Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Nature of vertical excited states of metal containing dyes for DSSCs applications: insights from TD-DFT and density based indexes

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SUPPORTING INFORMATION

Complementary results on N3.

	N°	E / eV	λ / nm	f / a.u.
PBE0	1	1.93	643	0.04
	2	1.98	627	0.02
	3	2.19	567	0.00
	4	2.21	560	0.00
	5	2.28	544	0.14
	6	2.39	518	0.03
	7	2.73	454	0.09
	8	2.80	443	0.08
	9	2.89	429	0.03
	10	2.90	427	0.01
	11	2.96	419	0.03
	12	2.96	419	0.06
	13	2.99	415	0.01
	14	3.00	413	0.00
	15	3.00	413	0.04
CAM	1	2.51	493	0.06
	2	2.54	487	0.02
	3	2.79	444	0.06
	4	2.84	437	0.00
	5	2.87	432	0.14
	6	3.02	410	0.04
EXP		2.30	538	
		3.12	398	

Table S1: Computed and experimental[1] transitions of N3. Experimental values are obtained in ethanol.

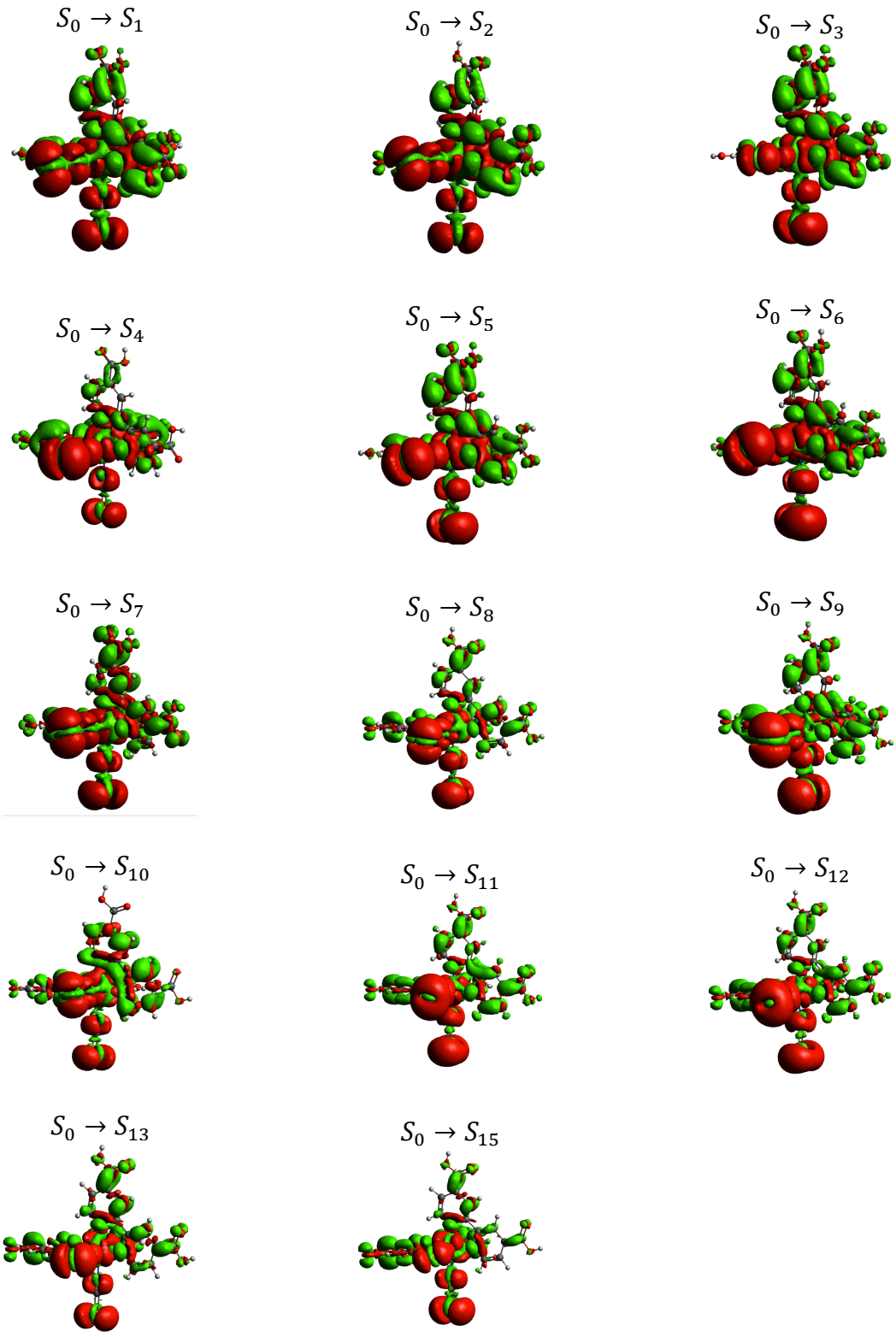

Figure S1: Electronic density variation computed for N3 at PBE0 level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

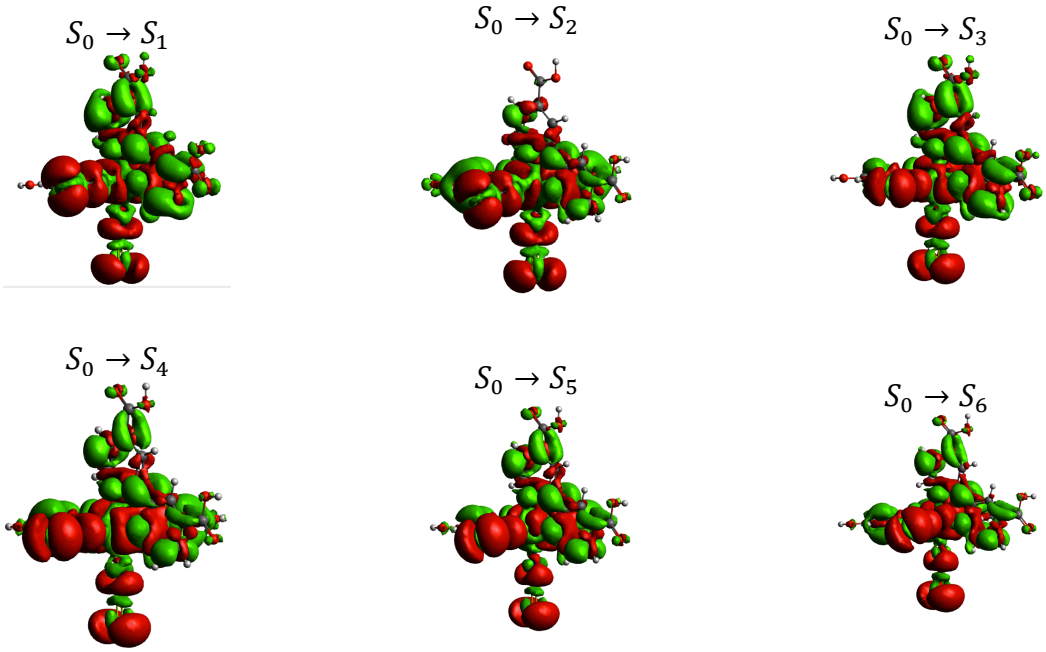

Figure S2: Electronic density variation computed for N3 at CAM-B3LYP level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

Complementary results on Z907.

	N°	E / eV	λ / nm	f / a.u.
PBE0	1	1.83	678	0.03
	2	2.05	604	0.00
	3	2.26	549	0.09
	4	2.44	509	0.02
	5	2.64	469	0.12
	6	2.71	458	0.01
	7	2.79	445	0.08
	8	2.84	437	0.01
	9	2.87	432	0.02
	10	2.90	427	0.06
	11	2.95	420	0.03
CAM	1	2.37	522	0.03
	2	2.63	471	0.00
	3	2.79	444	0.15
	4	3.03	409	0.02
EXP		2.41	515	
		3.31	375	

Table S2: Computed and experimental[2] transitions of Z907. Experimental values are obtained in ethanol.

