Supporting Information

Synthesis of Zinc Phthalocyanine with Large Steric Hindrance and Its Photovoltaic Performance for Dye-Sensitized Solar Cells

Li Lin,[a] Bosi Peng,[a] Wenye Shi,[a] Yingying Guo[a] and Renjie Li[*a]
[a]College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, China.
*Corresponding author. Fax: (+86) 27 6875 6679; Tel: +86-27 6875 6679; *E-mail*: lirj@whu.edu.cn (Li, R.)

Tables and Figures Captions

Fig. S1. MALDI-TOF mass spectrum of Zn-*tri*-PcNc-8a.

Fig. S2. MALDI-TOF mass spectrum of Zn-*tri*-PcNc-8.

Fig. S3. ^{1}H MNR (in DMSO-d_6) spectrum of the molecular ion of Zn-*tri*-PcNc-8a

Fig. S4. ^{1}H MNR (in DMSO-d_6) spectrum of the molecular ion of Zn-tri-PcNc-8

Fig. S5. UV-vis absorption spectra and Fluorescence emission spectra and of Std-ZnPc in THF solution (C=1 ×10^{-5} M) with excitation fixed at 620 nm.

Fig. S6. UV-vis absorption spectra and Fluorescence emission spectra and of Zn-*tri*-PcNc-8 in THF solution (C=1 ×10^{-5} M) with excitation fixed at 480 nm.

Fig. S7. UV-Vis absorption spectra of Zn-*tri*-PcNc-8 in THF at different concentration

Fig. S8. IR spectra of Zn-*tri*-PcNc-8.

Fig. S9. The typical cyclic voltammogram of Zn-*tri*-PcNc-8 in o-DCB containing 0.1M [NBu_4][ClO_4] at a scan rate of 20 mV S^{-1}.

Fig. S10. The frontier molecular orbitals of Zn-*tri*-PcNc-8, full optimized at B3LYP/6-31G level.

Table S1. Fluorescence emission data of zinc phthalocyanines in THF.

Table S2. Electrochemical data of Zn-*tri*-PcNc-8**.**

Table S3. TD-DFT calculated spectra selected (lowest-excited energies (ΔE), absorption wavelengths, oscillator strengths (*f*), and domination excitation characters for low-lying singlet state) of Zn-*tri*-PcNc-2 and Zn-*tri*-PcNc-8

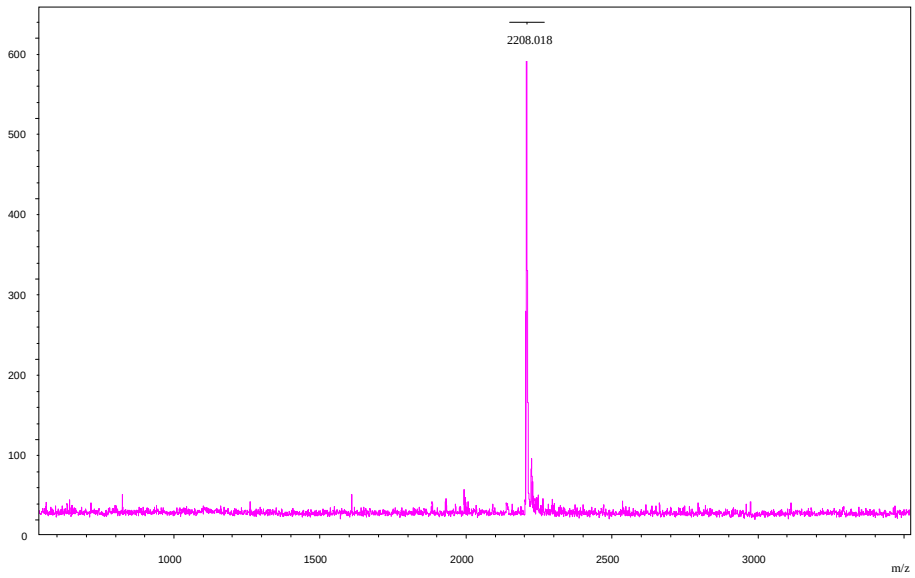

Fig. S1. MALDI-TOF mass spectrum of Zn-*tri*-PcNc-8a.

