

Supporting Information for

Construction of Multidimension Nanostructure by Self-assembly of Porphyrin Analogue

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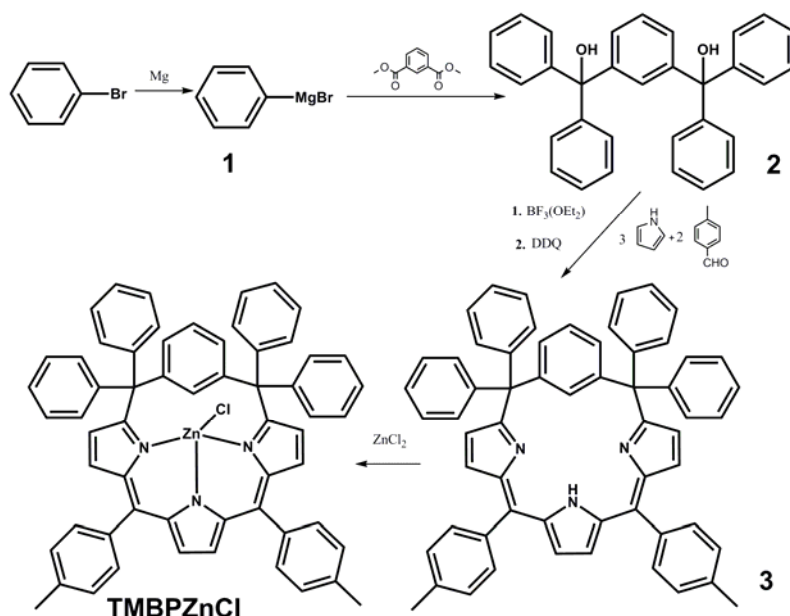
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General Remarks. Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich Chemicals and were used without further purification. Column chromatography (CC): SiO₂ (200-300 mesh). TLC glass plates coated with silica (F254) were visualized under UV light. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 25°C. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometric measurements were performed on a Bruker Biflex III MALDI-TOF instrument. UV/Vis spectra were measured on a Hitachi U-3010 spectrometer, and FTIR spectra were recorded as KBr pellets on a Perkin - Elmer System 2000 spectrometer. Fluorescence excitation and emission spectra were recorded with a Hitachi F-4500 FL fluorimeter at a constant temperature of 25°C. SEM images were taken using a field emission scanning electron microscope (SEM) (Hitachi 4300F and DB-235 FIB), operated at an acceleration voltage of 5-15kV. Transmission electron microscopy (TEM) images were taken using a JEOL-2011 microscope operated at 200kV. The samples were prepared by transferring the samples from the silicon slides by carbon-copper grids wetted with methanol. All single crystal X-ray diffraction data were collected on a Rigaku Saturn X-ray diffractometer with graphite-monochromator

Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K. Intensities were collected for absorption effects using the multi-scan technique SADABS. The structures were solved by direction methods and refined by a full matrix least squares technique based on F2 using SHELXL 97 program (Sheldrick, 1997). The extended packing plots and data from crystal packing were obtained using the software Mercury 1.4.1.

Experimental



Scheme s1. Synthesis of the porphyrin analogue TMBPZnCl.

Phenylmagnesium bromide (1)

In an oven-dried 1000ml three-necked flask equipped with a condenser, dropping funnel, mechanical stirrer, and nitrogen system were placed magnesium turnings (6.1 g, 250 mmol) with dry tetrahydrofuran (400 ml). Bromobenzene (36.9 g, 235 mmol) in dry tetrahydrofuran (100 ml) was added dropwise over 1h with gentle heating; when the reaction started the heat was removed. The reaction was allowed to go for 2 h. A brown color was observed. The solvent was removed under reduced pressure to give a black solid of crude compound **1** which was directly used in the next reaction.

