Electronic Supplementary Material (ESI) for Chemical Communications

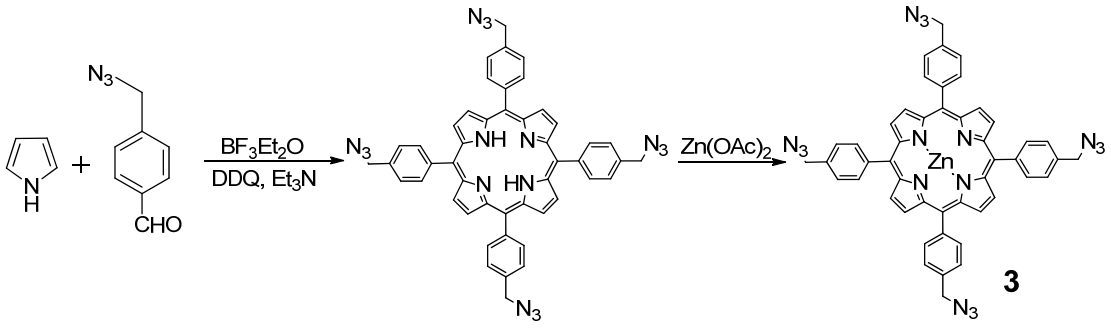
Supporting Information

smart Porphyrin Cage for Recognizingazide anion

Jianhong Zhang[a,b], Yongjun Li*[a], Wenlong Yang[a,b], Sui-Wai Lai[c], Chunjie Zhou[a,b],Huibiao Liu [a], Chi-Ming Che[c], Yuliang Li*[a]

Table of contents

1. Synthesis of 1 and 3:

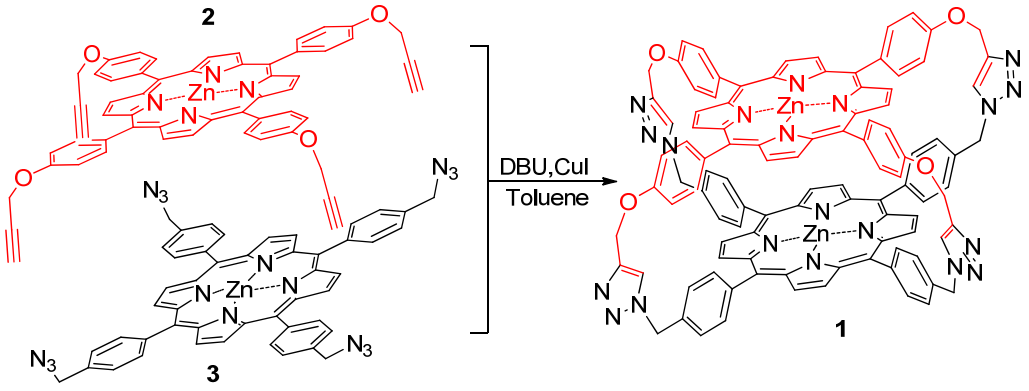


The synthesis of 3:

To a solution of 4-（azidomethyl）benzaldehyde (1.61 g, 10 mmol) and pyrrole

(0.67 g, 10 mmol) in $CHCl_3$ (400 mL), degassed (argon) for 30 minutes, were added $BF_3.Et_2O$ (356µl, 2.8 mmol). The solution was stirred at room temperature for 1 h and added DDQ (1.96 g, 8.6 mmol). The suspension was stirred for 0.5 h, then Et_3N m(389µl, 2.8 mmol) was added. Stirred for five minute, $Zn(AcO)_2$(4.53 g , 30 mmol) in CH_3OH (18 ml) was added. The solution was stirred for 12 h continuously. The solution was concentrated under reduced pressure. The residue was purified by column chromatography to give **3** (petroleum ether : $CHCl_3$ 1:1 as eluent) (2.6 g, yield = 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 8 H), 8.25 (d, *J* = 7.6Hz, 8H), 7.70 (d, *J* = 7.6Hz, 8H), 4.70 (s, 8H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 149.3, 142.5, 134.9, 134.4, 131.6, 126.6, 119.9, 53.7. MALDI-TOF, Calcd for $C_{48}H_{32}N_{16}Zn$: 896.2; Found 896.4. Anal. Calcd for $C_{48}H_{32}N_{16}Zn$: C, 64.18; H, 3.59; N, 24.95; Found: C, 64.16; H, 3.60; N, 24.93.