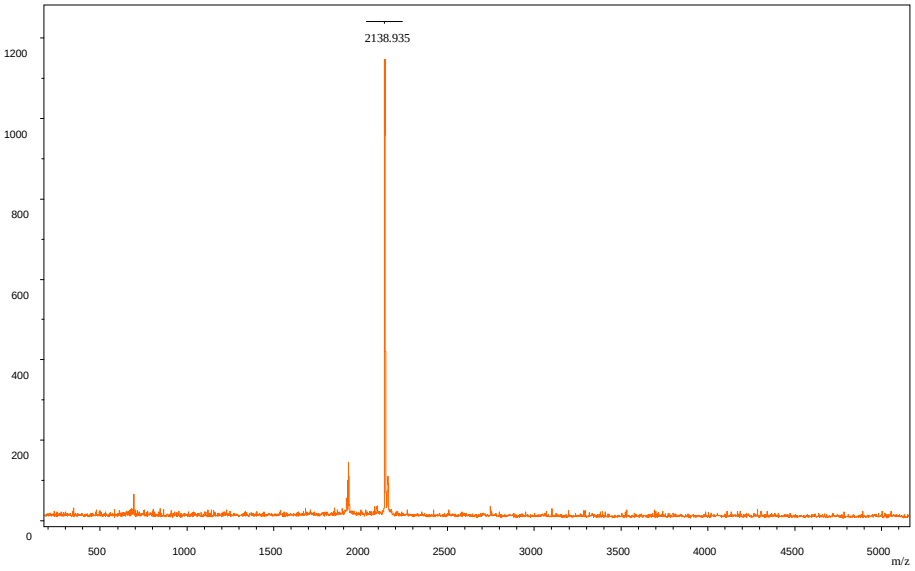

Fig. S2. MALDI-TOF mass spectrum of Zn-*tri*-PcNc-8.

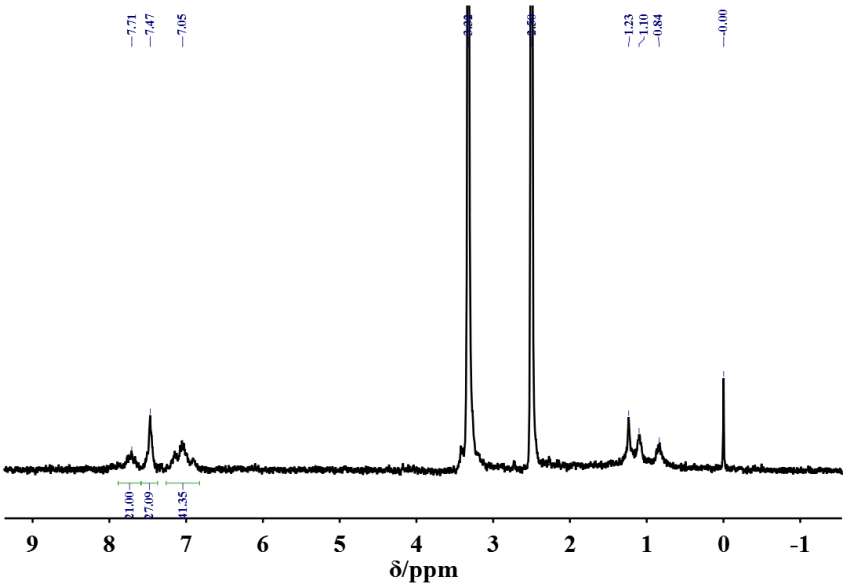

Fig. S3. ^{1}H MNR (in DMSO-d_6) spectrum of the molecular ion of Zn-*tri*-PcNc-8a