1,3-phenylenebis(diphenylmethanol) (2)

Dimethyl isophthalate (1.94 g, 10 mmol) was dissolved in 150 ml of dry degassed THF. Crude phenylmagnesium bromide (44 ml of a 1 M solution in diethyl ether, 44 mmol) was added. After being stirred for 1 h, the reaction mixture was hydrolyzed with aqueous ammonium chloride and extracted with dichloromethane. The extracts

were washed twice with water, and the solvent was removed under reduced pressure. The crude product was passed through column chromatography on silica gel and eluted with dichloromethane/acetic ether (v/v, 1:2, $R_f = 0.2$) for purification. Compound **2** is isolated as yellowish viscous oil slowly crystallizing on standing. Yield: 3.54g, approximately 80%. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.49$ (t, 1H), 7.15-7.35 (m, 23H), 3.25 (b, 2H). ^{13}C NMR (CDCl_3): $\delta = 146.6, 146.4, 127.9, 127.8, 127.6, 126.9, 126.8, 126.7, 82.0$. Anal for $\text{C}_{32}\text{H}_{26}\text{O}_2$, C, 86.85 H, 5.92; found: C 86.25, H 6.02. EI: $m/z = 442.2 \text{ M}^+$, calcd for $\text{C}_{32}\text{H}_{26}\text{O}_2 = 442.55$.

11,16-Bis(p-tolyl)-6,6,21,21-tetramethyl-m-benzi-6,21-porphodimethene (3)

Compound **2** (442 mg, 1 mmol), pyrrole (208 μl , 3 mmol), and 4-methylbenzaldehyde (240 mg, 2 mmol) were added to dry dichloromethane (900 ml) under the atmosphere of nitrogen gas. The $\text{Et}_2\text{O}\cdot\text{BF}_3$ (100 μl) was added. The solution was protected from light and stirred for 2 h. After this time, DDQ (454 mg, 2 mmol) was added and dissolved by continuous stirring, and the reaction solvent was removed under reduced pressure. The residue was passed through column chromatography on silica gel and eluted with CH_2Cl_2 until the purple material had completely eluted to obtain crude product. The crude product was passed through column chromatography on silica gel again and eluted with dichloromethane/ petroleum ether (v/v, 2:1, $R_f = 0.3$). The solution was concentrated and purified to give a red powder of compound **3**. Yield: 100 mg (12%). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.32$ (1H); 7.30 (1H); 7.28-7.20 (20H); 7.18 (2H); 7.08-7.04 (4H); 6.78 (4H); 6.66 (2H); 6.33 (2H); 6.15 (2H); 2.41 (6H). ^{13}C NMR (CDCl_3): $\delta = 177.6; 150.8; 144.6; 144.4; 138.3; 137.4; 136.6; 135.1; 134.6; 130.2; 129.3; 128.8; 127.6; 127.1; 126.7; 126.5; 125.6; 125.0; 124.9; 120.3; 62.8; 20.2$. Anal for $\text{C}_{60}\text{H}_{45}\text{N}_3$, C, 89.19 H, 5.61, N, 5.20; found: C, 88.68 H, 5.49, N, 5.83. MALDI-TOF MS: $m/z = 808.0 \text{ M}^+$, calcd for $\text{C}_{60}\text{H}_{45}\text{N}_3 = 808.02$.

{11,16-Bis(p-tolyl)-6,6,21,21-tetramethyl-m-benzi-6,21-porphodimethene}zinc(II) chloride (TMBPZnCl)

Compound **3** (80.8 mg, 0.1 mmol) was dissolved in 50 ml of chloroform/acetonitrile (1:2). Anhydrous zinc chloride (13.6 ml of a 10 M solution in acetonitrile, 1 mmol) was added. After being stirred for 10 min, one drop of 2,6-lutidine was added into the

solution. Dried residue was dissolved in dichloromethane and excess zinc salt was extracted using distilled water. The organic layer was collected and solvent was removed by reduced pressure. The crude product was passed through column chromatography on silica gel again and eluted with dichloromethane/ petroleum ether (v/v, 3:2, $R_f=0.2$) for purification. The compound **TMBPZnCl** was obtained as dark purple powder. Yield: 72.6mg, approximately 80%. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.33$ (1H); 7.30 (1H); 7.28 (16H); 7.18-7.15 (6H); 7.08-7.04 (4H); 6.78 (4H); 6.66 (2H); 6.33 (2H); 6.15 (2H); 2.41 (6H). ^{13}C NMR (CDCl_3): $\delta = 177.6$; 150.8; 144.6; 144.4; 138.3; 137.4; 136.6; 135.1; 134.6; 130.2; 129.3; 128.9; 127.6; 127.1; 126.7; 126.5; 125.6; 125.0; 124.9; 120.3; 62.8; 20.2. Anal for $\text{C}_{60}\text{H}_{44}\text{ClN}_3\text{Zn}$, C, 79.38 H, 4.88, N, 4.63; found: C 79.20, H 4.95, N, 4.22. MALDI-TOF MS: $m/z = 907.2 \text{ M}^+$, calcd for $\text{C}_{60}\text{H}_{44}\text{ClN}_3\text{Zn} = 907.87$.

