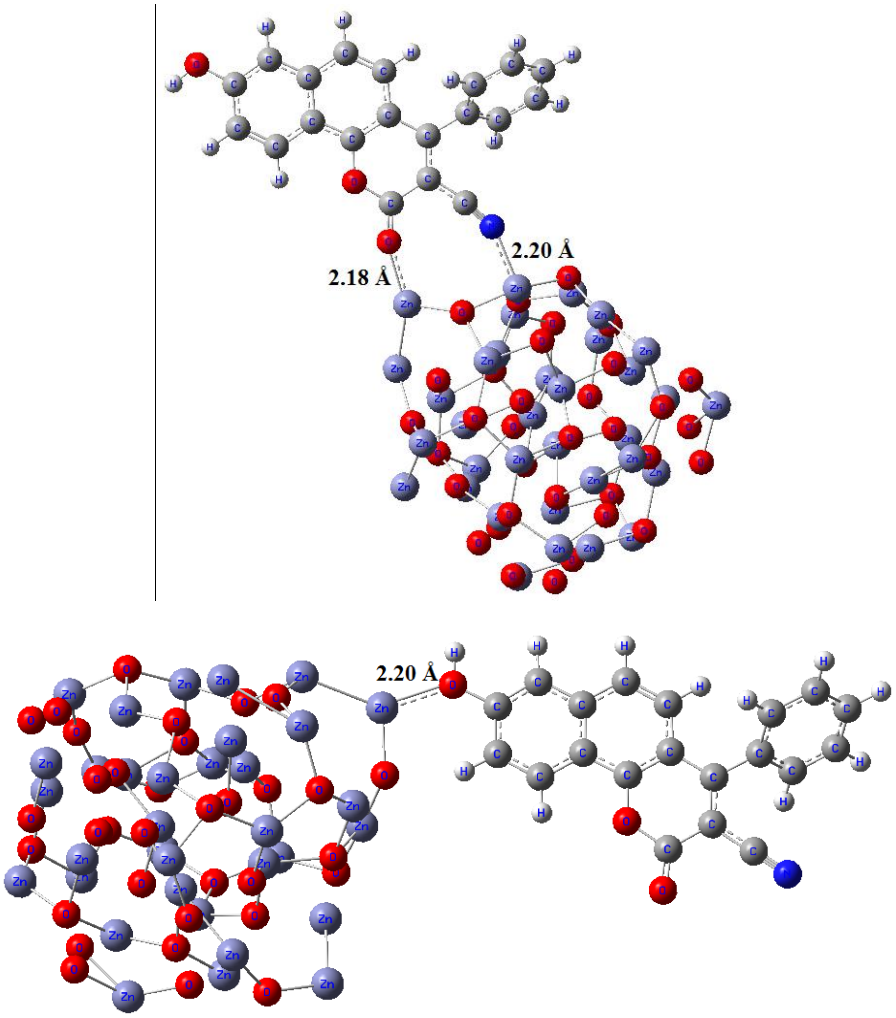






(e)





(f)

Figure S5. Ground state optimized structures of (a) BC5-$(ZnO)_3$, (b) BC5-$(ZnO)_6$, (c) BC5-$(ZnO)_9$, (d) BC5-$(ZnO)_{12}$, (e) BC5-$(ZnO)_{21}$ and (f) BC5-$(ZnO)_{34}$ for various mode of anchoring of the dye through cyano ($-C \equiv N$), carbonyl (C = O) and/or hydroxyl (-OH) group(s) in vacuum.

Table S7. Summary of major vertical transitions of the BC5-$(ZnO)_{34}$ obtained from TD-DFT calculations in solvent (THF).

Sample	Energy (eV)	Oscillator Strength (f)	Assignment
BC5-$(ZnO)_{34}$	0.66	0.697	[a]HOMO->[b]LUMO (99%)
”	0.92	0.059	HOMO->L+1 (98%)
”	1.01	0.077	HOMO->L+2 (98%)
”	1.88	0.177	H-1->L+2 (93%), H-1->L+1 (6%)
”	2.15	0.102	H-2->L+1 (76%), H-2->L+2 (16%)
”	2.20	0.075	H-1->L+3 (78%), HOMO->L+14 (11%) HOMO->L+15 (4%)
”	2.25	0.176	H-2->L+1 (76%), H-2->L+2 (16%)
”	2.32	0.064	H-2->L+1 (18%), H-2->L+2 (73%) HOMO->L+12 (4%)
”	2.38	0.083	HOMO->L+13 (22%), HOMO->L+15 (57%) HOMO->L+14 (4%), HOMO->L+18 (7%), HOMO->L+20 (3%)
”	2.49	0.145	HOMO->L+16 (16%), HOMO->L+17 (40%), HOMO->L+18 (20%)
”	2.53	0.083	H-1->L+6 (70%), H-1->L+7 (15%) HOMO->L+17 (4%)
”	2.61	0.064	H-1->L+6 (15%), H-1->L+7 (80%)

”	2.65	0.063	H-2->L+3 (89%) H-2->L+2 (2%), H-2->L+4 (5%)
”	2.87	0.105	H-6->LUMO (59%), HOMO->L+21 (15%) H-7->LUMO (8%), H-1->L+9 (4%)
”	3.02	0.034	H-2->L+6 (81%) H-2->L+8 (6%)