Supplementary Information for

Novel Porphyrin-Phthalocyanine Heterodimers and Heteropentamers: Synthesis, Characterization and Application in Organic Solar Cell[†]

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[†] Electronic supplementary information (ESI) available: Experimental and synthesis details, characterization for all new compounds.

Materials

Chemicals used in the present work, such as DMSO, *o*-dichlorobenzene and potassium carbonate are purchased from Beijing Chemical Reagent Corporation, PR China. 4-nitrophthalonitrile, DBU, subphthalocyanin and were purchased from Sigma-Aldrich. All chemicals used in the present work are analytical reagent grade.

Synthesis of compounds

meso-tetra [4-(3, 4-dicyanophenoxy) phenyl] – porphyrin (TDPP)

A mixture of HTPP (**2**) (0.1 g), 4-nitrophthalonitrile (0.155 g) and potassium carbonate (0.276g) in DMSO (50 mL) was heated at 80 °C for 10 h with stirring under nitrogen atmosphere. DMSO was dried over alumina before use. After cooling to room temperature, the mixture was added to 40 mL ethanol and filtrated, then washed with 100 mL water three times to remove potassium carbonate and DMSO. Column chromatography on silica gel with the mixture solvent (DMF: toluene = 5:1) as eluent gave one band. Removal of the mixture solvent by evaporation gave 0.162 g (92.8%) of a purple–red solid. The TDPP (molecule structure seen in Fig. S1a) has been characterized by IR spectrum, UV-vis absorption spectrum, ^{1}HNMR, and mass spectrum, respectively. IR [(KBr) m_{max}/cm^{-1}]: 2231 (CN), 1250 (C–O–C); UV-Vis [DMSO, $k_{max/nm}$]: 420, 515, 550, 591; ^{1}HNMR (400 MHz, $CDCl_3$), δ 8.69-8.66 (br d, 8H, pyrrole-H), 8.62 (br s, 8H, phthalonitrile H), 7.95–7.98 (d, 4H, phthalonitrile H), 7.64-7.74 (d, 16H, phenyl-H), -2.83 (s, 2H, pyrrole N-H); MALDI-TOF-MS *m*/*z*: calc. 1181.2; found 1183.6 [M+2]$^+$.

Dimer 1 (ZnPor-O-ZnPc)

A mixture of TDPP (0.05 g), subphthalocyanin (0.1g), hydrous zinc acetate (0.1 g) and DBU (2 drops) in DMSO (20 mL) was heated at 120 °C for 23 h with stirring under nitrogen atmosphere. DMSO was dried over alumina before use. After cooling to room temperature, the mixture was added to 200 mL deionized water and filtrated, then washed with 100 mL water three times to remove excess zinc acetate, acetic acid and DMSO. Column chromatography on silica gel with the mixture solvent (acetic ether: toluene = 1:2) as eluent gave the first band. Removal of the mixture solvent by evaporation gave 0.024 g (33.4%) of a blue-green solid. The dimer has been characterized by IR spectrum, UV-vis absorption spectrum, ^{1}HNMR, and mass spectrum, respectively (see Fig. S2-S5). IR [(KBr) m_{max}/cm^{-1}]: 2231 (CN), 1250 (C–O–C), 1334, 1166, 1117 and 888 (phthalocyanin ring); UV-Vis [DMSO, $k_{max/nm}$]: 340, 426, 560, 603, 668; ^{1}HNMR (400 MHz, $CDCl_3$), δ 9.01 (s, 3H, phthalocyanin-H), 8.27-8.39 (br s, 8H, pyrrole-H), 7.81-7.94 (d, 16H, phenyl-H), 7.68–7.80 (d, 12H, phthalocyanin-H), 7.46–7.66 (d, 9H, phenoxy-H); MALDI-TOF-MS *m*/*z*: calc. 1697.3; found 1697.34 $[M]^+$.

