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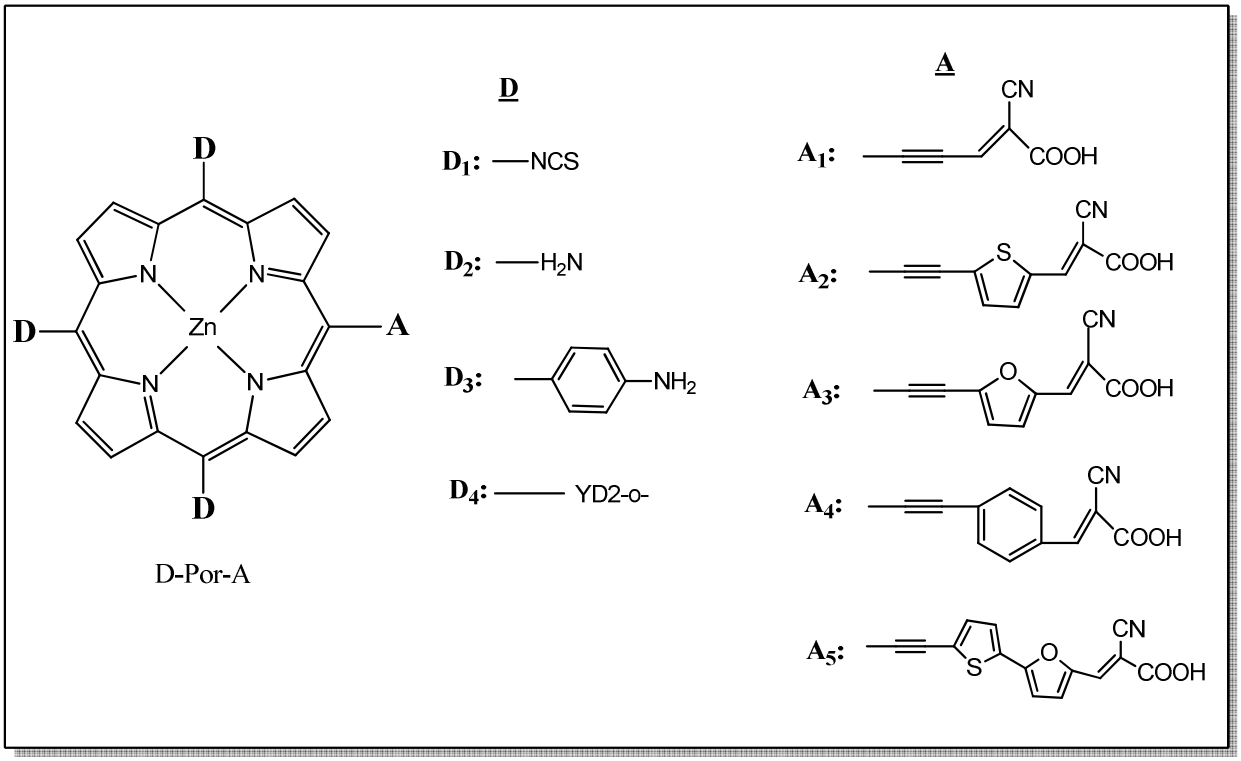
Supporting Information

Molecular Design of Porphyrins for Dye-Sensitized Solar Cells: A DFT/TDDFT Study

N.Santhanamoorthi, Chien-Min Lo and Jyh-Chiang Jiang,*

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, R.O.C.



Scheme S1. Structure of porphyrin with different donors(D) and acceptors(A).

Table S1. Molecular orbital energy levels (eV) for all the investigated porphyrin dyes calculated at CAM-B3LYP level of theory.

System	HOMO	LUMO	HOMO-LUMO gap
Dye 1	-5.626	-1.649	3.977
Dye 2	-5.227	-1.637	3.590
Dye 3	-5.163	-1.504	3.659
Dye 4	-5.052	-1.457	3.595
Dye 5	-5.590	-1.637	3.953
Yd2-o-C8	-5.639	-1.523	4.116

Table S2. The absorption energy of reference dye (YD2-o-C8) calculated at different DFT methods.