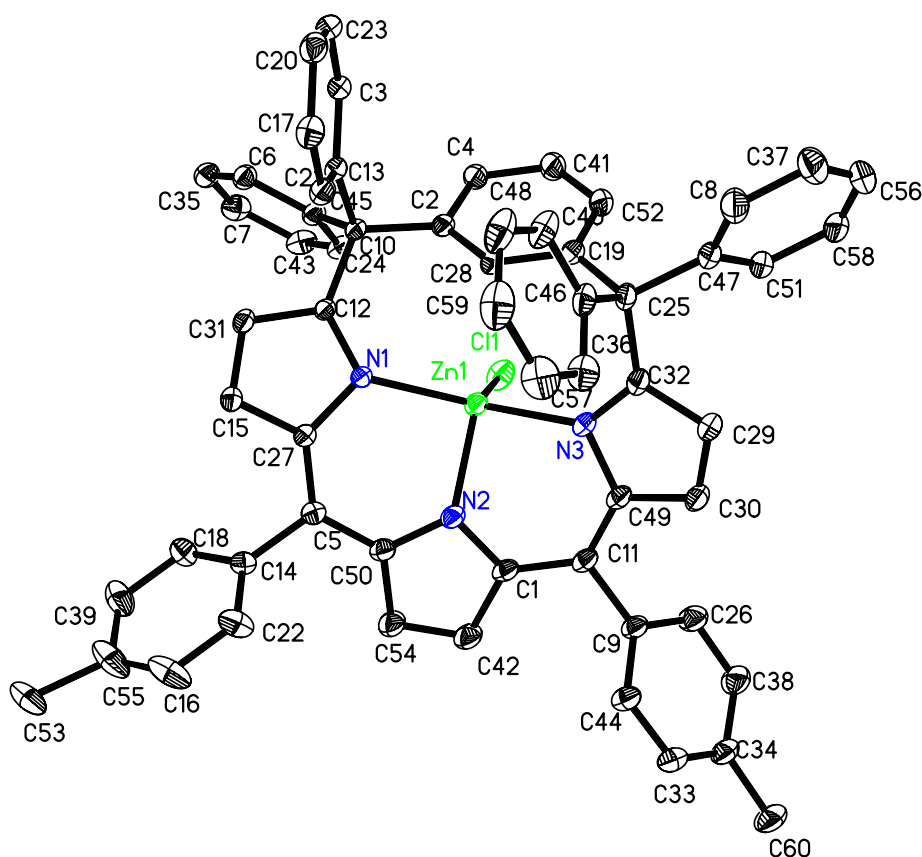


Fig. S1. The ORTEP diagram of TMBPZnCl in 50% probabilities of ellipsoids. In order to restrain the thermal movement of the atom of the molecule and tune the temperature impact factor, no less than 463 least-squares restraints were used in this refinement.

Chemical formula: $C_{60}H_{44}ClN_3Zn$

Formula weight (M): 907.80

Unit-cell dimensions (angstrom or pm, degrees) and volume, with estimated standard deviations:

$$\begin{aligned} a &= 10.586(2) \text{ \AA} & \alpha &= 100.74(3) \text{ deg.} \\ b &= 14.091(3) \text{ \AA} & \beta &= 100.99(3) \text{ deg.} \\ c &= 17.994(4) \text{ \AA} & \gamma &= 106.80(3) \text{ deg.} \\ U &= 2437.8(8) \text{ \AA}^3 \end{aligned}$$

Temperature: 173(2) K

Crystal system: Triclinic

No. of formula units in unit cell (Z): 2, 1.237 Mg/m³

Number of reflections measured and number of independent reflections: 33080 / 11168

