Supporting Information

CAHM1: a Theory Based Proposal for a New DSSC D-A-π-A Dye

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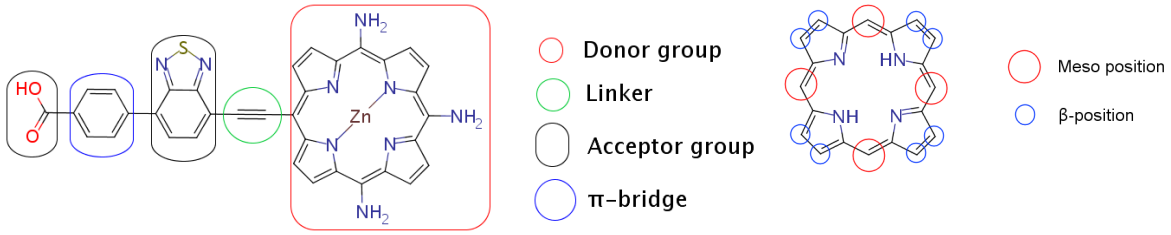
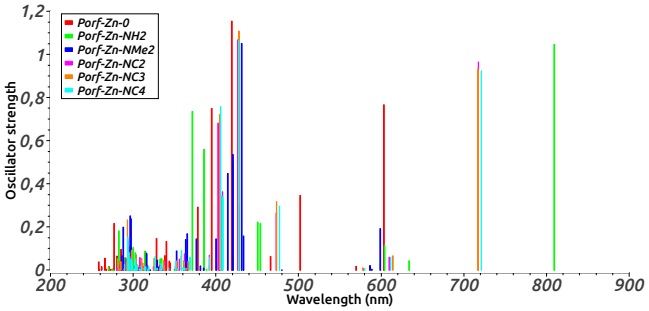


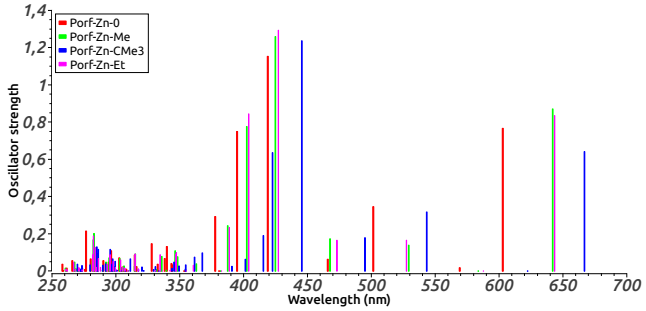
(a) Example of a D-A-π-A dye studied. Porphyrin ring as donor group, benzene ring as π bridge and BTD and carboxylic acid as acceptor group.

(b) Free metal porphyrin.

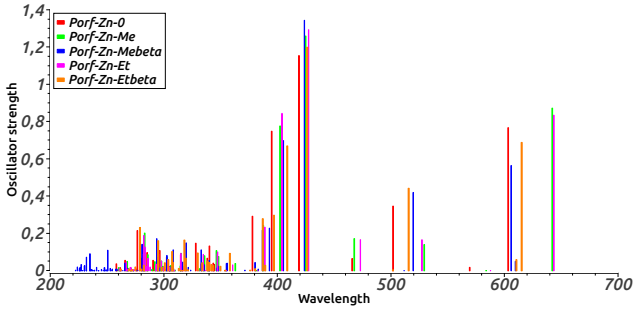
Figure S1: Nomenclature used in the description of studied systems.



