Supplementary material

Title:

A new family of A_2B_2 type porphyrin derivatives: Synthesis, Physicochemical Characterization and their Application in Dye-Sensitized Solar Cell.

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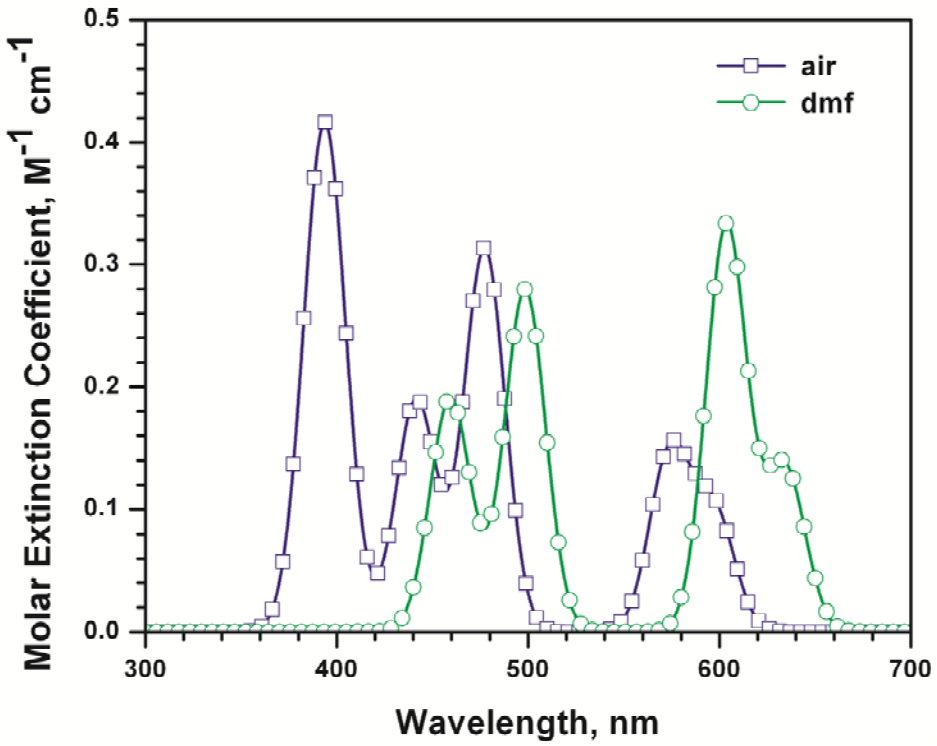

Figure S1: Simulated (fwhm = 25 nm) absorption spectra of the **P2** in the gas phase (blue) and DMF (green).

