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

Supplementary Information

Femtosecond Insights into Direct Electron Injection in Dye Anchored ZnO QDs following Charge Transfer Excitation

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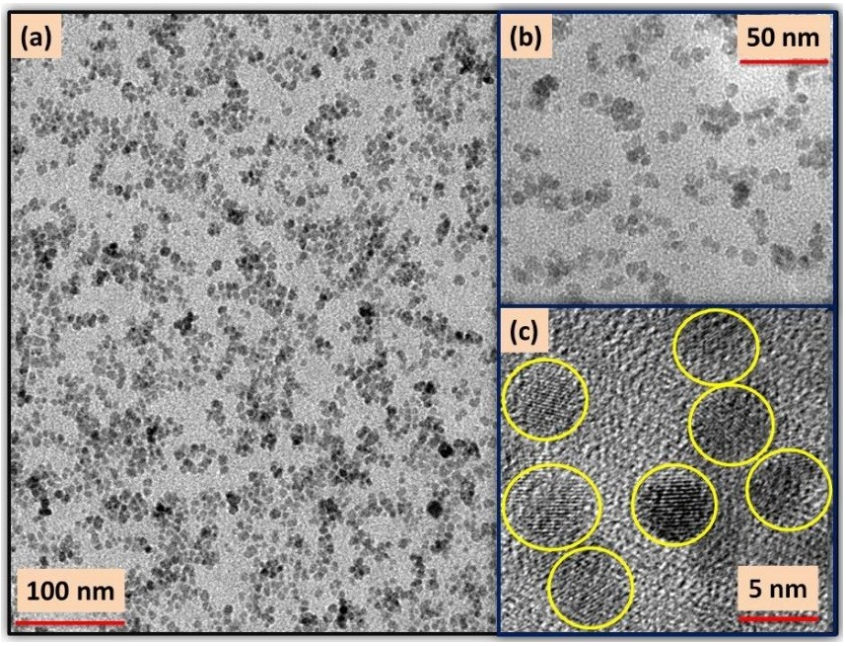


Figure S1. (**a, b**) TEM images with different resolutions and (**c**) HR-TEM images of ZnO QDs.

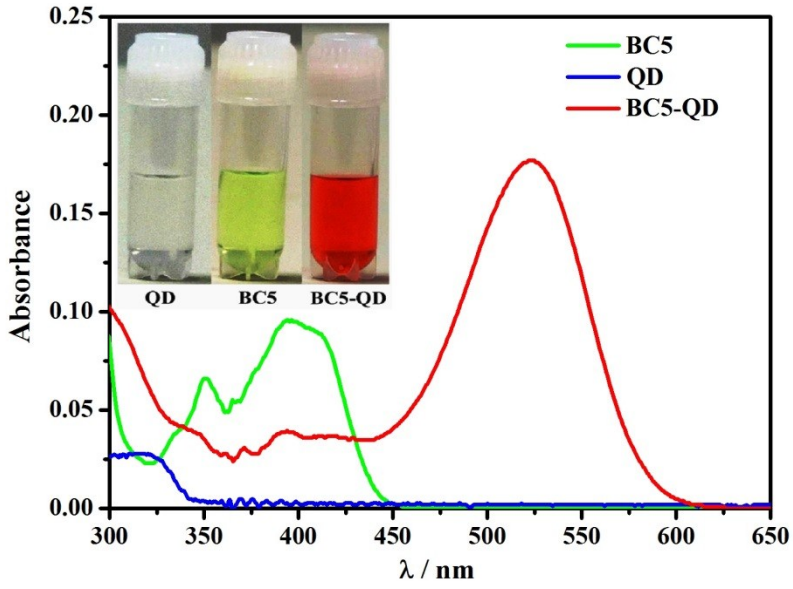


Figure S2. Absorption spectra of BC5 dye (12.66 μM), ZnO QD (58.10 nM) and their mixture in acetonitrile. Inset shows photographs of ZnO QD (white), BC5 dye (light green), and their mixture (red) solutions.

