Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A "clicked" Porphyrin Cage with High Binding Affinity towards Fullerenes

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Huibiao Liu[a], Qikai Li[c], Zhigang Shuai[a], Yuliang Li[a]*

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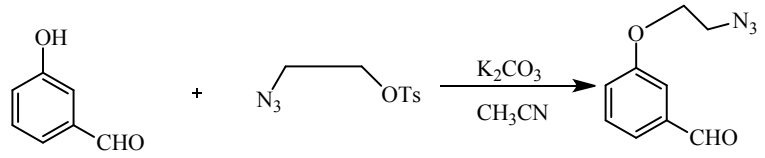
1. Synthesis of compounds



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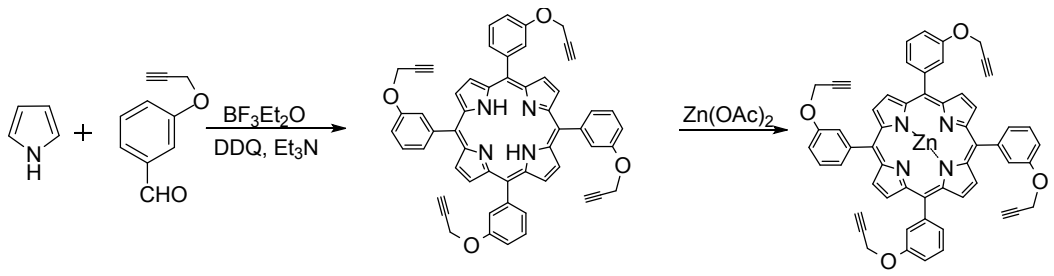
The synthesis of 5:

3-hydroxybenzaldehyde (2.4 g, 20 mmol) and 2-azidoethyl 4-methylbenzenesulfonate (4.8 g, 20 mL) was added to acetonitrile (60 mL), degassed (argon) for 10 minutes and heated to 80 °C while flushing with argon for 8 h. when the solution was cooled, washed with H_2O (100 mL) and CH_2Cl_2 (100 mL), the organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was concentrated in vacuo. The product was purified via chromatography (SiO_2, CH_2Cl_2 : petroleum ether 2 : 1) to afford the product (3.1g, 83% yield) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1 H), 7.50-7.45 (m, 2 H), 7.40 (d, J = 7.2 Hz, 1 H), 7.22 (t, J = 7.2 Hz, 1 H), 4.22 (t, J = 4.8 Hz, 2 H), 3.64 (t, J = 4.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 168.5, 142.2, 131.2, 124.3, 122.2, 113.7, 68.2, 50.2. EI, Calcd for $C_9H_9N_3O_2$: 191.1; Found 191.0. Anal. Calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74 N, 21.98; Found: C, 56.51; H, 4.73 N, 21.96.

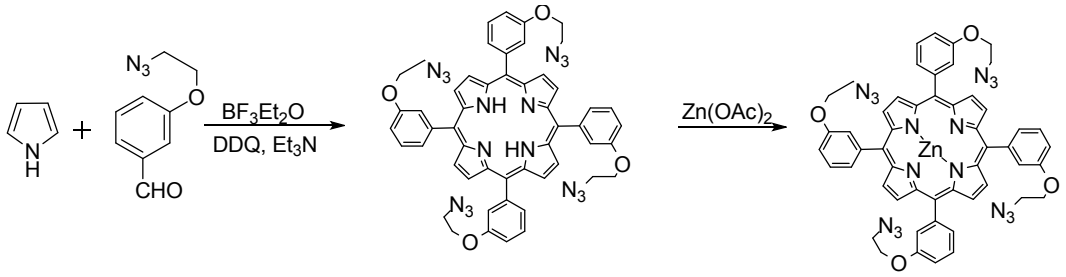


The synthesis of 3:

To a solution of 3-(prop-2-yn-1-yloxy)benzaldehyde (1.60 g, 10 mmol) and pyrrole (0.67 g, 10 mmol) in $CHCl_3$ (400 mL), degassed (argon) for 30 minutes, were added $BF_3.Et_2O$ (356 µl, 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 (389 µl, 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) (0.96 g, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.0 (s, 8 H), 7.85 (m, 8 H), 7.65 (t, *J* = 8 Hz, 4 H), 7.39 (m, 4 H), 4.82 (s, 8 H) 2.60 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 150.2, 144.2, 132.2, 128.6, 127.5, 121.4, 120.7, 114.5, 78.6, 75.9, 56.1. MALDI-TOF, Calcd for $C_{56}H_{36}N_4O_4Zn$: 894.2.; Found 894.7. Anal. Calcd for $C_{56}H_{36}N_4O_4Zn$: C, 75.21; H, 4.06; N, 6.26; Found: C, 75.23; H, 4.09 N, 6.23.