The porphyrin 3 was prepared by the literature (1) **:** Y. Liu, C.F Ke, H. Y. Zhang, J. Cui, F. Ding, *J. Am. Chem. Soc.*, 2008 , **130**, 600 - 605



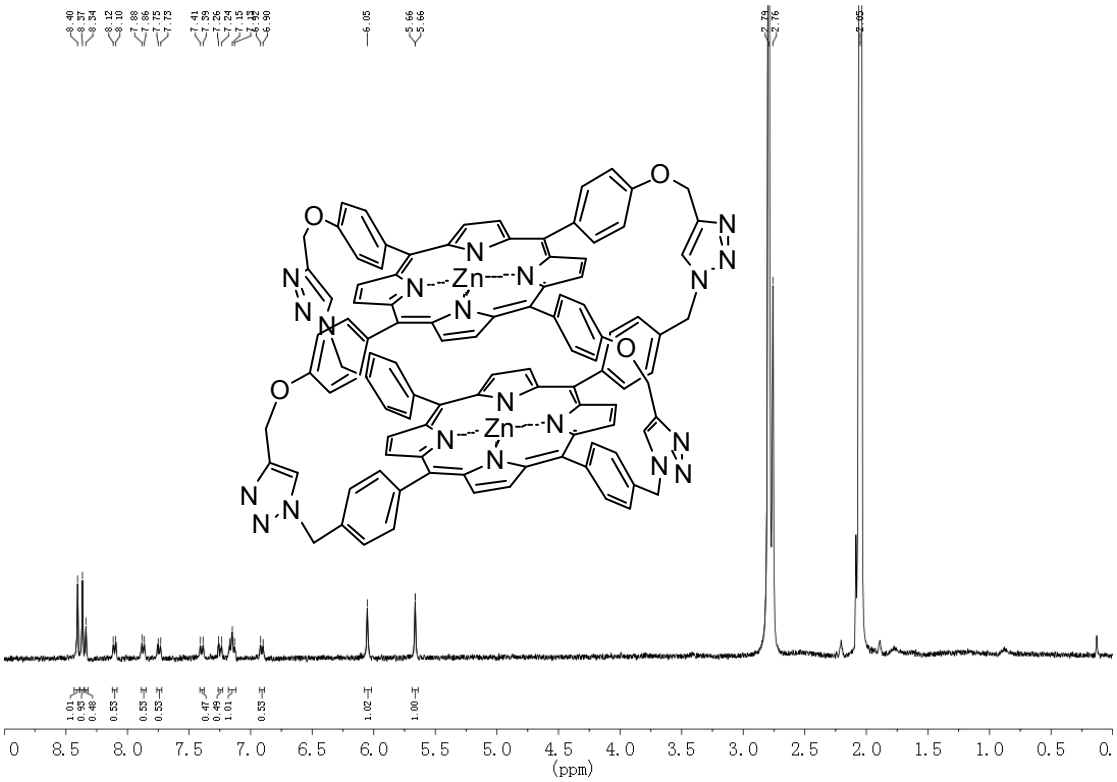
Synthesis of 1:

1, 8-Diaza [5.4.0] bicycloundec-7-ene (DBU) (4.0 mmol, 0.7 mL)was added to toluene (400 mL), degassed (argon) for 30 minutes and heated to 75 °C while flushing with argon. At 75 °C, CuI (0.05 mmol, 9.5 mg) was added to the mixture. A solution of the **2** (89.4 mg, 0.1 mmol) and **3 (**89.6 mg, 0.1 mmol) in THF (5 mL) and toluene (50 mL) was added to the solution slowly over 12 h and stirred for another 12 h under argon. The reaction was quenched with water and washed with H_2O (100 mL × 3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture

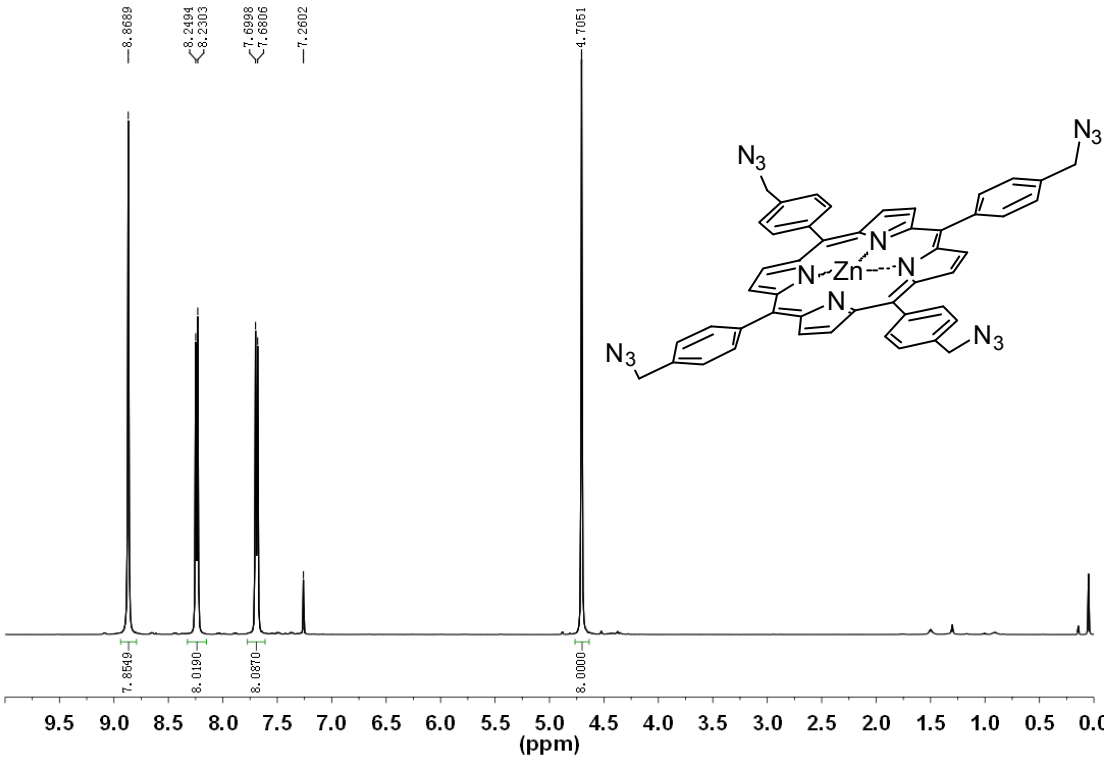
was concentrated in vacuo. The product was purified via chromatography (SiO_2, $CHCl_3$: methanol 30 : 1) to afford **1** (104 mg, 55% yield) as a purple solid. ^{1}H NMR (400 MHz, $(CD_3)CO$ δ 8.40 (s, 8H), 8.37 (s, 8H), 8.34 (s, 4H), 8.12 (d, J = 8 Hz, 1 H), 7.88 (d, J = 8 Hz, 1H), 7.75 (d, J = 8Hz, 1H), 7.40 (d, J = 8Hz, 1H), 7.26 (d, J = 8Hz, 1H), 7.15 (m, 2H), 6.92 (d, J = 8Hz, 1H), 6.05 (s, 8H), 5.66 (s, 8H) MALDI-TOF (M), Calcd for $C_{104}H_{68}N_{20}O_4Zn_2$ (M) 1788.4; Found 1788.6.

2. ^{1}H NMR and ^{13}C NMR

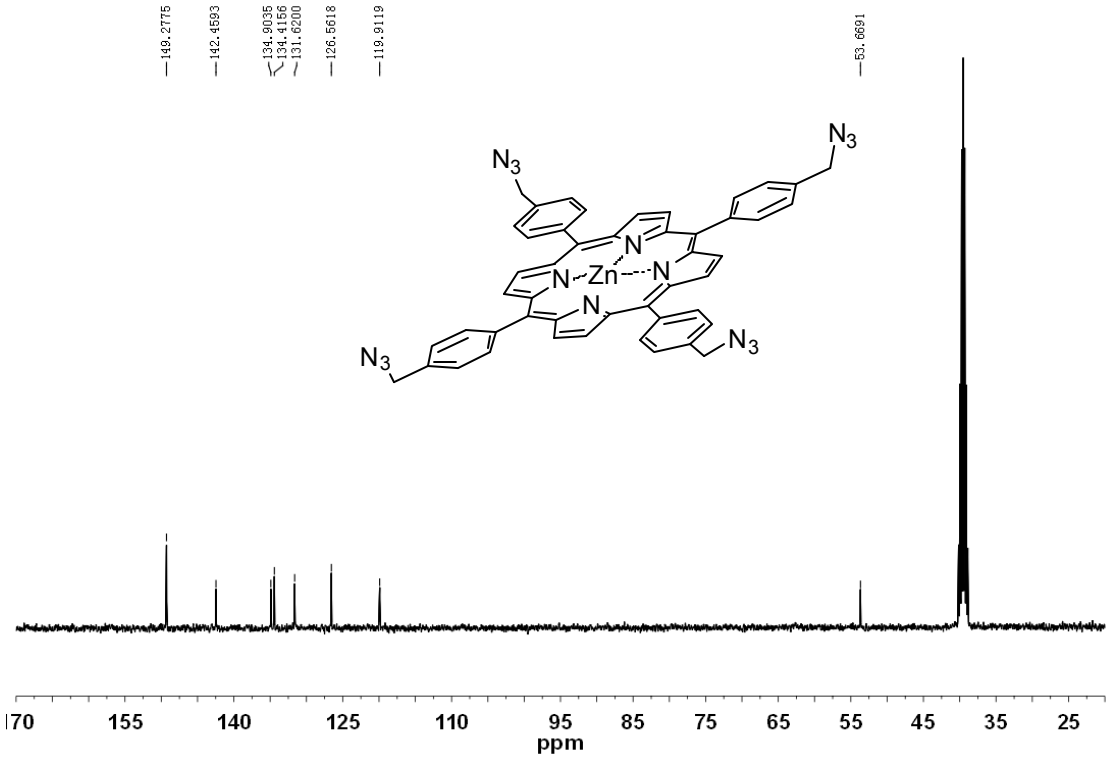
^{1}H NMR spectrum (400 MHz, 298 K, d_6-acetone)of **1**



