Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Theoretical analysis on absorption spectrum, electronic structure, excitation, and intramolecular electron transfer of D-A'-π-A porphyrin dyes for dye-sensitized solar cells

Zhijie Xu[a,*], Shaolei Gao[b], Xiaoqing Lu[b], Yuanyuan Li[a], Yameng Li[a], and Shuxian Wei [a,*]

[a] *College of Science, China University of Petroleum, Qingdao, Shandong, 266580, PR China.*

[b] *School of Materials Science and Engineering, China University of Petroleum, Qingdao, Shandong 266580, PR China.*

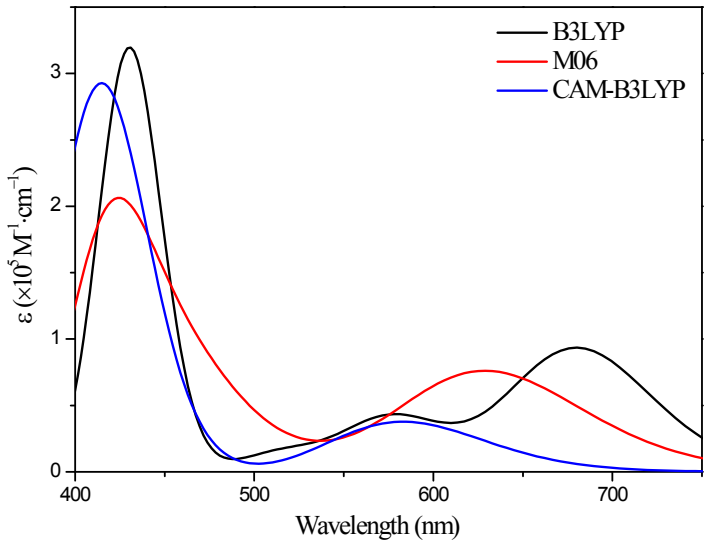


Fig. S1 Simulated absorption spectra of **CM-b** at the B3LYP/6-31G (d), CAM-B3LYP/6-31G (d) and M06/6-31G (d) levels.

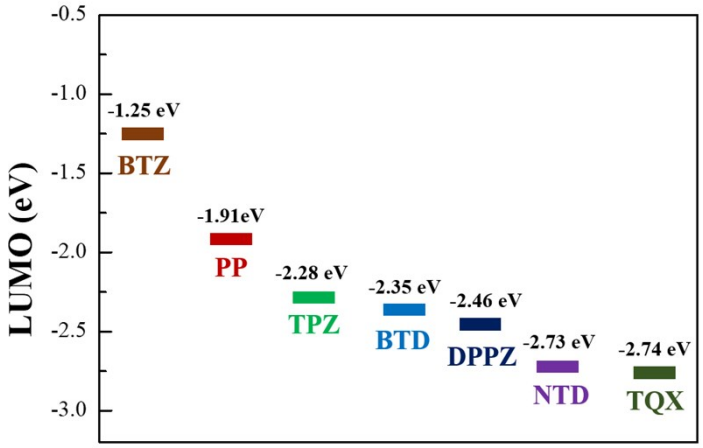


Fig. S2 LUMO levels alignment of BTD, TPZ, BTZ, PP, DPPZ, NTD, and TQX.