(a) Predicted absorption spectra for amine substituent in meso position

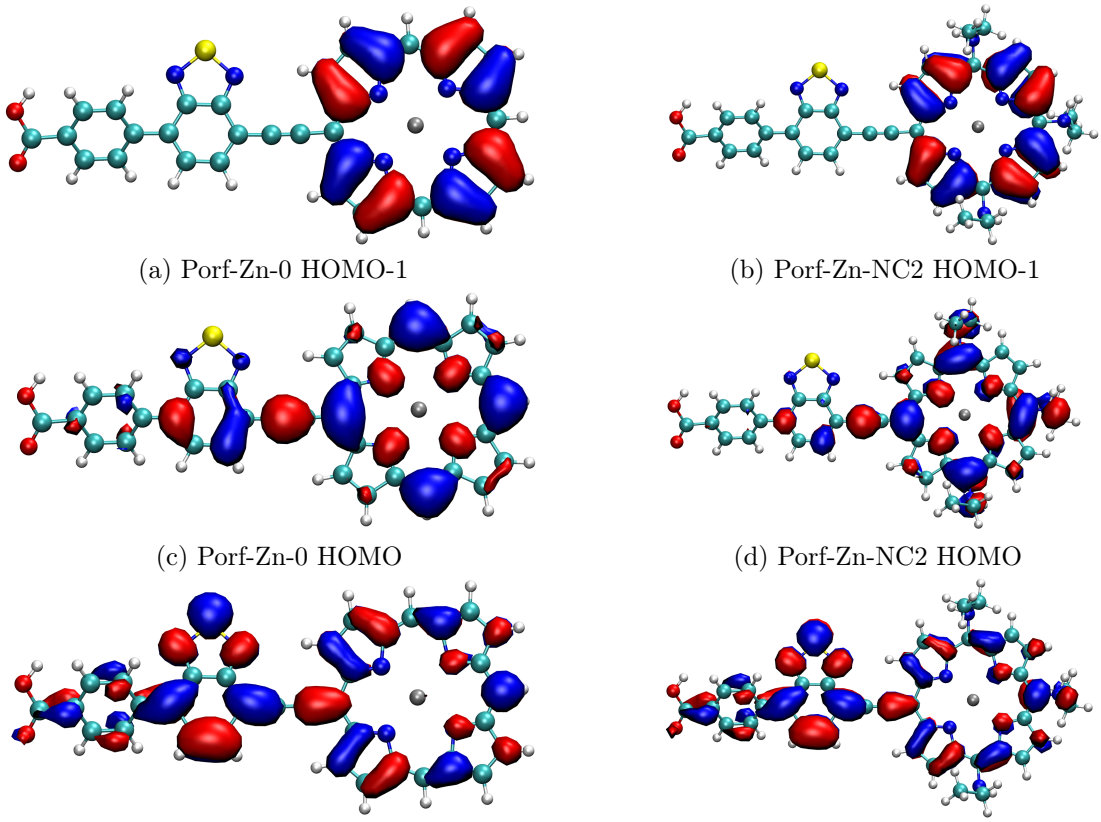


(b) Predicted absorption spectra for alkyl substituent in meso position



(c) Comparison between meso-alkyl substituion and β-alkyl substituion

Figure S2: Absorption spectra simulated for some compounds.



(a) Porf-Zn-0 HOMO-1

(b) Porf-Zn-NC2 HOMO-1

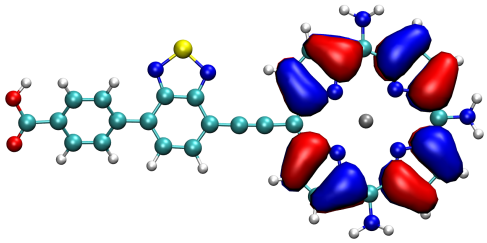
(c) Porf-Zn-0 HOMO

(d) Porf-Zn-NC2 HOMO

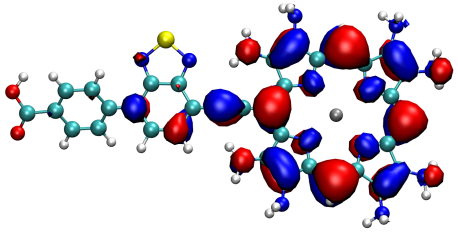
(e) Porf-Zn-0 LUMO

(f) Porf-Zn-NC2 LUMO

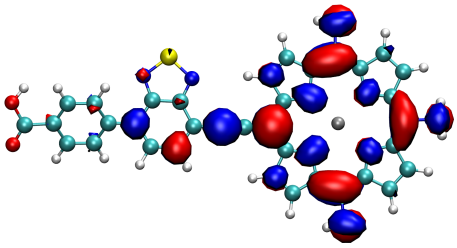
Figure S3: Comparison of Kohn-Sham orbitals for some compounds.