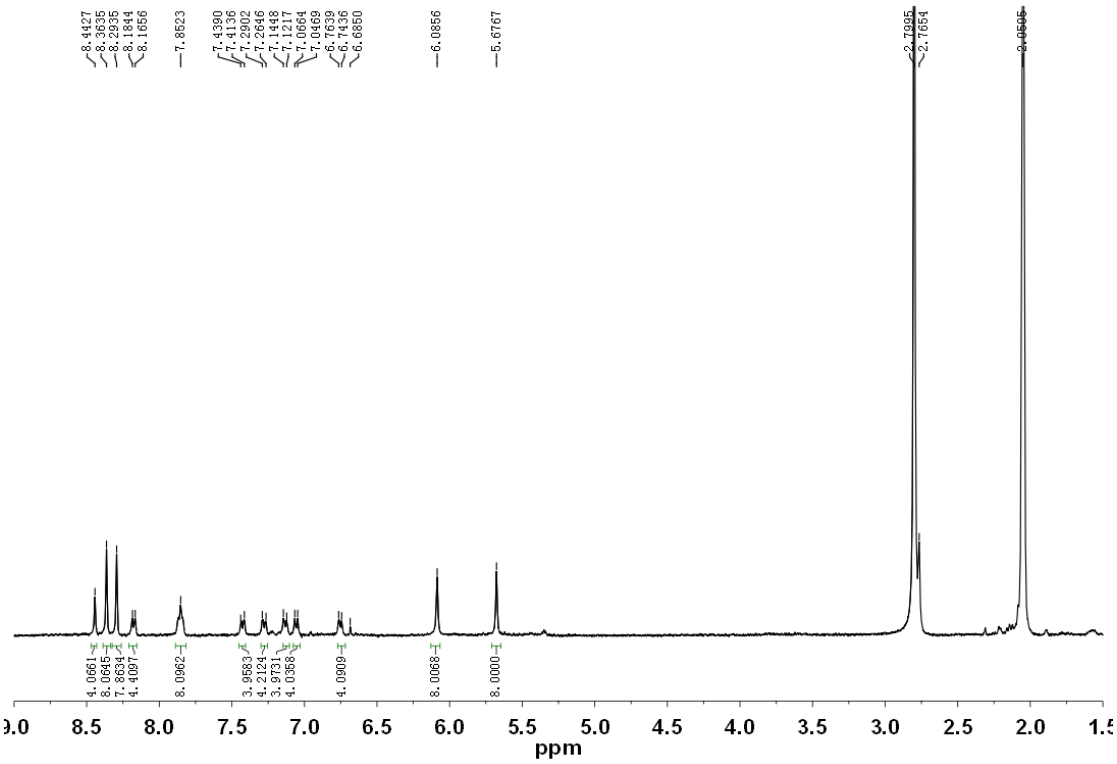
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **3**



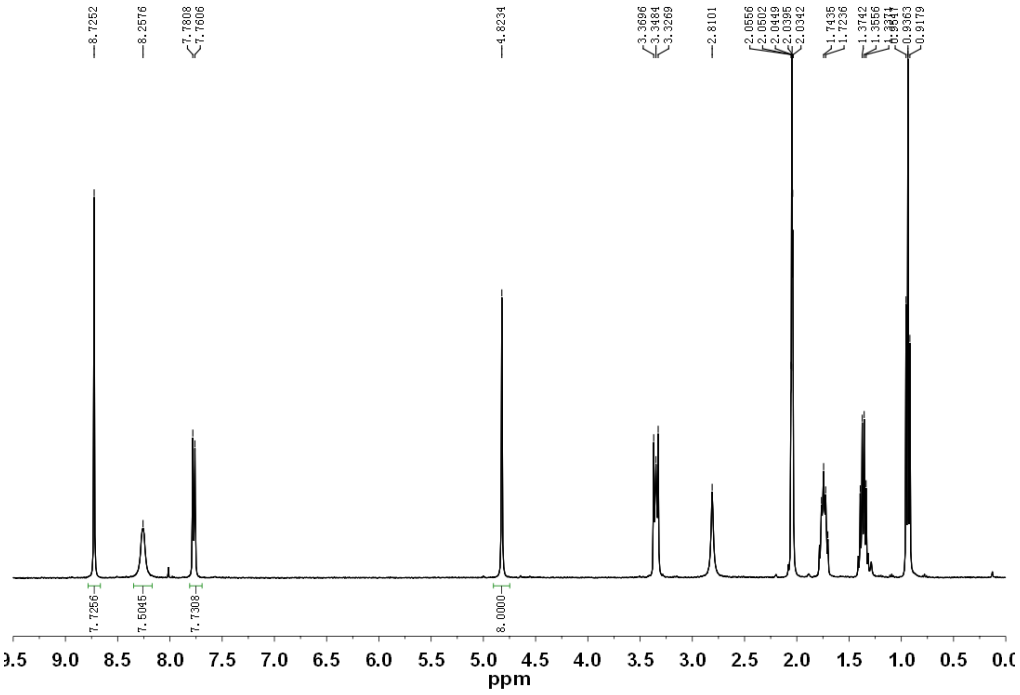
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **3**



