Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Chloroform-Selective Vapochromic Behavior Based on Crystal-State Host-Guest Complexation of Organic Cage

Zhen-an Cai,[1] Jing Du,[2] Tiefan Huang,[3] Yanjun Ding,*[1] Mingzai Wu *[1]

[1] School of Materials Science and Engineering, Anhui University, Hefei 230601, China.

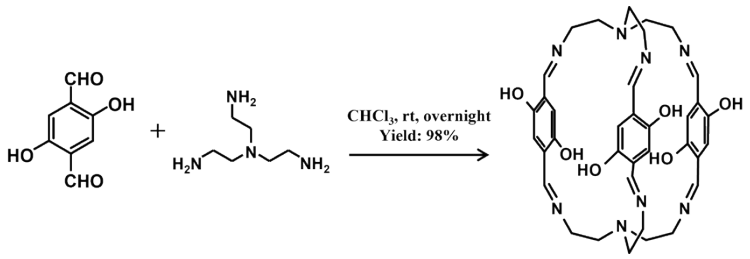
[2]Testing and Analysis Center, Hebei Normal University, Shijiazhuang 050024, China

[3]Functional Membrane Materials Engineering Research Center of Hunan Province, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, 411201, China.

1. Experimental Procedures

1.1. Materials. All chemicals were purchased from commercial sources and used as received.

1.2. Synthesis of DHTA-Cage. 2,5-Dihydroxyterephthalaldehyde (99.7 mg; 0.6 mmol) was dissolved in $CHCl_3$ (80 mL), then Tren (58.5 mg; 0.4 mmol) in $CHCl_3$ (60 mL) was added dropwise over 1 h. The reaction mixture stirred overnight at room temperature. After that, the solvent was evaporated and dried in vacuo to get the crude product in 98% yield. The crude product finally was purified via crystallization from dichloromethane and ethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 6.82 (s, 1H), 3.85 (d, J = 13.2 Hz, 1H), 3.47 (t, J = 12.7 Hz, 1H), 3.27 (t, J = 12.6 Hz, 1H), 2.18 (d, J = 13.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.93, 151.75, 119.36, 57.44, 53.75. HRMS (ESI) calcd for $C_{36}H_{44}N_8O_6Na$ [$(M+Na)^+$]: 705.3125, Found: 705.4144.



Scheme S1. Synthetic scheme of DHTA-Cage.

1.3. Single Crystal Growth. Single crystals of the crystalline DHTA-cage 1 were grown by liquid diffusion of diethyl ether into a dichloromethane solution at room temperature. Single crystals of DHTA-cage 2 were obtained by liquid diffusion of acetonitrile into a chloroform solution at room temperature.

1.4. Vapochromic Experiments. An open 5 mL vial containing 10 mg of crystalline DHTA-cage 1 was placed in a sealed 20 mL vial containing 1 mL of guest solution. Crystalline DHTA-cage 1 was exposed under saturated vapor pressure in the closed vessel at 25 ℃ for 12 h. Uptake of guest vapor by DHTA-cage 1 was measured by ^{1}H NMR by completely dissolving the crystals in CD_2Cl_2.

1.5. Adsorption Material Activation. Crystalline DHTA-cage 1 after adsorption was regenerated to release the adsorbed guests upon heating at 80 ℃ under vacuum for 4 h.

2. Methods

2.1. Solution NMR. NMR spectra were recorded on Bruker-400 (400 MHz for ^{1}H; 101 MHz for ^{13}C) instruments internally referenced to $SiMe_4$ signal.

2.2. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out using a TGA 5500 analyzer (TA Instruments) with an automated vertical overhead thermobalance. The samples were heated at 5 °C/min from 25 to 800 °C using N_2 as the protective gas.

2.3. Nitrogen Adsorption Experiment. Low-pressure gas adsorption measurement was performed using a BeiShiDe 3H-2000PS2 instrument. Samples were degassed under dynamic vacuum for 12 h at 60 °C prior to each measurement. N_2 isotherms were measured using a liquid nitrogen bath (77 K).

2.4. Powder X-Ray Diffraction. Powder X-ray diffraction (PXRD) patterns were obtained using a XRD Bruker D8-ADVANCE X-ray diffractometer (40 KV, 40 mA) with the Cu Kα radiation (λ = 1.5406 Å). Data were measured over the range of 3−50° in 2°/min steps.

2.5. Single Crystal X-ray Diffraction. Single crystal X-ray diffraction data were recorded on a STOE STADIVARI diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 150 K. All structures were solved with the ShelXT structure solution program using Intrinsic Phasing[1] and refined with the ShelXL refinement package using Least Squares minimization[2] operated in the OLEX2 interface.[3] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on organic carbon atoms were fixed in calculated positions. Crystal data and structural refinement for DHTA-cage 1 and DHTA-cage 2 are listed in Table S1.