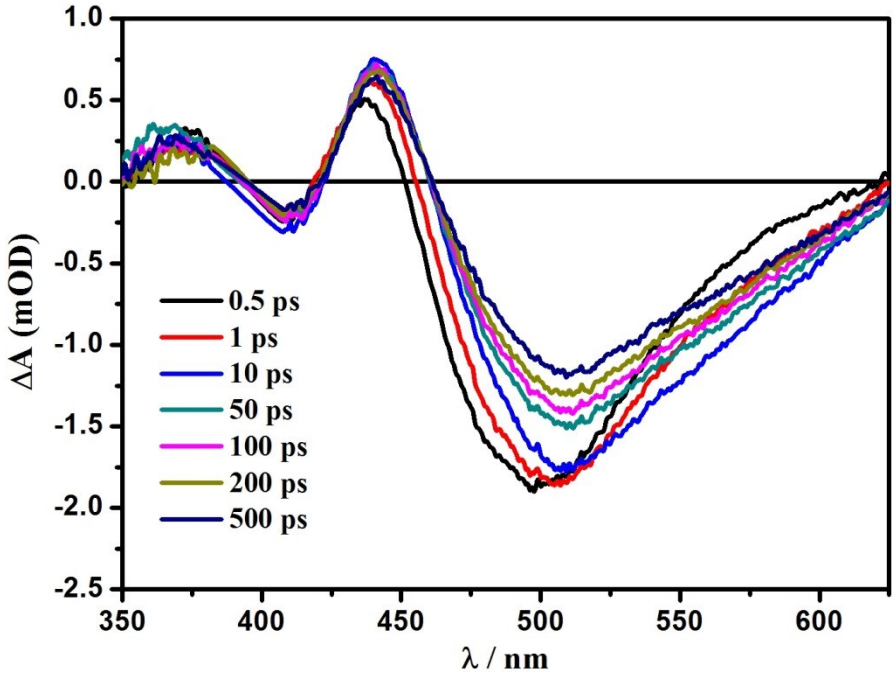


Figure S3. TA spectra of BC5 dye (excitation wavelength ~ 400 nm) in acetonitrile at different time delays.

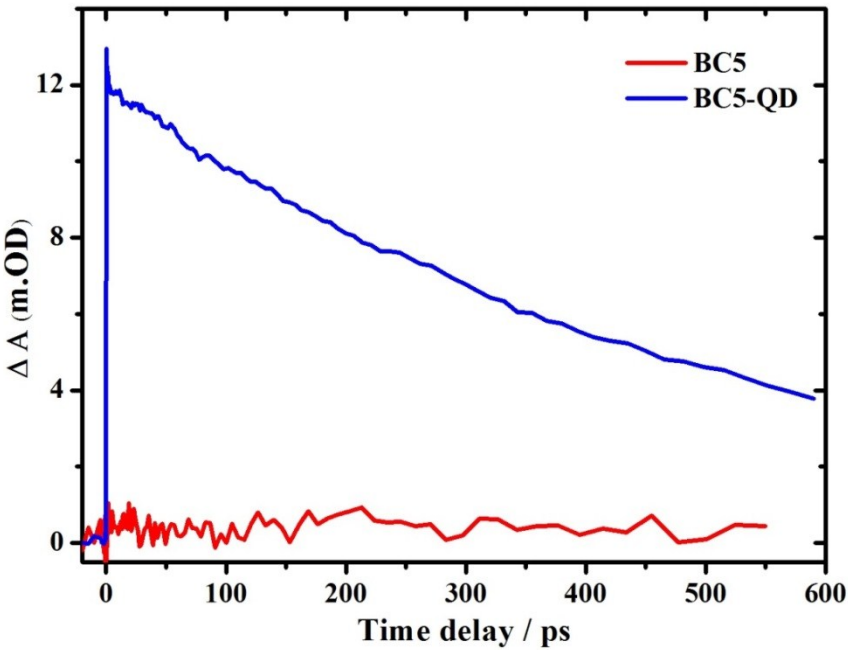


Figure S4. TA kinetics at 360 nm for BC5 and at 390 nm for BC5–ZnO complex.

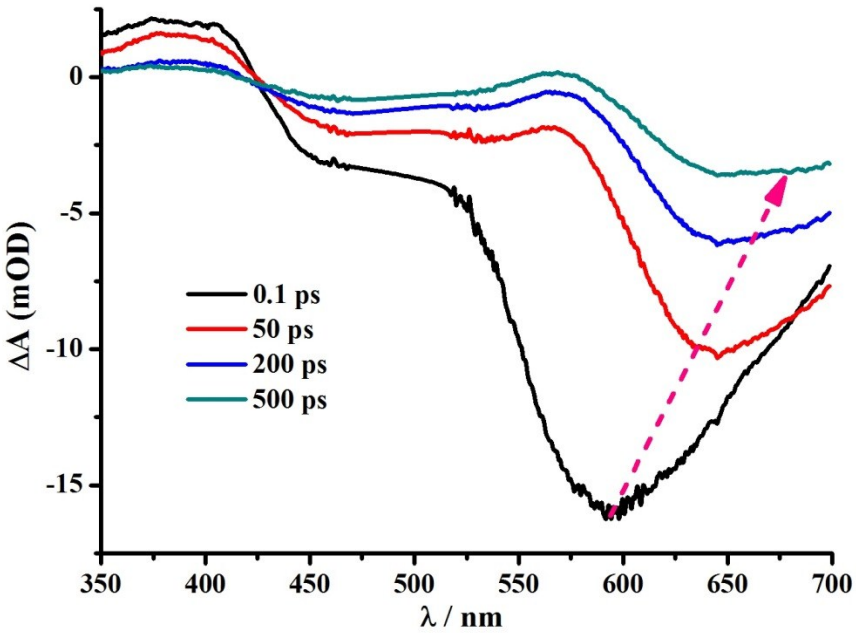


Figure S5. Shift of the negative TA band of BC5-ZnO complex with time.