Pentamer 2 (ZnPor-(O-ZnPc)$_4$)

A mixture of TDPP (0.05 g), *o*-benzenedinitrile(0.65g) and zinc chloride (0.1 g) in mixture of *o*-dichlorobenzene and *N,N*-dimethylaminoethanol (DMAE) (10 mL) was heated at 145 °C for 24 h with stirring under nitrogen atmosphere. The mixture of *o*-dichlorobenzene and *N, N*-dimethylaminoethanol (DMAE) was treated with ultrasound deaeration before use. After cooling to room temperature, the mixture was added to 100 mL methanol and filtrated, then washed with 100 mL water three times to remove excess zinc chloride, chloride acid and DMAE. Two of bright blue bands were eluted by the mixture of (acetonitrile: toluene = 1:2). The desired compound (navy blue band) was eluted using DMF: toluene = 1:3. Removal of the mixture solvent by evaporation gave 0.014 g (10.8%) of a blue solid. The pentamer has been characterized by IR spectrum, UV-vis absorption spectrum, ^{1}HNMR, and mass spectrum, respectively (see Fig. S6-S9). IR [(KBr) m_{max}/cm^{-1}]: 1285 (C–O–C), 1333, 1118, and 888 (phthalocyanin ring); UV-Vis [DMSO, $k_{max/nm}$]: 342, 428, 605, 670; ^{1}HNMR (400 MHz, $CDCl_3$), δ 9.35-943 (d, 48H, phthalocyanin-H), 8.23-8.29 (d, 8H, pyrrole-H), 7.92-7.98 (d, 16H, phenyl-H), 7.82–7.84 (d, 4H, phthalocyanin-H), 7.68–7.74 (d, 8H, phthalocyanin-H); MALDI-TOF-MS *m*/*z*: calc. 3045.79; found 3045.86 $[M]^+$.

Fabrication of Devices

Devices were fabricated on cleaned and patterned indium tin oxide (ITO) -coated glass substrates with a sheet resistance of 60 Ω/□. In all devices, porphyrin-phthalocyanine compoumds are used as the donors and [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM) is as the acceptor. The mixture solution of porphyrin-phthalocyanine compoumds (5 mg/mL) and PCBM with different weight ratio were deposited on substrates by spin coating method at 1500 rpm for 50 s. Then some devices were annealed in vacuum at different temperature, 100 °C, 120 °C, 140°C and 160 °C respectively for 20 min. The cathode Al for all devices was deposited by thermal evaporation under 1×10^{-3} Pa. The device ITO/PEDOT:PSS/ZnTPP:PCBM/LiF/Al (device 3) and ITO/PEDOT:PSS/ZnTCPc/ PCBM/LiF/Al (device 4) also were fabricated for comparison. The active area of each device is 0.1 cm^2 as limited by a shadow mask. The current-voltage (*I*-*V*) characteristics were measured using a Keithley 2400 parameter analyzer under a light intensity of 100 mW/cm^2 (AM 1.5G).