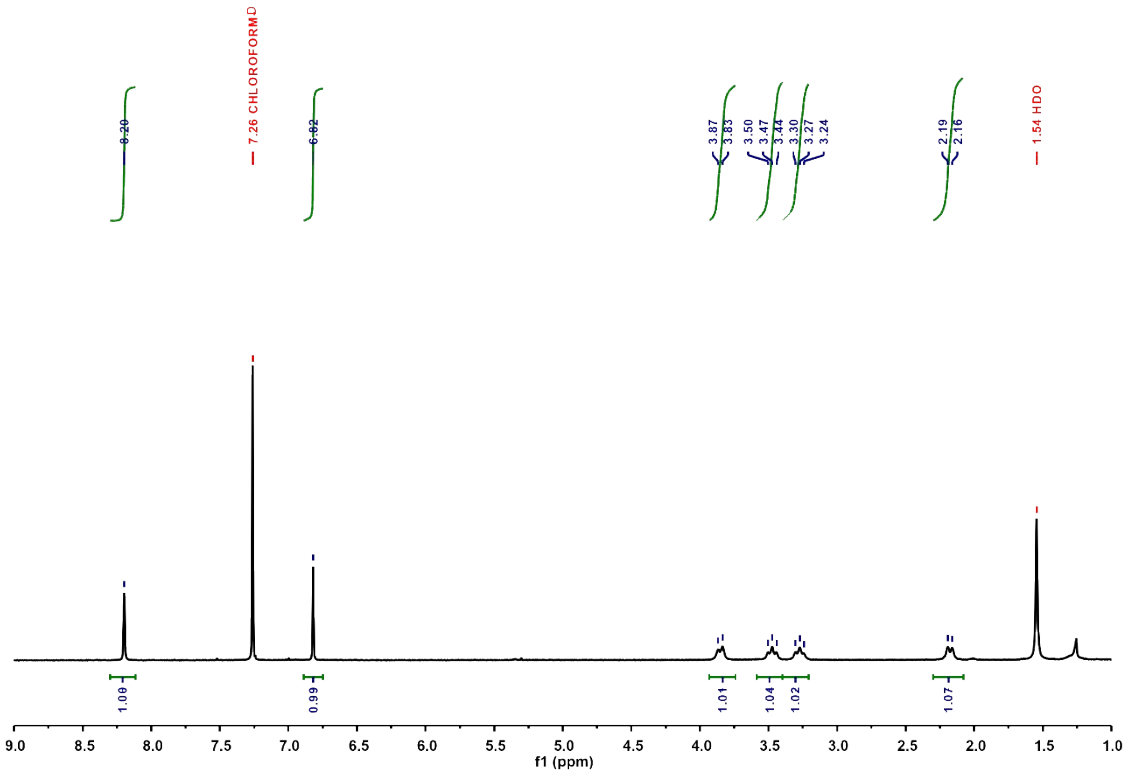


Figure S1. ^{1}H NMR spectrum (400 MHz, 298K, $CDCl_3$) of the **DHTA-cage** (HDO peak comes from trace amount of water in $CDCl_3$).