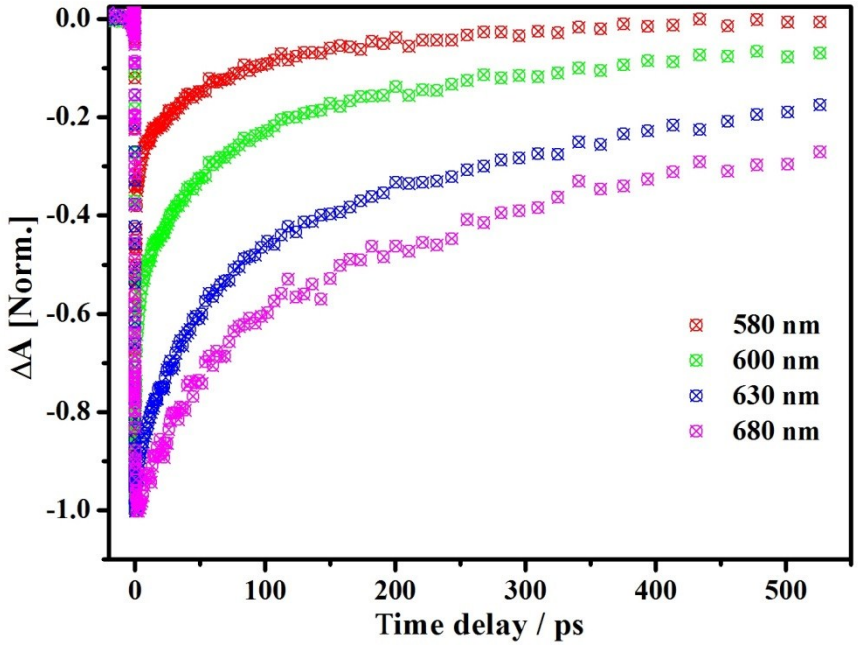


Figure S6. Normalised TA kinetic traces of the BC5-ZnO complex at 580, 600, 630, and 680 nm following excitation at 500 nm.