Rint: 0.0554

Final R values (and whether quoted for all or observed data): R1 = 0.0653, wR2 = 0.1597

R indices (all data): R1 = 0.0748, wR2 = 0.1673

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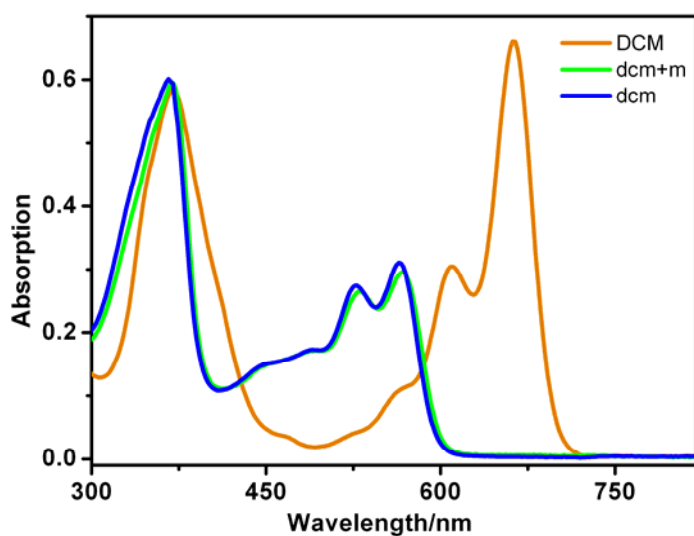


Fig. s2. UV-vis spectra of the compound **3** in CH_2Cl_2 (**dcm**), **3** in CH_2Cl_2/CH_3OH (v/v, 1/1) (**dcm+m**), **TMBPZnCl** in CH_2Cl_2 (**DCM**) at the concentration of 10^{-6} M.

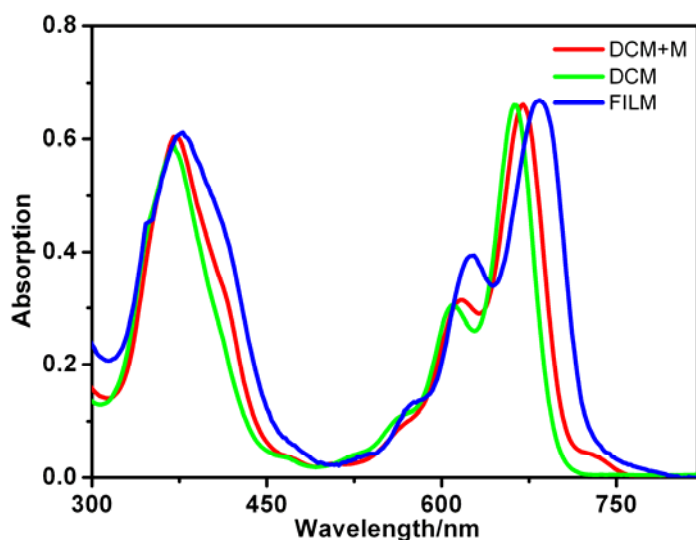


Fig. s3. UV-vis spectra of the compound **TMBPZnCl** in CH_2Cl_2 (**DCM**), **TMBPZnCl** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 1/1) (**DCM+M**) at the concentration of 10^{-6} M, and the film cast from the $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 1/1) solution (**FILM**).

Fig. s2 showed the UV-vis absorption spectra of **TMBPZnCl** resulted from CH_2Cl_2 , $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 1/1) at the concentration of 10^{-6} M and the film cast from the $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 1/1) solution of **TMBPZnCl**, respectively. The UV-vis spectra of the aggregated species were significantly different compared to the spectra of the corresponding porphyrin solutions. The absorption bands of the film were broadened and red-shifted compared with in the CH_2Cl_2 and $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 1/1). These observations demonstrated the methanol interacted with the porphyrin units and suggested “*J*” (edge-to-edge) type interaction in the vesicles.^{1,2}