Methods	**Basis set Combination**	**Absorption Energy(nm)**	
		Q band	**B band**
B3LYP	6-31G(d)	613.4	423.2
	6-31G(d)†	**642.6**	**437.2**
CAM-B3LYP	6-31G(d)	586.4	384.8
	6-311G(d)	606.3	389.8
	6-311+G(d)	599.1	393.3
	LANL2DZ for Zn, and 6-311G(d) for other atoms	597.6	388.9
	LANL2DZ for Zn, and 6-311+G(d) for other atoms	588.8	381.3
BHandHLYP	LANL2DZ for Zn, and 6-31+G(d) for other atoms †	568.6	399.9
	LANL2DZ for Zn, and 6-31G(d) for other atoms †	559.2	392.5
	6-31+G(d)	570.1	384.2
	LANL2DZ for Zn, and 6-31G(d) for other atoms	570.3	380.2
	LANL2DZ for Zn, and 6-31+G(d) for other atoms	580.9	387.4
	LANL2DZ for Zn, and 6-311+G(d) for other atoms	568.7	377.1
M062X	6-31G(d) †	566.3	391.3
	6-31G(d)	555.5	378.2
M06HF	6-31G(d) †	580.3	370.1
	6-31G(d)	573.1	372.3
Exp[a]		645	448

†Performed in THF medium, [a] Taken from Ref.[1]

Table S3. The calculated absorption energies (λ), oscillator strengths (f) and electronic transition configurations for the selected porphyrin sensitizers and reference dyes (YD2-o-C8 and N3) calculated at TDB3LYP/6-31G* in THF.

