Supplementary Information

Morphology controlled supramolecular assemblies *via* complexation between (5, 10, 15, 20-tetrakisphenyl-porphine) zinc and 4, 4'-bipyridine: from nanospheres to microrings

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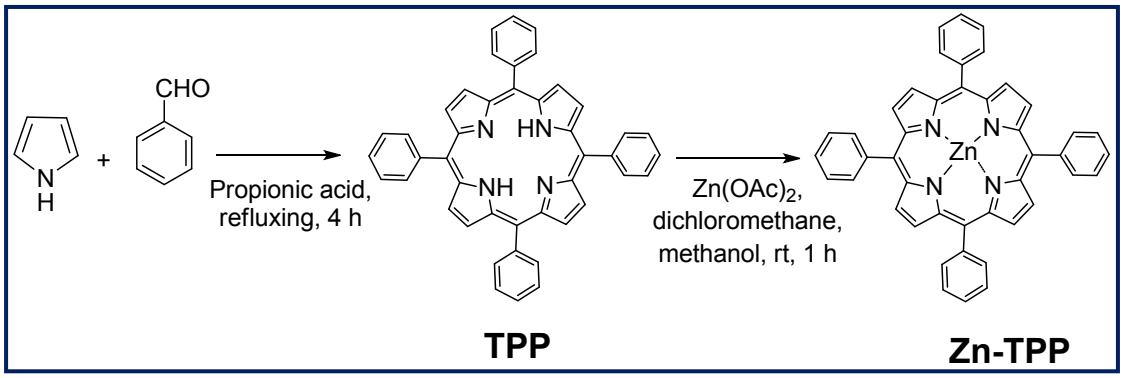
Materials

Pyrrole, benzaldehyde and 4, 4'-bipyridine were purchased from Aladdin-chemicals and used as received. Chloroform, dichloromethane, carbon tetrachloride and other chemicals were purchased from Sinopharm Chemical Reagent.

Characterization

^{1}H-NMR, and ^{13}C-NMR spectra were recorded at 400 MHz, using BRUKER AV400 spectrophotometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. Mass spectra were recorded on Waters LCT Premier XE Spectrometer. Absorption spectra were recorded at SHIMADZU UV-2550 UV spectrophotometer using in quartz Cuvette with 1 cm beam path length, and emission spectra were recorded at Varian's Cary Eclipse fluorescence spectrophotometer at 420 nm as excitation wavelength. Dynamic light scattering (DLS) measurements were carried out on NICOMP TM 380ZLS of PSS-NICOMP particle sizer systems, USA. Transmission electron microscopy (TEM) images were taken on a JEOL JEM1400 electron microscopes operated at 100 KV with carbon-coated copper grid. Atomic force microscope (AFM) images were taken on a Nano naviE-Sweep of Digital Instruments

using Tapping Mode. The AFM samples were prepared by drying 10 μL droplet of solution onto freshly cleaved mica. FTIR spectroscopy was carried out on Nicolet Nexus 670 FTIR spectrometer using KBr pellets.



Scheme S1. Synthesis of 5, 10, 15, 20-tetraphenylporphyrin (H_2TPP) and (tetrakisphenyl-porphine) zinc(Zn-TPP)

Synthesis of 5, 10, 15, 20-tetraphenylporphyrin (H_2TPP)

A three-necked flask (500 mL) was charged with a magnetic stirring bar. Propionic acid (300 mL) in redistilled pyrrole (7.0 mL, 0.1 mol), and benzaldehyde (7.6 mL, 0.1 mol) were added into above flask and the solution was refluxed for 4 h under stirring. Propionic acid was removed under reduced pressure, and then methanol (100 mL) was added. The reaction mixture was filtered after putting in fridge for 12 h. The final product was purified by silica gel column with chloroform/methanol (95/5, v/v) as the eluent to afford 0.5 g, yield 23%. ^{1}H NMR (400 MHz, $CDCl_3$,δ): 8.88 (s, 8H, py), 8.25 (m, 8H, 2, 6-ph), 7.79 (m, 12H, 3, 4, 5-ph), -2.76(s, 2H,-NH-py); ^{13}C (100 MHz, $CDCl_3$, δ) 120.2, 126.8, 127.8, 131.4, 134.7 and 142.3; TOF-MS (EI, m/z): calcd for $C_{44}H_{30}N_4$, 614.3.

Synthesis of (5, 10, 15, 20-tetrakisphenyl-porphine) zinc (ZnTPP)

In a 250 mL round-bottom flask, 5, 10, 15, 20-tetraphenylporphyrin, TPP (0.1 g, 0.16 mmol) was dissolved in 80 mL mixture solvent of DCM and methanol (v/v, 3/1). Zinc acetate (0.3 g, 1.6 mmol) was then added, and the reaction mixture was stirred for 5 h at room temperature. After reaction, the solvent was removed under reduced pressure.

The crude product was purified by silica gel column with chloroform to afford 0.11g, yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.95 (s, 8H, py), 8.26 (m, 8H, 2,6-ph), 7.78 (m, 12H, 3, 4, 5-ph). TOF-MS (EI, m/z): calcd for $C_{44}H_{28}N_4Zn$, 676.2.