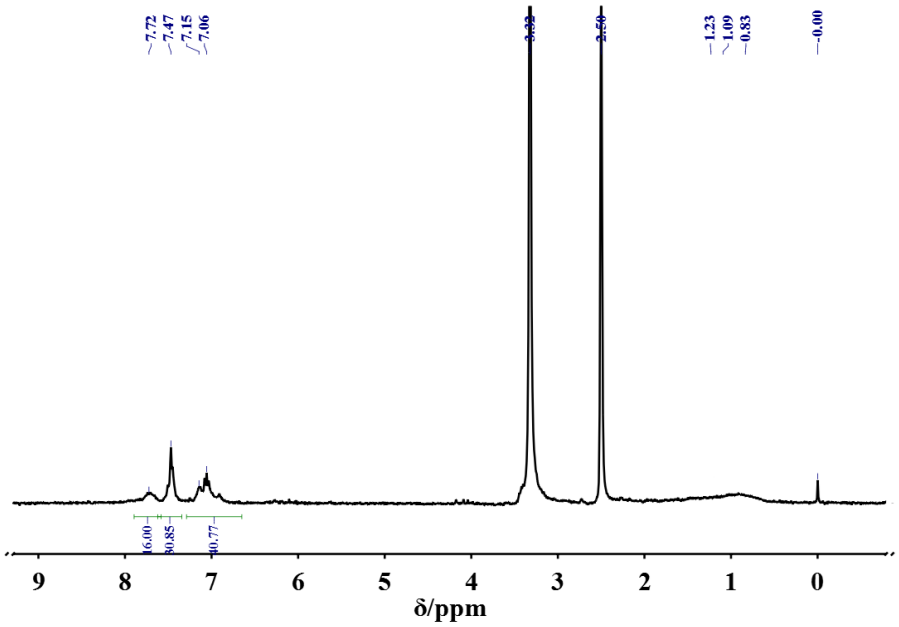

Fig. S4. ^{1}H MNR (in DMSO-d_6) spectrum of the molecular ion of Zn-*tri*-PcNc-8

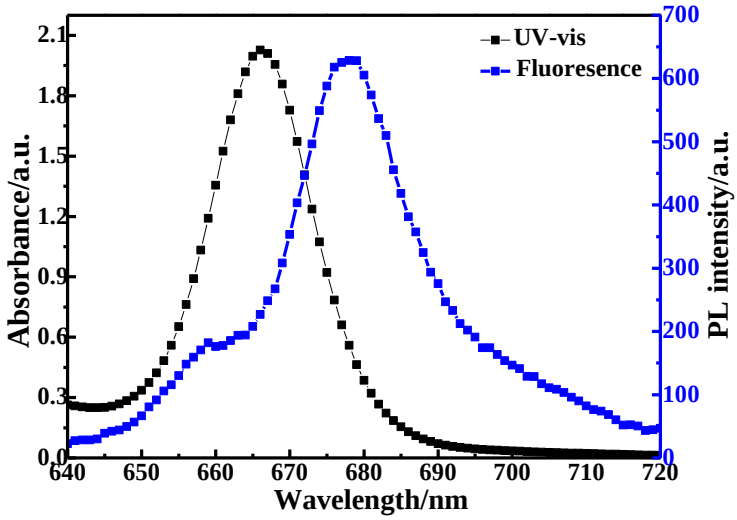

Fig. S5. UV-vis absorption spectra and Fluorescence emission spectra and of Std-ZnPc in THF solution (C=1 ×10^{-5} M) with excitation fixed at 620 nm.