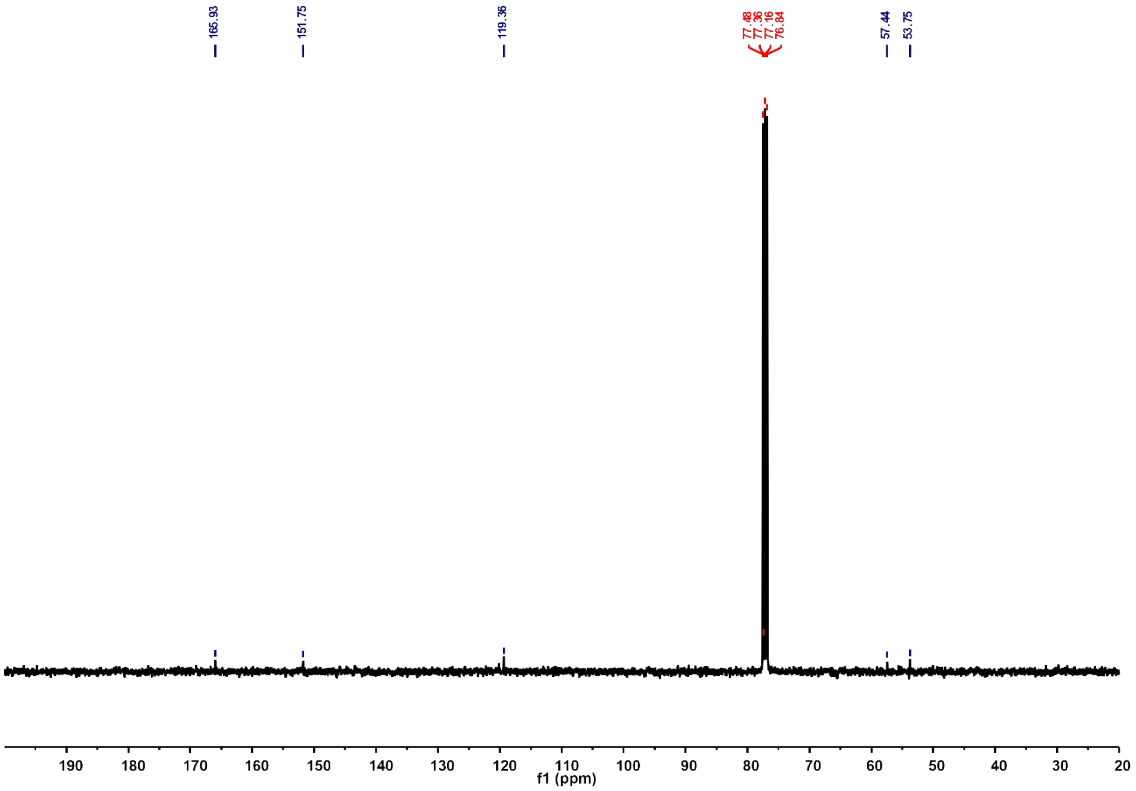


Figure S2. ^{13}C NMR spectrum (101 MHz, 298K, $CDCl_3$) of the **DHTA-cage 1**.

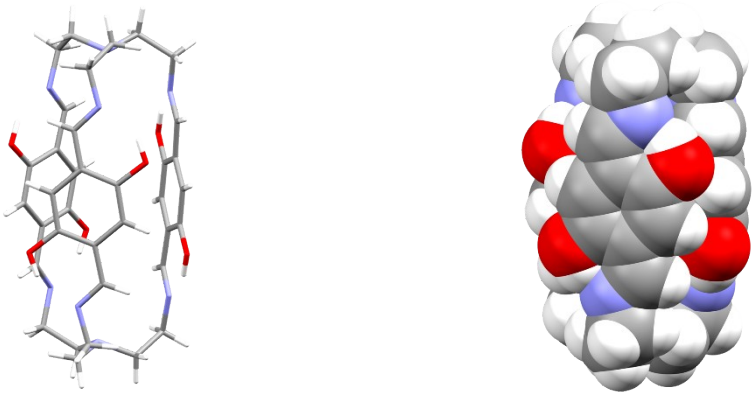


Figure S3. Single crystal structure and the space filling structure of crystalline DHTA-cage 1.

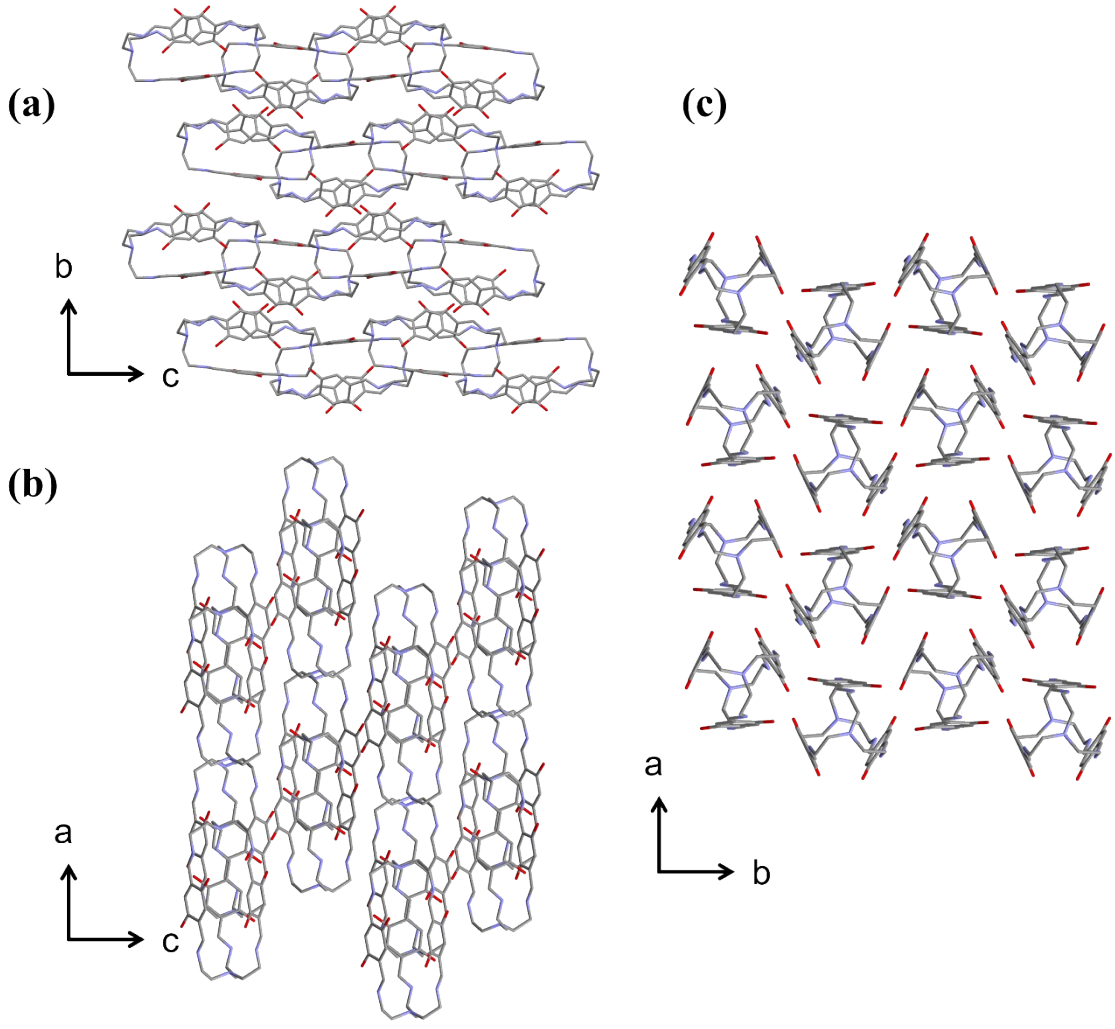


Figure S4. Packing arrangement of crystalline **DHTA-cage 1** along (a) *a*-axis (b) *b*-axis and (c) *c*-axis.