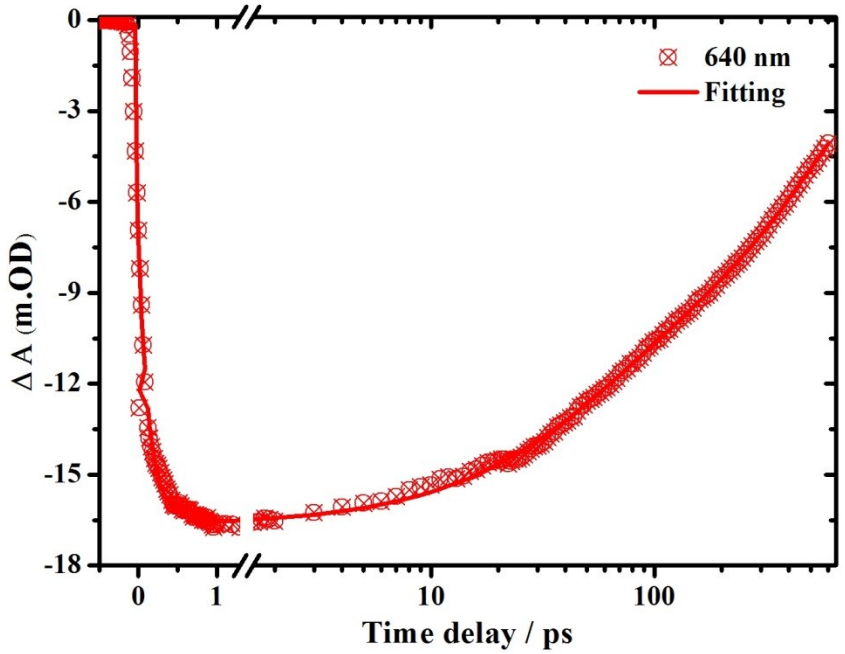
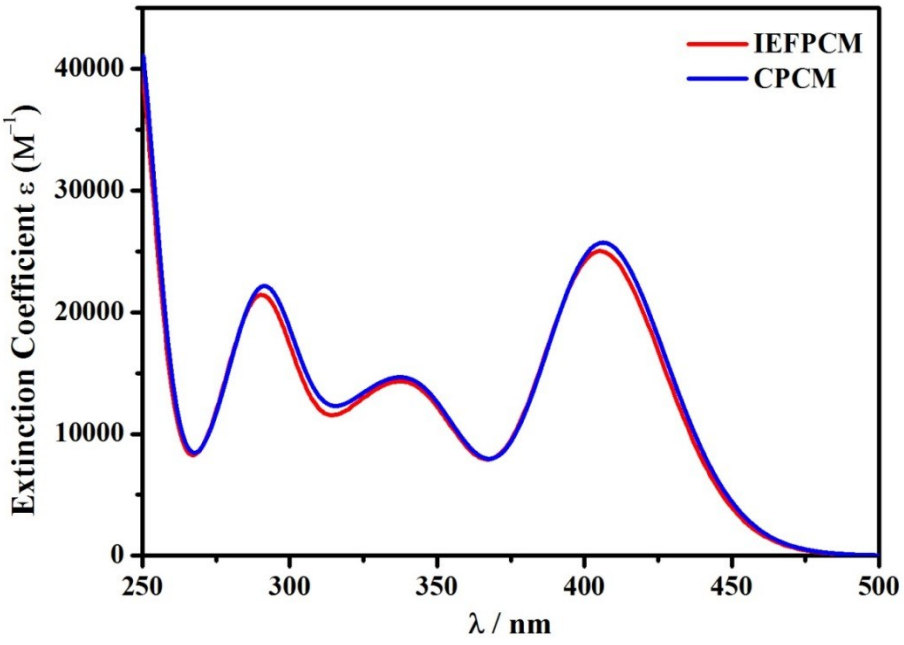
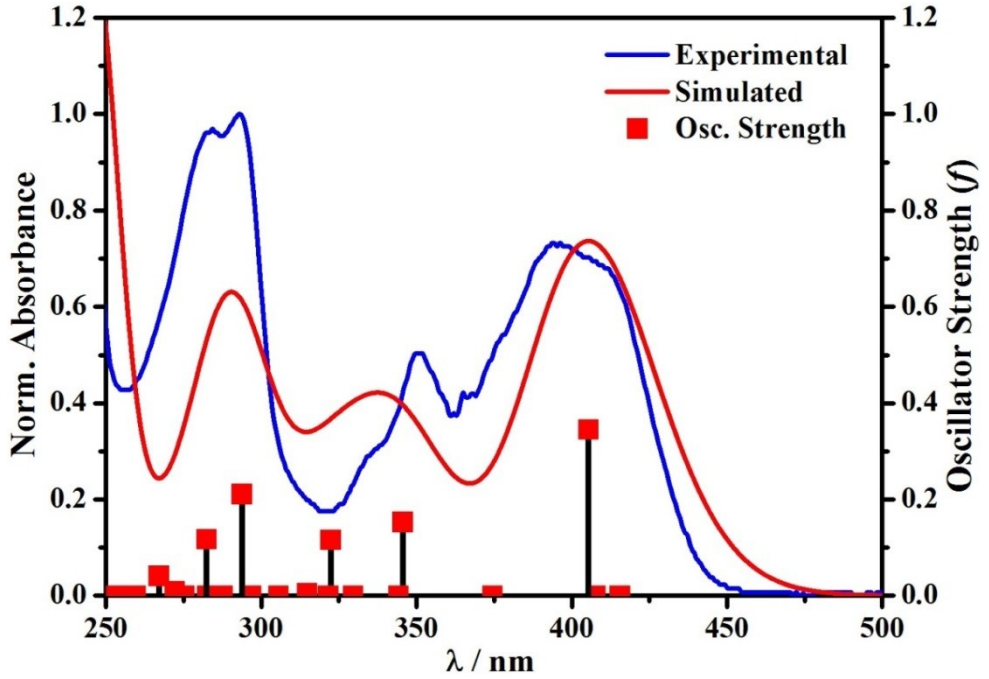


Figure S7. TA kinetics of the BC5-ZnO complex monitored at 640 nm (excitation wavelength ~ 500 nm). Solid red line represents fitting result.



(a)



(b)

Figure S8. **(a)** Simulated absorption spectra of BC5 dye in acetonitrile for two different solvation models. **(b)** Experimental and simulated absorption spectra of BC5 dye with calculated oscillator strengths in acetonitrile.