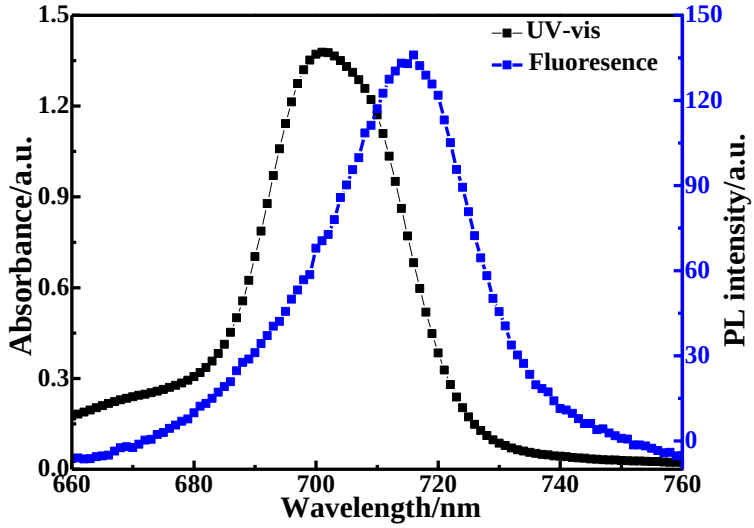

Fig. S6. UV-vis absorption spectra and Fluorescence emission spectra and of Zn-*tri*-PcNc-8 in THF solution (C=1 ×10^{-5} M) with excitation fixed at 480 nm.

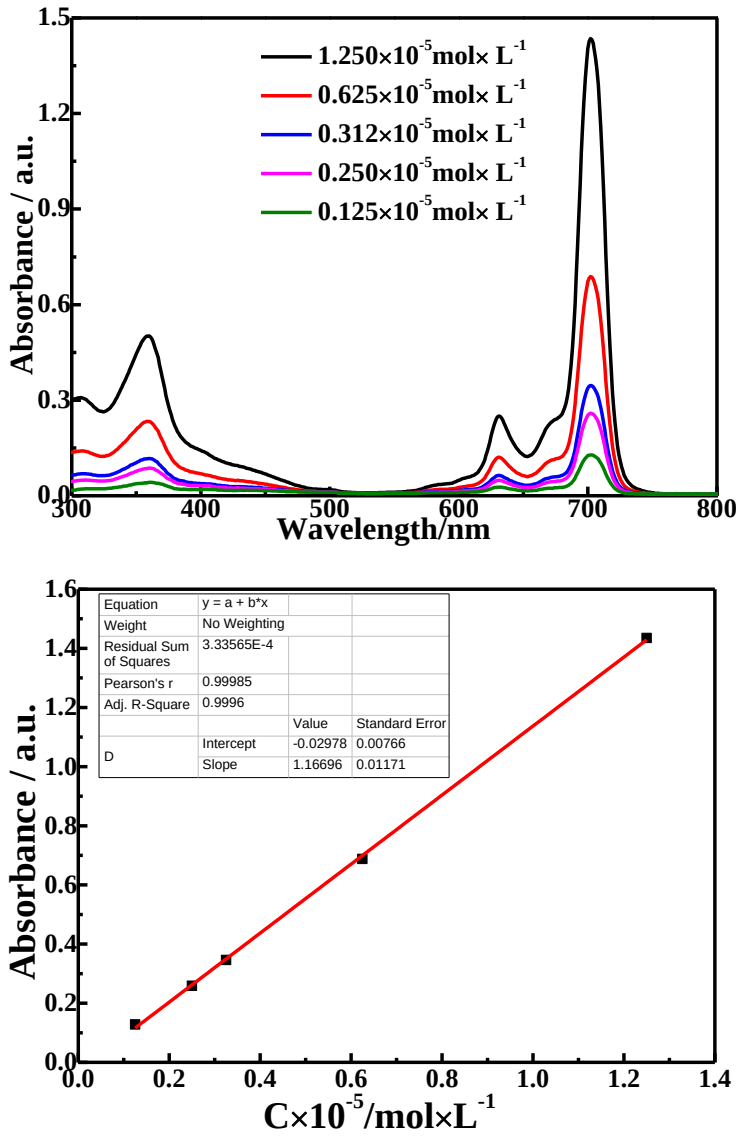

Fig. S7. UV-Vis absorption spectra of Zn-*tri*-PcNc-8 in THF at different concentration.