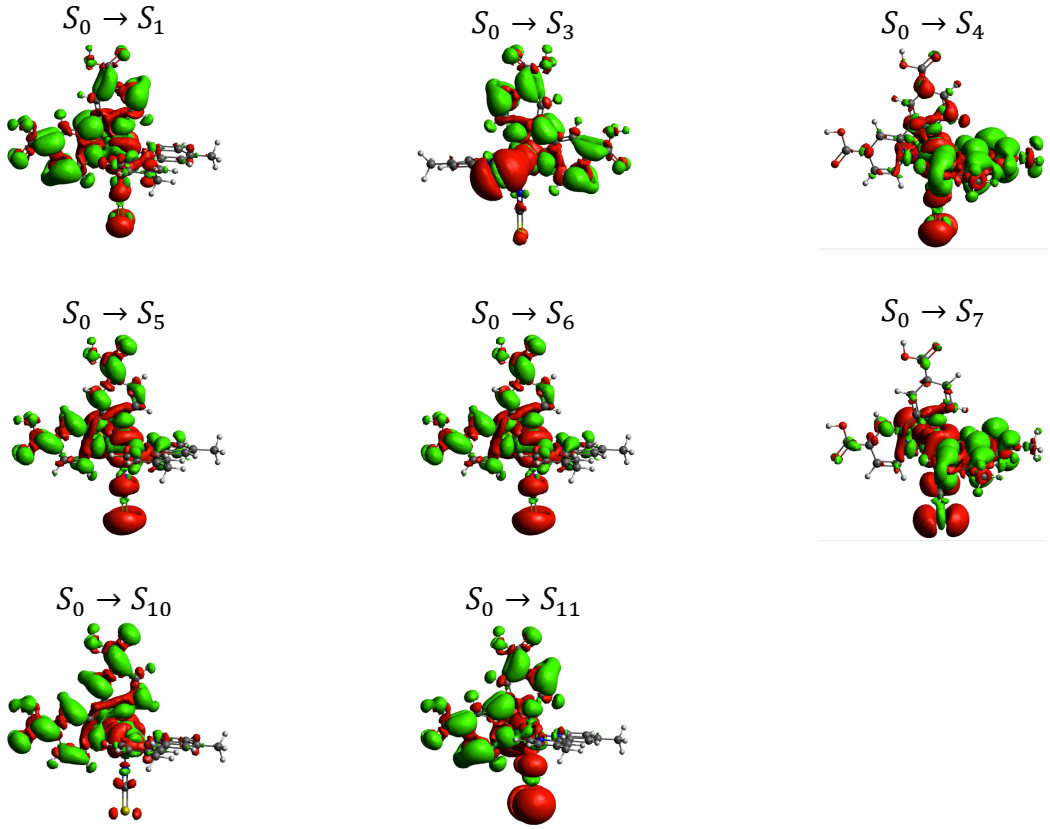

Figure S3: Electronic density variation computed for Z907 at PBE0 level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

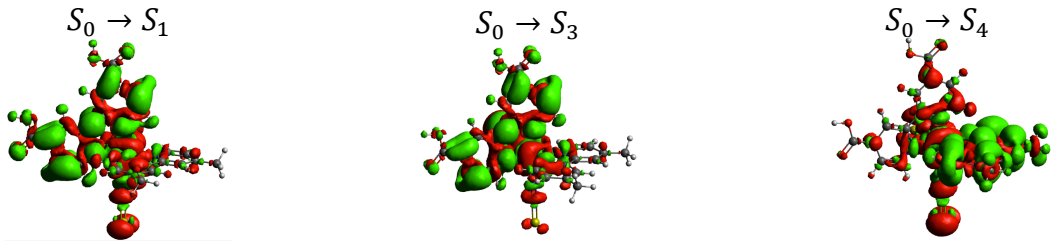

Figure S4: Electronic density variation computed for Z907 at CAM-B3LYP level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

Complementary results on CYC-B11.