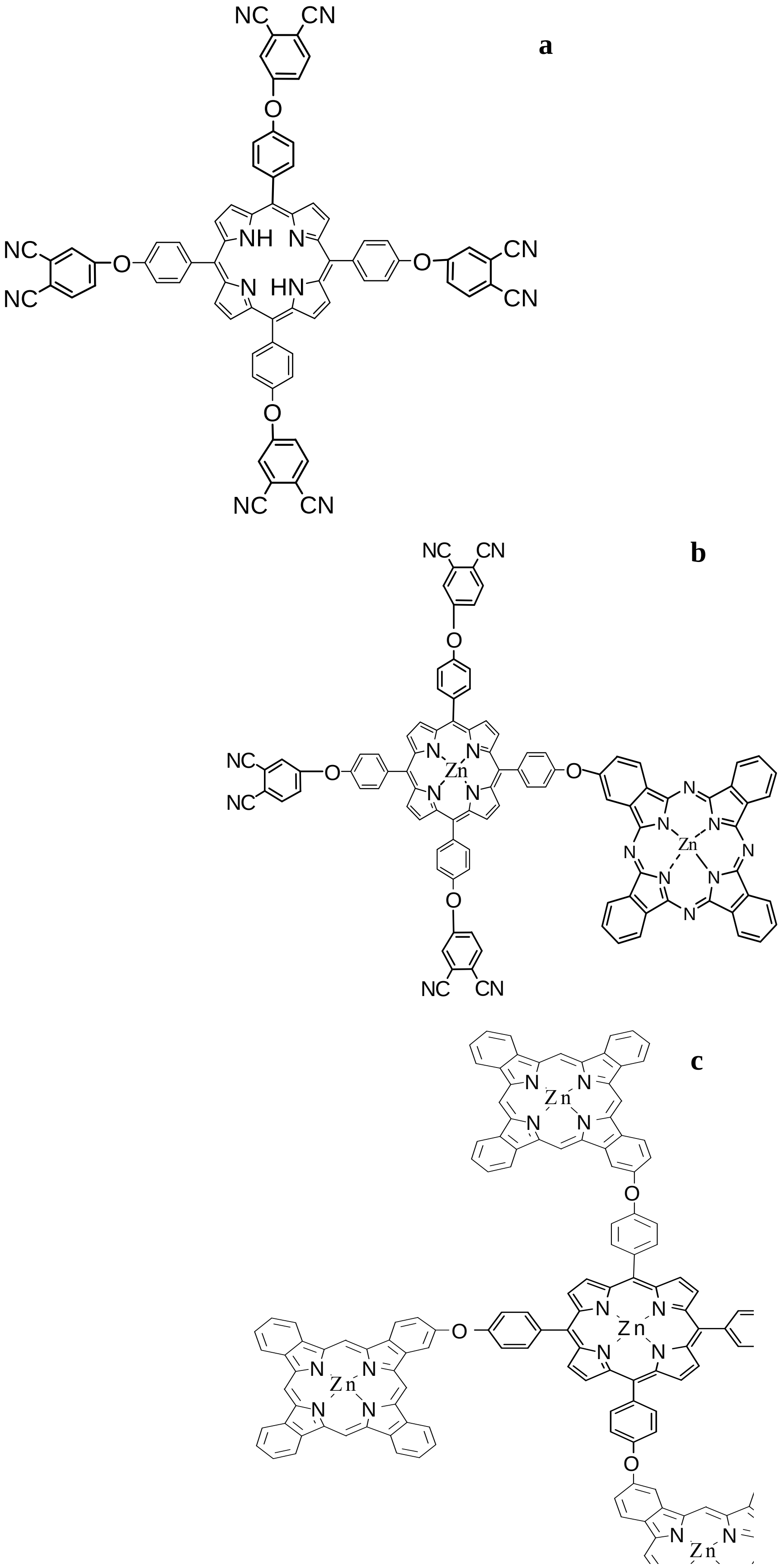

Fig. S1 Molecular structure of TDPP (a), ZnPor-O-ZnPc (b), and ZnPor-(O-ZnPc)$_4$ (c).

Characterization results of Dimer 1 (ZnPor-O-ZnPc)