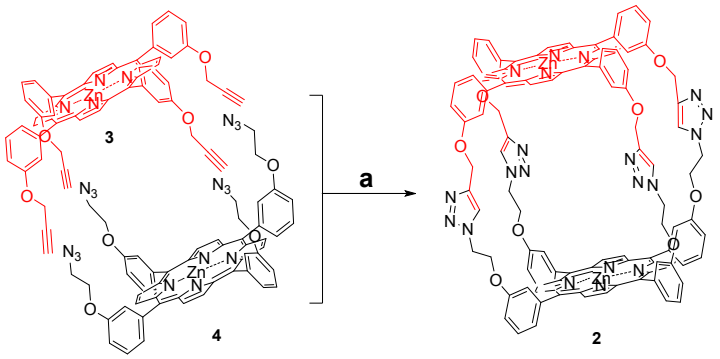
The synthesis of 4:



To a solution of 3-(2-azidoethoxy)benzaldehyde (1.91 g, 10 mmol) and pyrrole (0.67 g, 10 mmol) in $CHCl_3$ (400 mL), degassed (argon) for 30 minutes, were added $BF_3.Et_2O$ (356 µl, 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 **4** (petroleum ether : $CHCl_3$ 1:1 as eluent) (0.9 g, 28% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 8 H), 7.88 (m, 4 H), 7.81(s, 4 H) 7.67 (t, *J* = 8.2 Hz, 4 H), 7.37 (m, 4 H), 4.34 (t, *J* = 4.8 Hz, 8 H), 3.68 (t, *J* = 4.8 Hz, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 143.6, 130.4, 130.0, 121.1, 119.8, 107.3, 63.5, 50.3. MALDI-TOF, Calcd for $C_{52}H_{40}N_{16}O_4Zn$: 1018.3; Found 1018.6. Anal. Calcd for $C_{52}H_{40}N_{16}O_4Zn$: C, 61.33; H, 3.96; N, 22.01; Found: C,61.36; H, 3.94; N, 22.03.

Porphyrins **3** and **4** were prepared according to the literature procedures previously described (1) **:** Y. Liu, C.F Ke, H. Y. Zhang, J. Cui, F. Ding, *J. Am. Chem. Soc.*, 2008 , **130**, 600 - 605

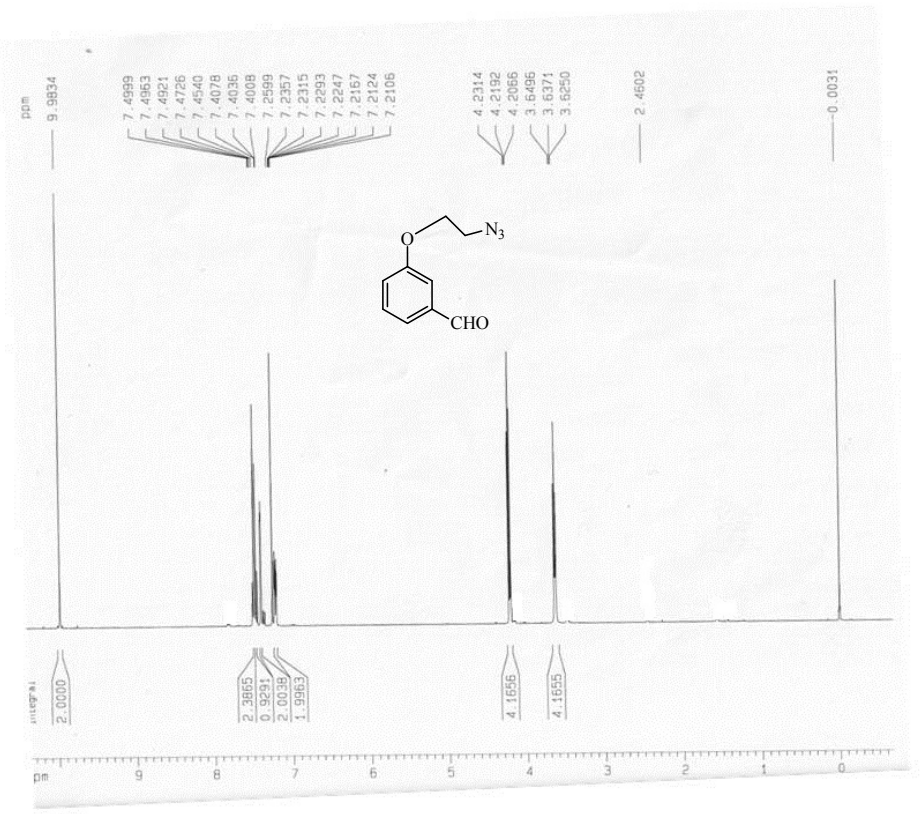
Synthesis of cage 2:



