Controlling the Directionality of Charge Transfer in Phthalocyaninato Zinc Sensitizer for Dye-Sensitized Solar Cell: Density Functional Theory Studies

Liang Wan, ^a Dongdong Qi, ^a Yuexing Zhang, ^a and Jianzhuang Jiang*^a

^a Department of Chemistry, University of Science and Technology Beijing, Beijing

100083, China

E-mail: jianzhuang@ustb.edu.cn



Figure S1. Schematic molecular structure of designed complexes exampled with $ZnPc-\beta-A-I-NH_2$. "ZnPc" refers to the phthalocyaninato zinc ring, " β " corresponds to the position of the acceptor, "A" refers to the "(E)-2-cyano-3-(5-vinylthiophen-2-yl) acrylic acid acceptor, and "I" refers to the position of NH₂ donors.



Figure S2. Molecular orbital maps of HOMO and LUMO of ZnPc-β-A, ZnPc-β-A-I-NH₂, ZnPc-β-A-II-NH₂, ZnPc-β-A-III-NH₂, ZnPc-β-A-I,II-NH₂, ZnPc-β-A-I,III-NH₂, ZnPc-β-A-II,III-NH₂, and ZnPc-β-A-I,II,III-NH

Table S1. Calculated atomic charge distribution (in e) of ZnPc ring, donor and acceptor with NBO method for ZnPc- β -A-I,III-NH₂ and ZnPc- β -A-I,III-NH₂'. (The relative error is calculated by $|(X-Y)/Y| \times 100\%$, where X is the charge distribution on ZnPc- β -A-I,III-NH₂' and Y is the charge distribution on ZnPc- β -A-I,III-NH₂.)

	$ZnPc-\beta-A-I,III-NH_2$	ZnPc-β-A-I,III-NH ₂ '	Relative error
acceptor	-0.036	-0.030	16.7%
donors	-0.214	-0.277	29.4%
ZnPc ring	0.250	0.307	22.8%

Table S2. Calculated energy data (in eV) of orbitals from HOMO-2 to LUMO+2 of ZnPc- β -A-I,III-NH₂ and ZnPc- β -A-I,III-NH₂'. (The energy variation is the orbital energy difference for the six orbitals between ZnPc- β -A-I,III-NH₂ and ZnPc- β -A-I,III-NH₂'.)

 $ZnPc-\beta-A-I,III-NH_2$ $ZnPc-\beta-A-I,III-NH_2$ ' Energy variation

LUMO+2	-2.579	-2.623	0.044
LUMO+1	-2.649	-2.690	0.041
LUMO	-3.013	-3.043	0.030
НОМО	-4.774	-4.844	0.070
HOMO-1	-5.516	-5.733	0.217
НОМО-2	-5.538	-5.750	0.212

(only the tran	isitions with contribut	tion >10% is considered)		
,				
λ /nm	f		Electronic transition nature [H=HOMO, L=LU	[OMU]
680.7	0.7115	(80%)H-0→L+0		
603.0	0.4094	(73%)H-0→L+1		
574.2	0.1859	(80%)H-1→L+2		
487.7	0.5492	(75%)H-1→L+0		
475.7	0.1181	(95%)H-1→L+1		
426.8	0.7725	(74%)H-1→L+2		
361.5	0.1289	(31%) H-1 \rightarrow L+0	(24%)H-5→L+0	(11%)H-2→L+1
337.4	0.1334	(22%)H-10→L+0	(20%)H-5→L+0	(13%)H-4→L+0
333.0	0.1170	(24%)H-7→L+1	(20%)H-6→L+1	(15%)H-5→L+1
326.4	0.2433	(22%)H-5→L+1	(20%)H-6→L+1	(16%)H-10→L+1
326.2	0.1779	(28%)H-8→L+1	(15%)H-2→L+2	(11%)H-6→L+1
315.1	0.2919	(63%)H-4→L+2		

Table S4. Calculated wavelength (λ m), oscillator strength (f), and electron transition nature in the electronic absorption spectra of

ZnPc- β -A-II-NH₂. (only the transitions with contribution >10% is considered)