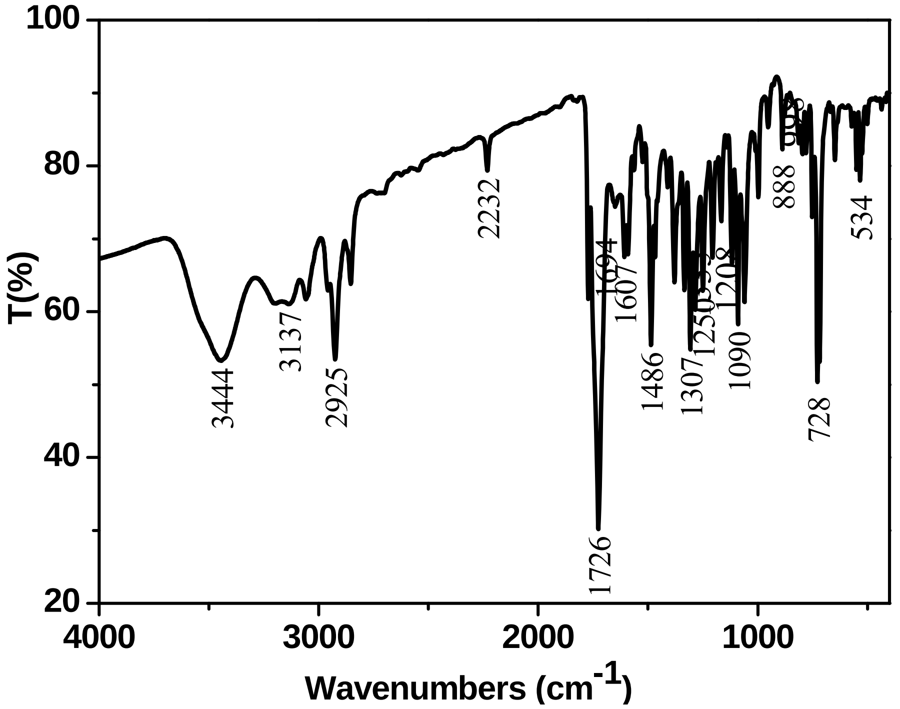

Fig. S2. IR spectrum of the ZnPor-O-ZnPc.

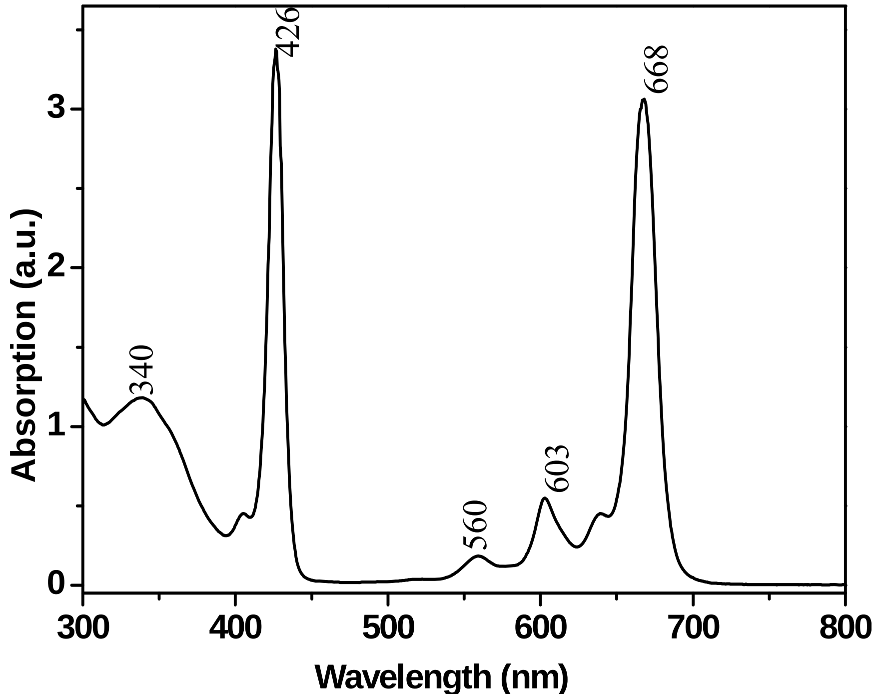

Fig. S3. UV-visible absorption spectrum of the ZnPor-O-ZnPc.