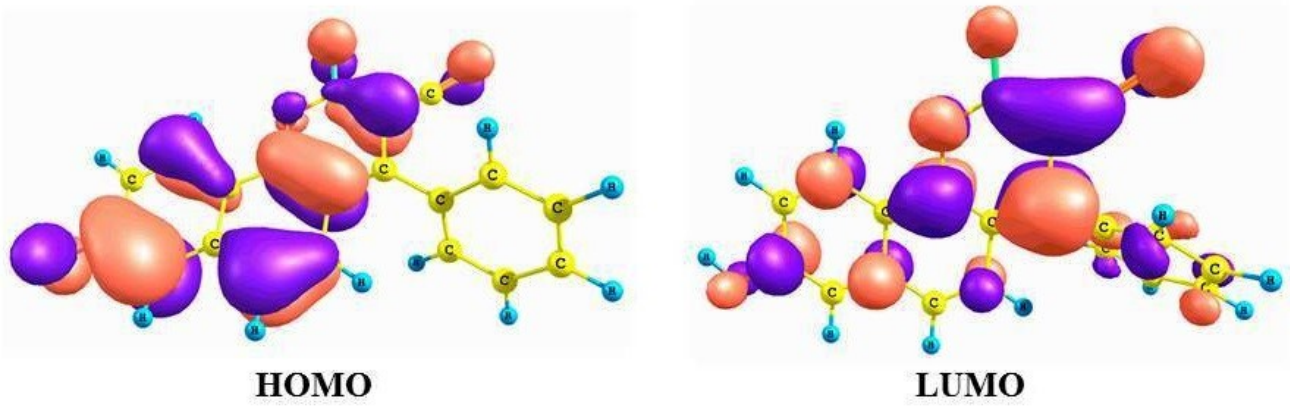


Figure S9. HOMO and LUMO of BC5 dye in acetonitrile.

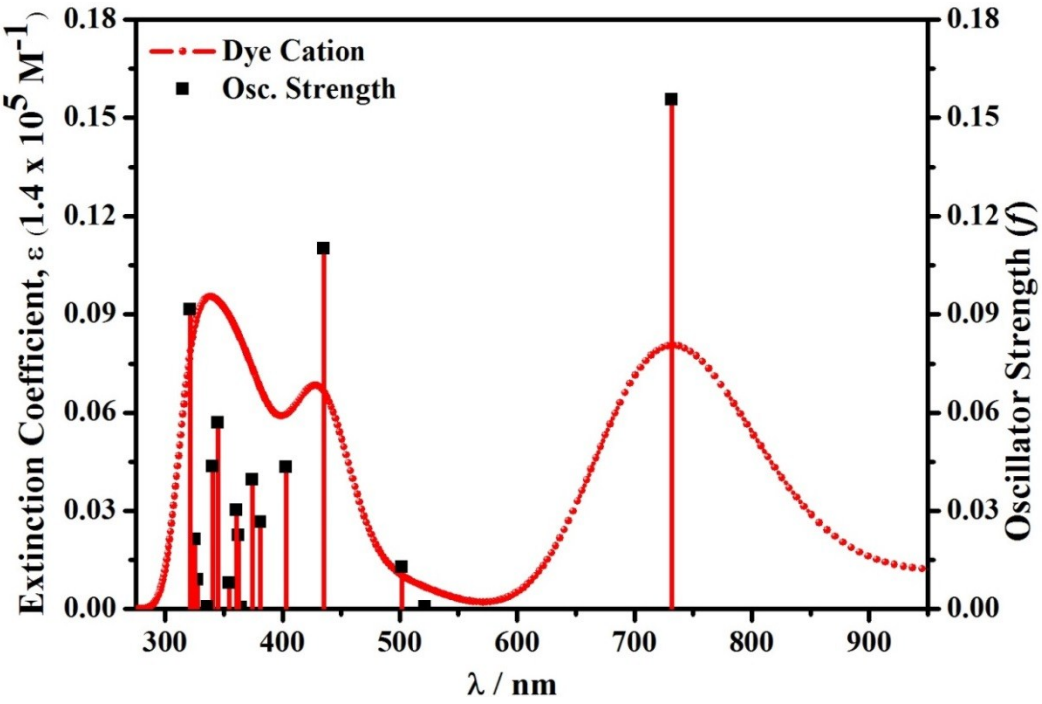


Figure S10. Simulated absorption spectra of the cation radical ($Dye^{\bullet+}$) of BC5 dye with major vertical transitions obtained by TD-DFT/B3LYP/6-31G (d)/CPCM in acetonitrile.

Table S1. Vertical electronic transitions of BC5 cation radical having reasonably high oscillator strengths (f) along with orbital contributions calculated by TD-DFT (IEFPCM) in acetonitrile.