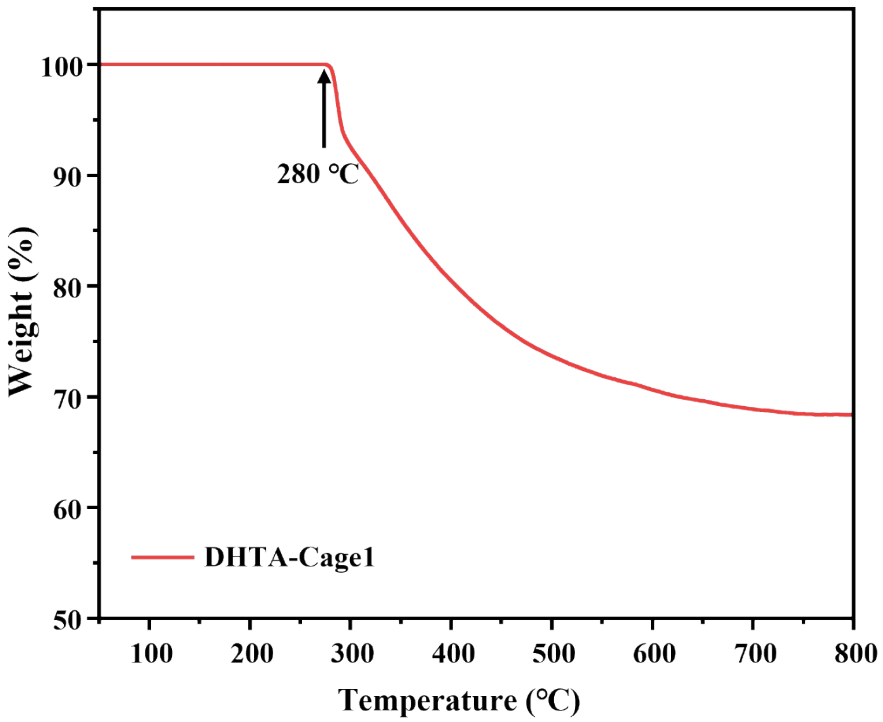


Figure S5. Thermogravimetric analysis: the as synthesized crystalline DHTA-cage 1.

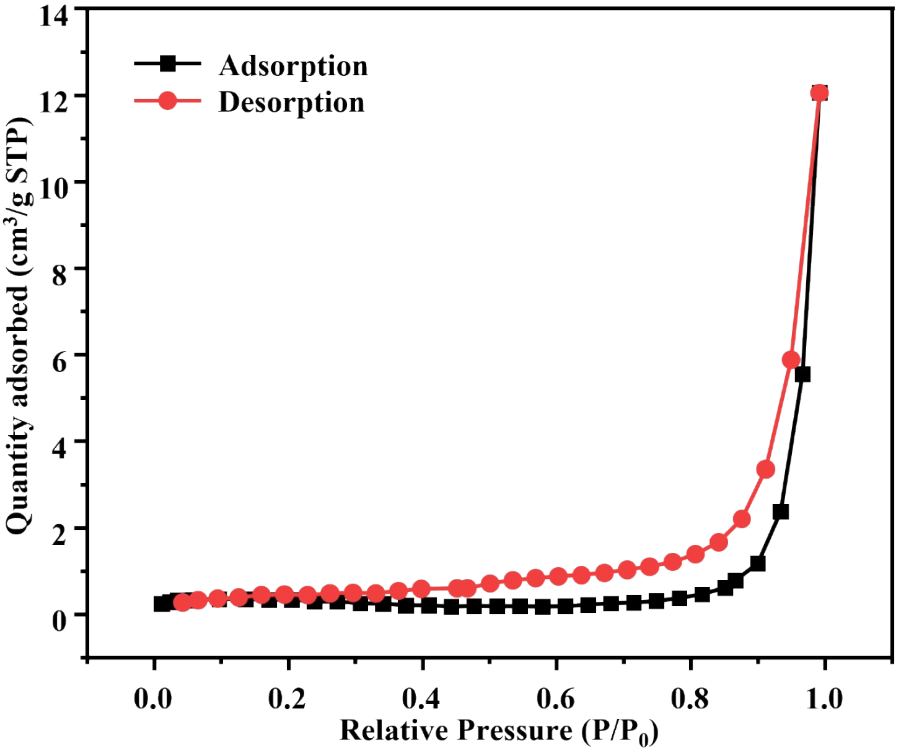


Figure S6. Nitrogen adsorption isotherm at 77 K for crystalline DHTA-cage 1. The calculated BET surface area is 0.8 m^2/g.