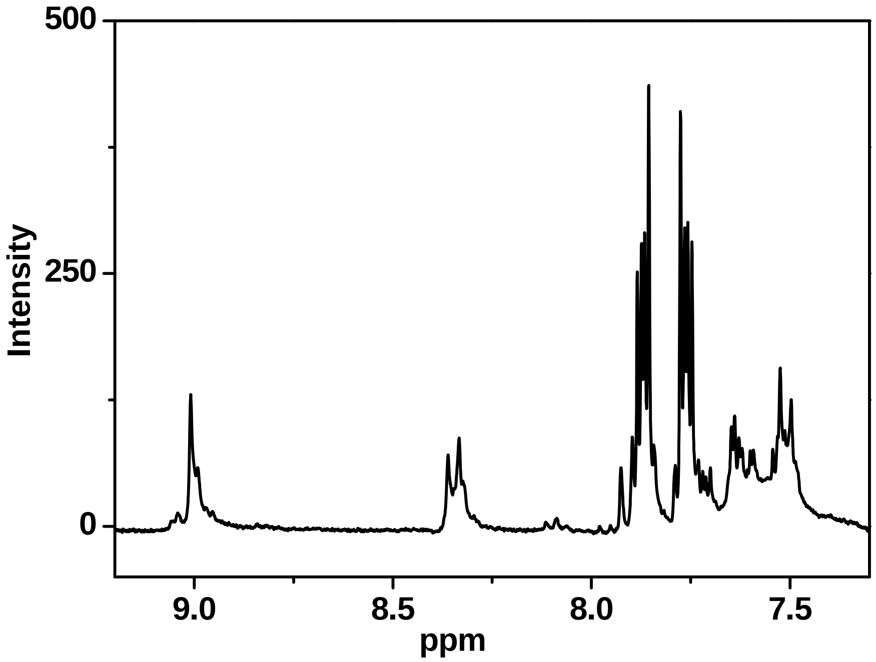

Fig. S4. ^{1}HNMR spectrum of the ZnPor-O-ZnPc.

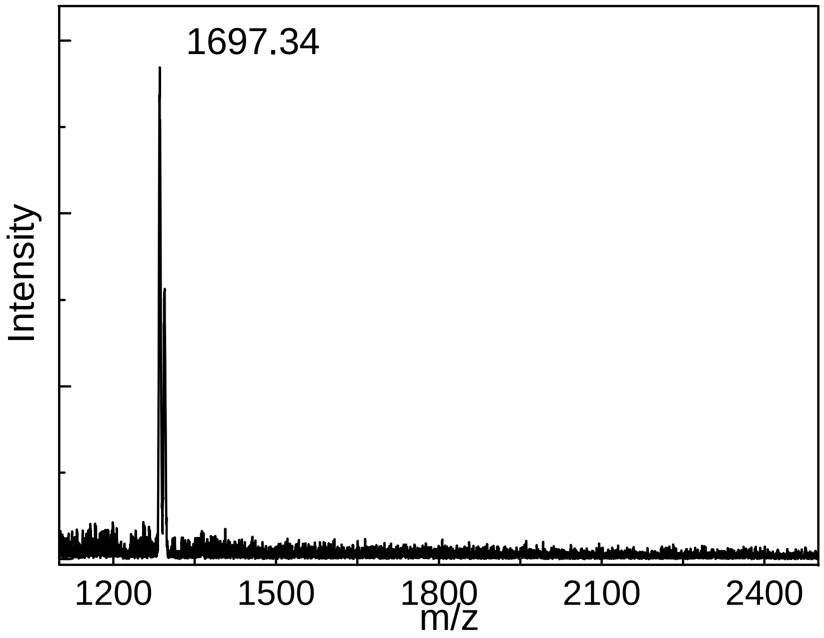

Fig. S5. Mass spectrum of the ZnPor-O-ZnPc.