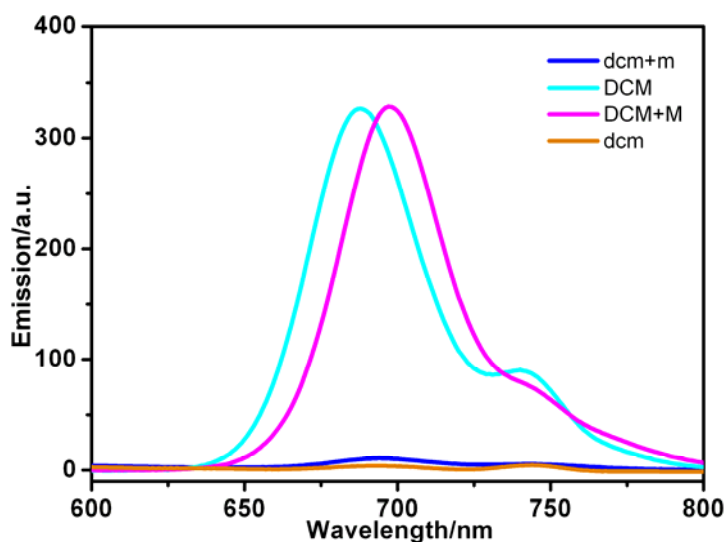


Fig. s4. Fluorescence spectra of the compound **3** in CH_2Cl_2 (**dcm**), **3** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 1/1) (**dcm+m**), **TMBPZnCl** in CH_2Cl_2 (**DCM**), **TMBPZnCl** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 1/1) (**DCM+M**) at the concentration of 10^{-6} M.

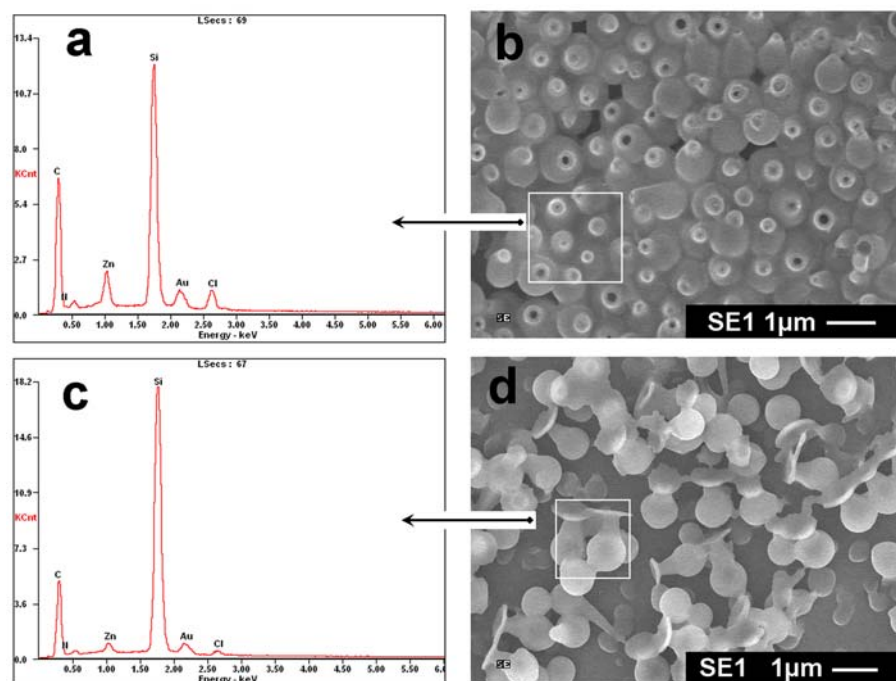


Fig. S5. The corresponding Energy Dispersive X-ray spectras (EDX), which show clearly that Zn peaks are present and that no other impurities are responsible for the observed self-assembly.

For energy-dispersive X-microanalysis, the aubergine-like and Ω -like vesicles of **TMBPZnCl** on the silicon slice were used directly. The results of energy-dispersive spectrum (EDS) showed that vesicles of **TMBPZnCl** on the silicon slice were composed of zinc, chlorine, nitrogen and carbon elements. The aurum was plating for pre-treatment of SEM samples.

