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Theoretical investigations on the unsymmetrical effect of β-link Zn-porphyrin sensitizers on the performance for dye-sensitized solar cells

Miao Xie[a], Fu-Quan Bai[b], Jinjian Wang[a], Yue-Qing Zheng[*a], and Zhenyang Lin[*b]

a *Research Center of Applied Solid State Chemistry, Chemistry Institute for Synthesis and Green Application, Ningbo University, 818 Fenghua Road, Ningbo, Zhejiang Province, 315211 People's Republic of China. E-mail: zhengcm@nbu.edu.cn*

b *Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR 999077, People's Republic of China. E-mail: chzlin@ust.hk*

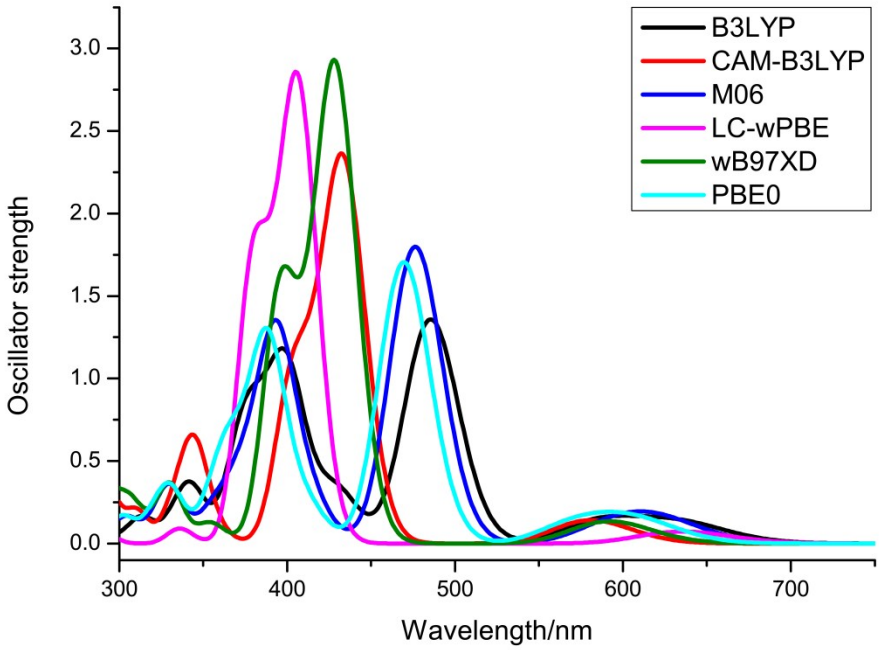

Fig. S1. Absorption spectra of the dye GD2 in DMF solution under different exchange-correlation functional with 6-31G (d) basis set.

Table S1 Partial molecular orbital compositions (%) of YD2-O-C8 dye in THF solution with different electric field strengths (the abbreviations: the Zn-Phy is Zn-porphyrin, the **4-MPH** is 4-methylphenyl group and the **BPA** is bis(4-methylphenyl)amine group.).

