

Supporting Information

Benzothiadiazole-based self assembled cage for cadmium detection

Zong-Cheng Wang¹, Ying-Zi Tan¹, Hui Yu¹, Wen-Hu Bao¹, Lin-Li Tang¹ and Fei Zeng^{1,*}

¹*Hunan University of Science and Engineering, YongZhou 425199, China*

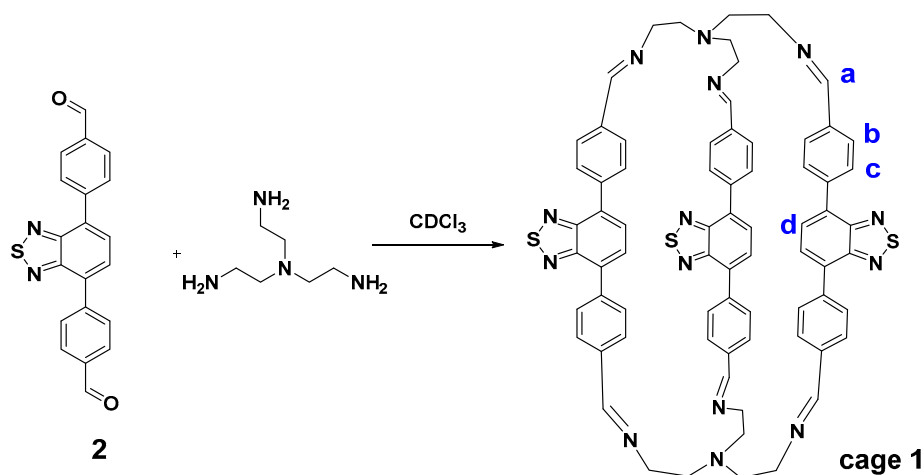
E-mail: zengfei@hseu.edu.cn

Content

1. Experiment section.....	2
2. ¹ H NMR and ¹³ C NMR spectra of cage 1.....	3
3. ¹ H - ¹ H COSY and ¹ H- ¹ H NOESY spectra of cage 1	4
4. Fluorescence photographs of cage 1 after additon of Cd ²⁺	5
5. ESI-MS spectrum of cage 1	5
6. ¹ H NMR spectroscopic of cage 1 after additon of Cd ²⁺	6
7. Reference.	6

1. Experiment section.

General. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker DMX400 NMR spectrometer. Commercial reagents were used without further purification. 4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde **2** was prepared according to the reported literature^{S1}. Electrospray ionization mass spectra (ESI-MS) were recorded on the Thermo Fisher® Exactive LC-MS spectrometer.



Scheme S1 Synthesis of the cage **1**

Synthesis of cage 1. The cage **1** was obtained by condensing **2** (1.24 mg, 6 mM) and tris(2-aminoethyl)amine (TREN) (0.36 mg, 4 mM) in CDCl_3 (0.6 mL). The solution was sealed in a NMR tube without stirring for 12h to let the system to reach the equilibrium. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 6H), 7.59 (d, $J = 8.0$ Hz, 12H), 7.39 (d, $J = 8.0$ Hz, 12H), 6.71 (s, 6H), 3.91 (s, 12H), 2.90 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.96, 153.58, 137.89, 136.15, 132.17, 129.05, 128.41, 127.11, 57.90, 52.22. ESI-MS cald. for $[\text{M}+\text{Na}]^+$: 1239.42. Found: 1239.15.