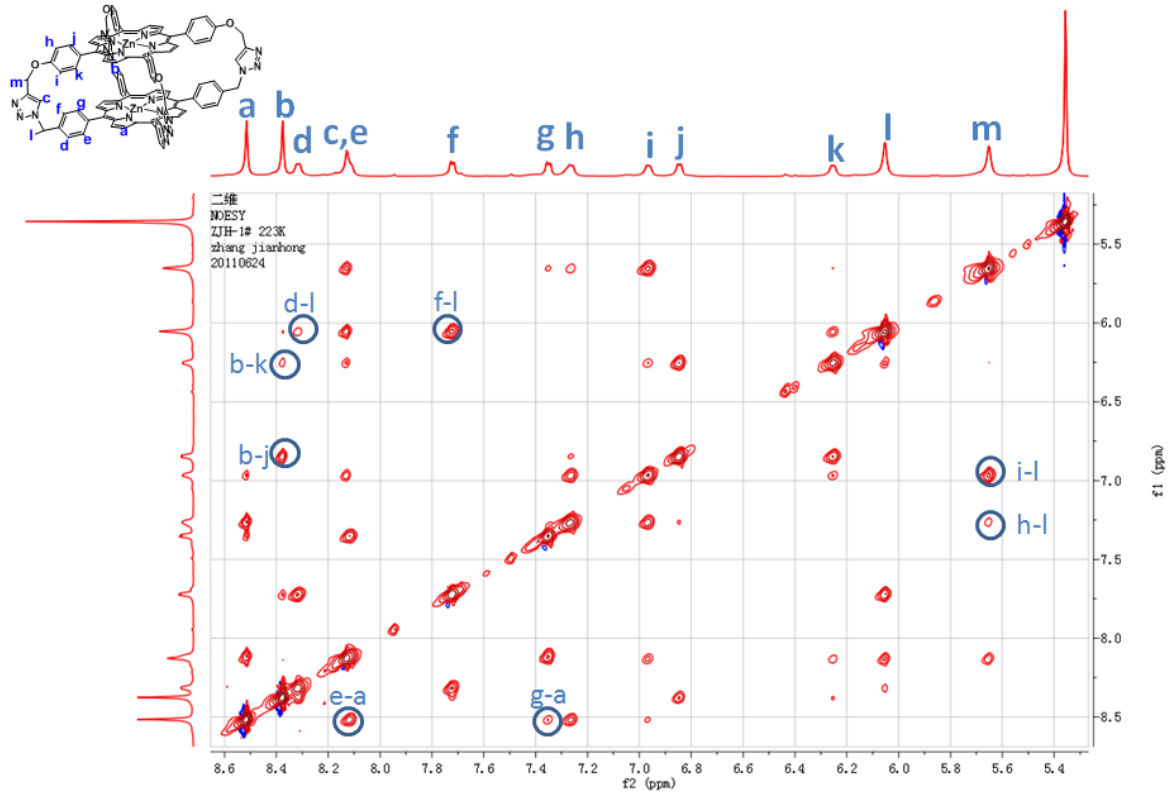
^{1}H NMR spectrum (400 MHz, 298 K, d_6-acetone) of **1+pyridine**



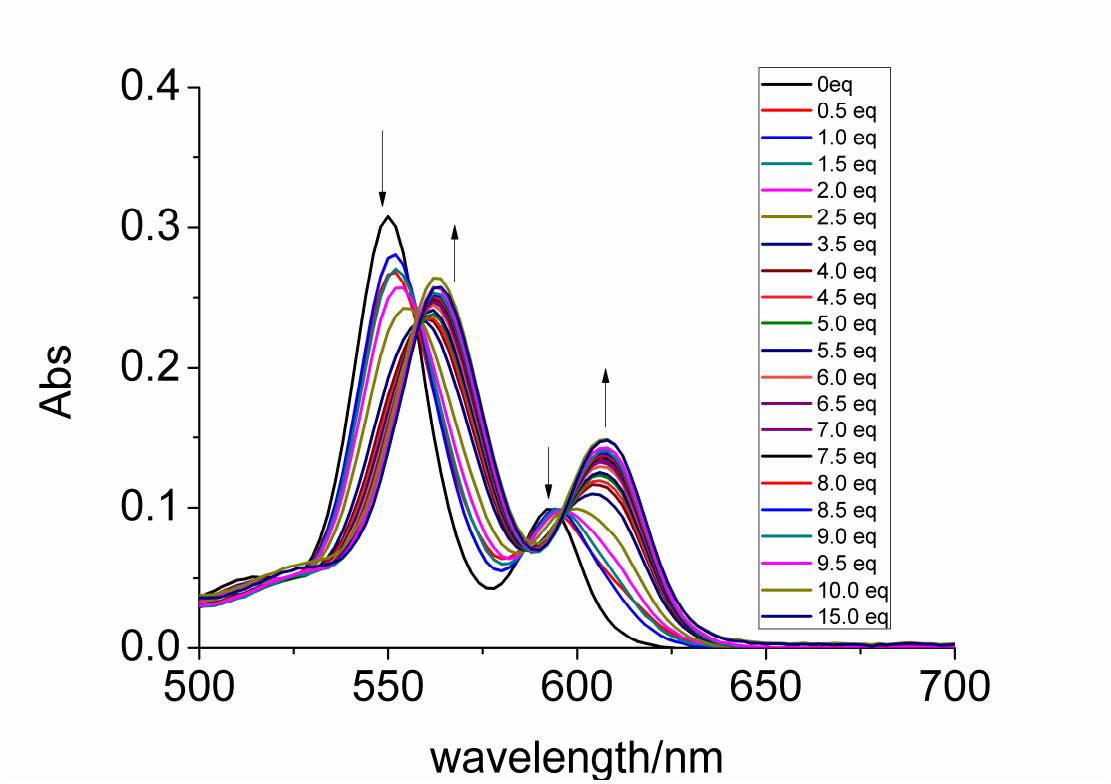
^{1}H NMR spectrum (400 MHz, 298 K, d_6-acetone) of **2+ TBAN$_3$**