	N°	E / eV	λ / nm	f / a.u.
PBE0	1	2.01	615	0.11
	2	2.11	588	0.09
	3	2.18	567	0.00
	4	2.18	536	0.41
	5	2.35	527	0.01
	6	2.46	503	0.11
	7	2.62	472	0.70
	8	2.71	457	0.31
	9	2.77	447	0.19
	10	2.80	443	0.04
	11	2.82	439	0.09
	12	2.85	435	0.28
	13	2.90	427	0.05
	14	2.97	417	0.12
	15	3.01	413	0.01
	16	3.01	413	0.02
	17	3.08	403	0.02
CAM	1	2.59	479	0.13
	2	2.69	461	0.22
	3	2.81	442	0.09
	4	2.88	431	0.57
	5	3.01	412	0.03
	6	3.05	406	0.36
EXP		2.24	554	
		3.20	388	

Table S3: Computed and experimental[3] transitions of CYC-B11. Experimental values are obtained in DMF.

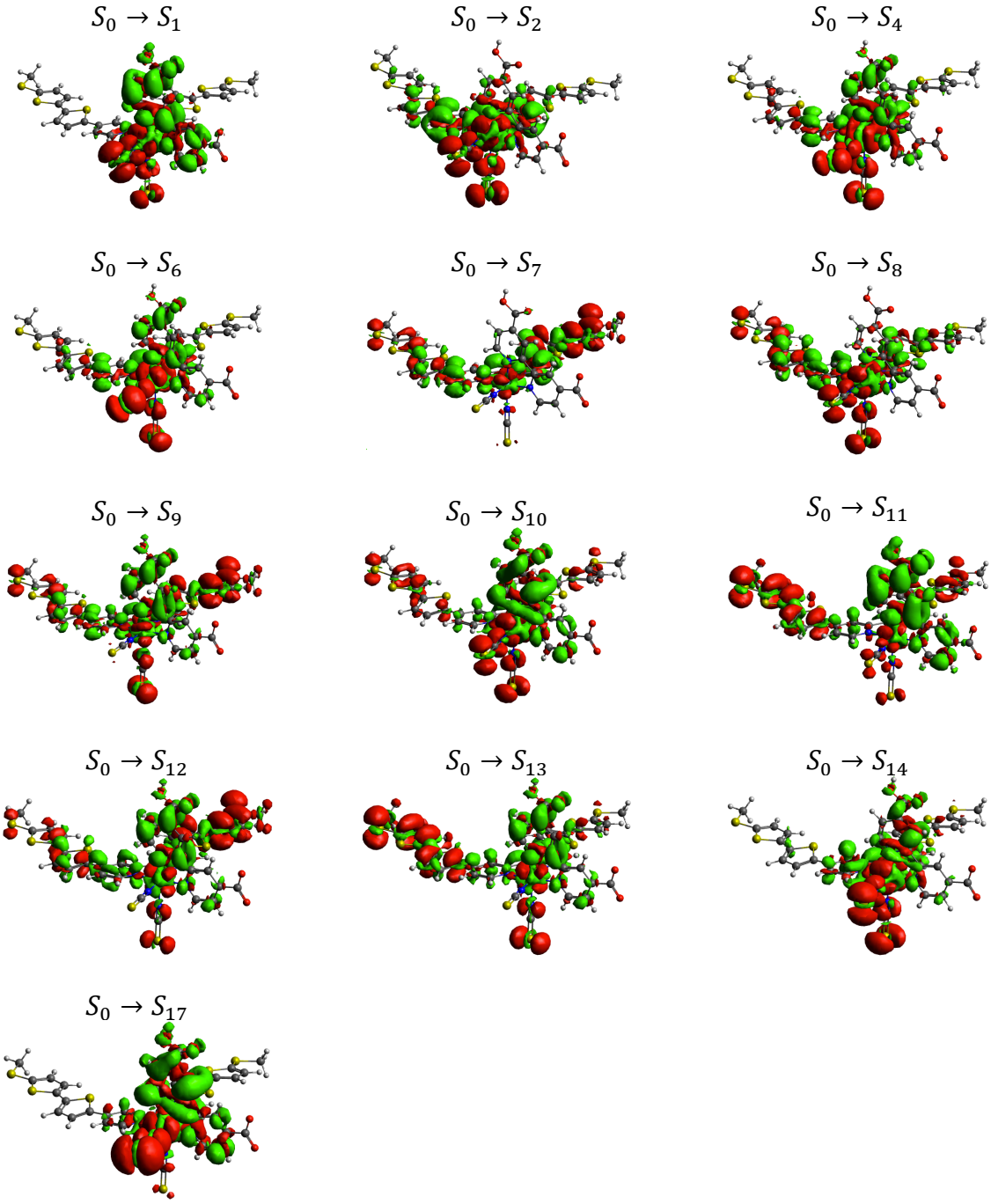