2. ^1H NMR and ^{13}C NMR spectra of cage 1

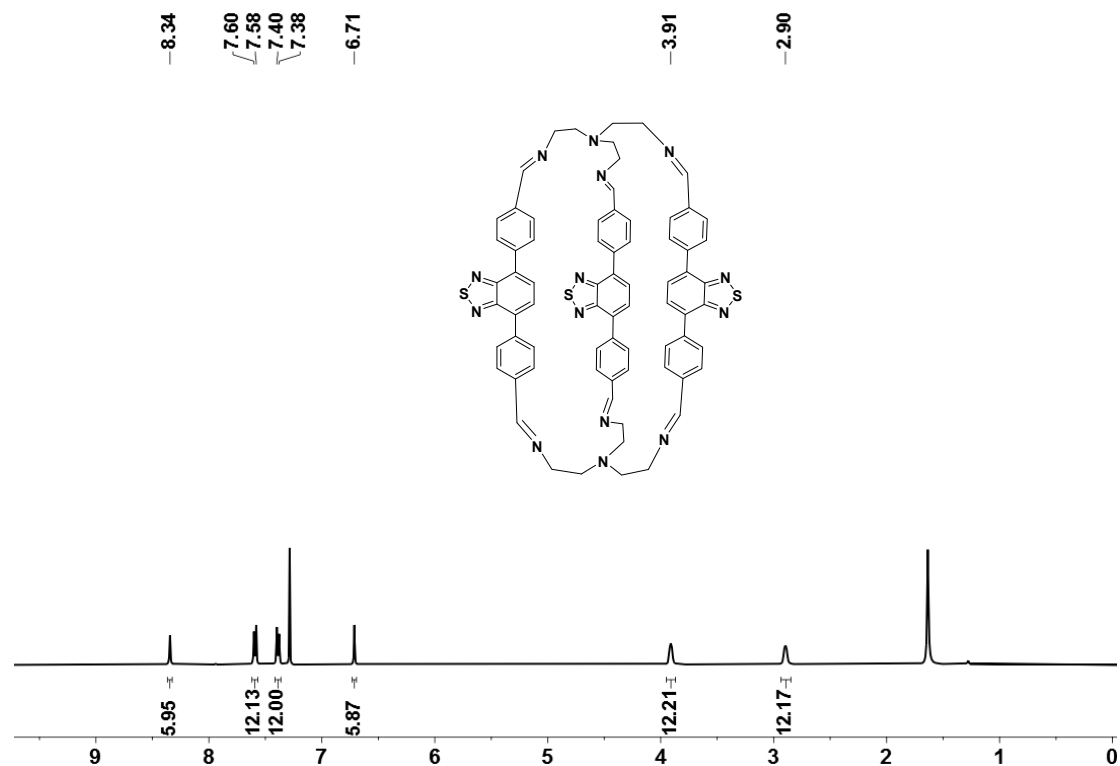


Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of cage 1.

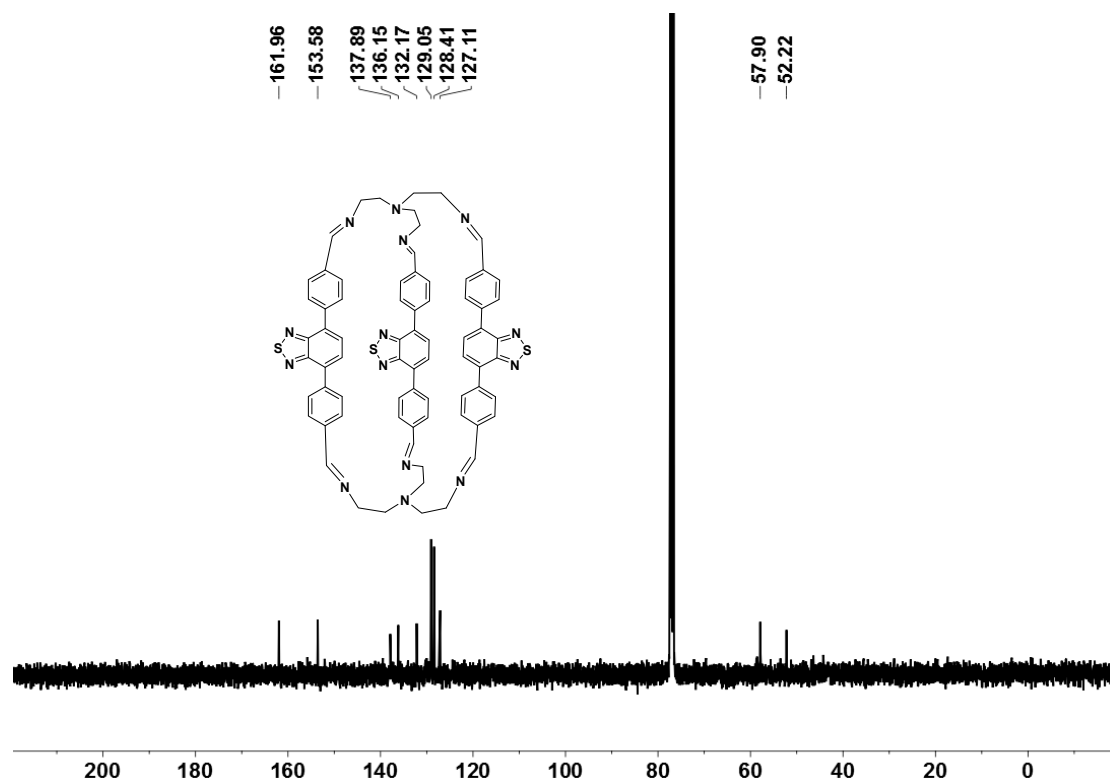


Figure S2. ^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of cage 1.