Compound	λ_{max} (nm)	Oscillator strength (f)	Assignment
Dye cation	729.52	0.1518	H-3(B)->LUMO(B)(91%) HOMO(A) -> LUMO(A) (3%) H-2(B) -> LUMO(B) (2%)
”	434.84	0.1059	HOMO(A)-> LUMO(A) (53%), HOMO(B) -> L+1(B) (18%) H-4(A) -> LUMO(A) (3%), H-3(A) -> L+1(A) (2%), H-2(A) -> LUMO(A) (3%) ,

			H-2(A) -> L+1(A) (2%), H-3(B) -> LUMO(B) (2%), H-3(B) -> L+1(B) (5%)
”	403.06	0.044	H-2(A) -> LUMO(A) (44%), HOMO(A) -> LUMO(A) (16%), HOMO(B) -> L+1(B) (19%) H-3(A) -> LUMO(A) (4%), H-3(A) -> L+1(A) (2%), H-5(B) -> LUMO(B) (3%), H-2(B) -> L+1(B) (2%)
”	381.54	0.0231	H-1(A) -> LUMO(A) (62%) H-3(A) -> LUMO(A) (9%), H-2(A) -> LUMO(A) (2%), H-1(A) -> L+1(A) (2%), HOMO(A) -> LUMO(A) (2%), H-7(B) -> LUMO(B) (3%), H-6(B) -> LUMO(B) (2%), H-2(B) -> L+1(B) (4%), H-1(B) -> L+1(B) (9%)
”	374.49	0.0421	H-3(A) -> LUMO(A) (28%), H-1(A) -> LUMO(A) (24%), H-7(B) -> LUMO(B) (11%), H-2(B) -> L+1(B) (11%) H-2(A) -> LUMO(A) (6%), H-8(B) -> LUMO(B) (3%), H-6(B) -> LUMO(B) (4%)
”	344.51	0.0525	H-3(A) -> L+1(A) (13%), HOMO(A) -> L+1(A) (29%), H-2(B) -> L+2(B) (12%) H-3(A) -> LUMO(A) (2%), H-3(A) -> L+2(A) (3%), H-2(A) -> L+1(A) (5%), HOMO(A) -> LUMO(A) (4%),

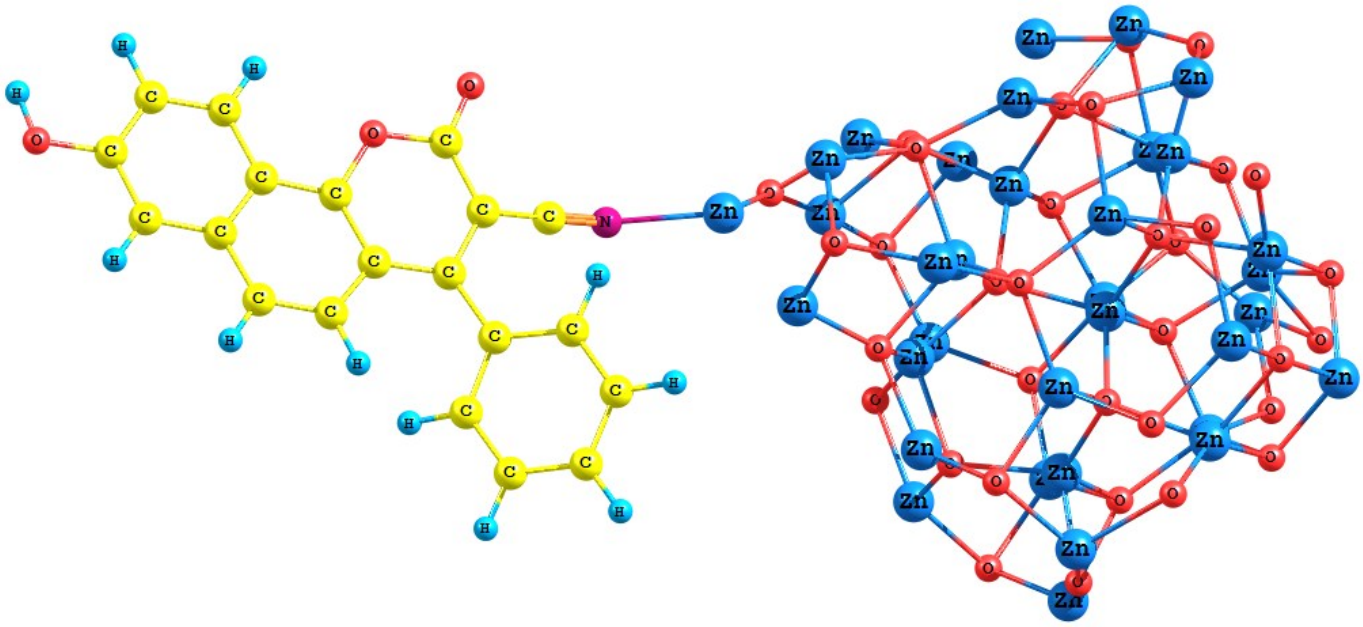
			H-10(B) -> LUMO(B) (2%), H-3(B) -> L+1(B) (2%), H-2(B) -> L+1(B) (8%), HOMO(B) -> L+1(B) (3%), HOMO(B) -> L+2(B) (2%)
”	320.84	0.0891	H-3(A) -> LUMO(A) (13%), H-10(B) -> LUMO(B) (15%), H-2(B) -> L+1(B) (29%) H-4(A) -> LUMO(A) (2%), H-3(A) -> L+1(A) (7%), HOMO(A) -> L+1(A) (8%), HOMO(A) -> L+2(A) (3%), H-12(B) -> LUMO(B) (2%), H-11(B) -> LUMO(B) (3%), H-2(B) -> L+2(B) (9%)