Complexes	Orbital	Energy(eV)	Main Component (%)					Assignment
			Zn-Phy	4-MPH	π-bridge	COOH	BPA	
GD2	LUMO+2	-2.029	52	2	34	12		π*(Zn-Phy)+π*(π-bridge)
	LUMO+1	-2.439	95	5	0	0		π*(Zn-Phy)
	LUMO	-2.875	59	3	29	8		π*(Zn-Phy)+π*(π-bridge)
	HOMO	-5.457	87	12	1			π(Zn-Phy)
	HOMO-1	-5.697	92	2	5	1		π(Zn-Phy)
	HOMO-2	-6.448	46	4	41	9		π(Zn-Phy)+ π(π-bridge)
	HOMO-3	-6.828	17	83	0	0		π(4-MPH)+ π(Zn-Phy)
	HOMO-5	-6.919	9	90	1	0		π(4-MPH)
	HOMO-9	-7.215	11	88	0	0		π(4-MPH)
	HOMO-12	-7.263	24	75	0	0		π(4-MPH)+ π(Zn-Phy)
GD2-N1	LUMO+2	-2.059	51	2	34	12	1	π*(Zn-Phy)+π*(π-bridge)
	LUMO+1	-2.508	94	3	0	0	2	π*(Zn-Phy)
	LUMO	-2.892	61	3	28	8	1	π*(Zn-Phy)+π*(π-bridge)
	HOMO	-5.226	39	3	0	0	57	π(BPA)+ π(Zn-Phy)
	HOMO-1	-5.720	87	2	6	1	4	π(Zn-Phy)
	HOMO-2	-5.781	58	7	0	0	35	π(Zn-Phy)+π(BPA)
	HOMO-3	-6.467	45	5	41	9	0	π(Zn-Phy)+π(π-bridge)
	HOMO-4	-6.866	12	87	0	0	0	π(4-MPH)
	HOMO-8	-7.067	66	15	0	0	19	π(Zn-Phy)+ π(BPA)

	HOMO-11	-7.230	4	71	0	0	24	π(4-MPH)+ π(BPA)
	HOMO-14	-7.278	28	67	1	0	4	π(4-MPH)+π(Zn-Phy)
	HOMO-15	-7.371	58	38	2	1	0	π(Zn-Phy)+ π(4-MPH)
GD2-N2	LUMO+2	-2.072	50	2	35	12	1	π*(Zn-Phy)+π*(π-bridge)
	LUMO+1	-2.478	95	4	0	0	1	π*(Zn-Phy)
	LUMO	-2.904	61	2	27	7	1	π*(Zn-Phy)+π*(π-bridge)
	HOMO	-5.227	40	3	0	0	56	π(BPA)+ π(Zn-Phy)
	HOMO-1	-5.715	88	2	5	1	4	π(Zn-Phy)
	HOMO-2	-5.787	57	6	0	0	36	π(Zn-Phy)+π(BPA)
	HOMO-3	-6.464	45	4	42	9	0	π(Zn-Phy)+π(π-bridge)
	HOMO-5	-6.920	14	83	1	0	1	π(4-MPH)
	HOMO-9	-7.107	11	5	0	0	84	π(BPA)
	HOMO-11	-7.224	9	89	0	0	1	π(4-MPH)
	HOMO-14	-7.250	20	75	0	0	4	π(4-MPH)+π(Zn-Phy)
GD2-2N	LUMO+2	-2.102	49	1	36	12	2	π*(Zn-Phy)+π*(π-bridge)
	LUMO+1	-2.543	94	2	0	0	3	π*(Zn-Phy)
	LUMO	-2.930	63	2	26	7	2	π*(Zn-Phy)+π*(π-bridge)
	HOMO	-5.149	37	2	0	0	61	π(BPA)+π(Zn-Phy)
	HOMO-1	-5.476	7	0	0	0	93	π(BPA)
	HOMO-2	-5.744	89	1	6	1	3	π(Zn-Phy)
	HOMO-3	-5.955	58	5	0	0	36	π(Zn-Phy)+π(BPA)
	HOMO-4	-6.471	45	4	41	9	1	π(Zn-Phy)+π(BPA)
	HOMO-5	-6.912	11	83	0	0	5	π(4-MPH)
	HOMO-7	-6.946	19	26	1	0	55	π(BPA)+ π(4-MPH)
	HOMO-15	-7.253	15	53	1	0	32	π(4-MPH)+π(BPA)

Table S2 Assignments of optical absorption bands of dye GD2, GD2-N1, GD2-N2 and GD2-2N based on TD-DFT calculations.