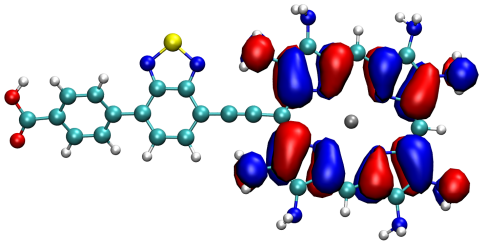
(a) Porf-Zn-NH2 HOMO-1



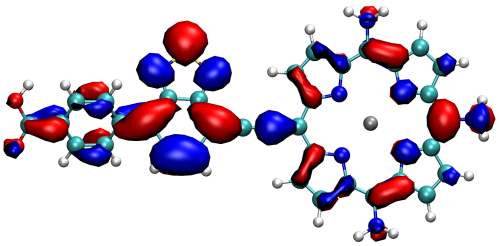
(b) Porf-Zn-NH2beta HOMO-1



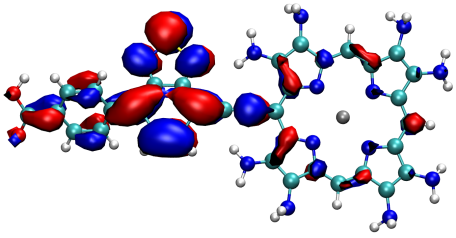
(c) Porf-Zn-NH2 HOMO



(d) Porf-Zn-NH2beta HOMO

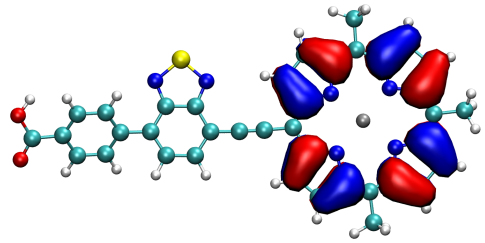


(e) Porf-Zn-NH2 LUMO

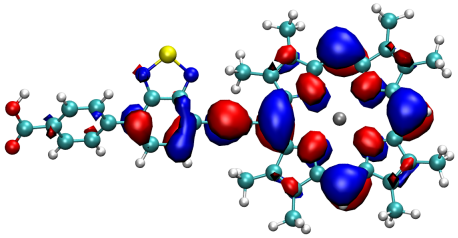


(f) Porf-Zn-NH2beta LUMO

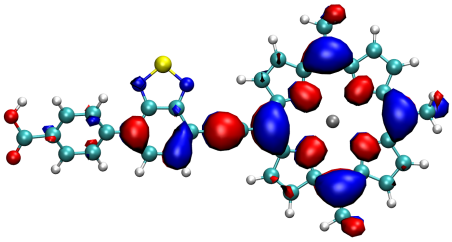
Figure S4: Comparison of Kohn-Sham orbitals for some compounds.