										(10%)H-8→L+2	
)MO, L=LUMO]								(10%)H-4→L+2		(10%)H-2→L+3	
ansition nature [H=HC							(14%)H-3→L+2	(10%)H-6→L+1	(11%)H-5→L+2	(11%)H-6→L+2	
Electronic tra					(10%)H-2→L+1		(15%)H-8→L+0	(12%)H-8→L+1	(21%)H-4→L+2	(13%)H-4→L+2	
	(83%)H-0→L+0	(69%)H-0→L+1	(77%)H-0→L+2	(81%)H-1→L+1	(64%)H-2→L+0	(72%)H-2→L+2	(36%)H-10→L+0	(14%)H-4→L+1	(43%)H-10→L+1	(34%)H-1→L+3	(69%)H-10→L+2
f	0.6290	0.3755	0.2176	0.3650	0.6053	0.5985	0.1234	0.4443	0.1144	0.2249	0.1572
λ/nm	706.8	613.7	588.2	515.6	476.4	426.8	339.1	324.9	321.9	315.9	305.0

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Table S5. Calculated wavelength (Nnm), oscillator strength (f), and electron transition nature in the electronic absorption spectra of

ZnPc- β -A-III-NH₂. (only the transitions with contribution >10% is considered)

														(10%)H-10→L+1	
MO, L=LUMO]														(10%)H-5→L+2	
transition nature [H=HO														(16%)H-8→L+2	
Electronic						(10%)H-2→L+2					(13%)H-4→L+2	(11%)H-14→L+0		(16%)H-6→L+2	(12%)H-0→L+7
	(83%)H-0→L+0	(68%)H-0→L+1	(75%)H-0→L+2	(80%)H-1→L+0	(82%)H-1→L+1	(73%)H-2→L+0	(93%)H-2→L+1	(75%)H-2→L+2	(70%)H-3→L+1	(49%)H-8→L+0	(50%)H-0→L+6	(13%)H-0→L+6	(48%)H-1→L+3	(16%)H-2→L+3	(30%)H-6→L+2
f	0.5692	0.3562	0.2093	0.1703	0.1014	0.7425	0.2108	0.5178	0.1153	0.1650	0.1330	0.1357	0.1803	0.2169	0.1257
λ/nm	716.2	610.2	591.4	545.7	522.9	480.4	458.0	425.8	365.8	343.0	327.7	324.8	321.3	315.7	311.7

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Table S6. Calculated wavelength (λ m), oscillator strength (f), and electron transition nature in the electronic absorption spectra of

ZnPc- β -A-I,II-NH₂. (only the transitions with contribution >10% is considered)

										(10%)H-1→L+3			(11%)H-0→L+7	
=LUMO]										(11%)H-5→L+2			(13%)H-15→L+0	
nic transition nature [H=HOMO, L					(11%)H-3→L+0					(12%)H-9→L+1	(13%)H-9→L+1	(10%) H-0 \rightarrow L+7	(13%)H-10→L+1	(11%)H-10(196)→L+2(209)
Electro					(12%)H-1→L+1	(28%)H-2→L+2				(14%)H-10→L+1	(22%)H-9→L+2	(12%)H-7→L+	(14%)H-10→L+2	(21%)H-12→L+0
	0+T←0-H(%98)	(66%)H-0→L+1	(73%)H-0→L+2	(76%)H-2→L+0	(68%)H-2→L+1	(37%)H-3→L+0	(92%)H-3→L+1	(75%)H-3→L+2	(76%)H-6→L+0	(18%)H-7→L+1	(27%)H-7→L+2	(30%)H-10→L+1	(17%)H-9→L+2	(47%)H-15→L+0
f	0.5391	0.3942	0.2750	0.1028	0.4682	0.6561	0.1058	0.3125	0.1067	0.3402	0.1469	0.1482	0.1856	0.1506
λ/nm	748.4	617.0	601.4	537.4	496.4	462.5	448.4	424.8	362.7	324.3	314.7	311.4	309.0	307.0

Table S7. Calculated wavelength (λ /nm), oscillator strength (f), and electron transition nature in the electronic absorption spectra of

ZnPc- β -A-I,III-NH₂. (only the transitions with contribution >10% is considered)