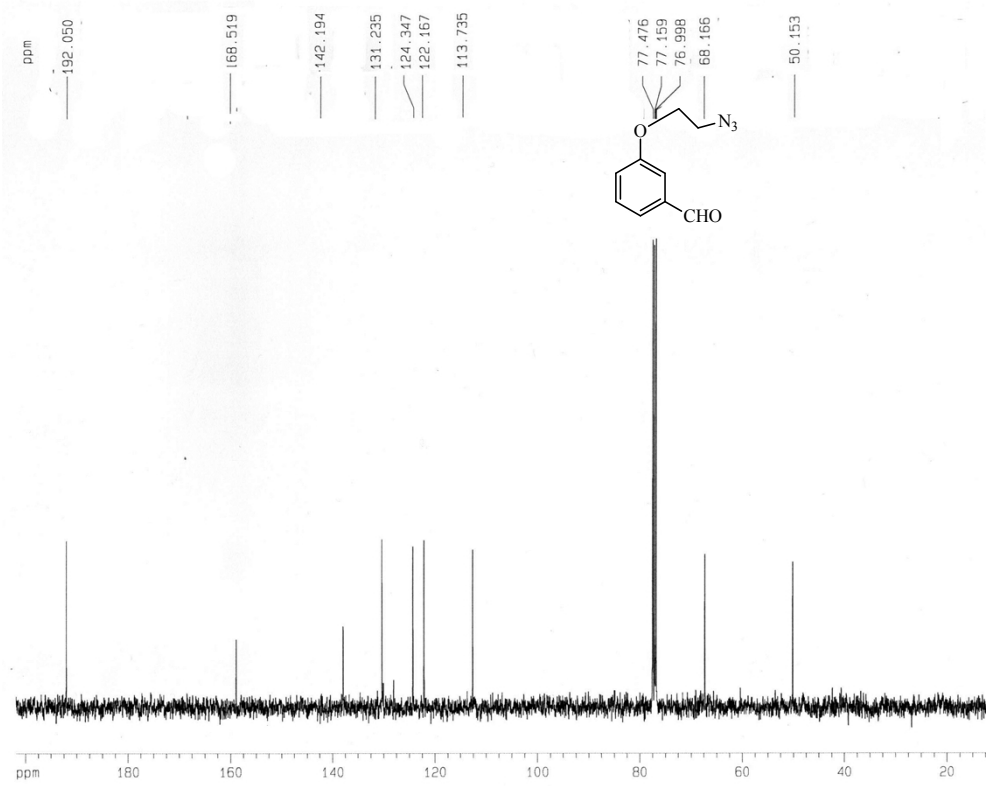
1,8-Diaza [5.4.0] bicycloundec-7-ene (DBU) (4.0 mmol, 0.7 mL)was added to toluene (400 mL), degassed (argon) for 30 minutes and heated to 75 °C while flushing with argon. At 75 °C, CuI (0.05 mmol, 9.5 mg) was added to the mixture. A solution of the **3** (89.6 mg, 0.1 mmol) and **4 (**102 mg, 0.1 mmol) 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** (50 mg, 26% yield) as a purple solid. ^{1}H NMR (400 MHz, 1,2-dichloroethane-d4), δ 8.74 (s, 8 H), 8.70 (s, 8 H), 7.81 (s, 4 H), 7.72 (d, J = 6.5 Hz, 4 H), 7.63 ~7.50 (m, 12 H), 7.33 (s, 4 H), 7.19 (s, 4 H), 5.22 (s, 8 H), 4.90 (s, 8 H), 4.58 (s, 8 H). MALDI-TOF (M), Calcd for $C_{108}H_{76}N_{20}O_8Zn_2$ (M) 1912.6; Found 1913.1.