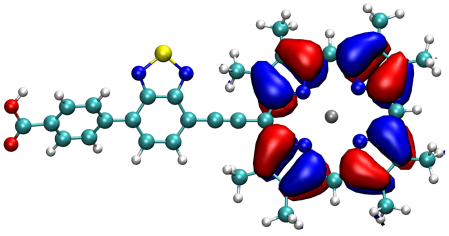
(a) Porf-Zn-Me HOMO-1



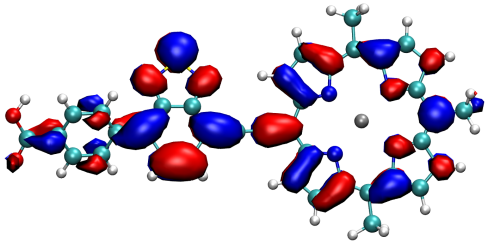
(b) Porf-Zn-Mebeta HOMO-1



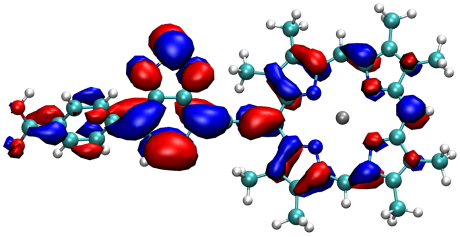
(c) Porf-Zn-Me HOMO



(d) Porf-Zn-Mebeta HOMO

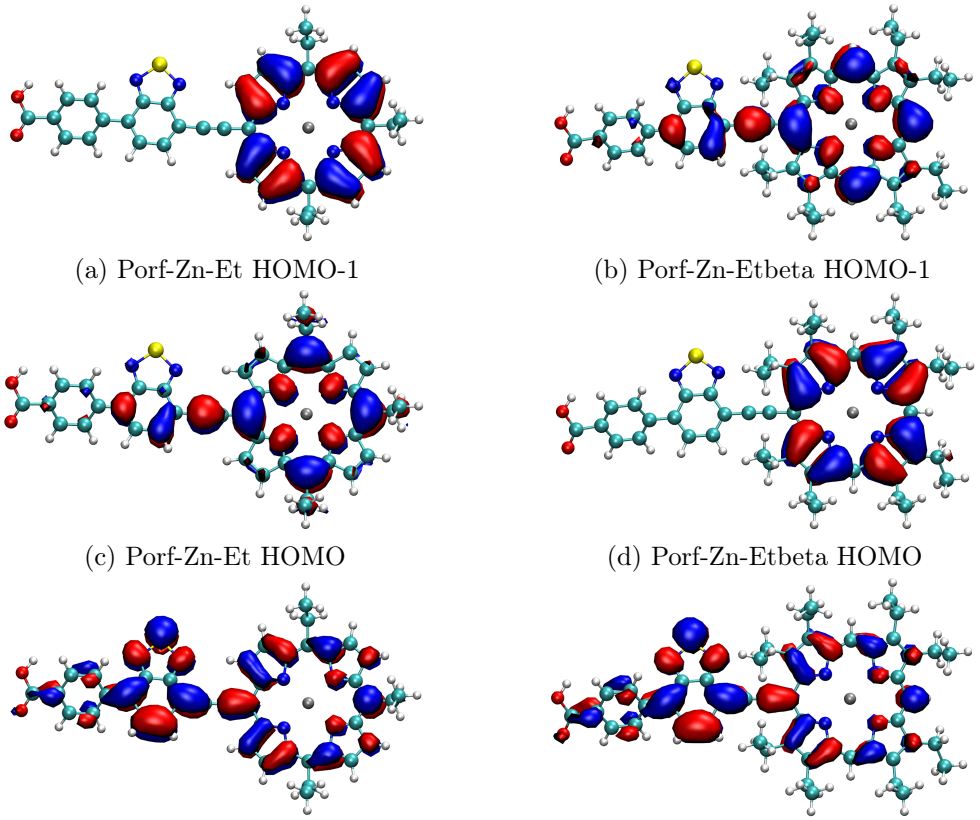


(e) Porf-Zn-Me LUMO



(f) Porf-Zn-Mebeta LUMO

Figure S5: Comparison of Kohn-Sham orbitals for some compounds.



(a) Porf-Zn-Et HOMO-1

(b) Porf-Zn-Etbeta HOMO-1

(c) Porf-Zn-Et HOMO

(d) Porf-Zn-Etbeta HOMO

(e) Porf-Zn-Et LUMO

(f) Porf-Zn-Etbeta LUMO

Figure S6: Comparison of Kohn-Sham orbitals for some compounds.