Table S1 The optimized geometries of the studied porphyrin dyes

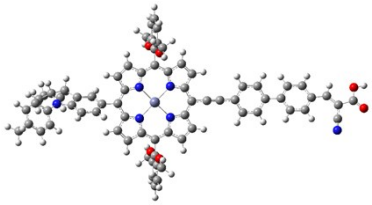
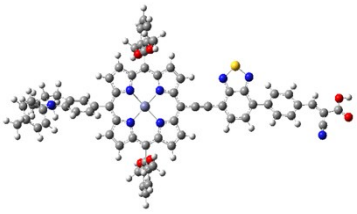
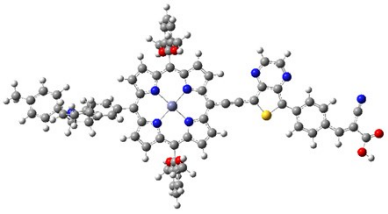
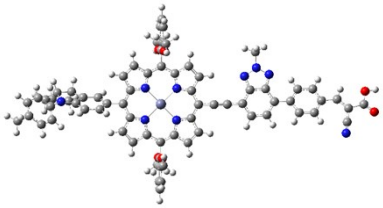
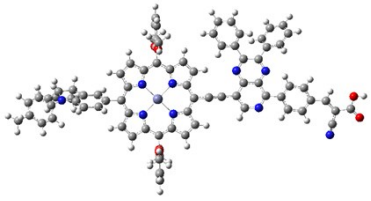
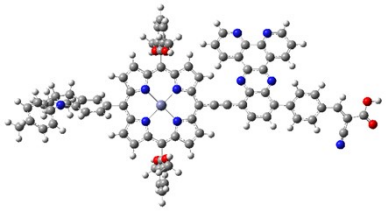
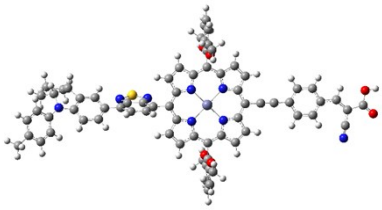
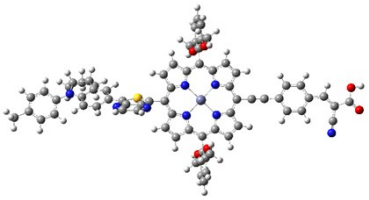
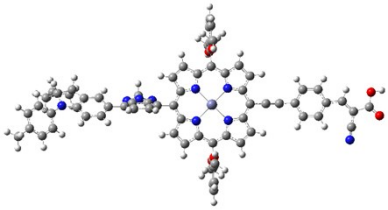
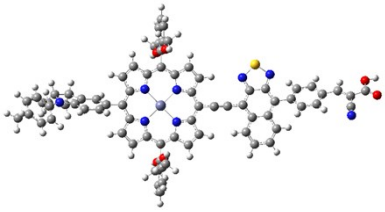
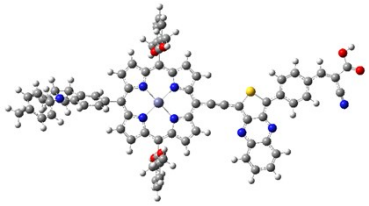
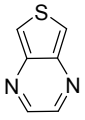
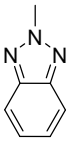
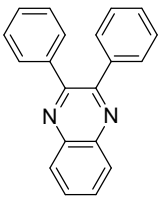
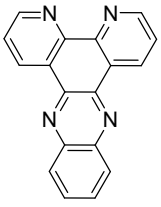
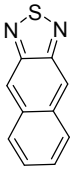
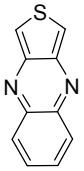
Dyes	REF	AA1	AA2
Optimized geometries			
Dyes	**AA3**	**AA4**	**AA5**
Optimized geometries			
Dyes	**AX1**	**AX2**	**AX3**
Optimized geometries			
Dyes	**AY1**	**AY2**	
Optimized geometries			

Table S2 The structures and LOMO levels of BTD, TPZ, BTZ, PP, DPPZ, NTD, and TQX.

Units	BTD	TPZ	BTZ	PP	DPPZ	NTD	TQX
Structure							
LUMO (eV)	-2.35	-2.28	-1.25	-1.91	-2.46	-2.73	-2.74

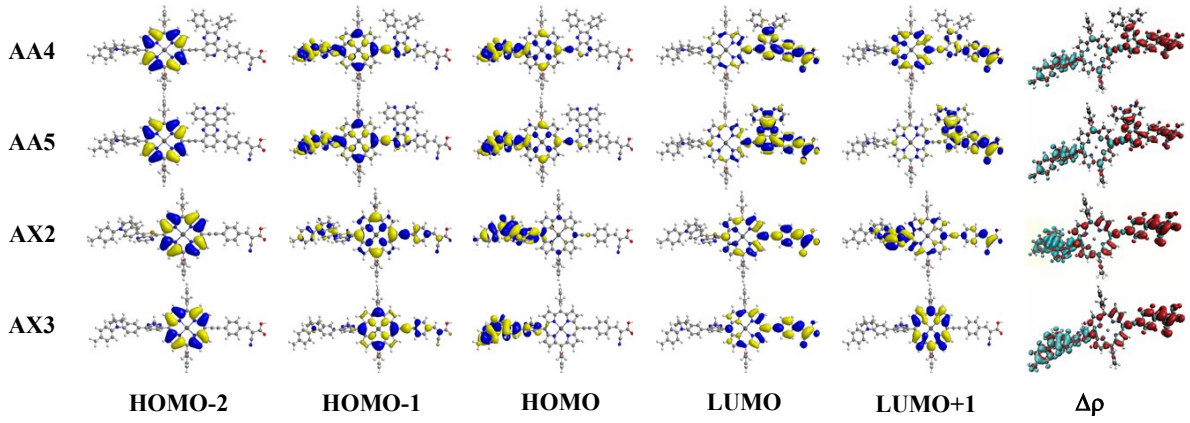


Fig. S3 The frontier molecular orbitals from HOMO-2 to LUMO+1 and charge density differences (Δρ) of AA4, AA5, AX2, and AX3 porphyrin dyes. Isodensity contour =0.02.