Complexes	Main transitions	ΔEcal(eV)	λcal(nm)	*f*	Character
GD2	HOMO→ LUMO (86%)	2.0411	607 (612)*	0.1398	π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-1→ LUMO (65%)	2.1679	571 (571)	0.1210	π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	HOMO→ L+1 (33%)				π(Zn-Phy) → π*(Zn-Phy)
	HOMO→ L+1 (47%)	2.6385	469 (444)	1.6580	π(Zn-Phy) → π*(Zn-Phy)
	H-1→ LUMO (30%)				π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	HOMO→ L+2 (43%)	3.1898	388	1.2138	π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-1→ L+1 (40%)				π(Zn-Phy) → π*(Zn-Phy)
	H-2→ L+1 (25%)	3.3723	367 (364)	0.2458	π(Zn-Phy)+ π(π-bridge) → π*(Zn-Phy)
	H-1→ L+2 (18%)				π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-3→ LUMO (17%)				π(4-MPH)+π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-5→ LUMO (16%)				π(4-MPH) → π*(Zn-Phy)+π*(π-bridge)
	H-2→ L+2 (41%)	3.7710	328 (319)	0.1426	π(Zn-Phy)+π(π-bridge) → π*(Zn-Phy)+π*(π-bridge)
	H-12→ LUMO (21%)				π(4-MPH)+ π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-9→ LUMO (16%)				π(4-MPH) → π*(Zn-Phy)+π*(π-bridge)
GD2-N1	HOMO→ LUMO (93%)	1.8331	676	0.0884	π(BPA)+ π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-1→ LUMO (50%)	2.2932	540	0.5140	π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-2→ LUMO (20%)				π(Zn-Phy)+π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-2→ L+1 (17%)				π(Zn-Phy)+π(BPA) → π*(Zn-Phy)
	H-2→ L+1 (55%)	2.7334	453	1.1157	π(Zn-Phy)+π(BPA) → π*(Zn-Phy)
	H-1→ LUMO (16%)				π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-1→ L+2 (15%)				π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-1→ L+1 (40%)	2.9441	421	0.6538	π(Zn-Phy) → π*(Zn-Phy)
	HOMO→ L+2 (27%)				π(BPA)+ π(Zn-Phy) → π*(Zn-Phy)
	H-2→ L+2 (15%)				π(Zn-Phy)+π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-2→ LUMO (14%)				π(Zn-Phy)+π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-3→ L+1 (25%)	3.3340	371	0.3956	π(Zn-Phy)+π(π-bridge) → π*(Zn-Phy)
	H-1→ L+2 (23%)				π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-4→ LUMO (12%)				π(4-MPH) → π*(Zn-Phy)+π*(π-bridge)
	H-3→ L+2 (31%)	3.7288	332	0.2346	π(Zn-Phy)+π(π-bridge) → π*(Zn-Phy)+π*(π-bridge)
	H-8→ L+1 (16%)				π(Zn-Phy)+ π(BPA) → π*(Zn-Phy)