761.7 0.4829 $(85\%)H-0\rightarrow L+0$ 620.4 0.3646 $(69\%)H-0\rightarrow L+1$ 604.9 0.2194 $(69\%)H-0\rightarrow L+2$ 547.4 0.2163 $(77\%)H-1\rightarrow L+0$ 507.7 0.1904 $(56\%)H-1\rightarrow L+2$ 474.0 0.1287 $(56\%)H-1\rightarrow L+2$ 470.1 0.2873 $(58\%)H-3\rightarrow L+2$ 470.1 0.8873 $(58\%)H-3\rightarrow L+2$ 472.4 0.1240 $(78\%)H-3\rightarrow L+2$ 472.4 0.1940 $(78\%)H-3\rightarrow L+1$ 422.4 0.1940 $(78\%)H-3\rightarrow L+2$ 321.8 0.2703 $(17\%)H-12\rightarrow L+1$ 319.5 0.11112 $(43\%)H-10\rightarrow L+1$ 314.2 0.3079 $(17\%)H-7\rightarrow L+2$ 309.7 0.11198 $(20\%)H-9\rightarrow L+1$	Electronic transition na	ature [H=HOMO, L=LUMO]	
20.4 0.3646 $(69\%)H-0\rightarrow L+1$ 04.9 0.2194 $(69\%)H-0\rightarrow L+2$ 47.4 0.2163 $(77\%)H-1\rightarrow L+0$ 07.7 0.1904 $(56\%)H-1\rightarrow L+1$ 74.0 0.1287 $(36\%)H-1\rightarrow L+1$ 74.0 0.1287 $(36\%)H-1\rightarrow L+1$ 74.0 0.1287 $(36\%)H-1\rightarrow L+2$ 70.1 0.8873 $(58\%)H-3\rightarrow L+1$ 42.9 0.3077 $(91\%)H-3\rightarrow L+1$ 22.4 0.1940 $(78\%)H-3\rightarrow L+1$ 22.4 0.1940 $(78\%)H-3\rightarrow L+1$ 21.8 0.2705 $(27\%)H-5\rightarrow L+1$ 19.5 0.1112 $(43\%)H-10\rightarrow L+1$ 14.2 0.3079 $(17\%)H-12\rightarrow L+2$ 19.7 0.1198 $(20\%)H-9\rightarrow L+1$	0-		
$(04.9$ 0.2194 $(69\%)H-0\rightarrow L+2$ 47.4 0.2163 $(77\%)H-1\rightarrow L+0$ 07.7 0.1904 $(56\%)H-1\rightarrow L+1$ 74.0 0.1287 $(56\%)H-1\rightarrow L+2$ 70.1 0.8873 $(58\%)H-3\rightarrow L+2$ 70.1 0.8873 $(58\%)H-3\rightarrow L+2$ 42.9 0.3077 $(91\%)H-3\rightarrow L+2$ 22.4 0.1940 $(78\%)H-3\rightarrow L+2$ 22.4 0.1940 $(78\%)H-3\rightarrow L+2$ 22.4 0.1940 $(78\%)H-3\rightarrow L+2$ 21.8 0.2705 $(27\%)H-5\rightarrow L+1$ 21.8 0.2703 $(17\%)H-12\rightarrow L+0$ 19.5 0.1112 $(43\%)H-10\rightarrow L+1$ 14.2 0.3079 $(17\%)H-7\rightarrow L+2$ 09.7 0.1198 $(20\%)H-9\rightarrow L+1$	-		
47.4 0.2163 $(77\%)H-1 \rightarrow L+0$ 07.7 0.1904 $(56\%)H-1 \rightarrow L+1$ 74.0 0.1287 $(36\%)H-1 \rightarrow L+2$ 70.1 0.8873 $(58\%)H-3 \rightarrow L+0$ 42.9 0.3077 $(91\%)H-3 \rightarrow L+1$ 22.4 0.1940 $(78\%)H-3 \rightarrow L+1$ 22.4 0.1940 $(78\%)H-3 \rightarrow L+1$ 22.4 0.1940 $(78\%)H-3 \rightarrow L+1$ 21.8 0.2705 $(27\%)H-3 \rightarrow L+1$ 21.8 0.2703 $(17\%)H-12 \rightarrow L+1$ 19.5 0.1112 $(43\%)H-10 \rightarrow L+1$ 14.2 0.3079 $(17\%)H-7 \rightarrow L+2$ 09.7 0.1198 $(20\%)H-9 \rightarrow L+1$	-2		