Figure S7. Photographs showing the color changes of crystalline DHTA-cage 1 upon exposure to halogenated methane (CH_2Cl_2, $CHCl_3$ and CCl_4) vapor.

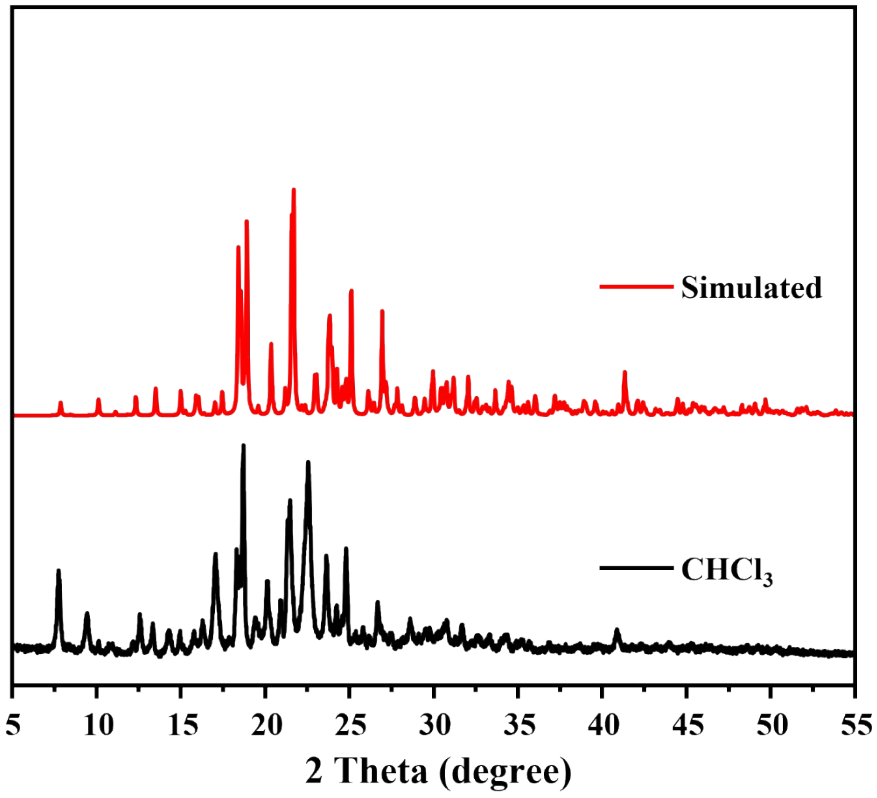


Figure S8. PXRD patterns of crystalline DHTA-cage 1 after exposure to chloroform (Black lines) and simulated from X-ray crystal structures of DHTA-cage 2 (Red lines).