3. ^1H - ^1H COSY and ^1H - ^1H NOESY spectra of cage 1

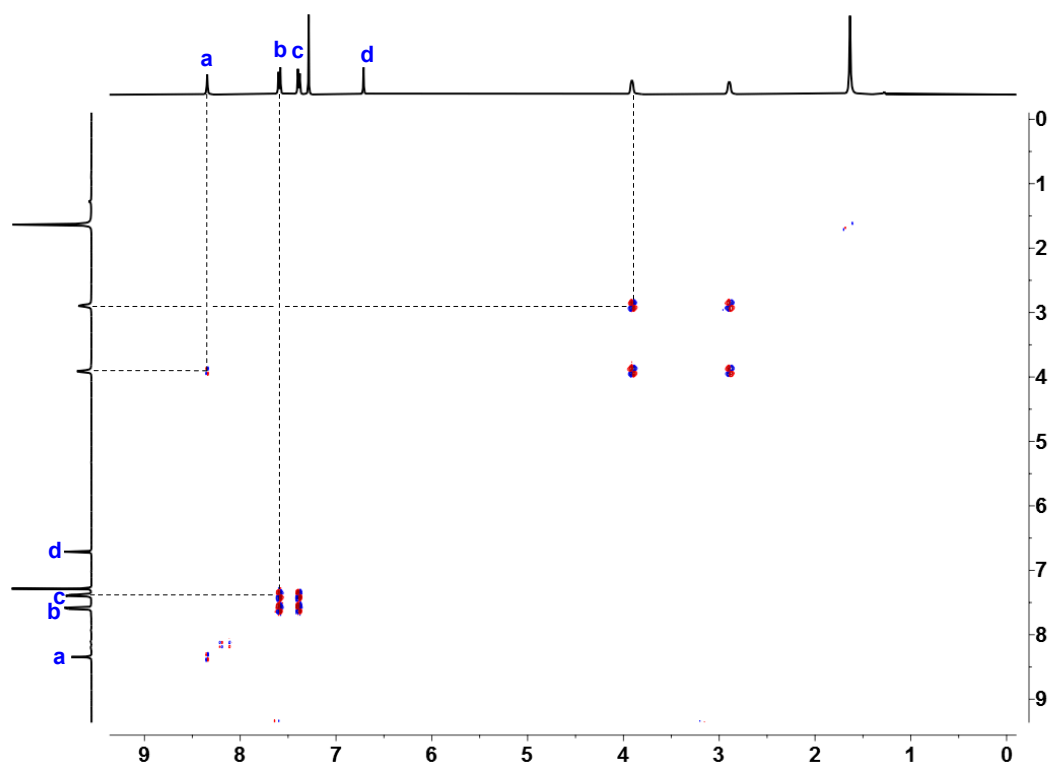


Figure S3. Partial ^1H - ^1H COSY spectrum (400 MHz, CDCl_3 , 298 K) of cage 1.