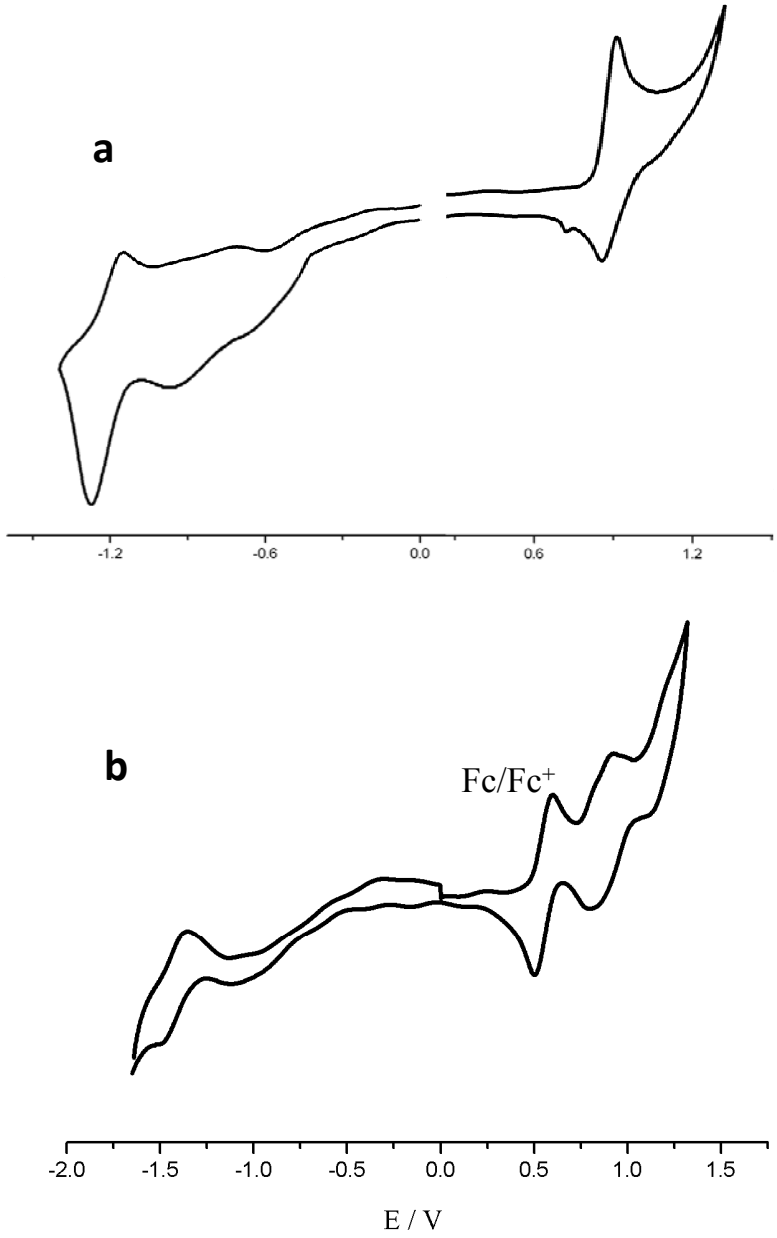

Figure S2. Cyclic voltammograms of **P1** (a) and **P2** (b) in THF. The voltages are *vs* the saturated calomel electrode (SCE).

Table S1. Vertical transitions with oscillator strength of **P2**, computed with B3LYP functional and LANL2DG/6-31G* basis sets.

Dye	Medium	λ_{max}, nm	Oscillator strength	Assignment	Dipole Moment, Debye	HOMO, eV	LUMO, eV	Band Gap, eV
P2	gas	597.3	0.097	HOMO→LUMO (84%) HOMO-2→LUMO+1 (16%)	0.000	-4.90	-2.46	2.44
		574.1	0.146	HOMO→LUMO+1 (75%) HOMO-2→LUMO (24%)				
		477.3	0.312	HOMO-3→LUMO+1 (60%) HOMO-2→LUMO (28%) HOMO→LUMO+1 (11%)				
		441.5	0.190	HOMO→LUMO+3 (87%)				
		395.3	0.300	HOMO-2→LUMO+3 (36%) HOMO-2→LUMO (24%) HOMO-3→LUMO+1 (17%) HOMO-1→LUMO+2 (16%) HOMO→LUMO+1 (5%)				
		389.7	0.128	HOMO-1→LUMO+2 (83%) HOMO-3→LUMO+1 (6%) HOMO-2→LUMO (6%)				
	dmf	634.2	0.134	HOMO→LUMO (91%) HOMO-3→LUMO+1 (8%)	0.000	-4.96	-2.65	2.31
		603.7	0.332	HOMO→LUMO+1 (87%) HOMO-3→LUMO (12%)				
		498.3	0.271	HOMO-2→LUMO+1 (55%) HOMO-3→LUMO (38%) HOMO→LUMO+1 (5%)				
		459.4	0.191	HOMO→LUMO+3 (89%) HOMO-3→LUMO+1 (5%)				

Table S2. Cyclic voltammetry data of **P1** and **P2** reported *vs* SCE[a]

Compound	$E_{1/2}^{Ox1}$ / V (ΔE_p / V)[b]	$E_{1/2}^{Red1}$ / V (ΔE_p / V)[b]
P1	0.86 (0.05)	-1.21 (0.138)
P2	0.85 (0.128)	-1.44(0.151)

[a] Experimental conditions: all measurements were performed at room temperature in degassed THF containing tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte with scan rate 100 mV s^{-1}. All reported waves are reversible and referenced to ferrocene/ferrocenium (Fc/Fc^+) couple. $E_{1/2}^{Ox}$ of the (Fc/Fc^+) couple is +0.55 V and ΔE_p is 0.09 V.