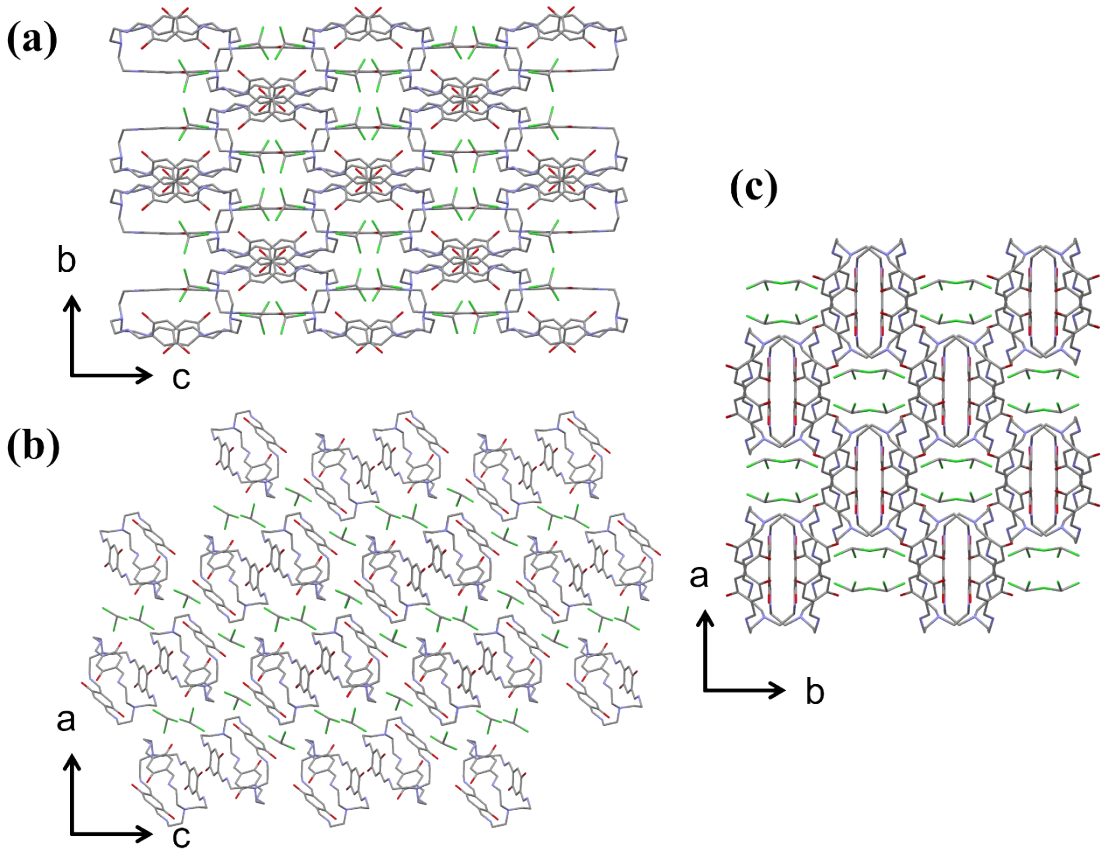


Figure S9. Packing arrangement of crystalline **DHTA-cage 2** along (a) *a*-axis (b) *b*-axis and (c) *c*-axis.

Figure S10. Photographs showing the color changes of crystalline DHTA-cage 1 upon exposure to equimolar mixtures of biphasic or tertiary solvent vapor.

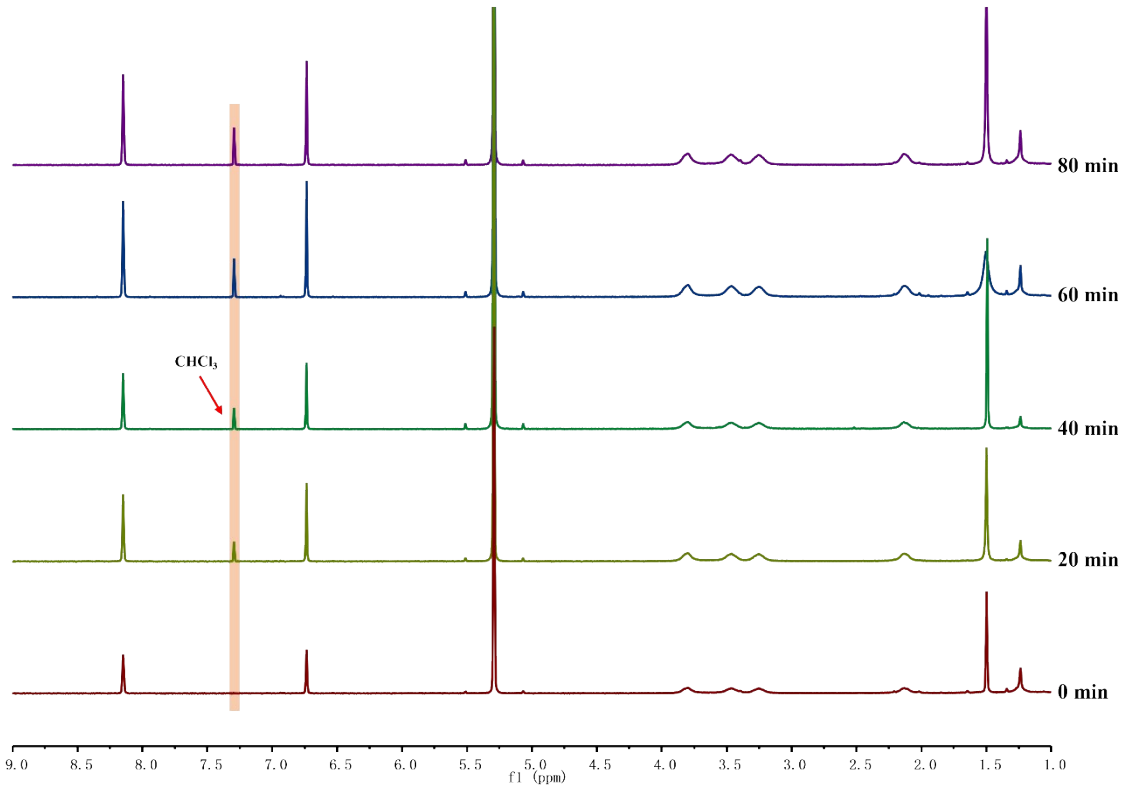


Figure S11. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of crystalline DHTA-cage 1 after exposure to chloroform over time.