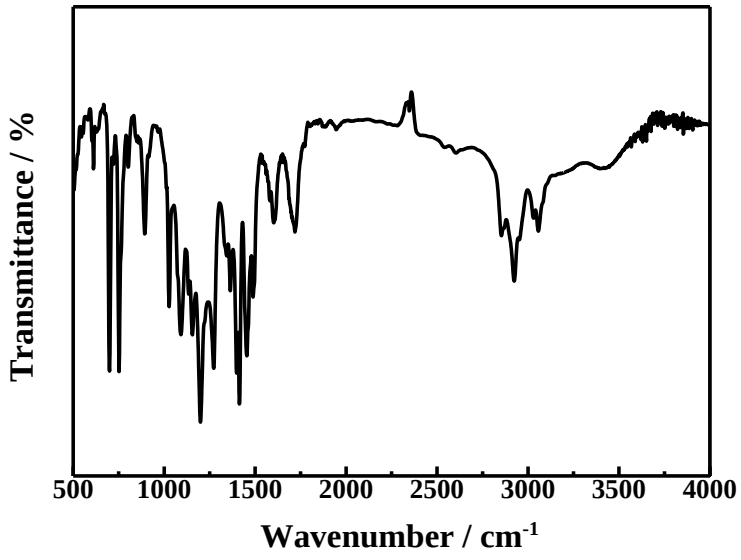

Fig. S8. IR spectra of Zn-*tri*-PcNc-8.

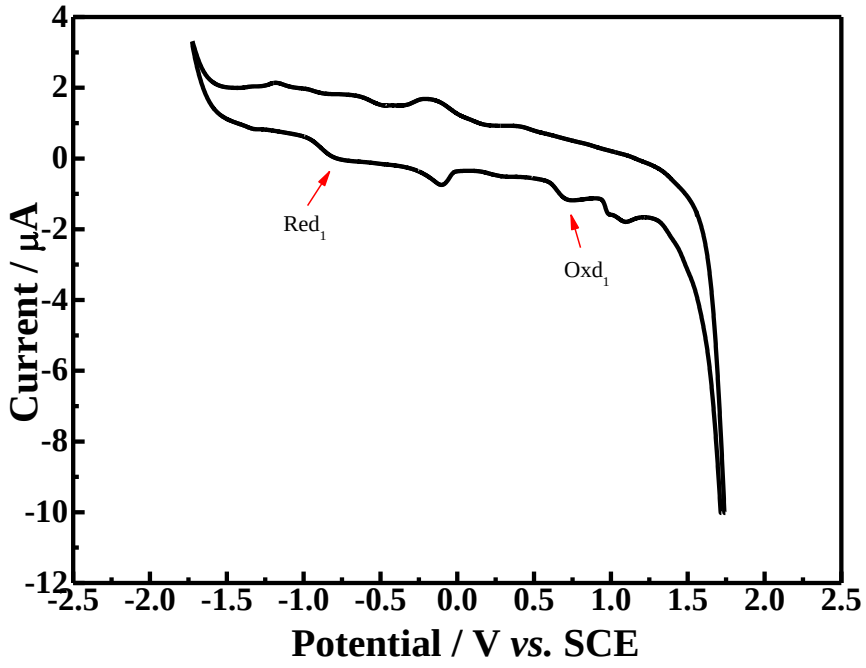

Fig. S9. The typical cyclic voltammogram of Zn-*tri*-PcNc-8 in o-DCB containing 0.1 M $[NBu_4][ClO_4]$ at a scan rate of 20 mV S^{-1}.

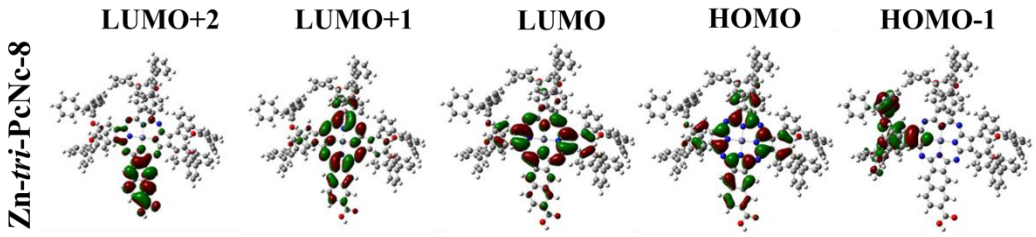

Fig. S10. The frontier molecular orbitals of Zn-*tri*-PcNc-8, full optimized at B3LYP/6-31G level.