Table S1: Mainly electronic transitions for meso-substituted amine porphyrins

	Wavelength (nm)	Associated energy (eV)	Oscilator strength	Most important transitions	Oscilator strength shift	Wavelength shift (nm)
Porf-Zn-0	418,69	2,9612	1,1541	HOMO-2 → LUMO (41%), HOMO-1 → LUMO+1 (29%), HOMO → LUMO+2 (27%)		
	602,86	2,0566	0,7663	HOMO → LUMO (86%), HOMO-1 → LUMO+1 (11%)		
Porf-Zn-NH2	385,3	3,2176	0,735	HOMO-1 → LUMO+1 (91%)	-0,4191 (-36,31 %)	-33,39 (-7,97 %)
	420	2,9519	0,4976	HOMO-2 → LUMO (86%)		
	450,4	2,7524	0,222	HOMO → LUMO+3 (94%)		
	809	1,5327	1,0459	HOMO → LUMO (99%)	0,2796 (36,49 %)	206,14 (34,19 %)
Porf-Zn-NMe2	413,8	2,9958	0,4481	HOMO-3 → LUMO+1 (20%), HOMO-3 → LUMO+2 (35%), HOMO-2 → LUMO+1 (15%)		
	420,2	2,9503	0,5354	HOMO-3 → LUMO+1 (35%), HOMO-1 → LUMO+1 (21%), HOMO → LUMO+2 (11%)		
	427,3	2,9015	0,2961	HOMO-3 → LUMO+1 (20%), HOMO-2 → LUMO+1 (22%), HOMO-2 → LUMO+2 (25%), HOMO-1 → LUMO+1 (12%)		
	430,8	2,8781	1,0512	HOMO-1 → LUMO+2 (36%), HOMO-3 → LUMO+2 (21%)	-0,1029 (-8,92 %)	12,11 (2,89 %)
	598	2,0722	0,1908	HOMO → LUMO+1 (74%), HOMO-1 → LUMO+2 (22%)	-0,5755 (-75,10 %)	-4,86 (-0,81 %)
Porf-Zn-NC2	402,3	3,0815	0,6806	HOMO-1 → LUMO+1 (53%), HOMO-1 → LUMO+2 (32%)		
	426,2	2,9089	1,0672	HOMO-2 → LUMO (62%), HOMO-1 → LUMO+1 (14%), HOMO-1 → LUMO+2 (17%)	-0,0869 (-7,53%)	7,51 (1,79%)
	717,4	1,728	0,9639	HOMO → LUMO (96%)	0,1976 (25,79%)	114,54 (19%)
Porf-Zn-NC3	404,8	3,063	0,7223	HOMO-1 → LUMO+1 (40%), HOMO-1 → LUMO+2 (46%)		
	427,6	2,8994	1,1093	HOMO-2 → LUMO (59%), HOMO-1 → LUMO+1 (20%), HOMO-1 → LUMO+2 (14%)	-0,0448 (-3,88%)	8,91 (2,13%)
	716,9	1,7294	0,9327	HOMO → LUMO (95%)	0,1664 (21,71%)	114,04 (18,92 %)
Porf-Zn-NC4	405,5	3,0573	0,7571	HOMO-1 → LUMO+1 (59%), HOMO-1 → LUMO+2 (25%)		
	427,2	2,9024	1,0636	HOMO-2 → LUMO (61%), HOMO-1 → LUMO+1 (11%), HOMO-1 → LUMO+2 (21%)	-0,0905 (-7,84%)	8,51 (2,03%)
	721,1	1,7194	0,9239	HOMO → LUMO (96%), HOMO-1 → LUMO+2 (2%)	0,1576 (20,57%)	118,24 (19,61%)