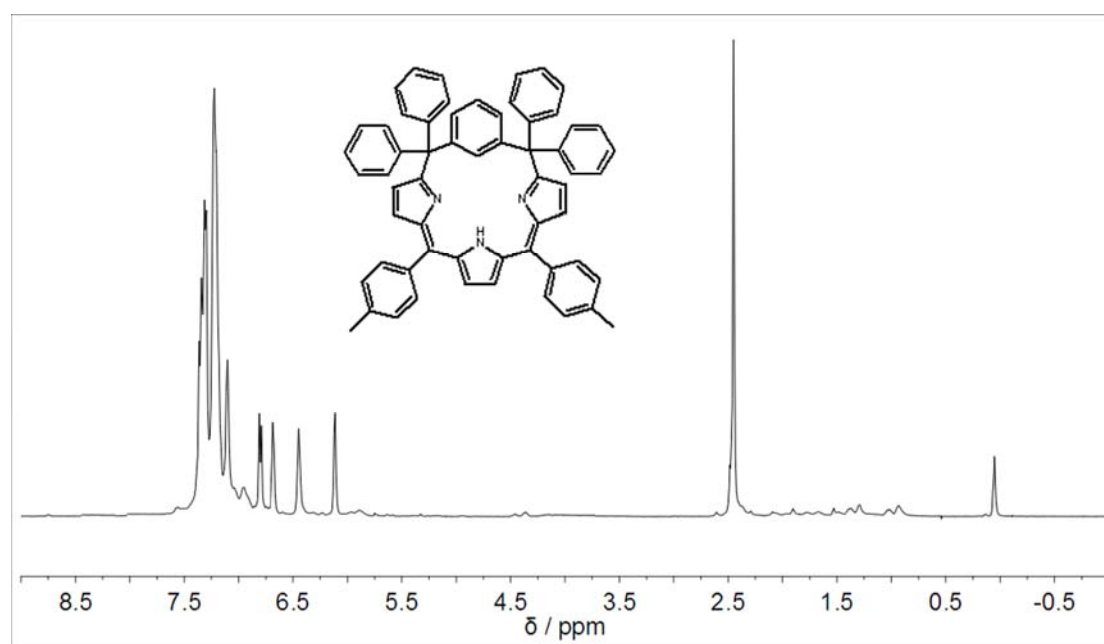


Fig. S6. The ¹H-NMR spectrum of compound 3.