	H-11→ LUMO (14%)				π(4-MPH)+ π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-14→ L+1 (31%)	4.0644	305	0.1452	π(4-MPH)+π(Zn-Phy) → π*(Zn-Phy)
	H-15→ L+1 (23%)				π(Zn-Phy)+ π(4-MPH) → π*(Zn-Phy)
GD2-N2	HOMO→ LUMO (93%)	1.8164	682	0.2106	π(BPA)+ π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-1→ LUMO (53%)	2.3585	525	0.6344	π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	HOMO→ L+1 (27%)				π(BPA)+ π(Zn-Phy) → π*(Zn-Phy)
	H-2→ L+1 (18%)				π(Zn-Phy)+π(BPA) → π*(Zn-Phy)
	H-2→ L+1 (56%)	2.7559	449	0.9883	π(Zn-Phy)+π(BPA) → π*(Zn-Phy)
	H-1→ L+1 (36%)	2.9389	421	0.6473	π(Zn-Phy) → π*(Zn-Phy)
	HOMO→ L+2 (21%)				π(Zn-Phy)+π(BPA) → π*(Zn-Phy)+ π*(π-bridge)
	H-2→ L+2 (42%)	3.2979	375	0.4464	π(Zn-Phy)+π(BPA) → π*(Zn-Phy)+ π*(π-bridge)
	H-5→ LUMO (14%)				π(4-MPH)π*(Zn-Phy)+π*(π-bridge)
	H-9→ LUMO (42%)	3.7391	331	0.1183	π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-3→ L+2 (24%)				π(Zn-Phy)+π(π-bridge) → π*(Zn-Phy)+ π*(π-bridge)
	H-14→ L+1 (22%)	4.0948	302	0.1127	π(4-MPH)+π(Zn-Phy) → π*(Zn-Phy)
	H-9→ L+1 (20%)				π(BPA) → π*(Zn-Phy)
	H-11→ L+1 (17%)				π(4-MPH) → π*(Zn-Phy)
GD2-2N	HOMO→ LUMO (94%)	1.7163	722	0.1642	π(BPA)+π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-1→ LUMO (95%)	2.0249	612	0.0655	π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-2→ LUMO (59%)	2.3369	530	0.7256	π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-1→ L+1 (15%)				π(BPA) → π*(Zn-Phy)
	H-3→ L+1 (53%)	2.8160	440	0.7571	π(Zn-Phy)+π(BPA) → π*(Zn-Phy)
	H-2→ L+2 (15%)				π(Zn-Phy) → π*(Zn-Phy)+π*(π-bridge)
	H-2→ L+1 (46%)	2.9401	421	0.7124	π(Zn-Phy) → π*(Zn-Phy)
	H-3→ LUMO (23%)				π(Zn-Phy)+π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-3→ L+2 (37%)	3.4592	358	0.5518	π(Zn-Phy)+π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-5→ LUMO (13%)				π(4-MPH) → π*(Zn-Phy)+π*(π-bridge)
	H-7→ LUMO (10%)				π(BPA)+ π(4-MPH) → π*(Zn-Phy)+π*(π-bridge)
	H-15→ LUMO (19%)	3.7061	334	0.1133	π(4-MPH)+π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-4→ L+2 (14%)				π(Zn-Phy)+π(BPA) → π*(Zn-Phy)+π*(π-bridge)
	H-5→ L+1 (13%)				π(4-MPH) → π*(Zn-Phy)