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

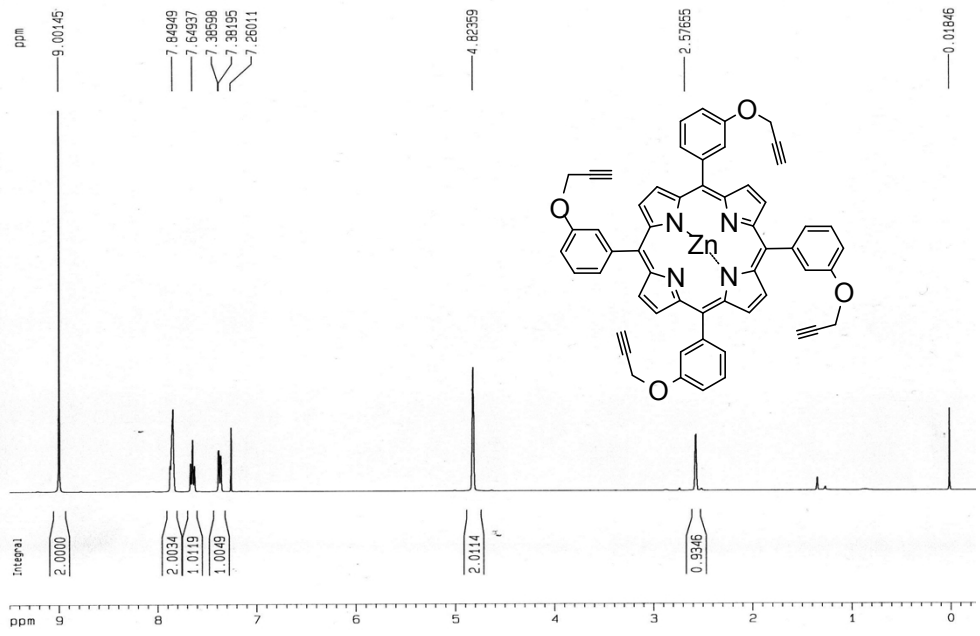
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **5**



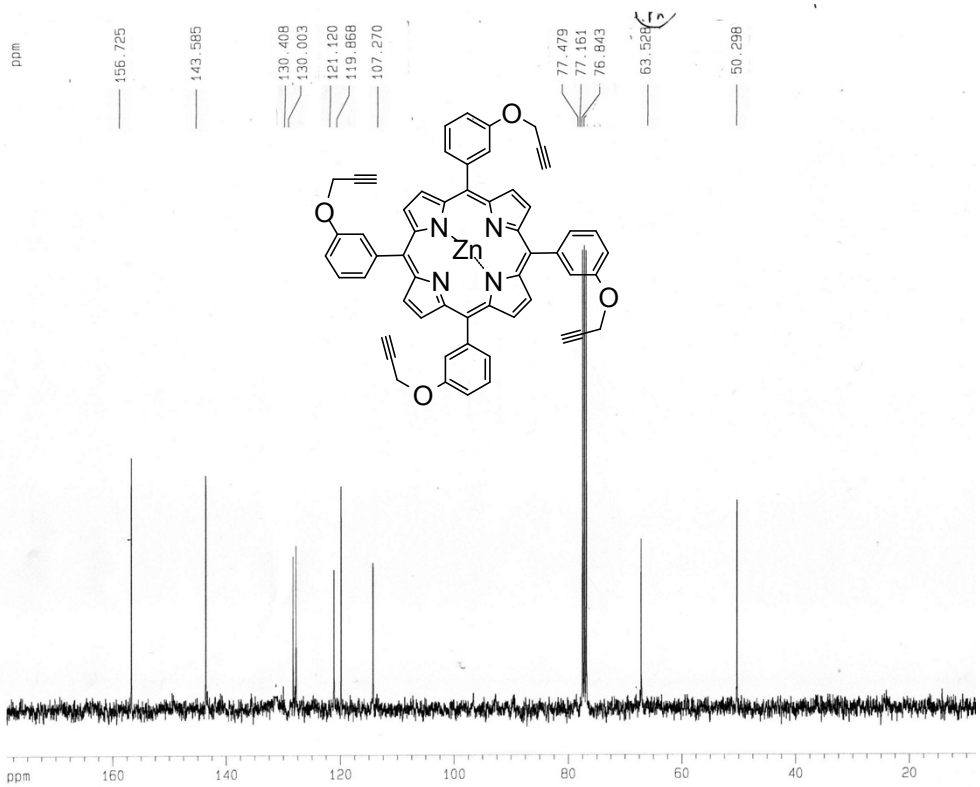
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **5**