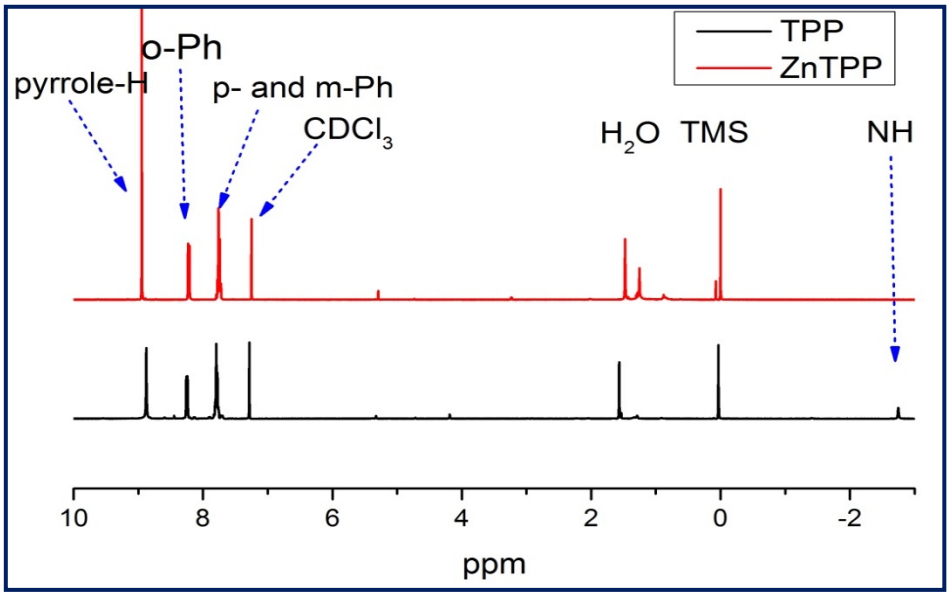


Fig. S1. 1H NMR spectrum of H2TPP and ZnTPP.

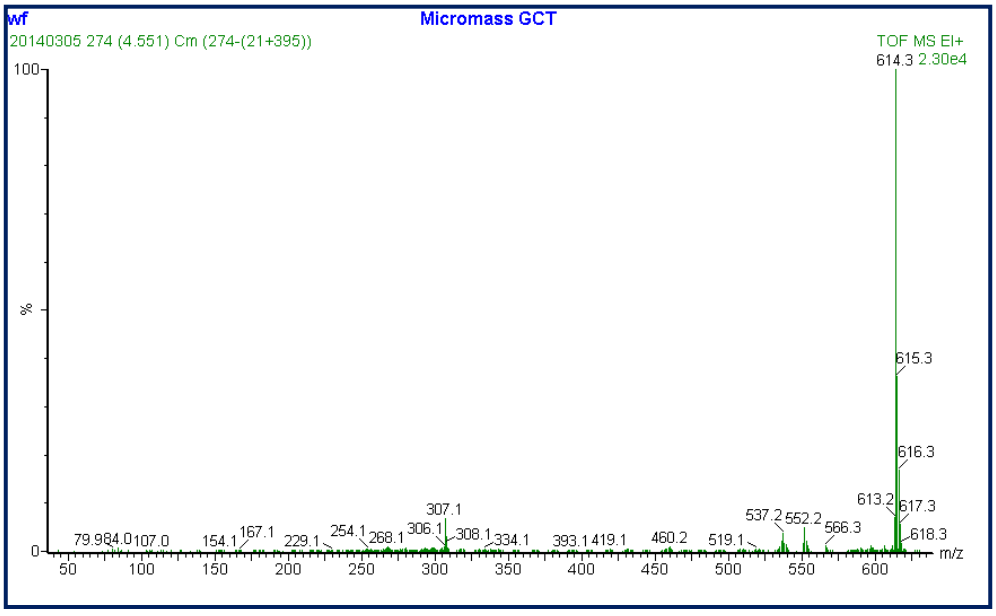


Fig. S2. TOF-MS spectrum for H_2TPP, calcd for $C_{44}H_{30}N_4$, 614.3.