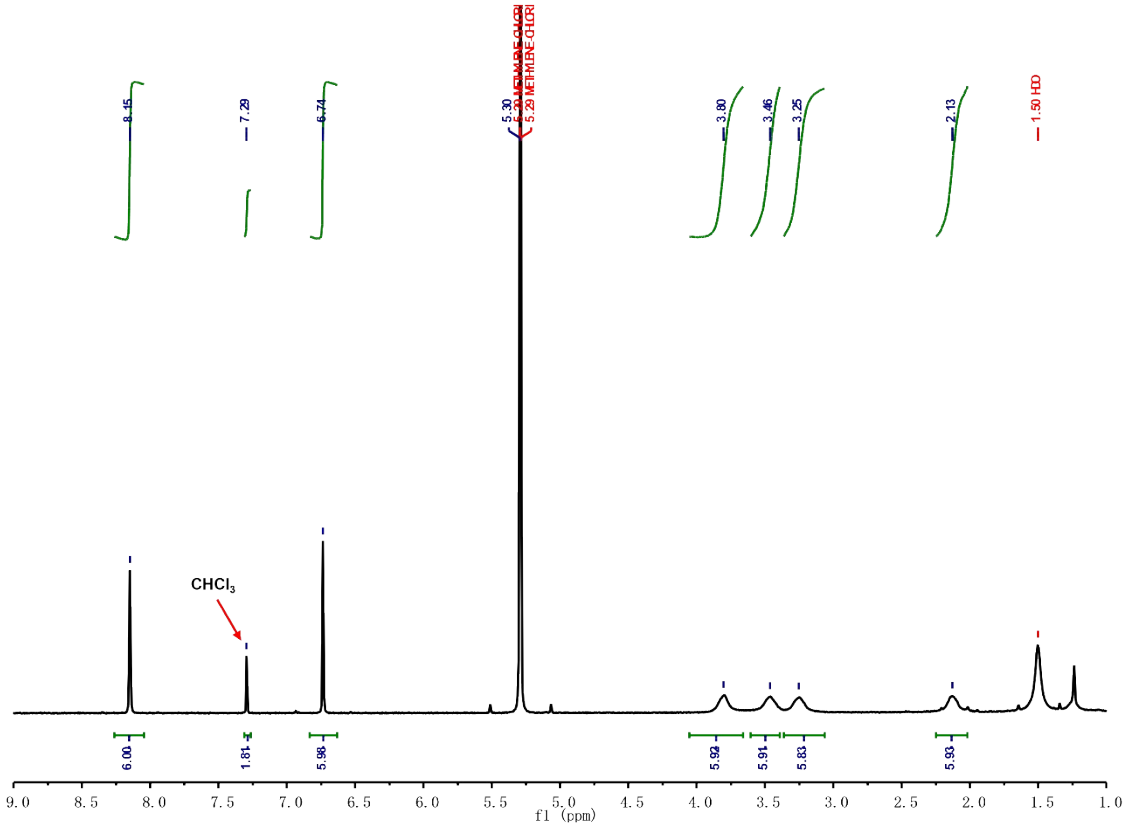


Figure S12. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of crystalline DHTA-cage 1 after exposure to chloroform at saturation.

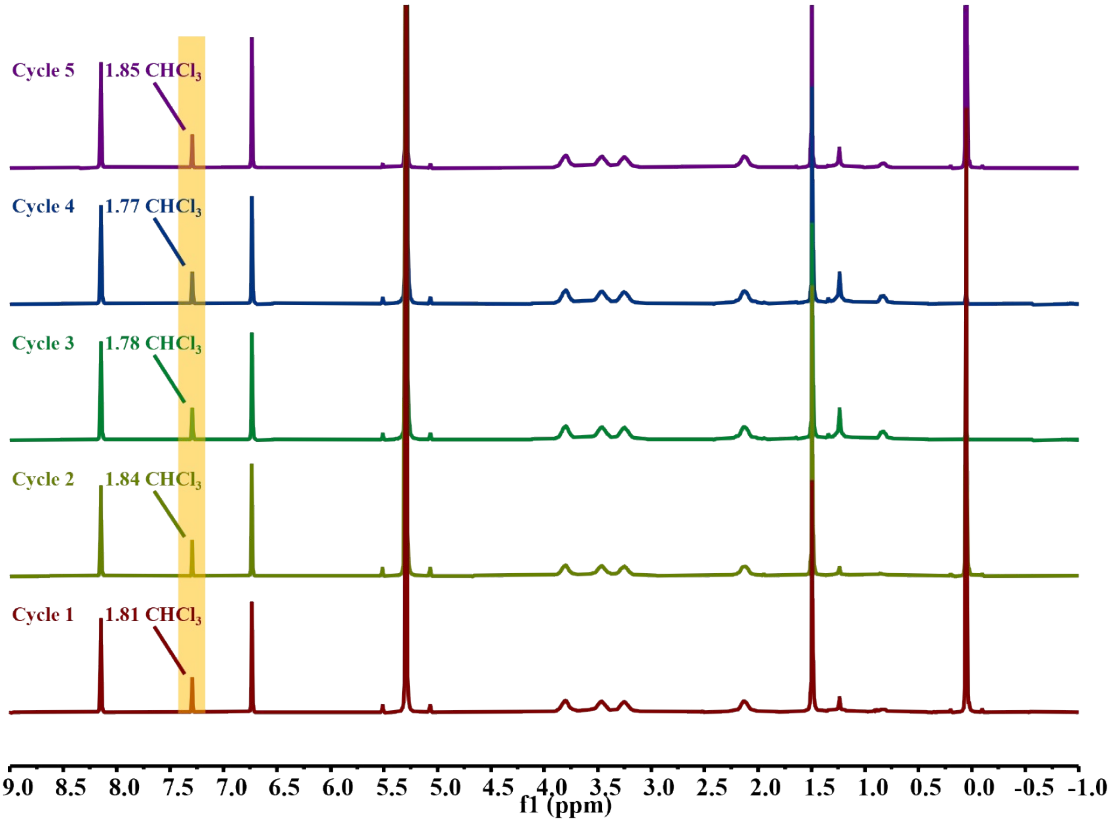


Figure S13. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of Uptake amounts of crystalline DHTA-cage 1 towards $CHCl_3$ molecules in five cycles.