Table S2: Mainly electronic transitions for meso-substituted alkyl porphyrins

	Wavelength (nm)	Associated energy (eV)	Oscilator strength	Most important transitions	Oscilator strength shift	Wavelength shift (nm)
Porf-Zn-0	418,69	2,9612	1,1541	HOMO-2 → LUMO (41%), HOMO-1 → LUMO+1 (29%), HOMO → LUMO+2 (27%)		
	602,86	2,0566	0,7663	HOMO → LUMO (86%), HOMO-1 → LUMO+1 (11%)		
Porf-Zn-Me	402,2	3,0826	0,7758	HOMO-1 → LUMO+2 (57%), HOMO → LUMO+1 (22%), HOMO-1 → LUMO+1 (10%)		
	424,7	2,9192	1,2598	HOMO-2 → LUMO (40%), HOMO-1 → LUMO+1 (36%), HOMO → LUMO+2 (14%)	0,1057 (9,16 %)	0,1057 (1,44%)
	641,7	1,9319	0,8711	HOMO → LUMO (91%)	0,1048 (13,68%)	38,84 (6,44%)
Porf-Zn-CMe3	422,4	2,9349	0,6356	HOMO-1 → LUMO+2 (54%), HOMO → LUMO+1 (23%), HOMO-3 → LUMO (14%)		
	445,2	2,7847	1,2374	HOMO-1 → LUMO+1 (42%), HOMO → LUMO+2 (30%), HOMO-2 → LUMO (25%),	0,0833 (7,22%)	26,51 (6,33%)
	543	2,2832	0,3173	HOMO → LUMO+2 (61%), HOMO-1 → LUMO+1 (27%), HOMO → LUMO (11%),		
	666,6	1,8598	0,6419	HOMO → LUMO (84%), HOMO-1 → LUMO+1 (12%),	-0,1244 (-16,23 %)	63,74 (10,57 %)
Porf-Zn-Et	404	3,0689	0,8441	HOMO-1 → LUMO+2 (65%), HOMO → LUMO+1 (28%)		
	427,2	2,9022	1,2931	HOMO-2 → LUMO (41%), HOMO-1 → LUMO+1 (38%), HOMO → LUMO+2 (18%)	0,139 (12,04%)	8,51 (2,03%)
	643,4	1,927	0,8342	HOMO → LUMO (89%)	0,0679 (8,86%)	40,54 (6,72%)

Table S3: Mainly electronic transitions for β-substituted porphyrins

	Wavelength (nm)	Associated energy (eV)	Oscilator strength	Most important transitions	Oscilator strength shift	Wavelength shift (nm)
Porf-Zn-0	418,69	2,9612	1,1541	HOMO-2 → LUMO (41%), HOMO-1 → LUMO+1 (29%), HOMO → LUMO+2 (27%)		
	602,86	2,0566	0,7663	HOMO → LUMO (86%), HOMO-1 → LUMO+1 (11%)		
Porf-Zn-NH2beta	429	2,8901	0,4699	HOMO-1 → LUMO+2 (24%), HOMO-1 → LUMO+1 (21%), HOMO → LUMO+3 (15%), HOMO → LUMO+2 (10%),		
	435,2	2,8492	0,9651	HOMO-1 → LUMO+2 (31%), HOMO-1 → LUMO+1 (24%), HOMO-5 → LUMO+1 (11%), HOMO → LUMO+1 (8%), HOMO → LUMO+2 (8%)	-0,189 (-16,38 %)	16,51 (3,94%)
	568,3	2,1817	0,338	HOMO → LUMO+1 (61%), HOMO-1 → LUMO+2 (21%), HOMO-1 → LUMO (11%), HOMO → LUMO+2 (4%)		
	661,6	1,8739	0,5134	HOMO-1 → LUMO (87%), HOMO → LUMO+1 (8%)	-0,2529 (-33%)	58,74 (9,74%)
Porf-Zn-Mebeta	405,09	3,0606	0,697	HOMO-1 → LUMO+2 (45%), HOMO → LUMO+1 (30%), HOMO-3 → LUMO (14%)		
	423,54	2,9273	1,3428	HOMO-1 → LUMO+1 (37%), HOMO-2 → LUMO (35%), HOMO → LUMO+2 (23%)	0,1887 (16,35%)	4,85 (1,16 %)
	519,32	2,3874	0,4191	HOMO-1 → LUMO+1 (40%), HOMO → LUMO+2 (37%), HOMO-1 → LUMO (14%),		
	605,59	2,0473	0,5643	HOMO-1 → LUMO (82%), HOMO → LUMO+2 (13%)	-0,202 (-26,36%)	2,73 (0,45%)
Porf-Zn-Etbeta	408,54	3,0348	0,6694	HOMO-1 → LUMO+2 (39%), HOMO → LUMO+1 (28%), HOMO-3 → LUMO (15%)		
	426,07	2,9099	1,1983	HOMO-2 → LUMO (34%), HOMO-1 → LUMO+1 (33%), HOMO → LUMO+2 (23%)	0,0442 (3,83%)	7,38 (1,76%)
	515,33	2,4059	0,4412	HOMO-1 → LUMO+1 (48%), HOMO → LUMO+2 (38%), HOMO-1 → LUMO (11%)		
	614,93	2,0162	0,6881	HOMO-1 → LUMO (83%), HOMO → LUMO+2 (11%)	-0,0782 (-10,20%)	12,07 (2%)