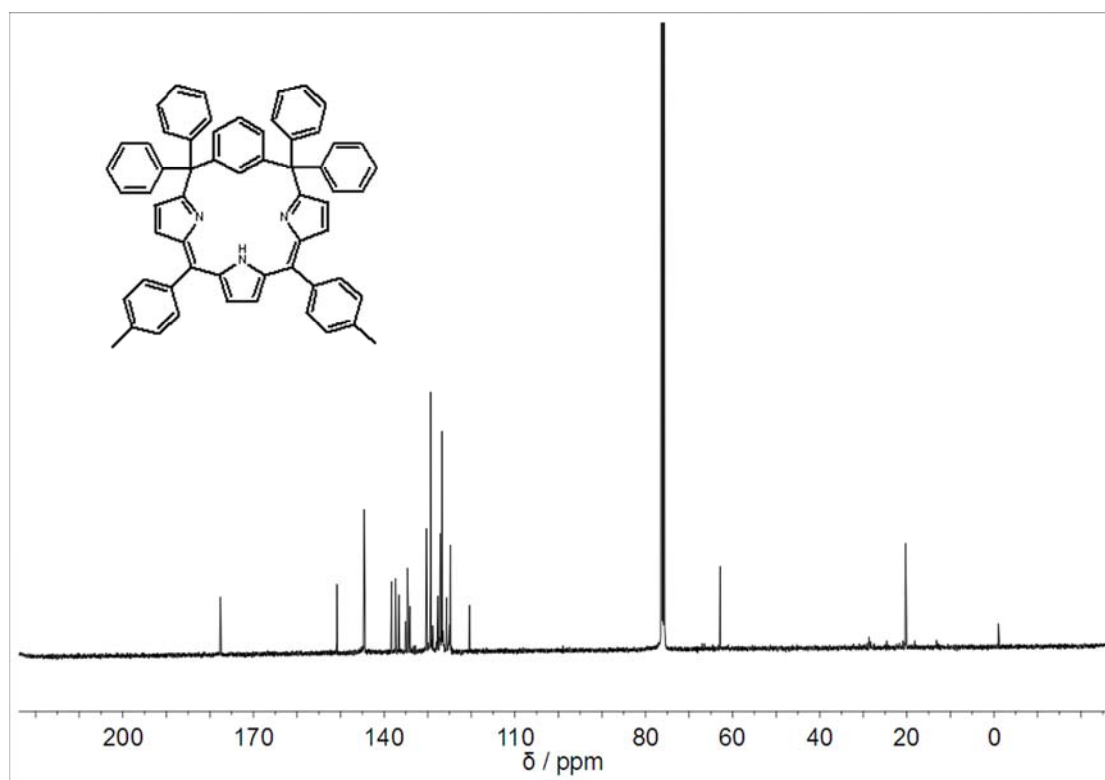


Fig. s7. The ^{13}C -NMR spectrum of compound 3.

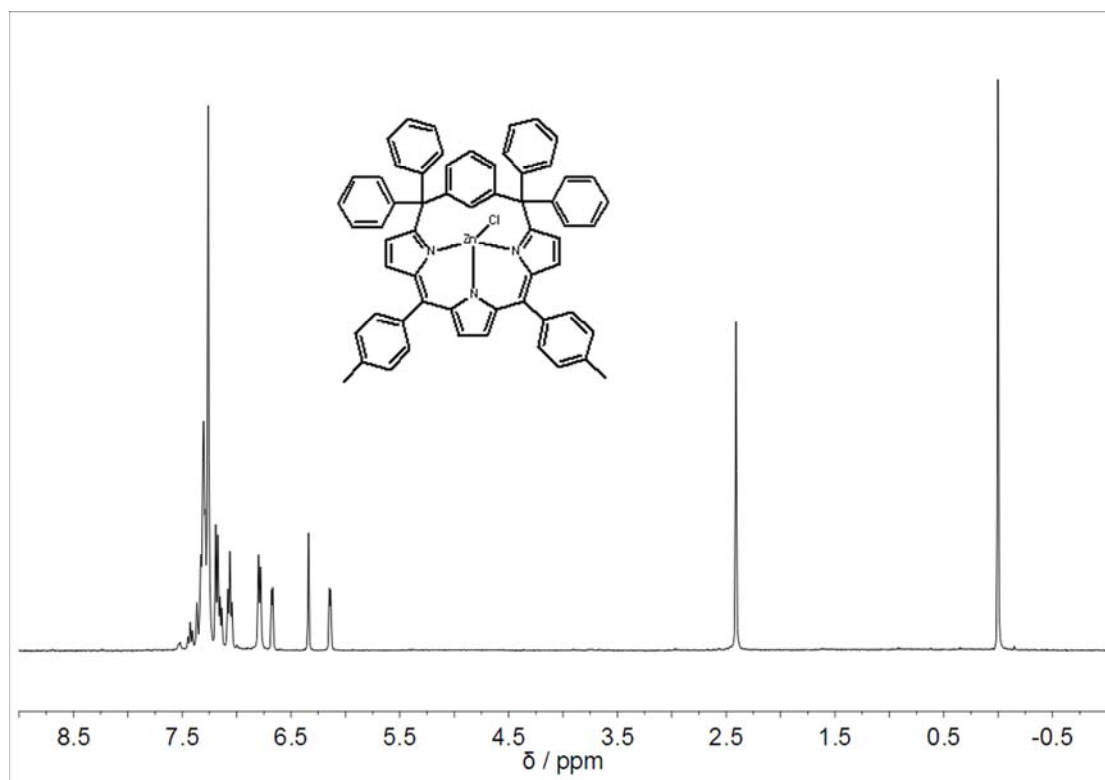


Fig. s8. The ^1H -NMR spectrum of compound 4.