Table S2. Vertical electronic transitions of BC5 cation radical having reasonably high oscillator strengths (f) along with orbital contributions calculated by TD-DFT (CPCM) in acetonitrile.

Compound	λ_{max} (nm)	Oscillator strength (f)	Assignment
Dye cation	731.63	0.1555	H-3(B)-> LUMO(B) (91%) HOMO(A) -> LUMO(A) (3%), H-2(B) -> LUMO(B) (2%)
”	434.95	0.1101	HOMO(A) -> LUMO(A) (54%), HOMO(B) -> L+1(B) (17%) H-4(A) -> LUMO(A) (3%), H-3(A) -> L+1(A) (2%), H-2(A) -> LUMO(A) (3%), H-2(A) -> L+1(A) (2%),

			H-3(B) -> LUMO(B) (2%), H-3(B) -> L+1(B) (5%)
”	402.92	0.0434	H-2(A) -> LUMO (44%), HOMO(A) -> LUMO(A) (16%), HOMO(B) -> L+1(B) (19%) H-3(A) -> LUMO(A) (4%), H-3(A) -> L+1(A) (2%), H-5(B) -> LUMO(B) (3%), H-2(B) -> L+1(B) (2%)
”	381.14	0.0265	H-3(A) -> LUMO(A) (11%), H-1(A) -> LUMO(A) (57%) H-2(A) -> LUMO(A) (3%), HOMO(A) -> LUMO(A) (2%), H-7(B) -> LUMO(B) (3%), H-6(B) -> LUMO(B) (2%), H-2(B) -> L+1(B) (5%), H-1(B) -> L+1(B) (8%)
”	374.31	0.0395	H-3(A) -> LUMO(A) (27%), H-1(A) -> LUMO(A) (29%), H-7(B) -> LUMO(B) (10%), H-2(B) -> L+1(B) (11%) H-2(A) -> LUMO(A) (4%), H-8(B) -> LUMO(B) (3%), H-6(B) -> LUMO(B) (3%)
”	344.63	0.0569	H-3(A) -> L+1(A) (14%), HOMO(A) -> L+1(A) (30%), H-2(B) -> L+2(B) (12%) H-3(A) -> LUMO(A) (2%), H-3(A) -> L+2(A) (3%), H-2(A) -> L+1(A) (5%), HOMO(A) -> LUMO(A) (4%), H-10(B) -> LUMO(B) (2%), H-3(B) -> L+1(B) (2%),

			H-2(B) -> L+1(B) (8%), HOMO(B) -> L+1(B) (3%), HOMO(B) -> L+2(B) (2%)
”	320.99	0.0915	H-3(A) -> LUMO(A) (13%), H-10(B) -> LUMO(B) (16%), H-2(B) -> L+1(B) (29%) H-4(A) -> LUMO(A) (2%), H-3(A) -> L+1(A) (7%), HOMO(A) -> L+1(A) (8%), HOMO(A) -> L+2(A) (3%), H-12(B) -> LUMO(B) (2%), H-11(B) -> LUMO(B) (3%), H-2(B) -> L+2(B) (8%)



BC5 **$(ZnO)_{34}$**

Figure S11. Optimised geometry of BC5-$(ZnO)_{34}$ complex in acetonitrile. Colour code: yellow for carbon atoms, light blue for hydrogen atoms, magenta for nitrogen atoms, red for oxygen atoms and dark blue for zinc atoms, respectively.

Table S3. Major vertical electronic transitions of BC5-$(ZnO)_{34}$ complex along with high oscillator strengths (f), respective orbital contributions calculated by TD-DFT/B3LYP/LanL2DZ/ CPCM in acetonitrile.