Table S3. The energy levels of the frontier molecular orbitals from HOMO-2 to LUMO+2 of all the investigated dyes.

Dyes	H-2	H-1	HOMO	LUMO	L+1	L+2
REF	-2.22	-2.37	-2.75	-4.80	-5.13	-5.28
AA1	-2.24	-2.45	-2.99	-4.81	-5.16	-5.31
AA2	-2.27	-2.39	-3.14	-4.81	-5.10	-5.34
AA3	-2.23	-2.38	-2.84	-4.81	-5.12	-5.29
AA4	-2.23	-2.42	-2.99	-4.83	-5.15	-5.30
AA5	-2.34	-2.51	-2.94	-4.81	-5.16	-5.31
AX1	-2.29	-2.38	-2.90	-4.89	-5.15	-5.36
AX2	-2.30	-2.37	-2.92	-4.77	-5.19	-5.37
AX3	-2.26	-2.28	-2.89	-4.83	-5.13	-5.34
AY1	-2.32	-2.55	-3.13	-4.80	-5.08	-5.31
AY2	-2.36	-2.46	-3.35	-4.79	-5.06	-5.35

Note: All energies are in eV, where H = HOMO and L = LUMO.

Table S4. Relevant information of electron excitation involved oscillator strengths (f) and relative orbital contributions at the corresponding wavelengths (λ, nm) of dyes AA4, AA5, AX2, AX3, and AY1.