507.7 0.1904 $(56\%)H-1 \rightarrow L+1$ 174.0 0.1287 $(36\%)H-1 \rightarrow L+2$ 170.1 0.8873 $(58\%)H-3 \rightarrow L+0$ 170.1 0.8873 $(58\%)H-3 \rightarrow L+2$ 142.9 0.3077 $(91\%)H-3 \rightarrow L+1$ 122.4 0.1940 $(78\%)H-3 \rightarrow L+2$ 121.8 0.2793 $(17\%)H-12 \rightarrow L+0$ 114.2 0.3079 $(17\%)H-7 \rightarrow L+2$ 109.7 0.1198 $(20\%)H-9 \rightarrow L+1$	0-		
74.0 0.1287 $(36\%)H-1 \rightarrow L+2$ 770.1 0.8873 $(58\%)H-3 \rightarrow L+0$ 442.9 0.3077 $(91\%)H-3 \rightarrow L+1$ 22.4 0.1940 $(78\%)H-3 \rightarrow L+2$ 255.3 0.2705 $(27\%)H-3 \rightarrow L+2$ 555.3 0.2705 $(27\%)H-12 \rightarrow L+1$ 21.8 0.2793 $(17\%)H-12 \rightarrow L+0$ 19.5 0.1112 $(43\%)H-10 \rightarrow L+1$ 114.2 0.3079 $(17\%)H-7 \rightarrow L+2$ 09.7 0.1198 $(20\%)H-9 \rightarrow L+1$	-1 (18%)H-1→L+2	(10%)H-2→L+1	
70.1 0.8873 $(58\%)H-3 \rightarrow L+0$ 42.9 0.3077 $(91\%)H-3 \rightarrow L+1$ 122.4 0.1940 $(78\%)H-3 \rightarrow L+2$ 55.3 0.2705 $(27\%)H-5 \rightarrow L+1$ 51.8 0.2705 $(27\%)H-12 \rightarrow L+0$ 21.8 0.2793 $(17\%)H-12 \rightarrow L+0$ 19.5 0.1112 $(43\%)H-12 \rightarrow L+1$ 14.2 0.3079 $(17\%)H-17 \rightarrow L+2$ 09.7 0.1198 $(20\%)H-9 \rightarrow L+1$	-2 (23%)H-2→L+2	(20%)H-1→L+1	(10%)H-2→L+1
42.9 0.3077 $(91\%)H-3 \rightarrow L+1$ 22.4 0.1940 $(78\%)H-3 \rightarrow L+2$ 55.3 0.2705 $(27\%)H-5 \rightarrow L+1$ 55.3 0.2703 $(17\%)H-12 \rightarrow L+0$ 19.5 0.1112 $(43\%)H-10 \rightarrow L+1$ 114.2 0.3079 $(17\%)H-7 \rightarrow L+2$ 09.7 0.1198 $(20\%)H-9 \rightarrow L+1$	0-		
22.4 0.1940 $(78\%)H-3\rightarrow L+2$ (55.3) 0.2705 $(27\%)H-5\rightarrow L+1$ (21.8) 0.2793 $(17\%)H-12\rightarrow L+0$ (19.5) 0.1112 $(43\%)H-10\rightarrow L+1$ (14.2) 0.3079 $(17\%)H-7\rightarrow L+2$ (09.7) 0.1198 $(20\%)H-9\rightarrow L+1$	-1		
555.3 0.2705 $(27\%)H-5 \rightarrow L+1$ 21.8 0.2793 $(17\%)H-12 \rightarrow L+0$ 19.5 0.1112 $(43\%)H-10 \rightarrow L+1$ 114.2 0.3079 $(17\%)H-7 \rightarrow L+2$ 09.7 0.1198 $(20\%)H-9 \rightarrow L+1$	-2		
21.8 0.2793 $(17\%)H-12\rightarrow L+0$ $.19.5$ 0.1112 $(43\%)H-10\rightarrow L+1$ $.14.2$ 0.3079 $(17\%)H-7\rightarrow L+2$ $.09.7$ 0.1198 $(20\%)H-9\rightarrow L+1$	-1 (25%)H-7→L+0	(21%)H-6→L+0	
19.5 0.1112 $(43\%)H-10\rightarrow L+1$ 14.2 0.3079 $(17\%)H-7\rightarrow L+2$ 09.7 0.1198 $(20\%)H-9\rightarrow L+1$	$(16\%)H-6 \rightarrow L+1$	(14%)H-7→L+2	(11%)H-7→L+1
$\begin{array}{rrrr} .14.2 & 0.3079 & (17\%)H-7 \rightarrow L+2 \\ .09.7 & 0.1198 & (20\%)H-9 \rightarrow L+1 \end{array}$.+1 (14%)H-6→L+2		
$(09.7 0.1198 (20\%)H-9 \rightarrow L+1$	-2 (15%)H-10→L+2	(13%)H-7→L+1	
	-1 (14%)H-9→L+2	(14%)H-0→L+7	(14%)H-15→L+0
07.2 0.1020 (46%) H-15→L+0	,+0 (21%)H-12→L+0		