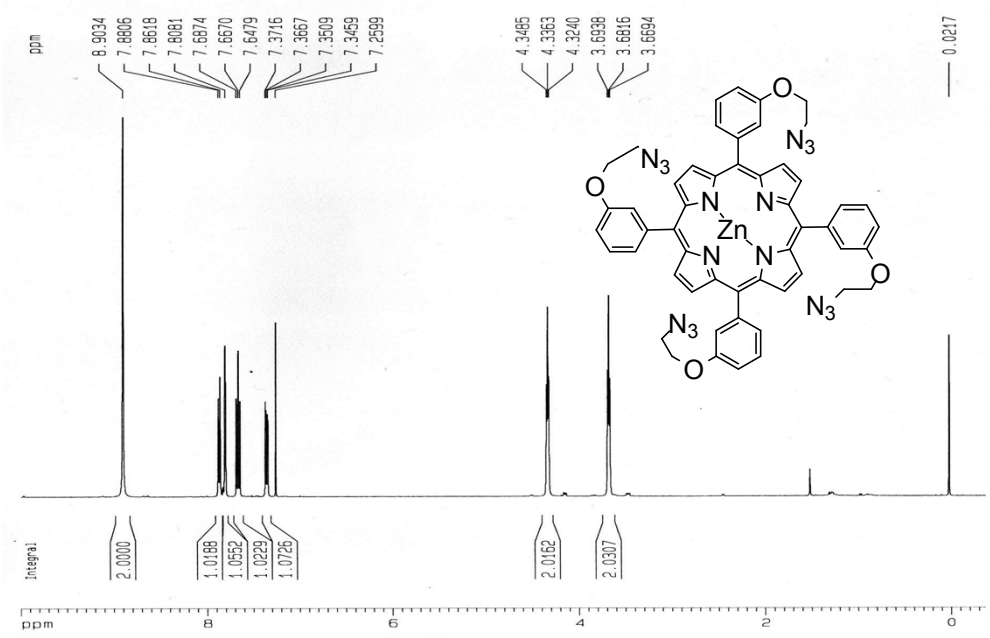
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **3**



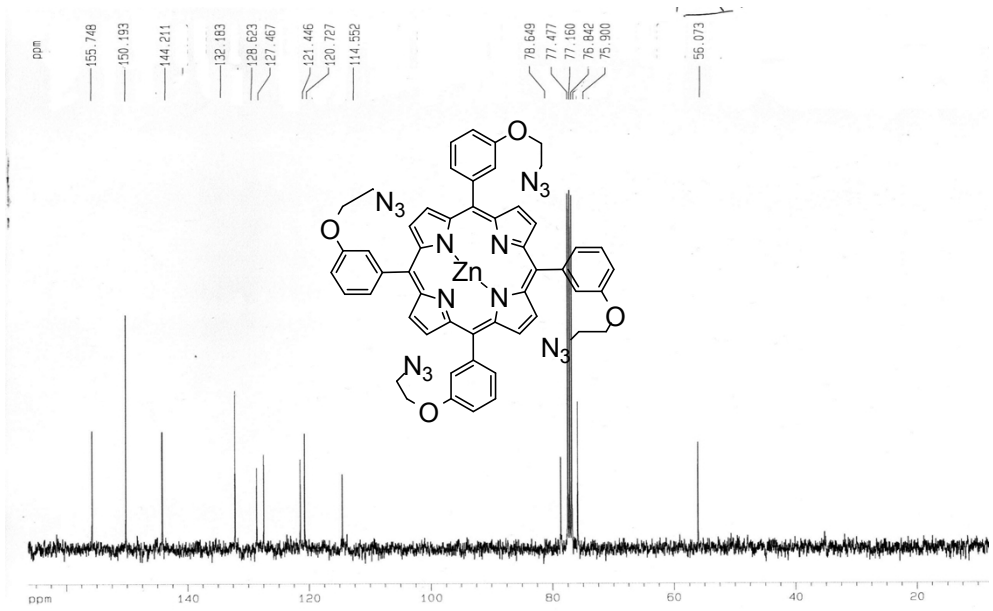
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **3**



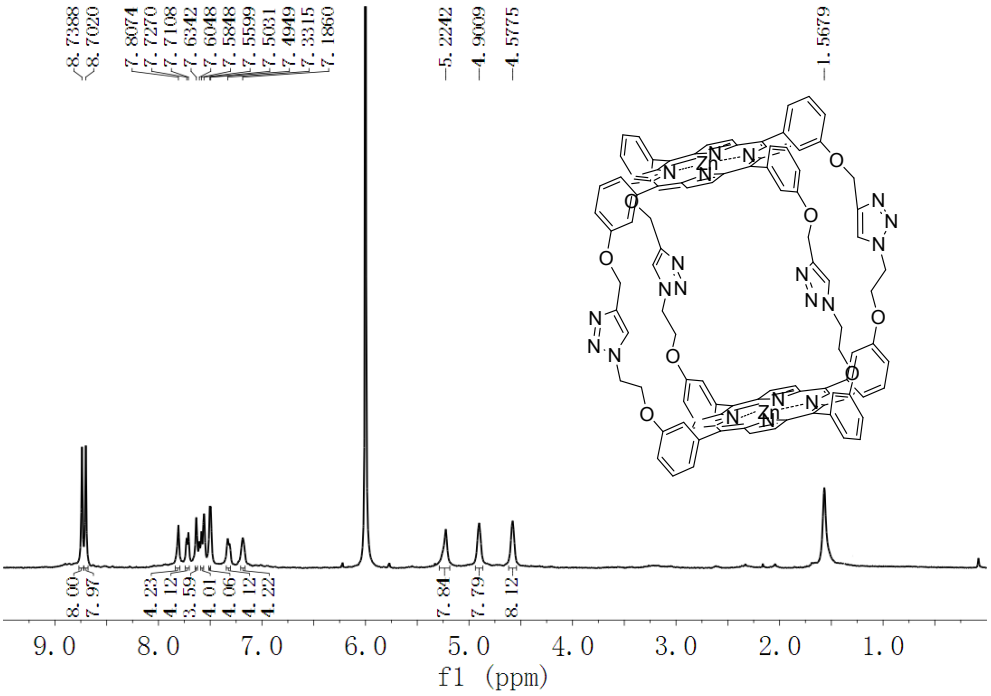
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **4**