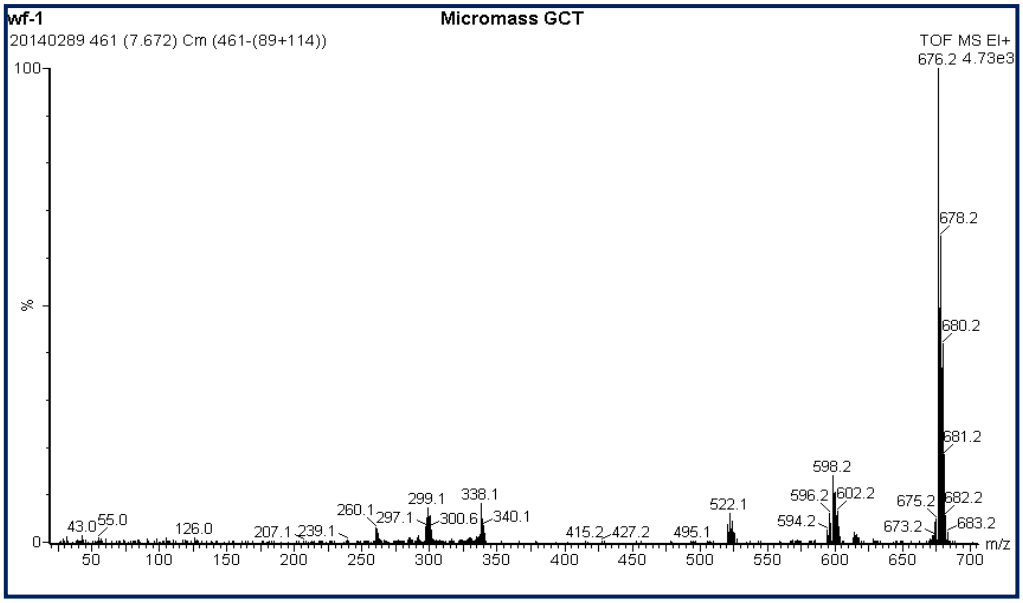


Fig. S3. TOF-MS spectrum for ZnTPP calcd for $C_{44}H_{28}N_4Zn$, 676.2.

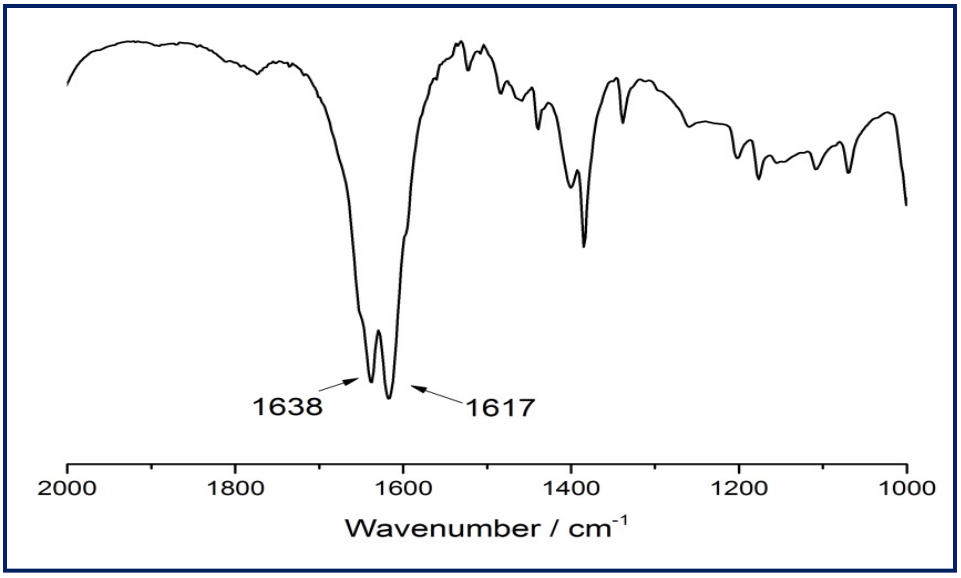


Fig. S4. FT-IR spectrum of Zn-TPP.

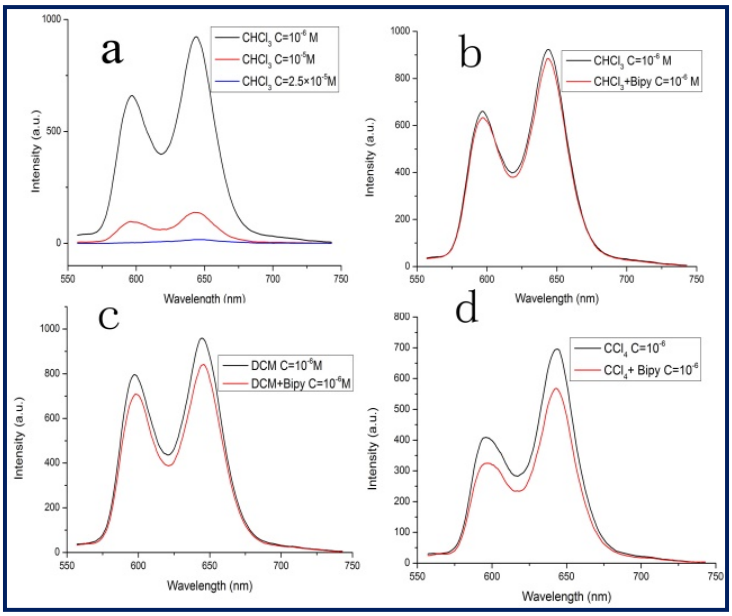


Fig. S5. Fluorescence spectra of ZnTPP in chloroform with different concentrations (a); and fluorescence spectra of ZnTPP in different solutions with and without Bipy at 1.0 × 10^{-6} M, (b) chloroform, (c) dichloromethane and (d) carbon tetrachloride.

References

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