System	λ(nm)	f	MO Character
Dye 1	680.8	1.10	H-0->L+0(92%)
	565.0	0.13	H-0->L+1(59%) H-2->L+0(28%)
	550.0	0.16	H-2->L+0(59%) H-0->L+1(25%) H-1->L+2(8%) H-2->L+1(6%)
	514.0	0.11	H-1->L+0(55%) H-0->L+2(26%) H-1->L+1(10%)H-2->L+2(8%)
	475.2	0.69	H-2->L+1(47%) H-1->L+2(27%) H-2->L+0(11%) H-3->L+0(11%)
	453.3	0.51	H-3->L+0(47%) H-2->L+1(34%) H-1->L+2(12%)
	423.3	0.60	H-1->L+1(43%) H-2->L+2(25%) H-0->L+2(16%) H-3->L+2(8%)
	396.2	0.14	H-3->L+0(33%) H-1->L+2(24%) H-3->L+1(13%) H-7->L+0(6%) H-0->L+1(6%) H-2->L+1(5%)
	387.3	0.22	H-0->L+3(53%) H-3->L+1(40%)
	367.4	0.15	H-3->L+1(34%) H-0->L+3(31%) H-10->L+0(10%) H-1->L+2(10%)
	365.7	0.13	H-3->L+2(27%) H-9->L+0(24%) H-11->L+0(14%) H-7->L+2(9%) H-9->L+1(7%) H-6->L+2(5%)
Dye 2	783.8	1.36	H-0->L+0(100%)
	584.2	0.10	H-0->L+2(80%) H-1->L+0(13%) H-1->L+1(6%)
	479.5	0.15	H-1->L+0(86%) H-0->L+2(11%)
	418.1	0.82	H-2->L+0(78%) H-0->L+3(11%)H-1->L+2(9%)
	385.6	0.24	H-1->L+1(63%) H-3->L+0(31%)
	381.8	0.34	H-3->L+0(53%) H-1->L+1(27%) H-5->L+0(6%)
	368.7	0.48	H-1->L+2(65%) H-2->L+0(+11%)H-0->L+1(5%)
Dye 3	772.3	1.31	H-0->L+0(100%)
	400.1	0.92	H-2->L+0(63%) H-0->L+3(23%) H-1->L+2(11%)
	391.4	0.10	H-0->L+3(62%) H-1->L+2(24%) H-2->L+0(8%)
	383.1	0.47	H-1->L+1(87%) H-0->L+2(6%) H-3->L+0(5%)
	374.3	0.14	H-3->L+0(85%)
	363.3	0.28	H-1->L+2(37%) H-4->L+0(20%) H-2->L+0(+16%) H-5->L+0(7%)
Dye 4	839.3	1.10	H-0->L+0(100%)
	644.2	0.20	H-0->L+1(94%)
	594.2	0.13	H-0->L+2(86%) H-1->L+1(9%) H-1->L+0(5%)
	472.3	0.09	H-1->L+0(94%) H-0->L+2(5%)
	463	0.89	H-2->L+0(61%) H-0->L+3(34%)
	396.9	0.46	H-1->L+1(85%) H-0->L+2(8%) H-2->L+2(5%)
	391.9	0.10	H-2->L+1(78%) H-1->L+2(12%) H-2->L+1(5%)
	384.6	0.13	H-0->L+4(61%) H-1->L+2(29%)
	365.3	0.12	H-2->L+2(54%) H-3->L+0(38%)
	361.7	0.20	H-1->L+2(30%) H-5->L+0(23%) H-0->L+4(17%) H-5->L+1(10%) H-4->L+0(8%)
	353.9	0.17	H-4->L+0(79%)
Dye 5	684.3	1.21	H-0->L+0(96%)
	507.3	0.21	H-1->L+0(62%) H-0->L+2(22%) H-1->L+1(15%)
	493.3	0.20	H-2->L+0(82%) H-4->L+0(7%) H-2->L+1(6%)
	492.3	0.14	H-3->L+0(83%) H-4->L+0(8%) H-3->L+1(6%)
	485.3	0.37	H-4->L+0(78%) H-2->L+0(8%) H-3->L+0(6%)
	446.3	0.82	H-5->L+0(40%) H-1->L+2(40%) H-5->L+1(5%) H-0->L+1(5%)
	436.5	0.79	H-1->L+1(44%) H-2->L+2(23%) H-0->L+2(+11%)H-4->L+2(9%) H-5->L+2(6%)
	357.5	0.13	H-8->L+0(48%) H-5->L+1(18%) -8->L+1(9%) H-0->L+3(7%)
	353.1	0.27	H-5->L+2(54%) H-6->L+2(18%) H-7->L+0(12%)
Yd2-o-C8	642.6	0.51	H-0->L+0(90%) H-1->L+1(7%)
	492.3	0.14	H-2->L+1(49%) H-1->L+0(31%) H-0->L+1(20%)
	437.2	1.67	H-1->L+1(50%) H-0->L+2(29%) H-2->L+0(9%) H-0->L+0(8%)
	425.5	0.18	H-3->L+0(42%) H-4->L+0(31%) H-2->L+1(13%) H-1->L+0(8%)
	422.2	0.56	H-2->L+1(34%) H-1->L+0(23%) H-4->L+0(19%) H-0->L+1(10%) H-3->L+0(8%)
	406.2	0.27	H-0->L+2(63%) H-1->L+1(16%) H-7->L+0(6%) H-8->L+0(6%)
	365.7	0.11	H-1->L+2(69%) H-10->L+0(19%) H-7->L+1(+6%)

	363.6	0.14	H-10->L+0(74%) H-1->L+2(18%)
	336.8	0.16	H-7->L+1(51%) H-8->L+1(20%) H-11->L+1(9%)
N3	692.7	0.04	H-0->L+0(95%)
	684.1	0.01	H-0->L+1(90%) H-1->L+1(5%)
	582.5	0.09	H-2->L+1(74%) H-1->L+0(21%)
	565.5	0.01	H-2->L+0(44%) H-1->L+1(41%) H-0->L+3(7%) H-0->L+1(6%)
	495.8	0.05	H-0->L+2(93%)
	473.7	0.05	H-3->L+0(51%) H-0->L+3(39%)
	473.5	0.04	H-3->L+1(95%)
	447.8	0.05	H-1->L+2(80%) H-2->L+3(10%) H-0->L+4(7%)
	443.2	0.02	H-2->L+3(81%) H-1->L+2(13%)
	397.8	0.09	H-4->L+1(74%) H-5->L+0(20%)
	382.6	0.01	H-3->L+2(90%)

Reference:

(1). Yella, A.; Lee, H. W.; Tsao, H. N.; Yi, C. Y.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W. G.; Yeh, C. Y.; Zakeeruddin, S. M.; Gratzel, M. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science* **2011,** *334*, 629-634.