^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **4**



^{1}H NMR spectrum (400 MHz, 298 K, 1,2-dichloroethane-d4) of **cage 2**



3. Binding Analysis for the receptor with C_{60} or C_{70}

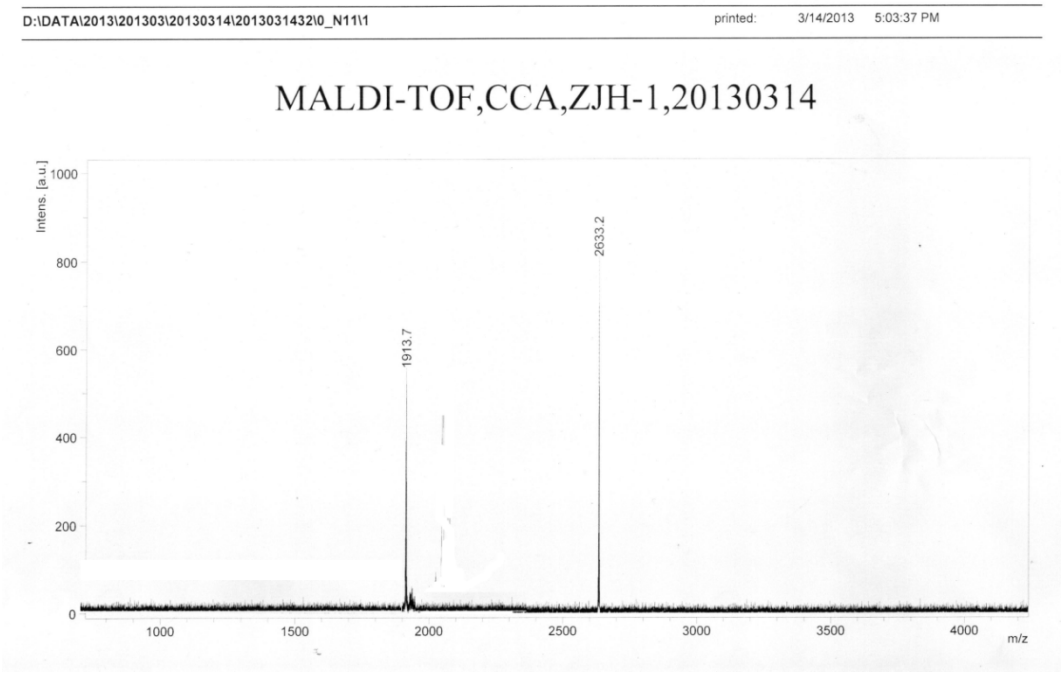


Figure S1. MALDI-MS spectra of cage **2** and cage **2**+C_{60}

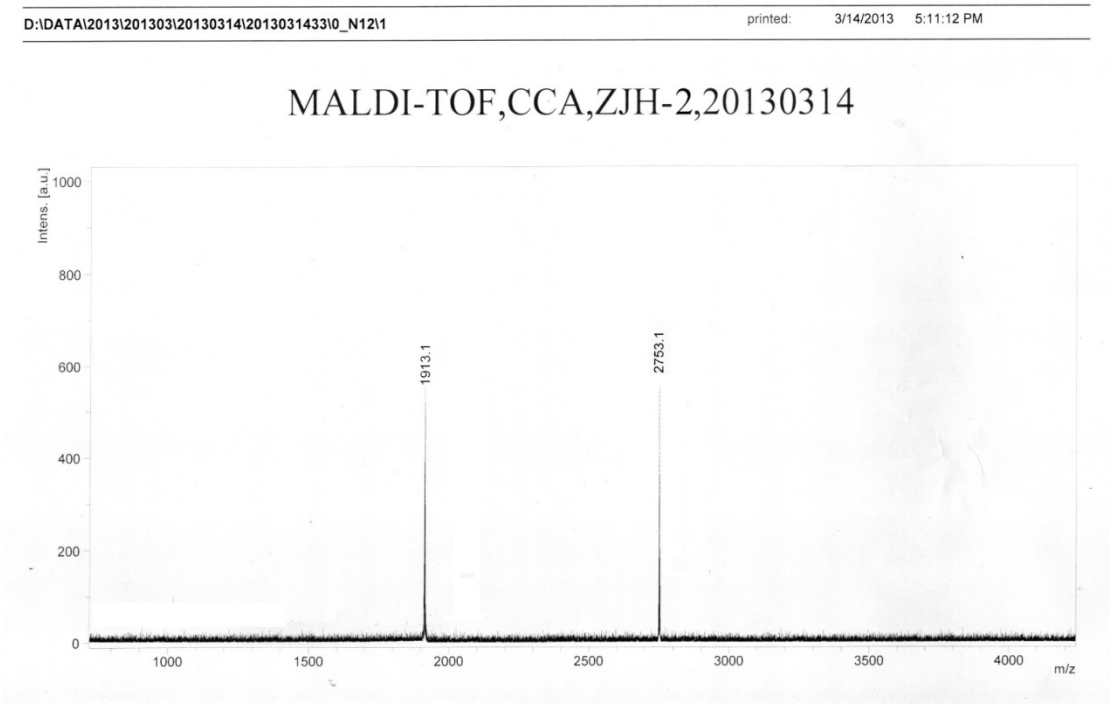