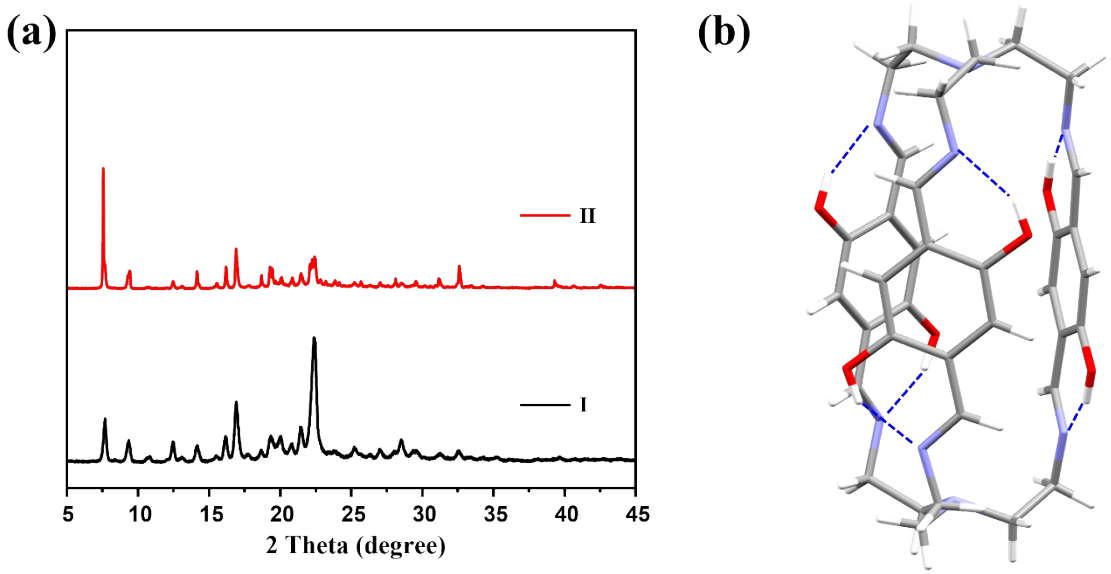


Figure S14. (a) Water stability of (Ⅰ) crystalline DHTA-cage 1 and (Ⅱ) crystalline DHTA-cage 1 soaked in boiling water for 24 h. (b) crystal structure of crystalline DHTA-cage 1 showing the hydrogen bonding (Blue lines).

Table S1. Experimental single crystal X-ray data.

Identification code	**DHTA-Cage 1**	**DHTA-Cage 2**
Empirical formula	$C_{36}H_{42}N_8O_6$[a]	$C_{36}H_{42}N_8O_6 \cdot 2CHCl_3$[a]
Formula weight	682.77	921.51
Temperature /K	150.0	150
Crystal system	Monoclinic	Monoclinic
Space group	*P 1 2$_1$/n 1*	*I 1 2/a 1*
a /Å	13.6491(8)	16.4758(8)
b /Å	16.3995(7)	14.6068(9)
c /Å	15.8476(9)	19.2419(10)
α /°	90.00	90.00
β /°	102.302(5)	114.749(4)
γ /°	90.00	90.00
Volume /Å^3	3465.8(3)	4205.4(4)
Z	4	4
ρ_{calc} g/cm^3	1.309	1.455
μ /mm^{-1}	0.747	4.194
F(000)	1448	1912
Radiation	CuKα (λ = 1.54186 Å)	CuKα (λ = 1.54186Å)
Theta range for data collection/°	3.89 to 69.44	3.94 to 64.9
Index ranges	-13≤ h ≤ 16, -8 ≤ k ≤ 19, -18 ≤ l ≤ 13	-19≤ h ≤18, -14≤ k ≤ 17, -22 ≤ l ≤ 18
Reflections collected	13127	7589
Independent reflections	5729 [R_{int} = 0.0348, R_{sigma} = 0.0382]	3458 [R_{int} = 0.0412, R_{sigma} = 0.0344]
Data/restraints/parameters	4231/0/457	2959/0/266
Goodness-of-fit on F^2	0.952	1.101
Final *R* indexes [I>=2σ (I)][b]	R_1 = 0.0407, wR_2 = 0.1011	R_1 = 0.0593, wR_2 = 0.1649
Final *R* indexes [all data][b]	R_1 = 0.0607, wR_2 = 0.1075	R_1 = 0.0675, wR_2 = 0.1720
CCDC	2287666	2287717

[a] Formula is given based on single-crystal X-ray data.
[b] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$, $wR_2 = \{ \Sigma[w(F_o^2-F_c^2)^2]/ \Sigma[w(F_o^2)^2]\}^{½}$

Reference

[1] G. M. Sheldrick, Acta Crystallogr. C Struct. Chem. 2015, 71, 3-8.

[2] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339-341.