Figure S5: Electronic density variation computed for CYC-B11 at PBE0 level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

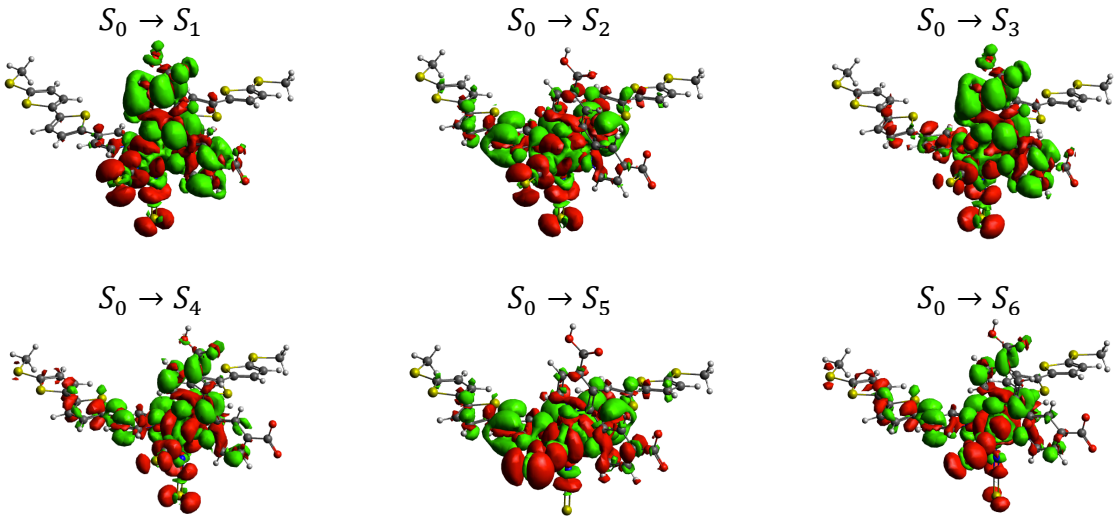

Figure S6: Electronic density variation computed for CYC-B11 at CAM-B3LYP level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

Complementary results on the Black Dye.

	N°	E / eV	λ / nm	f / a.u.
PBE0	1	1.79	692	0.01
	2	1.99	623	0.00
	3	2.07	598	0.10
	4	2.37	522	0.04
	5	2.50	496	0.06
	6	2.62	473	0.00
	7	3.09	402	0.00
CAM	1	2.25	550	0.02
	2	2.49	498	0.12
	3	2.50	495	0.00
	4	2.94	421	0.05
EXP		2.10	590	
		2.35	528sh	
		3.10	400	

Table S4: Computed and experimental[4] transitions of the Black Dye. Experimental values are obtained in ethanol.