Table S4: Mainly electronic transitions for differents CAHM1 conformations

	Wavelength (nm)	Oscilator strength	Most important transitions
CAHM1-32	409,15	0,2924	HOMO-1 → LUMO+2 (54%), HOMO → LUMO+4 (34%)
	429,75	0,7966	HOMO-2 → LUMO (63%), HOMO-1 → LUMO+2 (15%), HOMO-1 → LUMO+1 (10%)
	435,89	0,4407	HOMO-1 → LUMO+1 (75%), HOMO → LUMO+2 (10%), HOMO-2 → LUMO (7%)
	468,48	0,1281	HOMO → LUMO+3 (95%)
	522,21	0,2958	HOMO-1 → LUMO (90%), HOMO → LUMO+2 (8%)
	660,47	0,1538	HOMO → LUMO+1 (87%), HOMO-1 → LUMO+2 (5%)
	895,06	0,4793	HOMO → LUMO (99%)
CAHM1-155	407,24	0,3269	HOMO-1 → LUMO+2 (59%), HOMO → LUMO+4 (27%)
	424,37	0,3102	HOMO-1 → LUMO+1 (76%), HOMO-2 → LUMO (7%), HOMO → LUMO+4 (7%)
	435,31	0,5221	HOMO-2 → LUMO (72%), HOMO-1 → LUMO+2 (12%), HOMO-1 → LUMO+1 (10%),
	458,66	0,3865	HOMO → LUMO+3 (93%)
	514,07	0,2209	HOMO-1 → LUMO (84%), HOMO → LUMO+2 (14%)
	826,84	1,0236	HOMO → LUMO (98%)
CAHM1-(-)32	406,33	0,3528	HOMO-1 → LUMO+2 (60%), HOMO → LUMO+4 (21%)
	423,59	0,2805	HOMO-1 → LUMO+1 (78%), HOMO → LUMO+2 (6%)
	432,42	0,5277	HOMO-2 → LUMO (74%), HOMO-1 → LUMO+2 (14%), HOMO-1 → LUMO+1 (6%)
	457,98	0,3702	HOMO → LUMO+3 (93%)
	511,74	0,2509	HOMO-1 → LUMO (85%), HOMO → LUMO+2 (13%)
	825,96	1,0062	HOMO → LUMO (98%)

Table S5: HOMO and LUMO energies (in eV) for all compounds studied. LUMO values above the TiO_2 conduction band (-2.77 eV) are highlighted

Molecules	**HOMO (eV)**	**LUMO (eV)**
Porf-Zn-0	-5.59	-2.92
Porf-Zn-NH2	-4.62	-2.66
Porf-Zn-NMe2	-5.33	-2.70
Porf-Zn-NC2	-4.99	-2.77
Porf-Zn-NC3	-5.02	-2.80
Porf-Zn-NC4	-4.99	-2.78
Porf-Zn-Me	-5.38	-2.88
Porf-Zn-CMe3	-5.35	-2.91
Porf-Zn-Et	-5.39	-2.89
Porf-Zn-NH2beta	-4.91	-2.88
Porf-Zn-Mebeta	-5.44	-2.85
Porf-Zn-Etbeta	-5.49	-2.88
CAHM1-(-)32	-4.57	-2.62
CAHM1-32	-4.52	-2.62
CAHM1-155	-4.58	-2.63