[b] The anodic-cathodic peak separations (ΔE_p, in V) are given in parentheses

Table S3. Interplanar angles observed in tetrakis(4-iodophenyl)porphyrin[c]

No.	Label	Normal	Distance	Nearest Miller	Angle
1	Porphyrin	0.560 0.343 0.754	7.2348	(679)	0
2	Phenyl 1	-0.450 0.242 0.859	8.3547	(-15 18 51)	61.42
3	Phenyl 2	0.354 0.790 -0.500	-11.77	(12 -56 52)	72.27

Table S4. Interplanar angles observed in zinc complex of tetrakis(4-iodophenyl)porphyrin[c]

No.	Label	Normal	Distance	Nearest Miller	Angle
1	Porphyrin	0.847 -0.518 0.119	4.3264	(14 -8 0)	0
2	Phenyl 1	-0.062 0.394 0.917	-0.358648	(2 -10 -52)	81.51
3	Phenyl 2	0.161 0.928 -0.335	0.742777	(2 11 -9)	67.38

Table S5. Interplanar angles observed in aqua ZnTCPP[d]

No.	Label	Normal	Distance	Nearest Miller	Angle, º
1	Porphyrin	0.857 -0.000 -0.516	5.97308	(14 0 -4)	0
2	Phenyl	0.732 0.632 0.254	7.50758	(52 68 4)	60.31

All the phenyl groups are inclined from the porphyrin ring at 60.31º.

Table S6. Interplanar angles observed in tetrakis(N,N-dimethyl-amino-phenyl)porphinato Mn(II) [e]

No.	Label	Normal	Distance	Nearest Miller	Angle
1	Porphyrin	0.552 0.199 0.810	24.3893	(9 9 39)	0
2	Phenyl 1	-0.090 -0.606 0.790	16.3341	(-2 -30 48)	61.98
3	Phenyl 2	0.938 -0.344 -0.028	-9.11463	(-24 24 12)	64.73

Table S7. Interplanar angles observed for the geometry optimized free base dye (**P1**)[c]

No.	Label	Normal	Distance	Nearest Miller	Angle
1	Porphyrin	0.013 0.013 1.000	-5.74857e-005	(-1 0 -40)	0
2	Phenyl (donor)	0.044 0.898 -0.438	-0.00957236	(-1 -16 8)	64.79
3	Phenyl (acceptor)	0.916 -0.063 -0.396	-0.0214425	(-14 1 6)	64.81
4	Phenyl (donor)	0.044 0.898 -0.438	0.00972303	(1 16 -8)	67.38
5	Phenyl (acceptor)	.916 -0.063 -0.396	0.0214441	(14 -1 -6)	67.40

Table S8. Interplanar angles observed for the geometry optimized zinc complex dye (**P2**)[c]

No.	Label	Normal	Distance	Nearest Miller	Angle
1	Porphyrin	-0.002 -0.011 1.000	-1.51762e-005	(00-1)	0
2	Phenyl (donor)	0.199 0.889 0.413	0.0344808	(294)	66.21
3	Phenyl (acceptor)	0.909 -0.221 0.352	-0.0257206	(-82-3)	66.25
4	Phenyl (donor)	0.199 0.888 0.414	-0.0344881	(-2-9-4)	69.30
5	Phenyl (acceptor)	0.910 -0.221 0.352	0.0257227	(8-23)	69.32

c. Starting geometries for the compounds were taken from tetrakis(4-iodophenyl)porphyrin and its zinc(II) complex reported by M. Sankar and I. Goldberg, *Acta Cryst. C*, 2007, **63**, m300-m303.

d. Values were taken from the Crystal structure of aquazinc tetrakis(4-carboxyphenyl)porphyrin reported by Y. Diskin-Posner and I. Goldberg, *Chem. Commun.*, 1999, 1961-1962.

e. Values were taken from the Crystal structure of tetrakis(*N,N*-dimethyl-amino-phenyl)porphinato Mn(II) reported by D. Zhang, H. Wang, L. Tian, H-Z Kou, J. Jiang and Z-H Ni, *Cryst.Growth Des.* 2009, **9**, 3989.