E	*F*	Compositions[a]	E	*f*	Compositions[a]	E	*f*	Compositions[a]	E	*f*	Compositions[a]
		AA4			H-1→L+1(17%)			H-2→L+1(30%)	407.4	0.033	H-4→L(44%)
694.3	1.110	H→L(82%)	472.9	0.033	H-1→L+3(52%)			H-2→L(17%)			H→L+3(26%)
574.8	0.075	H-1→L(74%)			H→L+3(26%)	465.0	0.151	H-1→L+3(58%)	406.7	0.02	H-4→L(49%)
		H→L(11%)			H-2→L+2(15%)			H-2→L+2(11%)			H→L+3(22%)
522.9	0.072	H-2→L(43%)	444.2	0.038	H-1→L+1(66%)	453.7	0.023	H-2→L+3(54%)	403.1	1.111	H-2→L+2(59%)
		H→L+2(35%)			H-1→L+2(13%)			H-2→L+1(39%)			H-1→L+1(34%)
		H-2→L+1(12%)	436.9	0.024	H-2→L+1(78%)	416.3	0.885	H-3→L(24%)	387.5	0.013	H-7→L(34%)
488.1	0.264	H→L+1(30%)			H-2→L+2(18%)			H-2→L+2(20%)			H-5→L(32%)
		H-1→L+1(23%)	436.3	1.166	H-5→L(47%)			H-1→L+3(14%)	355.9	0.039	H-12→L(78%)
		H-2→L+2(15%)			H-1→L+2(28%)	414.2	0.051	H-4→L(91%)	344.8	0.0550	H-13→L(67%)
475.1	0.144	H→L+3(61%)			H-2→L+3(17%)	411.9	0.017	H-5→L(93%)			**AY1**
		H-1→L+1(28%)	412.9	0.925	H-2→L+2(37%)	406.9	0.186	H-3→L(55%)	800.5	1.206	H→L(89%)
434.9	1.392	H-5→L(45%)			H-1→L+3(35%)			H-2→L+2(10%)	639.8	0.016	H-2→L(52%)
		H-2→L+2(23%)	408.5	0.617	H-5→L(32%)	404.5	1.105	H-1→L+2(34%)			H-1→L(30%)
		H-1→L+1(20%)			H-2→L+3(29%)			H-2→L+3(30%)	630.3	0.029	H-1→L(57%)
420.0	0.200	H-2→L+1(43%)	366.8	0.606	H-5→L+1(48%)			H-2→L+1(20%)			H-2→L(27%)
		H-2→L+3(16%)			H-12→L(23%)	365.9	0.012	H-4→L+2(66%)	572.2	0.055	H→L+2(66%)
		H-1→L+3(14%)	360.6	0.072	H-5→L+2(17%)	365.4	0.052	H-8→L(36%)			H-2→L+3(18%)
415.8	0.329	H-1→L+3(48%)			H-11→L(12%)			H-4→L+2(17%)	546.7	0.060	H→L+3(53%)
		H-2→L+1(13%)	355.9	0.092	H-12→L(22%)	357.1	0.163	H-9→L+2(74%)			H-2→L+2(24%)
410.7	0.116	H-3→L(30%)			H-5→L+1(15%)			**AX3**	540.6	0.060	H→L+1(76%)
	0	H-8→L(14%)			**AX2**	633.6	1.023	H-1→L(48%)	523.0	0.187	H-3→L(86%)
406.2		H-2→L+3(56%)	685.1	1.050	H→L(80%)			H→L(39%)	484.7	0.119	H-1→L+2(56%)
		H-1→L+2(18%)			H-1→L(10%)	593.0	0.093	H→L(41%)			H-1→L+1(18%)
389.8		H-6→L(29%)	596.6	0.734	H-2→L(45%)			H-1→L(27%)	472.9	0.036	H-1→L+3(69%)
		H→L+4(20%)			H-1→L(16%)			H-2→L(16%)			H→L+3(16%)
383.6		H-18→L(29%)			H-1→L+2(16%)	586.5	0.023	H-2→L(45%)	434.5	1.037	H-2→L+2(47%)
380.3		H-8→L(40%)	595.2	0.289	H-1→L(55%)			H-1→L+1(20%)			H-3→L+2(21%)
		H→L+4(26%)			H-2→L(13%)			H→L(15%)	425.7	0.684	H-2→L+2(49%)
356.5		H-13→L(57%)			H→L(11%)	497.7	0.689	H-1→L+2(39%)			H-1→L+3(25%)
		AA5	571.7	0.2102	H→L+1(49%)			H-2→L+1(32%)	378.0	0.322	H-3→L+2(50%)
686.6	0.975	H→L(81%)			H→L+3(41%)			H→L+2(12%)			H-11→L(13%)
562.3	0.037	H-1→L(76%)	510.0	0.298	H→L+ (24%)	484.7	0.071	H→L+1(77%)			H-2→L+3(11%)
		H→L(11%)			H→L+1(22%)			H-2→L(13%)	374.7	0.195	H-11→L(27%)
520.1	0.075	H-2→L(52%)			H→L+3(20%)	471.1	0.116	H-1→L+1(35%)			H-12→L(25%)
		H→L+3(30%)	506.8	0.107	H→L+2(54%)			H-2→L+2(26%)			H-3→L+2(17%)
		H-2→L+2(15%)			H→L+3(15%)			H-2→L(22%)	370.3	0.341	H-3→L+3(32%)
513.4	0.033	H→L+1(74%)			H-2→L(15%)			H→L+1(14%)			H-12→L(21%)
		H→L+2(14%)	475.5	0.517	H-1→L+1(52%)	464.8	0.293	H→L+2(77%)	363.4	0.167	H-15→L(91%)
483.4	0.507	H-1→L+2(33%)			H-2→L+2(14%)	422.6	1.668	H→L+3(41%)	361.9	0.027	H-10→L(46%)
		H→L+2(18%)			H→L+3(14%)			H-1→L+2(27%)			H-9→L(17%)
		H-2→L+3(17%)	468.7	0.089	H-1→L+2(34%)			H-2→L+1(21%)	358.2	0.090	H-8→L+3(84%)

[a]Only oscillator strength $f > 0.01$ and orbital percentage > 10% are reported, where H = HOMO and L = LUMO.

Table S5 The lowest S_1 state for the selected porphyrin dyes calculated by TD M06 method. (H = HOMO and L = LUMO)

Dyes	λ_{max} (λ_{max} of absorption)/nm	$E_{\lambda max}$ /eV	f	Transition dipole moments (D)	Main configurations
AA1	857.4 (707.3)	1.446	1.925	54.35	LUMO→HOMO (91.0%)
AA2	966.9 (788.4)	1.282	2.180	69.39	LUMO→HOMO (93.3%)
AA3	794.1 (662.7)	1.561	2.254	58.93	LUMO→HOMO (88.9%)
AX1	753.1 (625.5)	1.646	1.977	49.01	LUMO→HOMO (78.8%)
AY1	993.4 (800.5)	1.248	1.631	53.35	LUMO→HOMO (93.1%)

Table S6. The *LHE* and *RLHE* values of all the investigated Zn-porphyrin dyes.

	REF	**AA1**	**AA2**	**AA3**	**AA4**	**AA5**	**AX1**	**AX2**	**AX3**	**AY1**	**AY2**
LHE	90.9%	95.1%	97.9%	95.9%	92.2%	89.4%	92.8%	91.2%	90.5%	93.8%	95.7%
RLHE	1.000	1.045	1.077	1.055	1.015	0.984	1.021	1.002	0.996	1.032	1.053