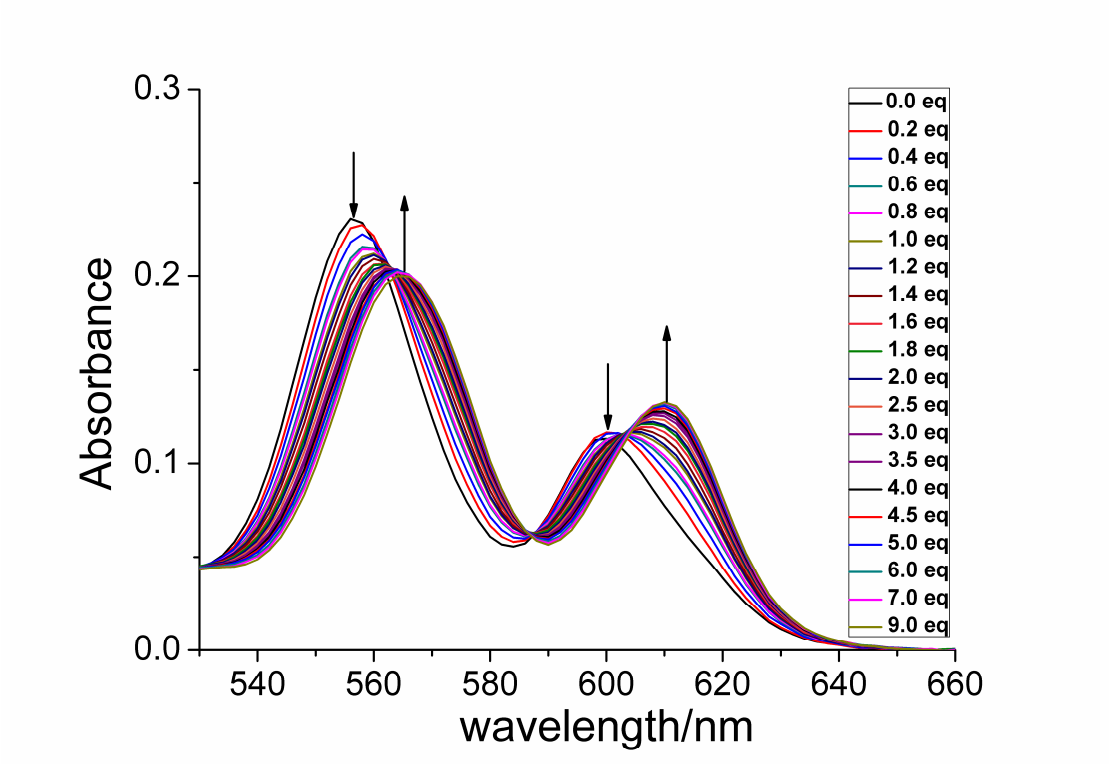
3.NOESY spectrum of 1 in d_6-acetone at 258 K