()* is experimental results from ref. 40

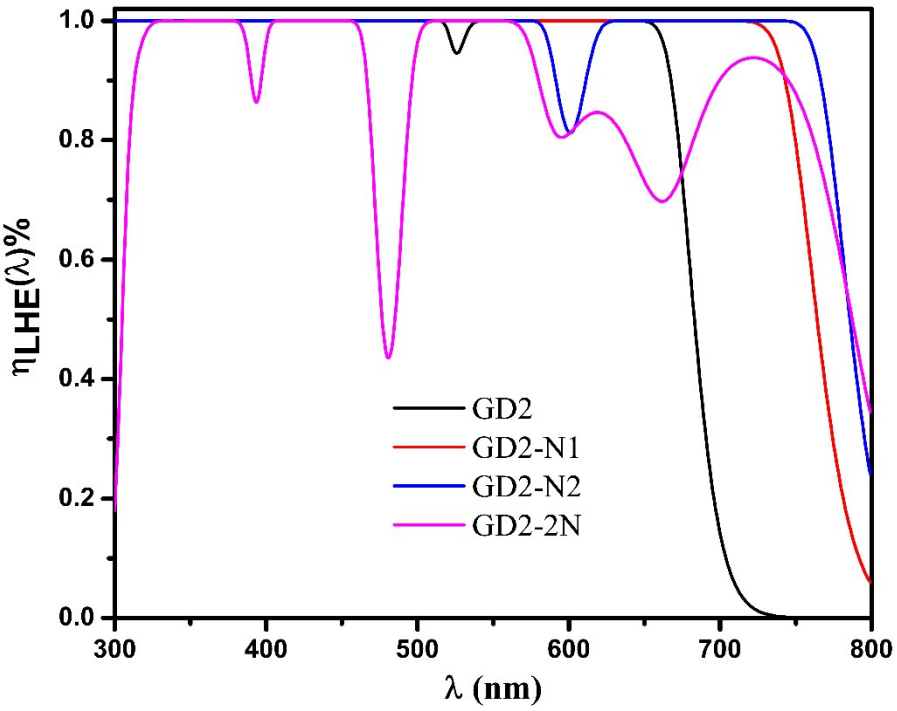

Fig. S2. The plots of the η_{LHE} (λ) curves for all sensitizers.

Table S3 Selected bond lengths (Å), bond angles (°) and torsion angles (°) of dye GD2, GD2-N1, GD2-N2 and GD2-2N on TiO_2 surface systems.

Parameters		A adsorption geometry				B adsorption geometry			
		GD2	GD2-N1	GD2-N2	GD2-2N	GD2	GD2-N1	GD2-N2	GD2-2N
Bond lengths (Å)									
	C_1—C_2	1.508	1.511	1.511	1.512	1.493	1.491	1.491	1.490
	C_1—C_3	1.507	1.509	1.504	1.506	1.504	1.504	1.504	1.504
	C_1—C_4	1.370	1.367	1.365	1.366	1.379	1.378	1.379	1.377
	C_2—O_1	1.228	1.228	1.227	1.227	1.313	1.308	1.309	1.307
	C_2—O_2	1.343	1.344	1.342	1.343	1.285	1.290	1.290	1.290
	C_3—O_3	1.336	1.337	1.336	1.337	1.261	1.261	1.260	1.261
	C_3—O_4	1.229	1.229	1.228	1.228	1.260	1.260	1.260	1.260
A	O_2—$Ti_{surface}$	1.941	1.943	1.950	1.951				
A	O_3—$Ti_{surface}$	1.898	1.891	1.884	1.887				
B	O_1—$Ti_{surface}$					2.190	2.225	2.216	2.227
B	O_2—$Ti_{surface}$					2.197	2.153	2.158	2.145
	H_1—$O_{surface}$	0.986	0.986	0.986	0.986	0.988	0.988	0.988	0.988
	H_2—$O_{surface}$	0.987	0.987	0.987	0.987	0.983	0.983	0.983	0.983
Bond angles (°)									
	C_2—C_1—C_3	128.70	127.83	126.29	126.57	117.60	118.29	118.173	118.52
	O_1—C_2—O_2	120.49	120.46	121.12	120.35	128.88	128.84	128.89	128.97
	O_3—C_3—O_4	120.68	120.41	120.56	120.62	125.51	125.58	125.62	125.47
Dihedral angle (°)									
	O_2—C_2—C_1—C_4	128.67	124.18	113.41	117.31	164.24	165.28	168.43	165.59
	O_3—C_3—C_1—C_4	156.30	163.80	171.85	169.07	97.25	92.65	93.66	96.06

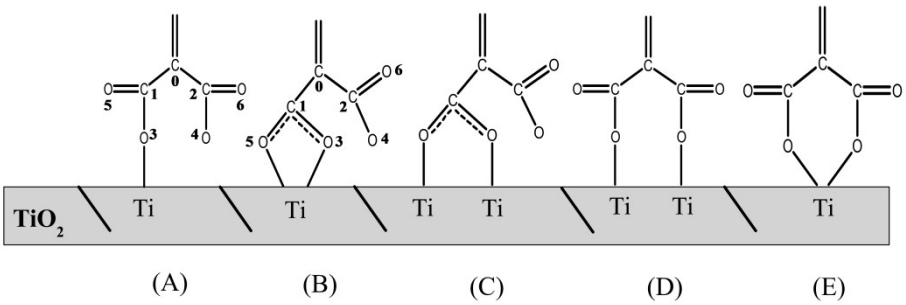

Fig. S3. Possible adsorption configurations of the sensitizers on the semiconductor surface.

