Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information for:

Theoretical studies on the spectroscopic properties of porphyrin derivatives for dye-sensitized solar cells application

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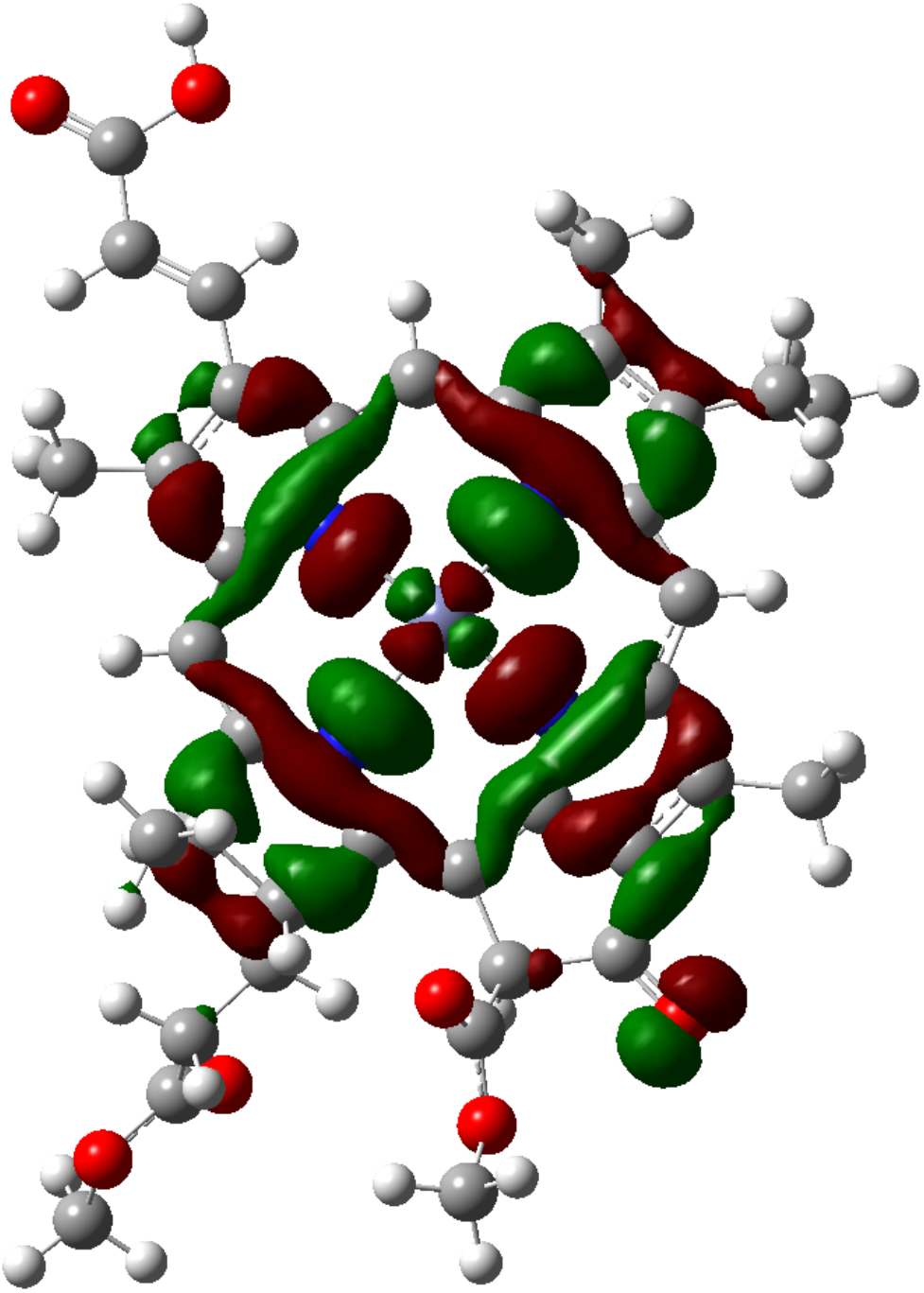