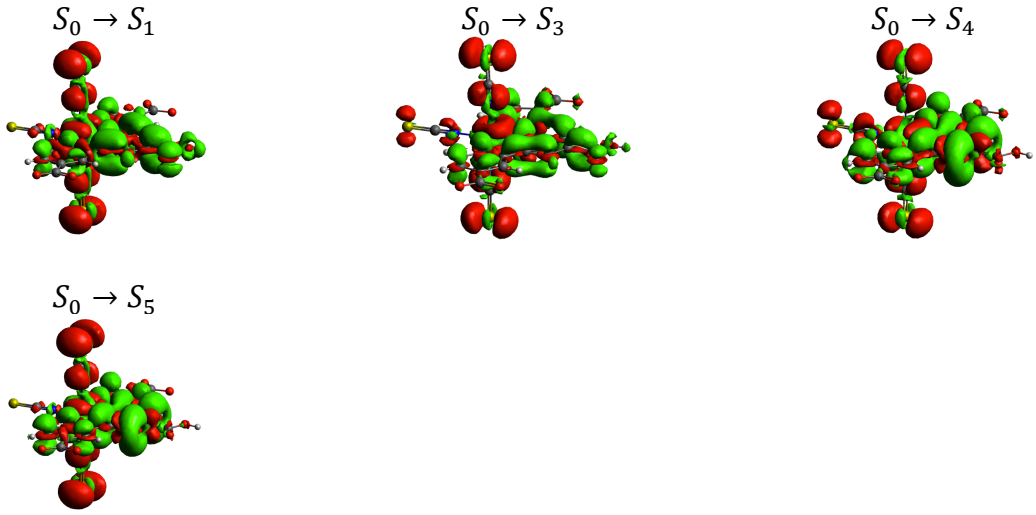

Figure S7: Electronic density variation computed for the Black Dye at PBE0 level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

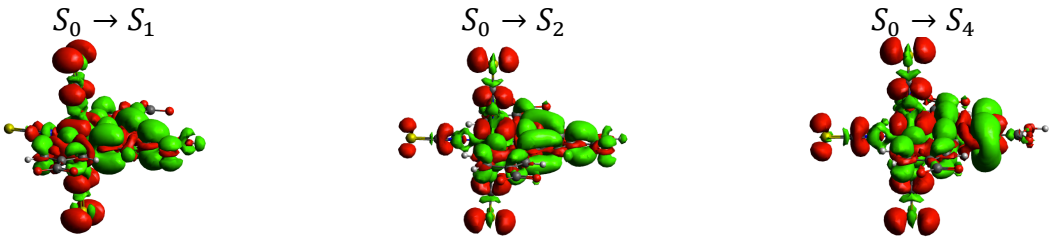

Figure S8: Electronic density variation computed for the Black Dye at CAM-B3LYP level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

Complementary results on YD2.

	N°	E / eV	λ / nm	f / a.u.
PBE0	1	1.83	676	0.57
	2	2.05	606	0.02
	3	2.31	537	0.03
	4	2.49	497	0.16
	5	2.83	438	1.65
	6	2.90	428	1.06
	7	3.05	407	0.28
CAM	1	1.95	636	0.44
	2	2.09	594	0.00
	3	2.72	455	0.24
	4	2.92	424	1.29
	5	3.02	410	1.95
EXP		1.92	646	
		2.12	586	
		2.80	443	

Table S5 : Computed and experimental[5] transitions of YD2. Experimental values are obtained in THF.