Figure S2. MALDI-MS spectra of cage **2** and cage **2**+C_{70}

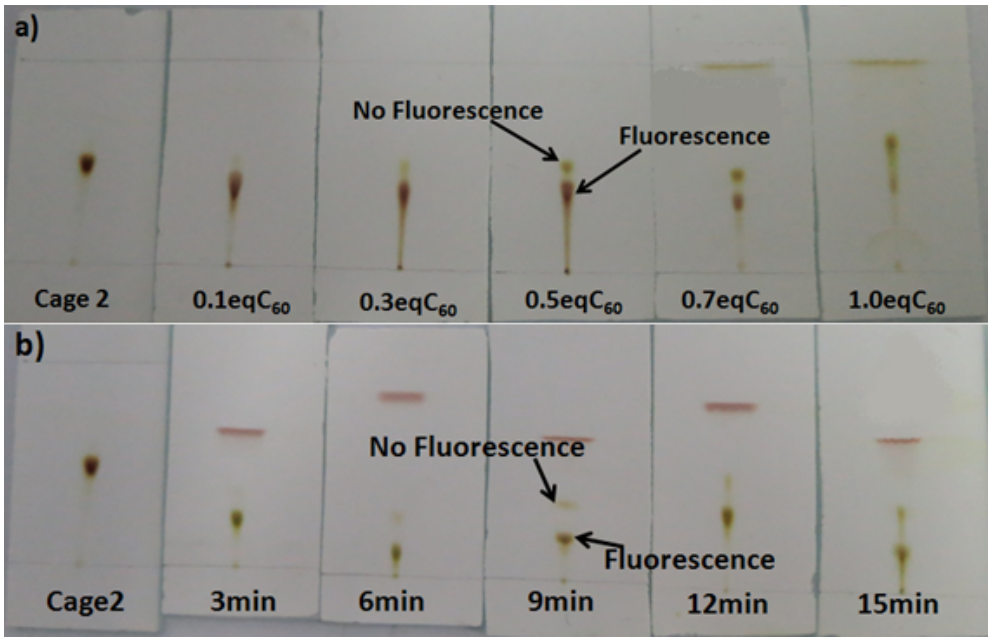


Figure S3. a) TLC of cage **2** in $CHCl_3$ at 298 K upon titrational addition of C_{60} in CS_2. b) TLC of cage **2** in $CHCl_3$+ C_{70} in CS_2（1:1） at 298 K with time as the basis. TLC condition: silica gel plate/ $CHCl_3$:CH_3OH=30:1