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Table S8. Calculated wavelength (λ m), oscillator strength (f), and electron transition nature in the electronic absorption spectra of

ZnPc- β -A-II,III-NH₂. (only the transitions with contribution >10% is considered)

										(11%)H-5→L+1					
nsition nature [H=HOMO, L=LUMO]										(14%)H-7→L+0			(11%)H-8→L+2		
										(15%)H-7→L+1	(11%)H-6→L+1	(15%)H-1→L+3	(12%)H-7→L+2		(10%)H-0→L+7
Electronic tra				(16%)H-1→L+0	(10%)H-3→L+0			(19%)H-5→L+0		(16%)H-6→L+0	(13%)H-12→L+0	(16%)H-8→L+1	(14%)H-10→L+1	(12%)H-8→L+1	(27%)H-12→L+0
	(86%)H-0→L+0	(68%)H-0→L+1	(74%)H-0→L+2	(64%)H-2→L+0	(75%)H-2→L+1	(60%)H-3→L+0	(73%)H-3→L+2	(65%)H-4→L+1	(49%)H-6→L+0	(33%)H-6→L+1	(25%)H-7→L+1	(25%)H-0→L+6	(16%)H-2→L+3	(33%)H-7→L+2	(37%)H-10→L+2
f	0.5200	0.3956	0.2667	0.1486	0.4554	0.7108	0.3434	0.1010	0.1008	0.1032	0.1993	0.1959	0.1623	0.1719	0.2556
λ/nm	745.7	615.3	600.7	532.7	497.7	470.5	424.7	369.7	367.2	352.9	324.6	318.2	314.3	311.1	307.1

Table S9. Calculated wavelength (Nnm), oscillator strength (f), and electron transition nature in the electronic absorption spectra of

 $ZnPc-\beta-A-I,II,III-NH_2.$

										(13%)H - 8→L+1			
O, L=LUMO]										(14%)H-7→L+2			(14%)H-7→L+1
ansition nature [H=HOM						(18%)H-3→L+1				(14%)H-7→L+1	(14%)H-7→L+2	(10%)H-8→L+1	(19%)H-0→L+7
Electronic tr				(15%)H-1→L+0	(20%)H-4→L+0	(18%)H-3→L+2		(24%)H-8→L+0		(15%)H-12→L+0	(29%)H-0→L+7	(10%)H-0→L+7	(20%)H-12→L+0
	(88%)H-0→L+0	(68%)H-0→L+1	(70%)H-0→L+2	(65%)H-3→L+0	(64%)H-3→L+1	(31%)H-4→L+0	(94%)H-4→L+1	(54%)H-7→L+0	(59%)H-10→L+0	(19%)H-8→L+2	(29%)H-10→L+1	(30%)H-7→L+2	(24%)H-10→L+1
f	0.4612	0.4384	0.2675	0.1381	0.6160	0.8247	0.1477	0.1431	0.1541	0.1176	0.1009	0.4628	0.2162
λ/nm	793.7	622.5	610.2	532.9	483.1	461.9	435.4	353.6	338.9	330.2	314.7	312.4	311.4