Characterization results of Pentamer 2 (ZnPor-(O-ZnPc)$_4$)

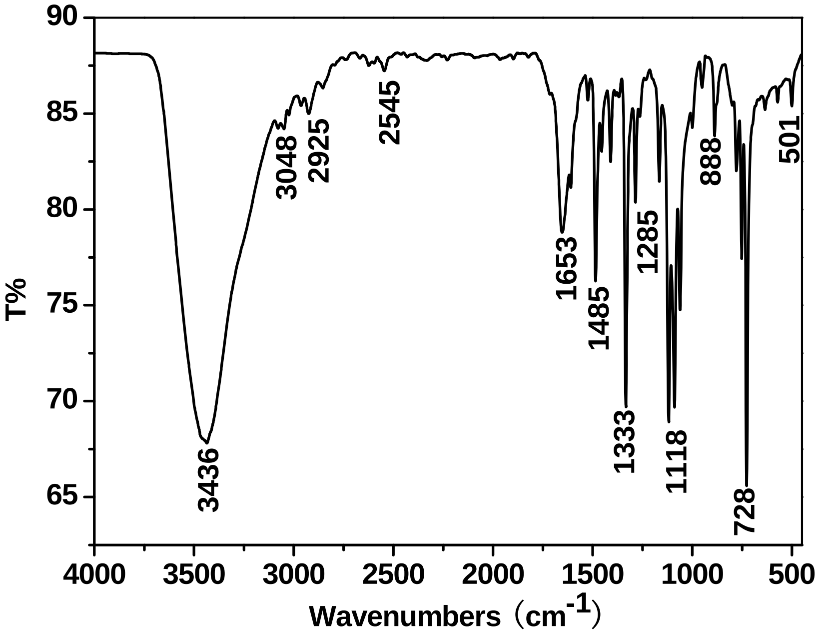

Fig. S6. IR spectrum of the ZnPor-(O-ZnPc)$_4$.

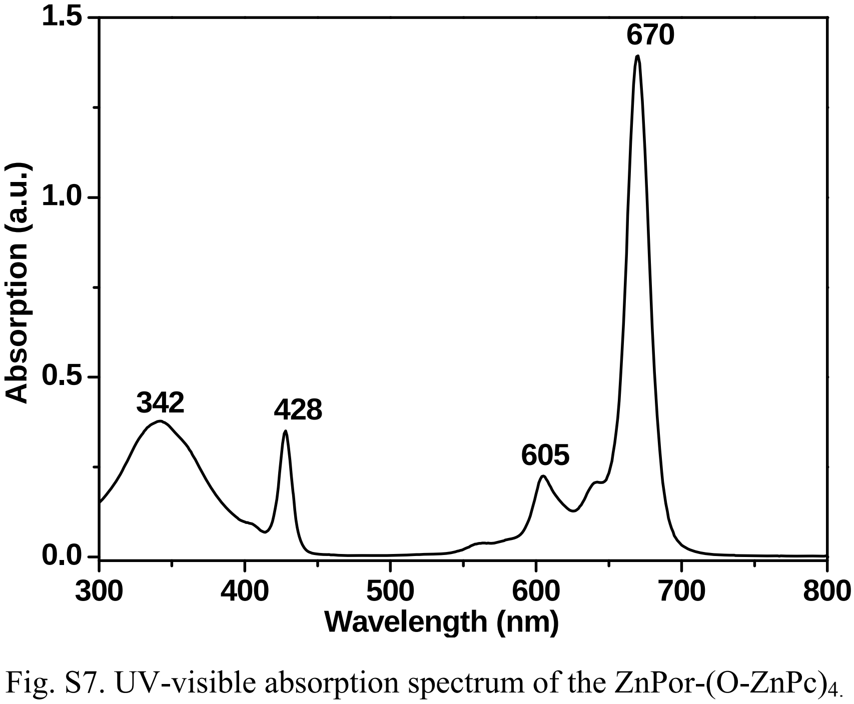

Fig. S7. UV-visible absorption spectrum of the ZnPor-(O-ZnPc)$_4$.