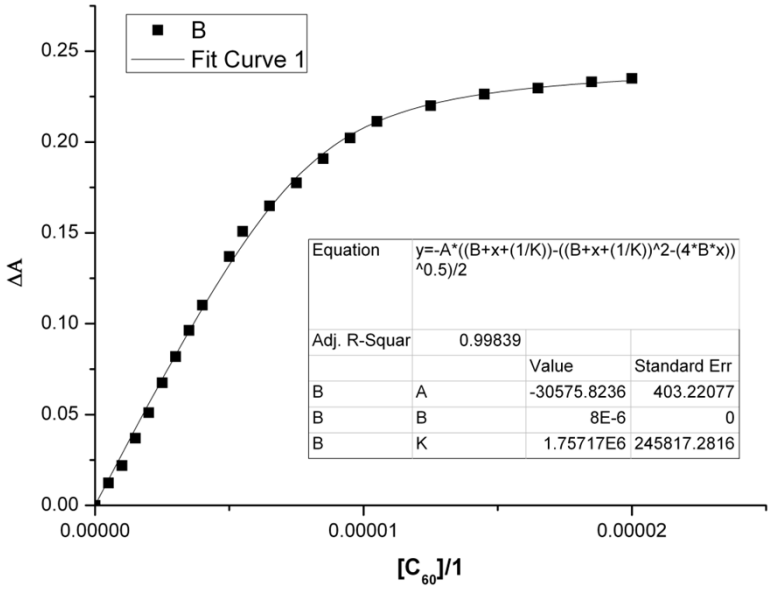


Figure S4. An association constant of cage **2** with C_{60} by the UV-vis titration

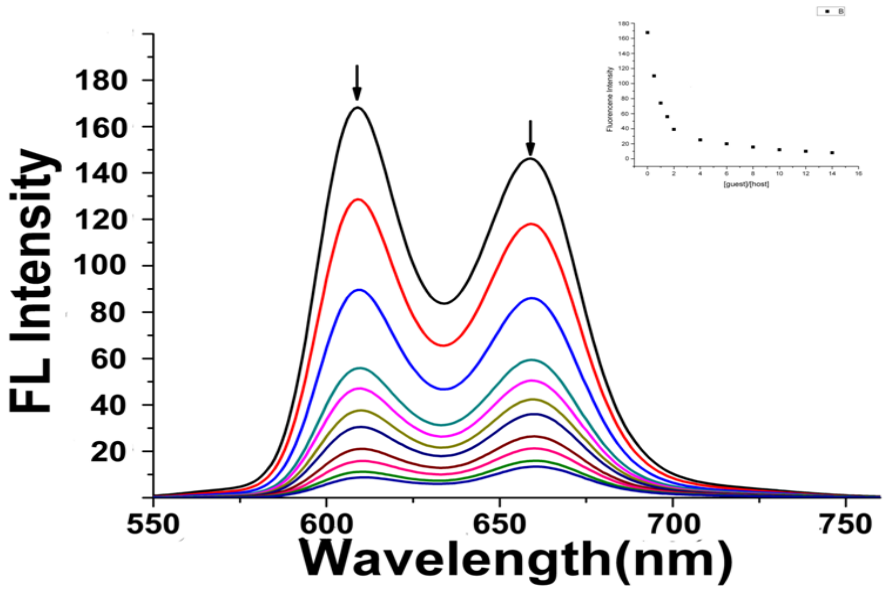


Figure S5. Fluorescence spectra during the titration of 2 (0.14 μM) with C_{70} in toluene at 298 K (λ_{ex} = 421 nm). Inset: plot of I_{609nm} against number of equivalents of C_{70} added.

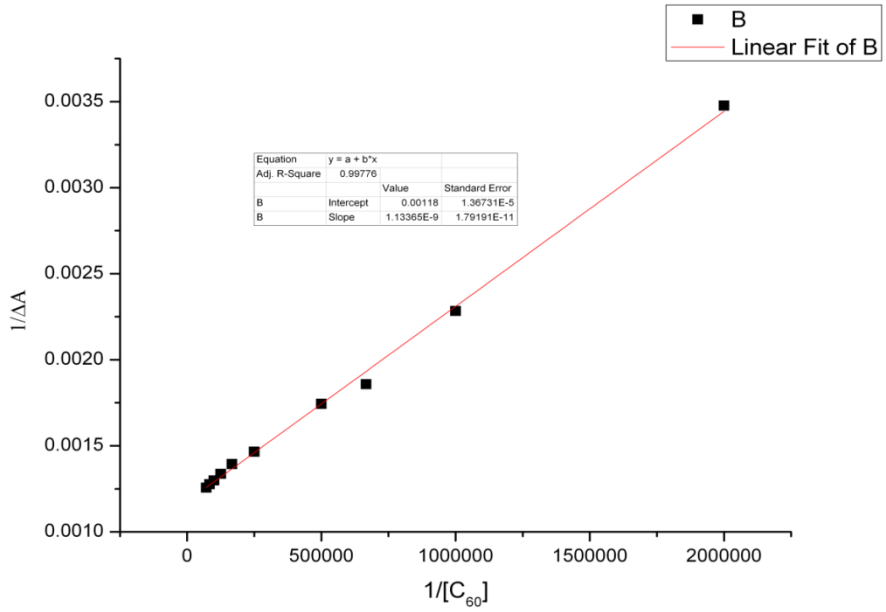


Figure S6. Benesi-Hildebrand analysis of cage 2 at different C_{70} concentrations.