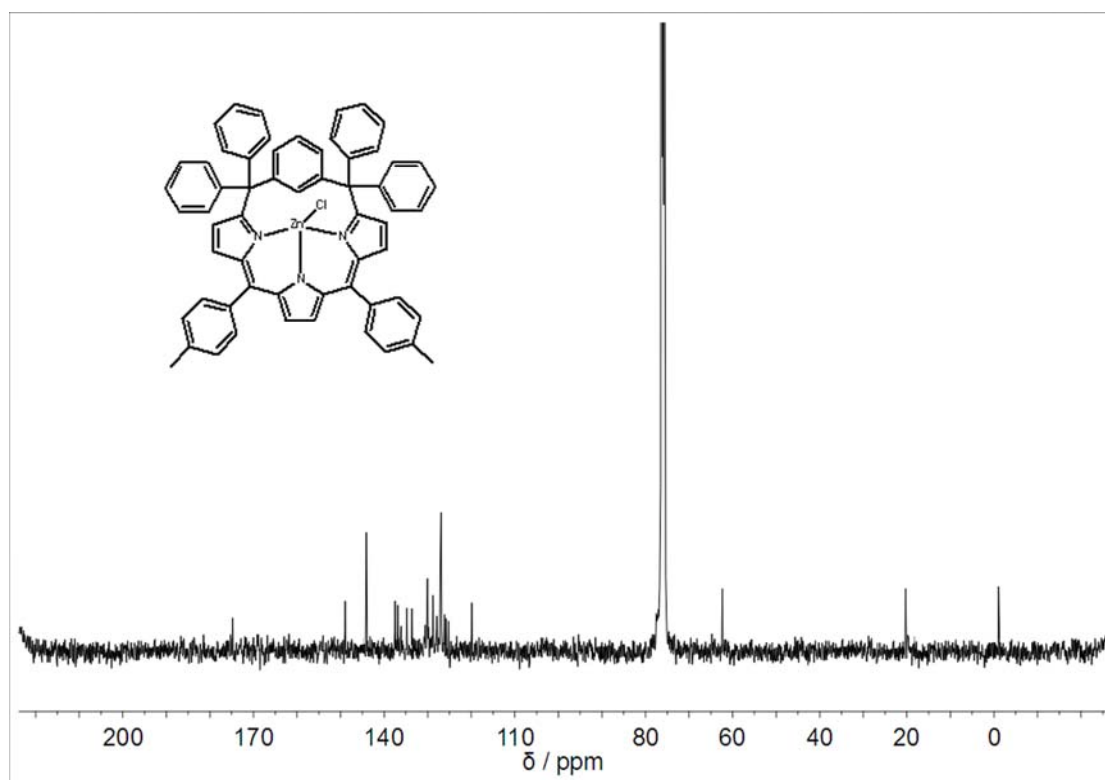


Fig. s9. The ^{13}C -NMR spectrum of compound 4.

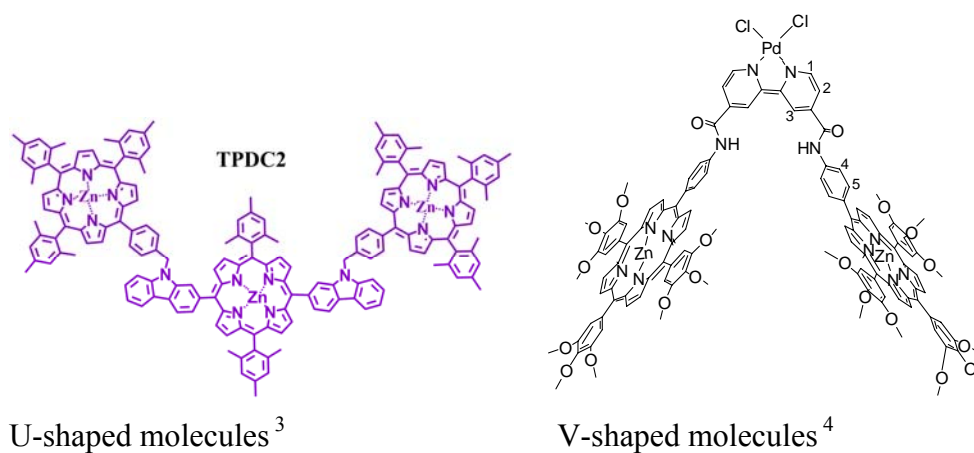


Fig. s10. The U-shaped molecules and V-shaped molecules for compare

Notes and references:

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