4. UV–vis spectrum of the cage 1 with N_3^- in CH_2CCl_2, THF, acetone

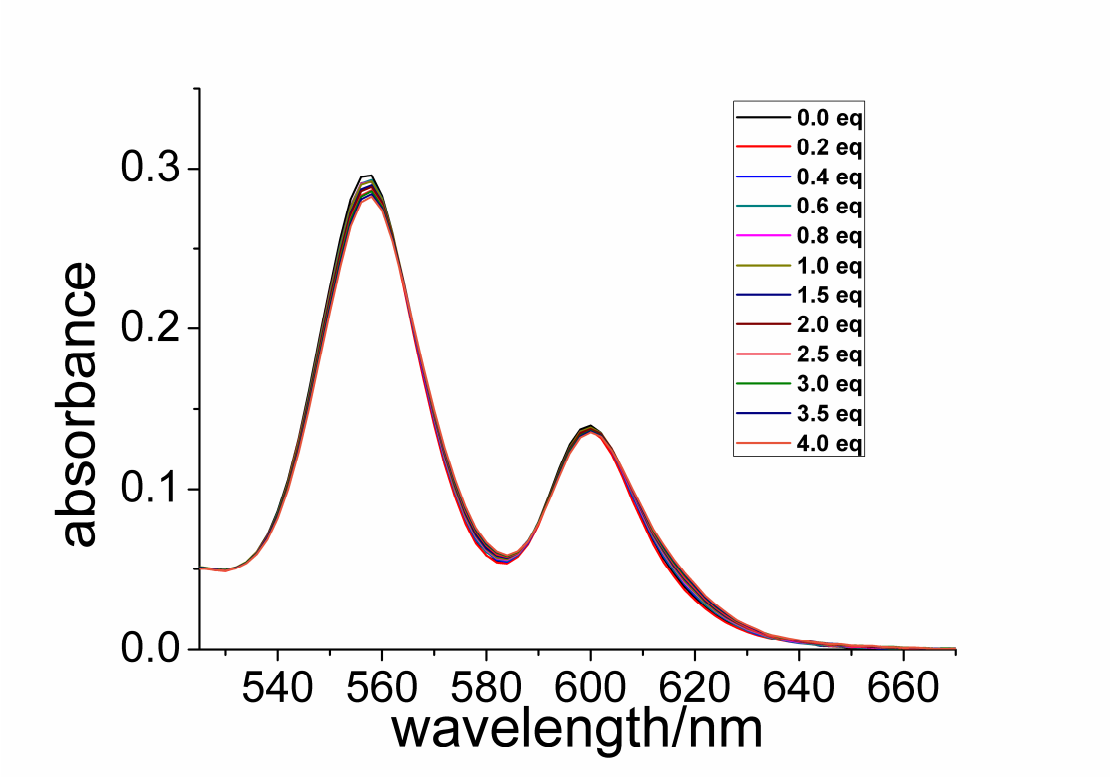


UV–vis titration of the cage 1 (10 μM in CH_2Cl_2) with N_3^-(up to 15 equal)



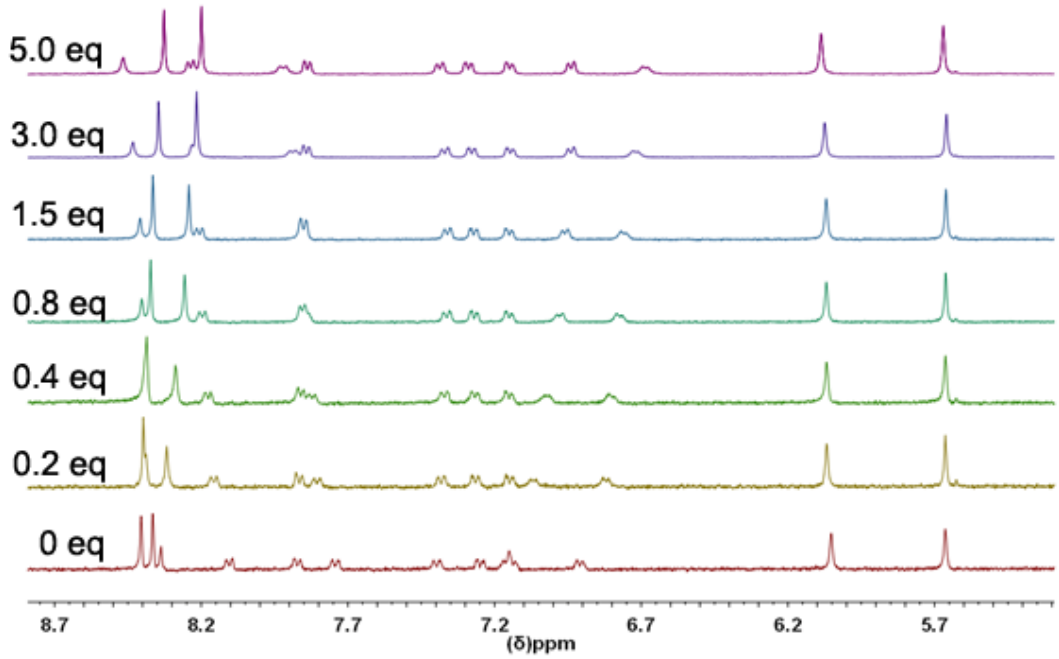
UV–vis titration of the cage 1 (10 μM in acetone) with N_3^-(up to 9

equal)