Compound	Energy (eV)	Oscillator strength (f)	Assignment
BC5-$(ZnO)_{34}$	0.84011	0.1039	HOMO -> LUMO (99%)
”	1.06515	0.0517	HOMO -> L+1 (43%), HOMO -> L+2 (48%) HOMO -> L+3 (6%)
”	1.4737	0.0464	HOMO -> L+6 (94%) HOMO -> L+5 (2%)
”	1.76094	0.0597	H-1-> LUMO (99%)
”	2.0923	0.0755	H-1 -> L+1 (14%), H-1-> L+2 (72%), HOMO -> L+11 (9%)
”	2.17892	0.1714	H-2 -> LUMO (78%), H-1 -> L+3 (6%), HOMO -> L+10 (4%), HOMO -> L+14 (2%), HOMO -> L+16 (4%)
”	2.21373	0.1408	HOMO -> L+14 (33%), HOMO -> L+16 (43%) H-2 -> LUMO (6%), HOMO -> L+11 (4%), HOMO -> L+12 (2%), HOMO -> L+13 (7%)
”	2.39637	0.2269	H-2 -> L+1 (78%), H-2 -> L+2 (11%) HOMO -> L+13 (3%)

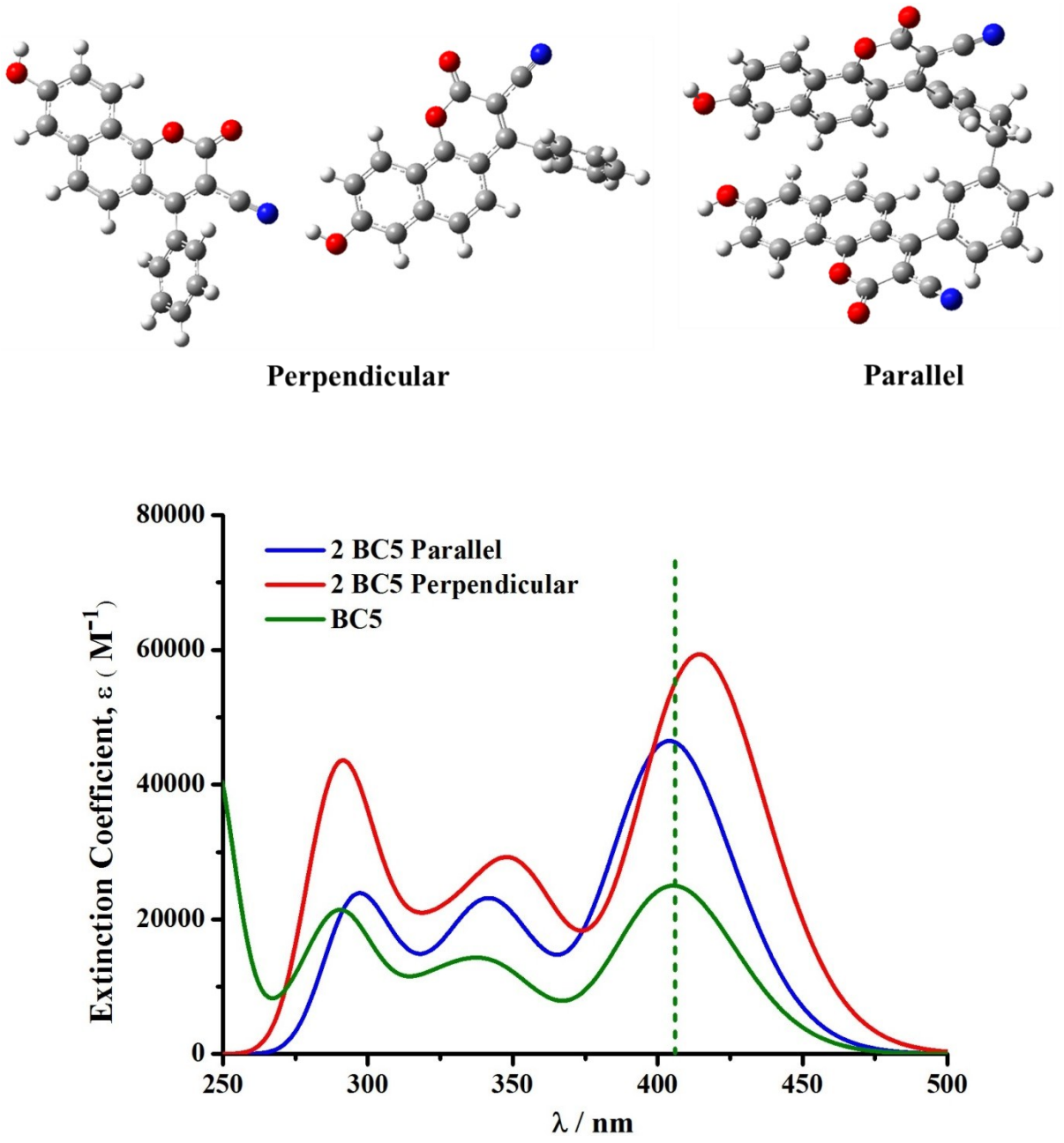


Figure S12. Simulated absorption spectra of a single BC5 dye (green) and aggregation of two dye molecules in parallel (blue) and perpendicular (red) mode in acetonitrile.