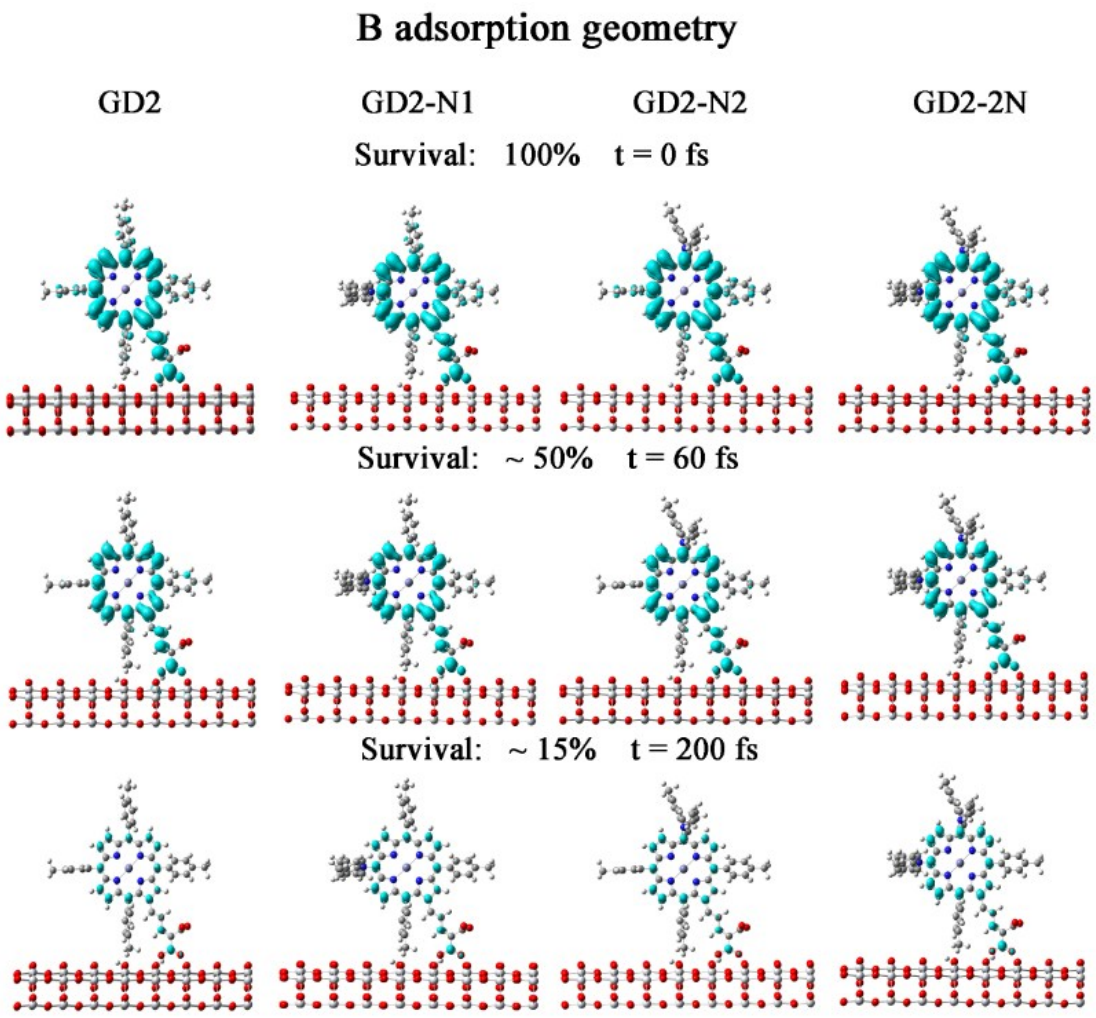

Fig. S4. Densities of photo-excited electrons for all dye sensitized TiO_2 systems under the condition of the B adsorption configuration.