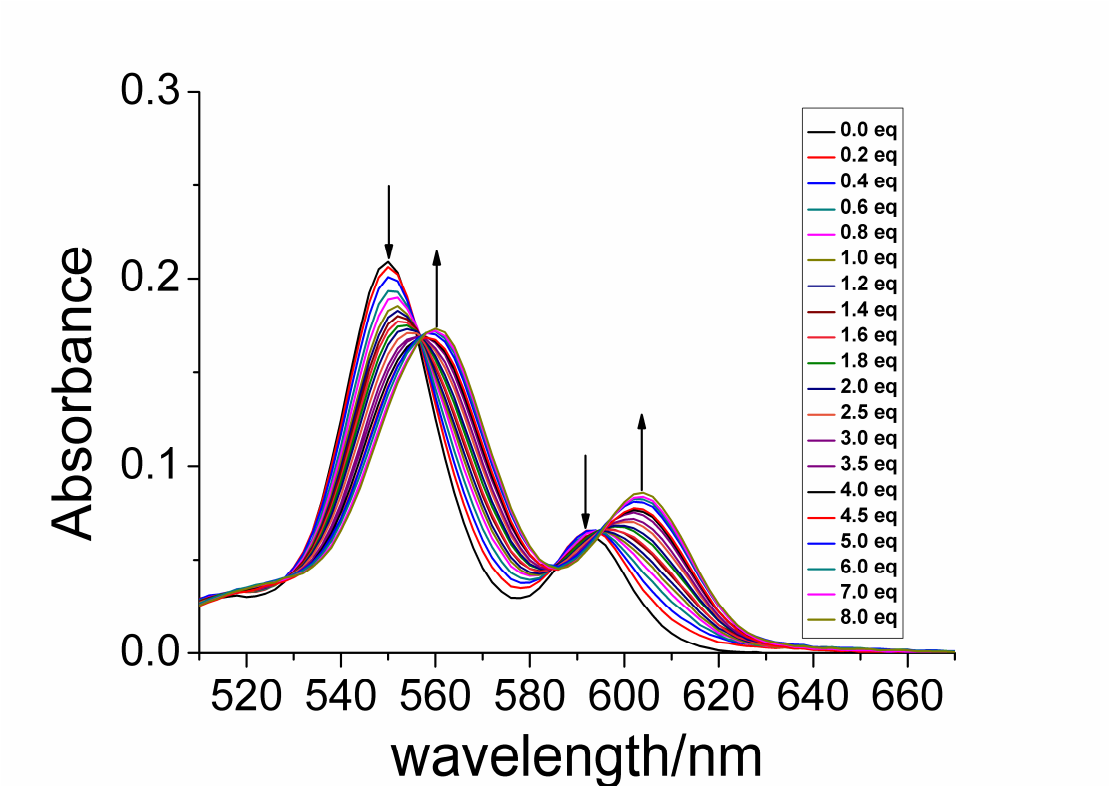
UV–vis titration of the cage 1 (10 μM in THF) with N_3^-(up to 4 equal)

5. ^{1}H NMR spectra of the cage 1 in d_6-acetone at 298 K upon titrational addition of TBASCN



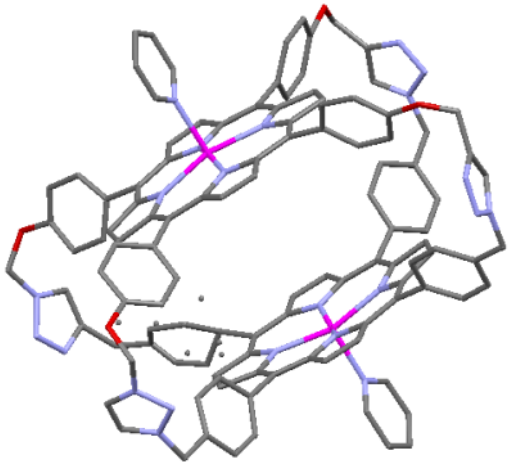
^{1}H NMR spectra of the cage 1 in d_6-acetone at 298 K upon titrational addition of TBASCN

6. UV–vis spectrum of the cage 1 with SCN^- in acetone

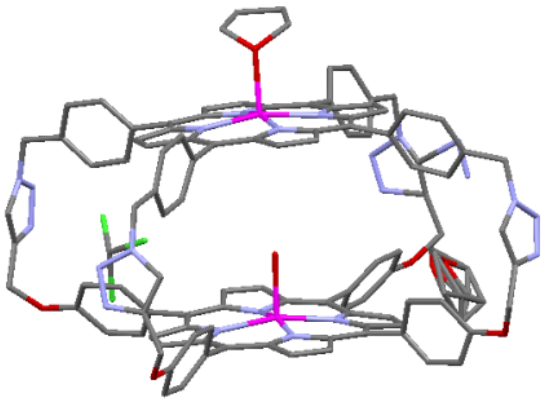


UV–vis titration of the cage 1 (10 μM in acetone) with SCN^- (up to 8 equal)

7. X-ray crystal structure of 1.



The crystal **A** of **1** was obtained in pyidine and acetone.



The crystal **B** of **1** was obtained in THF

(1) Y. Liu, C.F Ke, H. Y. Zhang, J. Cui, F. Ding, *J. Am. Chem. Soc.*, 2008 , **130**, 600 - 605.