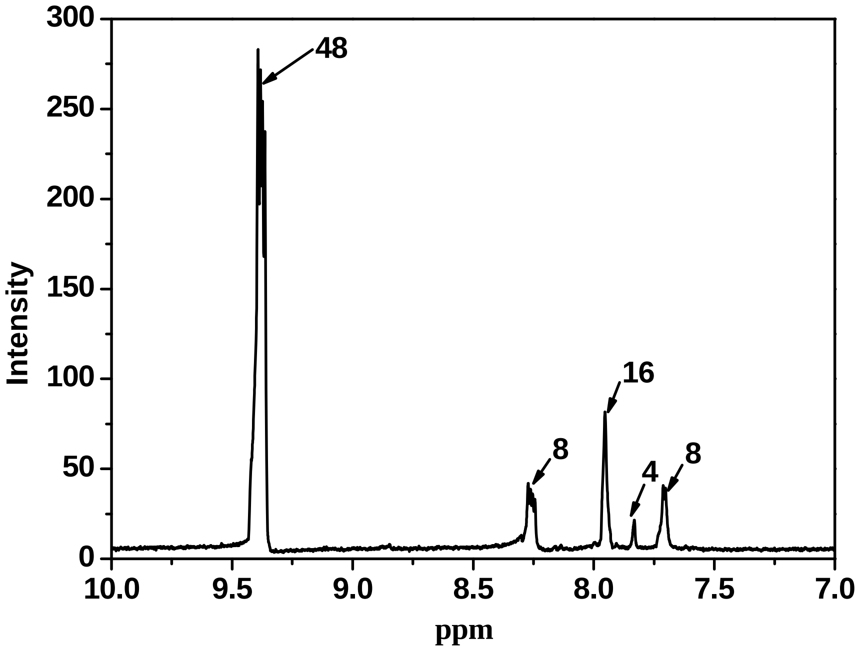

Fig. S8. ^{1}HNMR spectrum of the ZnPor-(O-ZnPc)$_{4.}$

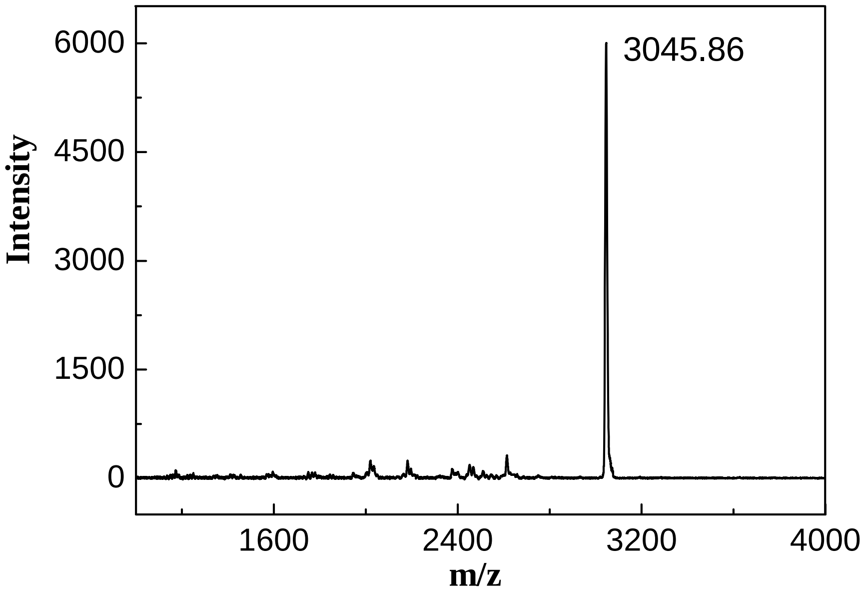

Fig. S9. Mass spectrum of the ZnPor-(O-ZnPc)$_{4.}$

References:

S1 Z.-F. Li, Y.-X. Wang and Y.-Q. Wang, *Journal of Shandong University of Technology (Sci & Tech),* 2003, **19**, 1-7.

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S3 Z. –X. Zhao, K. I. Ozoemena, D. M. Maree and T. Nyokong, *Dalton Trans.*, 2005, 1241-1248.