Figure S1 The HOMO-4 of the Zn-PHE

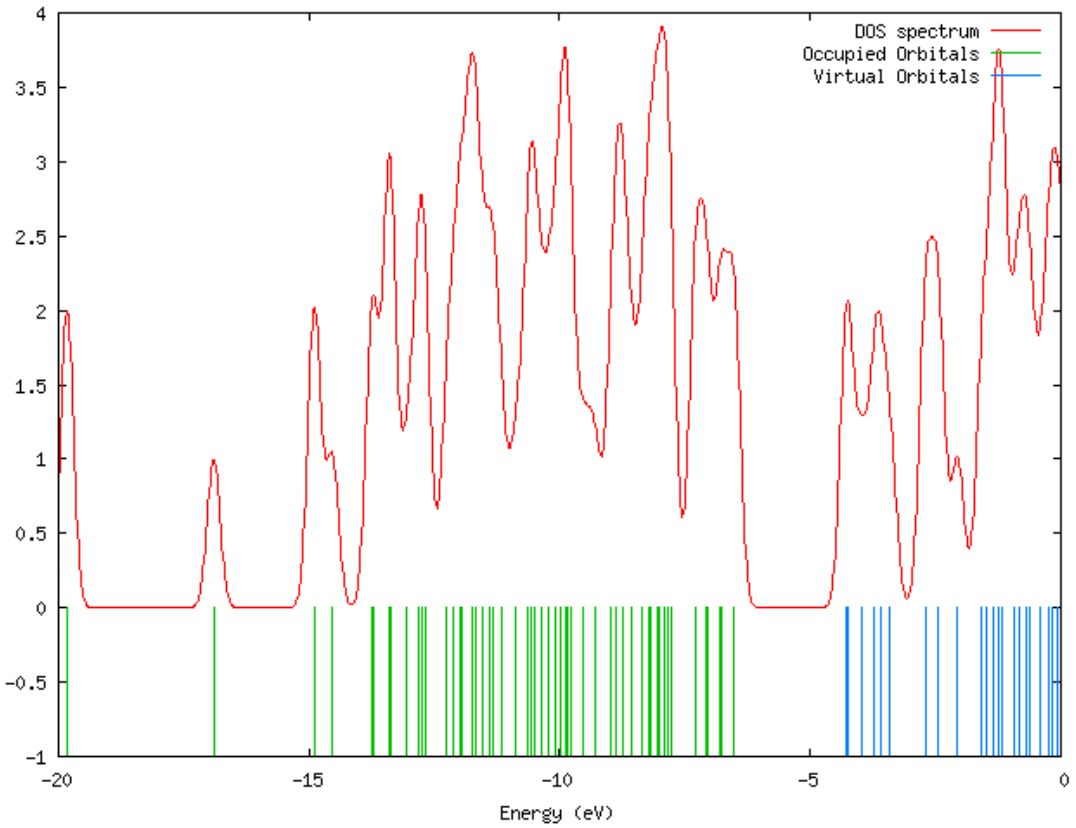

Figure S2. The density of states (DOS) plot for the bare $(TiO_2)_5$ model.

Table S1. Partial Molecular Orbital Compositions (%) for dye PHE, Mg-PHE and Zn-PHE in ethanol solution. (MC = metal center, TM = tetrapyrrole macrocycle. The green molecular orbital are the orbitals directly involve the transition.)