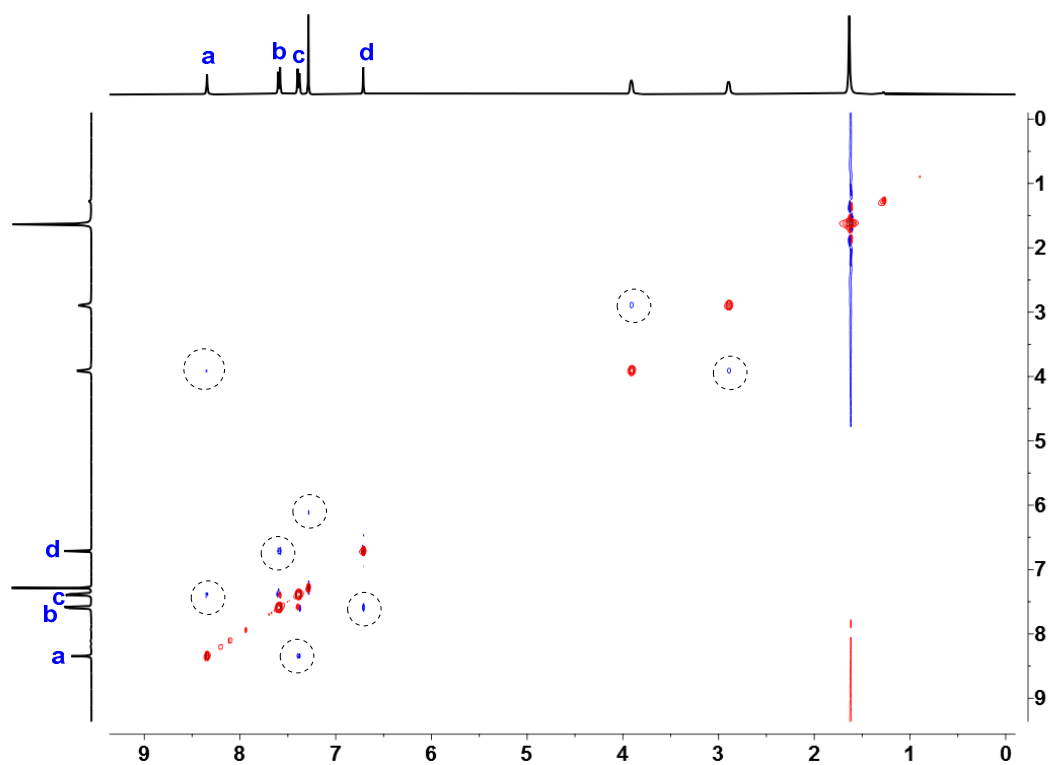


Figure S4. Partial ^1H - ^1H NOESY spectrum (400 MHz, CDCl_3 , 298 K) of cage 1.

4. Fluorescence photographs of cage 1 after additon of Cd^{2+}

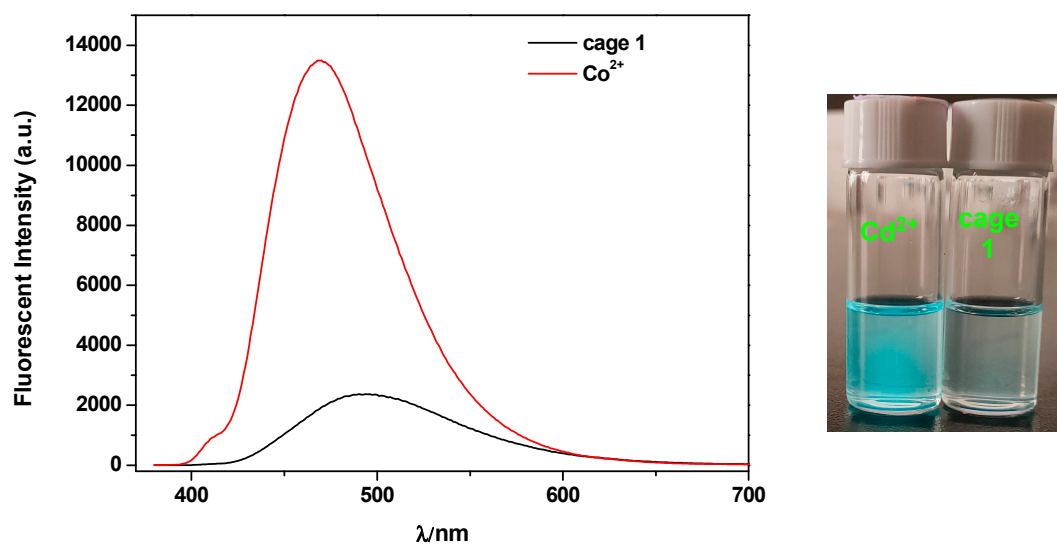


Figure S5. Fluorescence photographs of cage 1 after addition of 10 equiv of Cd^{2+} , $[\text{1}]_0 = 1.0 \times 10^{-5} \text{ M}$.

5. ESI-MS spectrum of cage 1

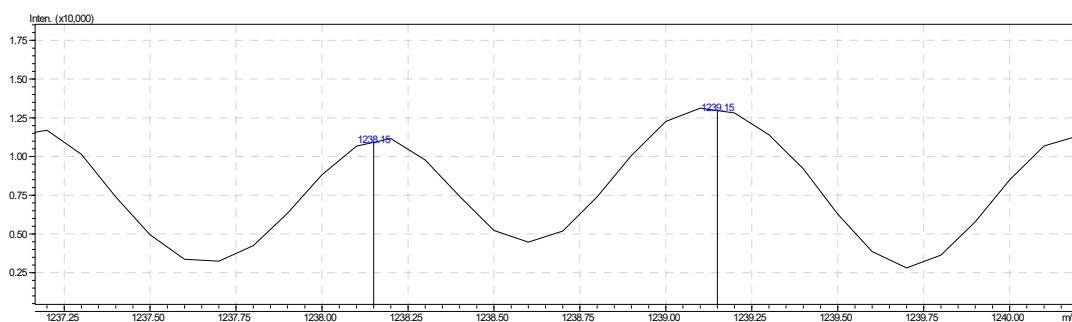


Figure S6. ESI-MS spectrum of cage 1.