Fluorescence quantum yields (ΦF): Fluorescence quantum yields (ΦF) of the studied Zn-tri-PcNc-8 was determined in THF by the comparative method using equation.[1-2]

$$\emptyset\mathrm{F} = \emptyset\mathrm{F(Std)}\frac{F \times A_{std} \times n^2}{F_{std} \times A \times n_{std}^2}$$

F and F_{Std} are the areas under the fluorescence emission curves of the Zn-*tri*-PcNc-8 and the unsubstituted zinc(II)Pc (the standard Std-ZnPc), respectively. *A* and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n^2 and n_{Std}^2 are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (Std-ZnPc) (ϕF = 0.30 in THF)[2] was employed as the standard.

1. N. Kobayashi, H. Ogata, N. Nonaka and E. A. Luk'yanets, *Chem. Eur. J.* 2003, **9**, 5123-5134.
2. M. M. Ayhan, G. A. Özpinar, M. Durmus and A. G. Gürek, *Dalton Trans.*, 2013, **42**, 14892-14904.

Table S1. Fluorescence Emission Data of Zinc Phthalocyanines in THF.

Dye	Excitation wavelength λ [nm]	Fluorescence peak maximum λ [nm]	Fluorescence quantum yield ϕF
Std-ZnPc	620	678	0.30
Zn-*tri*-PcNc-8	480	716	0.31

Table S2. Electrochemical Data of Zn-*tri*-PcNc-8**.**

Dye	Oxd_2	Oxd_1	Red_1	Red_2	$\Delta E^o_{1/2}$ [a]
Zn-*tri*-PcNc-8	0.99	0.62	-1.07	-1.39	1.69

[a] $\Delta E^o_{1/2}$ is the potential difference between the first oxidation and first reduction processes.

Table S3. TD-DFT Calculated Spectra Selected (Lowest-Excited Energies (ΔE), Absorption Wavelengths, Oscillator Strengths (*f*), and Domination Excitation Characters for Low-Lying Singlet State) of Zn-*tri*-PcNc-2 and Zn-*tri*-PcNc-8.

Dye	State	Theoretically calculated				Experimental	
		Δ*E*(eV)	λ(nm)	Main configuration	*f*	Δ*E*(eV)	λ (nm)
Zn-*tri*-PcNc-2	1	1.88	661	219[a]→220[b] 70%	0.625	1.76	694
	2	1.93	644	219→221 70%	0.828		
	3	2.61	475	219→222 70%	0.035		
	6	3.08	403	216→220 19%	0.028		
				217→220 15%			
				218→220 64%			
	7	3.14	394	214→220 13%	0.123		
				218→221 67%			
				219→223 10%			
	8	3.17	391	216→220 24%	0.018		
				217→220 58%			
				218→220 23%			
	9	3.23	384	216→220 52%	0.018		
				217→220 28%			
				217→221 23%			
	10	3.23	383	216→220 21%	0.023		
				216→221 35%			
				217→223 47%			
Zn-*tri*-PcNc-8	1	1.85	669	555[a]→556[b] 70%	0.625	1.75	702
	2	1.90	652	555→557 70%	0.772		
	3	2.56	484	553→557 13%	0.034		
				555→558 67%			
	4	2.58	479	553→556 35%	0.011		
				554→556 56%			
	5	2.62	472	553→557 26%	0.017		
				554→557 58%			

6	2.67	463	553→556	54%	0.117
			554→556	32%	
			554→557	25%	
7	2.72	455	553→557	63%	0.177
			554→556	13%	
			554→557	26%	
8	2.77	447	552→556	63%	0.094
			552→557	13%	
			553→556	13%	
9	2.87	432	551→557	18%	0.115
			552→556	14%	
			552→557	65%	

[a] HOMO; [b] LUMO.