Analogues	Orbital	Energy (eV)	Main Component (%)				Assignment
			MC	TM	π-bridge	COOH	
PHE	LUMO+9	1.626		96	1	3	π*(TM)
	LUMO+8	1.433		64	8	28	π*(TM) + p (COOH)
	LUMO+7	0.561		100			π*(TM)
	LUMO+6	0.158		95	1	4	π*(TM)
	LUMO+5	0.000		100			π*(TM)
	LUMO+4	-0.304		100			π*(TM)
	LUMO+3	-1.157		79	11	10	π*(TM)
	LUMO+2	-1.579		68	19	13	π*(TM) +π*(π-bridge)
	LUMO+1	-2.247		85	9	6	π*(TM)
	LUMO	-2.996		88	8	4	π*(TM)
	HOMO	-5.301		98	1	1	π(TM)
	HOMO-1	-5.488		98	2		π(TM)
	HOMO-2	-6.201		100			π(TM)
	HOMO-3	-6.682		62	31	7	π(TM) +π(π-bridge)
	HOMO-4	-7.093		100			π*(TM)
	HOMO-5	-7.285		100			π*(TM)
	HOMO-6	-7.341		100			π*(TM)
	HOMO-7	-7.425		100			π*(TM)
	HOMO-8	-7.474		100			π*(TM)
	HOMO-9	-7.583		2	6	92	p (COOH)
Mg-PHE	LUMO+9	1.067	76	23		1	p (MC) +π*(TM)
	LUMO+8	0.988	98	2			p (MC)
	LUMO+7	0.621	7	93			π*(TM)
	LUMO+6	0.312		94	2	4	π*(TM)
	LUMO+5	0.005		100			π*(TM)
	LUMO+4	-0.231		99			π*(TM)
	LUMO+3	-1.037		85	8	7	π*(TM)
	LUMO+2	-1.394		65	20	15	π*(TM) +π*(π-bridge)
	LUMO+1	-2.087		82	11	17	π*(TM) + p (COOH)
	LUMO	-2.887		89	7	4	π*(TM)
	HOMO	-5.106		98	2		π(TM)
	HOMO-1	-5.387	2	97			π(TM)
	HOMO-2	-6.234		89	8	2	π(TM)
	HOMO-3	-6.337	1	78	16	4	π(TM) +π(π-bridge)
	HOMO-4	-6.804	1	98			π(TM)
	HOMO-5	-6.933		100			π*(TM)
	HOMO-6	-7.170		97	2		π*(TM)
	HOMO-7	-7.472		94	3	3	π*(TM)

	HOMO-8	-7.495		11	6	83	p (COOH)
	HOMO-9	-7.561	1	94	1	4	π*(TM)
Zn-PHE	LUMO+9	1.122	90	10			p (MC)
	LUMO+8	0.930	68	30		2	p (MC) +π*(TM)
	LUMO+7	0.581	10	90			π*(TM)
	LUMO+6	0.297	1	94	1	3	π*(TM)
	LUMO+5	0.004		100			π*(TM)
	LUMO+4	-0.239		99			π*(TM)
	LUMO+3	-1.036		85	8	7	π*(TM)
	LUMO+2	-1.412		64	20	15	π*(TM) +π*(π-bridge)
	LUMO+1	-2.094		82	11	7	π*(TM)
	LUMO	-2.874		89	7	4	π*(TM)
	HOMO	-5.129		98	1		π(TM)
	HOMO-1	-5.460	2	96			π(TM)
	HOMO-2	-6.262		93	6	1	π(TM)
	HOMO-3	-6.376	2	76	18	4	π(TM) +π(π-bridge)
	HOMO-4	-6.474	18	82			π(TM)
	HOMO-5	-6.853	2	96	2		π(TM)
	HOMO-6	-6.987		99			π*(TM)
	HOMO-7	-7.207		97	2		π*(TM)
	HOMO-8	-7.504		92	3	5	π*(TM)
	HOMO-9	-7.520		6	6	88	p (COOH)

Table S2. Partial molecular orbital compositions (%) of the single-crystal anatase $(TiO_2)_5$ (101) model.

Complex	Orbital	Energy(eV)	Main Component (%)			Assignment
			Ti	O	H	
$(TiO_2)_5$	LUMO+9	-2.444	83	16	1	3d (Ti)
	LUMO+8	-2.454	75	21	4	3d (Ti)
	LUMO+7	-2.690	83	16	1	3d (Ti)
	LUMO+6	-2.704	82	15	3	3d (Ti)
	LUMO+5	-3.403	87	12	1	3d (Ti)
	LUMO+4	-3.607	86	13	1	3d (Ti)
	LUMO+3	-3.720	89	11	0	3d (Ti)
	LUMO+2	-3.974	87	13	0	3d (Ti)
	LUMO+1	-4.254	84	11	5	3d (Ti)
	LUMO	-4.281	86	10	4	3d (Ti)
	HOMO–LUMO Energy Gap (2.239 eV)					
	HOMO	-6.520	3	97	0	2p (O)
	HOMO-1	-6.522	3	97	0	2p (O)
	HOMO-2	-6.767	2	98	0	2p (O)
	HOMO-3	-6.794	2	98	0	2p (O)
	HOMO-4	-7.061	6	93	1	2p (O)
	HOMO-5	-7.095	7	92	1	2p (O)
	HOMO-6	-7.296	8	91	1	2p (O)
	HOMO-7	-7.302	8	90	2	2p (O)
	HOMO-8	-7.768	8	92	0	2p (O)
	HOMO-9	-7.850	13	86	1	2p (O)