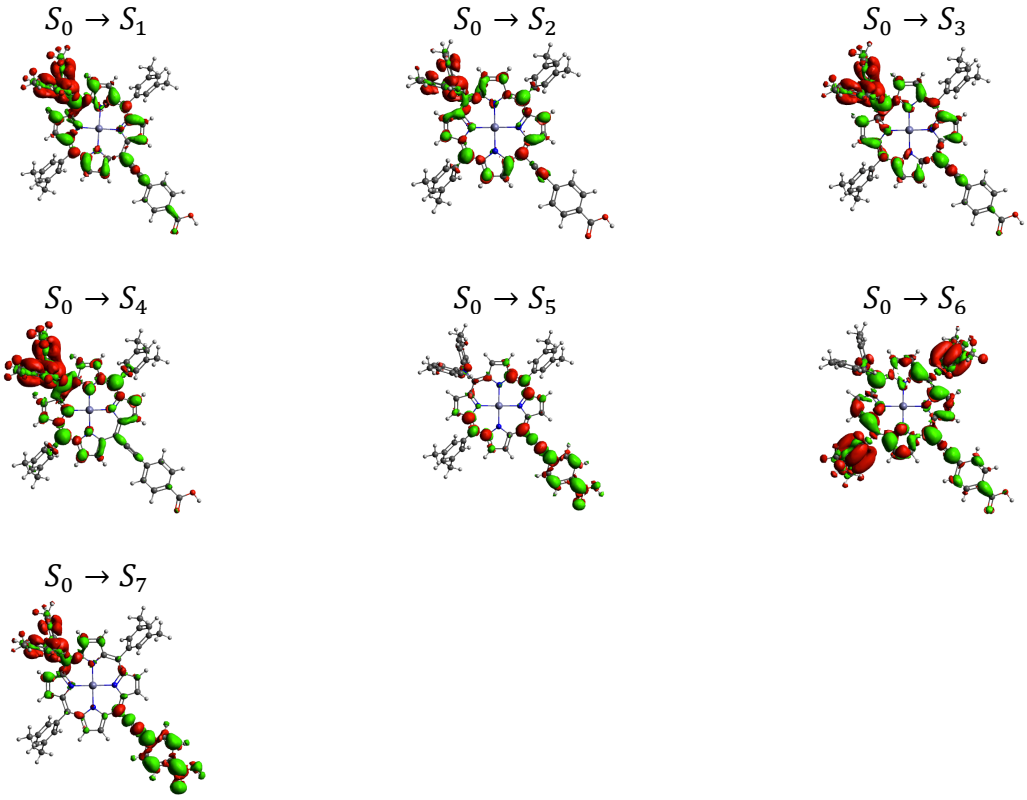

Figure S9: Electronic density variation computed for YD2 at PBE0 level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

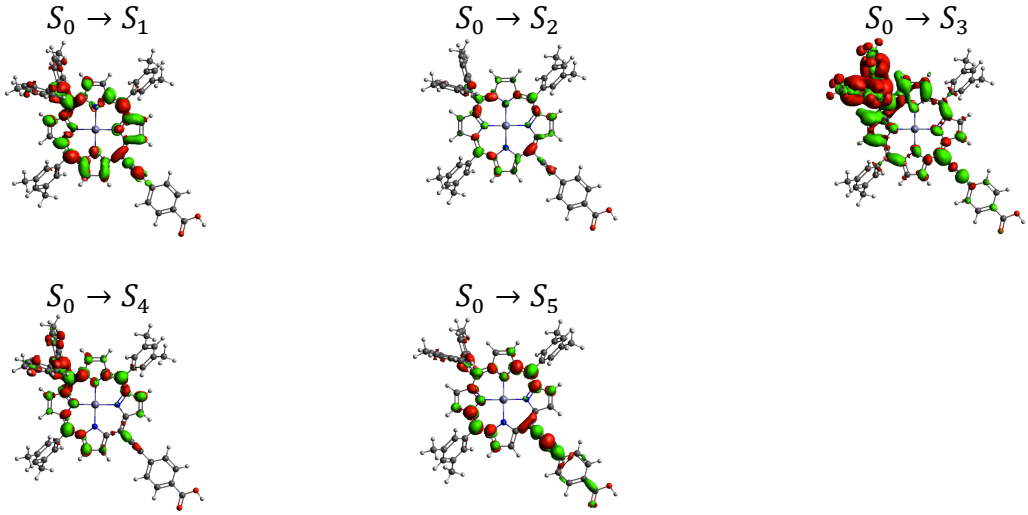

Figure S10: Electronic density variation computed for YD2 at CAM-B3LYP level (isolvalue 0.006 a.u.). The green and red volumes represent the regions of density increase and decrease upon transition, respectively.

1. M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer, and M. Grätzel, *Inorg. Chem.*, 1999, **38**, 6298–6305.

2. J. Preat, C. Michaux, D. Jacquemin, and E. A. Perpète, *J. Phys. Chem. C*, 2009, **113**, 16821–16833.

3. C. Chen, M. Wang, J. Li, N. Pootrakulchote, L. Alibabaei, J. Decoppet, J. Tsai, C. Gra, C. Wu, S. M. Zakeeruddin, and M. Gra, *ACSnano*, 2009, **3**, 3103.

4. M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. a Bignozzi, and M. Grätzel, *J. Am. Chem. Soc.*, 2001, **123**, 1613.

5. A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin, and M. Grätzel, *Science.*, 2011, **334**, 629.