Supplementary Material for PCCP

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

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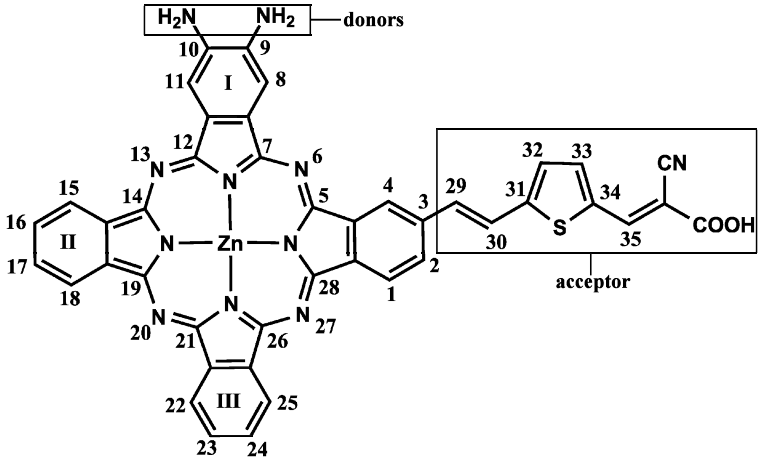

ZnPc-β-A-I-NH_2

Figure S1. Schematic molecular structure of designed complexes exampled with ZnPc-β-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 NH_2 donors.

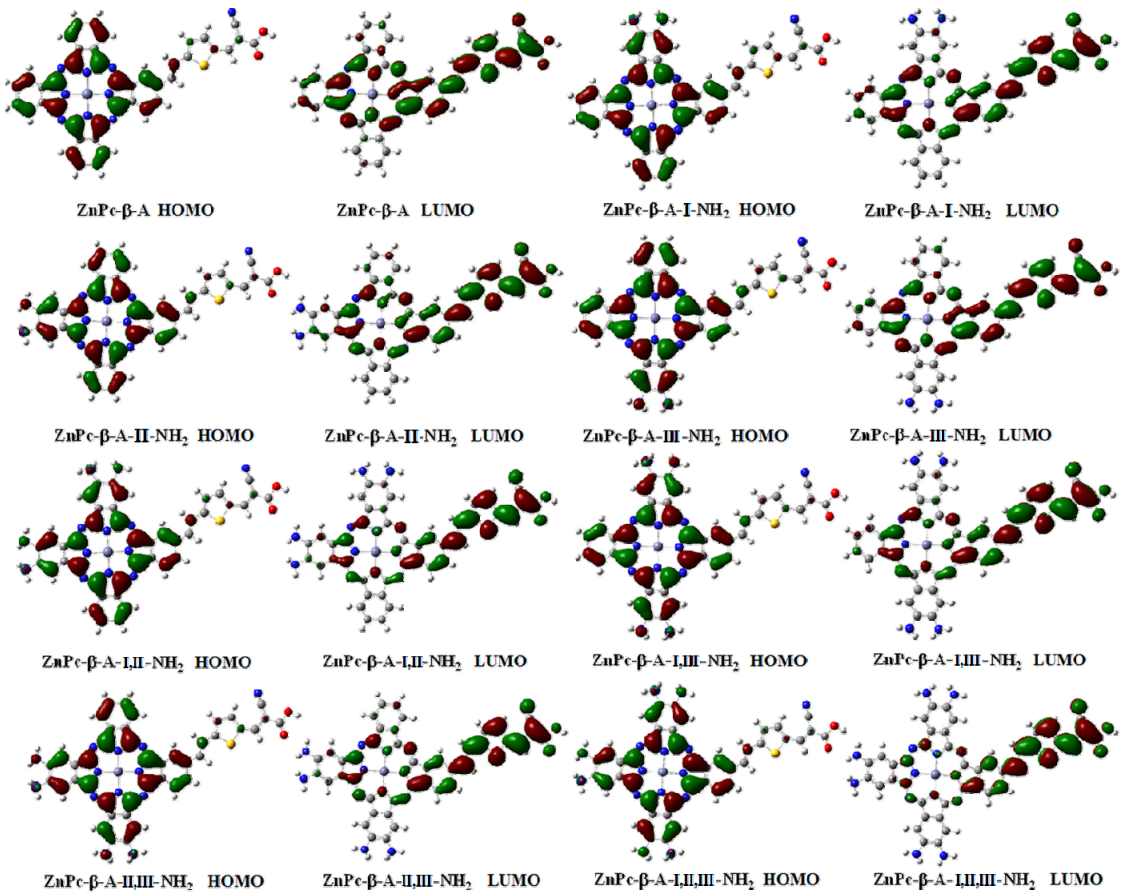

Figure S2. Molecular orbital maps of HOMO and LUMO of ZnPc-β-A, ZnPc-β-A-I-NH_2, ZnPc-β-A-II-NH_2, ZnPc-β-A-III-NH_2, ZnPc-β-A-I,II-NH_2, ZnPc-β-A-I,III-NH_2, ZnPc-β-A-II,III-NH_2, and ZnPc-β-A-I,II,III-NH

Table S1. Calculated atomic charge distribution (in e) of ZnPc ring, donor and acceptor with NBO method for ZnPc-β-A-I,III-NH_2 and ZnPc-β-A-I,III-NH_2'. (The relative error is calculated by $\left|(X-Y)/Y\right|\times100\%$, where X is the charge distribution on ZnPc-β-A-I,III-NH_2' and Y is the charge distribution on ZnPc-β-A-I,III-NH_2.)