6. ^1H NMR spectroscopic of cage 1 after additon of Cd^{2+}

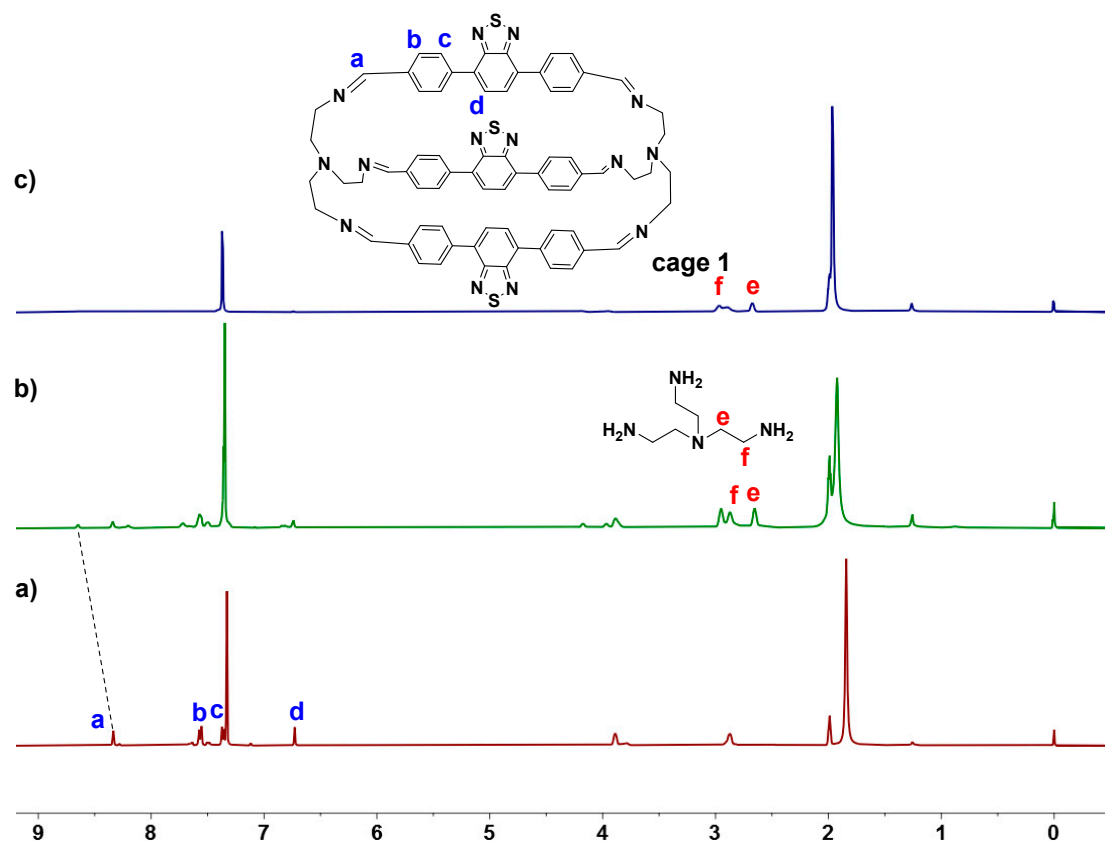


Figure S7. ^1H NMR spectrum (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN} = 10:1$, 298K) of a) cage 1, b) 1 and 0.5 equiv of Cd^{2+} , c) 1 and 1.0 equiv of Cd^{2+} . $[\mathbf{1}]_0 = 2.0$ mM. After addition of 0.5 equiv of Cd^{2+} cation, a small amount of yellow precipitation was formed. Further increase the amount of Cd^{2+} cation can produce more precipitation.

7. Reference.

1. S1 Tang Y, Huang H, Peng B, Chang Y, Li Y, Zhong C. A thiadiazole-based covalent triazine framework nanosheet for highly selective and sensitive primary aromatic amine detection among various amines. J. Mater. Chem. A 2020; 8: 16542-16550.