	ZnPc-β-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-NH_2 and ZnPc-β-A-I,III-NH_2'. (The energy variation is the orbital energy difference for the six orbitals between ZnPc-β-A-I,III-NH_2 and ZnPc-β-A-I,III-NH_2'.)

	ZnPc-β-A-I,III-NH_2	ZnPc-β-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
HOMO	-4.774	-4.844	0.070
HOMO-1	-5.516	-5.733	0.217
HOMO-2	-5.538	-5.750	0.212

Table S3. Calculated wavelength (λ/nm), oscillator strength (*f*), and electron transition nature in the electronic absorption spectra of ZnPc-β-A. (only the transitions with contribution >10% is considered)

λ/nm	*f*	Electronic transition nature [H=HOMO, L=LUMO]		
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→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/nm), oscillator strength (*f*), and electron transition nature in the electronic absorption spectra of ZnPc-β-A-II-NH_2. (only the transitions with contribution >10% is considered)

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

Table S5. Calculated wavelength (λ/nm), oscillator strength (*f*), and electron transition nature in the electronic absorption spectra of ZnPc-β-A-III-NH_2. (only the transitions with contribution >10% is considered)

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

Table S6. Calculated wavelength (λ/nm), oscillator strength (*f*), and electron transition nature in the electronic absorption spectra of ZnPc-β-A-I,II-NH_2. (only the transitions with contribution >10% is considered)

λ/nm	*f*	Electronic transition nature [H=HOMO, L=LUMO]				
748.4	0.5391	(86%)H-0→L+0				
617.0	0.3942	(66%)H-0→L+1				
601.4	0.2750	(73%)H-0→L+2				
537.4	0.1028	(76%)H-2→L+0				
496.4	0.4682	(68%)H-2→L+1	(12%)H-1→L+1	(11%)H-3→L+0		
462.5	0.6561	(37%)H-3→L+0	(28%)H-2→L+2			
448.4	0.1058	(92%)H-3→L+1				
424.8	0.3125	(75%)H-3→L+2				
362.7	0.1067	(76%)H-6→L+0				
324.3	0.3402	(18%)H-7→L+1	(14%)H-10→L+1	(12%)H-9→L+1	(11%)H-5→L+2	(10%)H-1→L+3
314.7	0.1469	(27%)H-7→L+2	(22%)H-9→L+2	(13%)H-9→L+1		
311.4	0.1482	(30%)H-10→L+1	(12%)H-7→L+	(10%)H-0→L+7		
309.0	0.1856	(17%)H-9→L+2	(14%)H-10→L+2	(13%)H-10→L+1	(13%)H-15→L+0	(11%)H-0→L+7
307.0	0.1506	(47%)H-15→L+0	(21%)H-12→L+0	(11%)H-10(196)→L+2(209)		

Table S7. Calculated wavelength (λ/nm), oscillator strength (*f*), and electron transition nature in the electronic absorption spectra of ZnPc-β-A-I,III-NH_2. (only the transitions with contribution >10% is considered)

λ/nm	*f*	Electronic transition nature [H=HOMO, L=LUMO]			
761.7	0.4829	(85%)H-0→L+0			
620.4	0.3646	(69%)H-0→L+1			
604.9	0.2194	(69%)H-0→L+2			
547.4	0.2163	(77%)H-1→L+0			
507.7	0.1904	(56%)H-1→L+1	(18%)H-1→L+2	(10%)H-2→L+1	
474.0	0.1287	(36%)H-1→L+2	(23%)H-2→L+2	(20%)H-1→L+1	(10%)H-2→L+1
470.1	0.8873	(58%)H-3→L+0			
442.9	0.3077	(91%)H-3→L+1			
422.4	0.1940	(78%)H-3→L+2			
355.3	0.2705	(27%)H-5→L+1	(25%)H-7→L+0	(21%)H-6→L+0	
321.8	0.2793	(17%)H-12→L+0	(16%)H-6→L+1	(14%)H-7→L+2	(11%)H-7→L+1
319.5	0.1112	(43%)H-10→L+1	(14%)H-6→L+2		
314.2	0.3079	(17%)H-7→L+2	(15%)H-10→L+2	(13%)H-7→L+1	
309.7	0.1198	(20%)H-9→L+1	(14%)H-9→L+2	(14%)H-0→L+7	(14%)H-15→L+0
307.2	0.1020	(46%)H-15→L+0	(21%)H-12→L+0		

Table S8. Calculated wavelength (λ/nm), oscillator strength (*f*), and electron transition nature in the electronic absorption spectra of ZnPc-β-A-II,III-NH_2. (only the transitions with contribution >10% is considered)

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

Table S9. Calculated wavelength (λ/nm), oscillator strength (*f*), and electron transition nature in the electronic absorption spectra of ZnPc-β-A-I,II,III-NH_2.

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