Supporting information

A new versatile crystalline sponge for organic structural analysis without the need of activation

Jin-Chang Liu[1], Wei-Ping Huang[1], Yu-Xin Tian[1], Wei Xu[1]*, Wen-Cai Ye[1,2]*, Ren-Wang Jiang[1,2]*

1 State Key Laboratory of Bioactive Molecules and druggability Assessment, College of Pharmacy, Jinan University, Guangzhou 510632, P. R. China;

2 International Cooperative Laboratory of Traditional Chinese Medicine Modernization and Innovative Drug Development of Ministry of Education (MOE) of China, College of Pharmacy, Jinan University, Guangzhou 510632, P. R. China.

Correspondence:

Ren-Wang Jiang: trwjiang@jnu.edu.cn

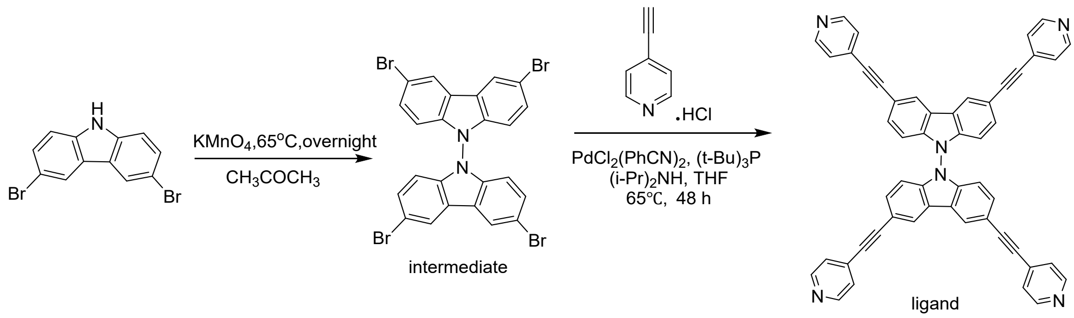
Wen-Cai Ye: chywc@aliyun.com

Wei Xu: xwnail2003@163.com

Tel: 8620-85221016; Fax: 8620-85221559

Table of contents

S1. Syntheses of intermediate and ligand



Scheme 1 synthesis of intermediate and ligand

(1) Synthesis of 3,3',6,6'-tetrabromo-9,9'-bicarbazole (intermediate)

To a solution of 3,6-dibromo-9H-carbazole 1g (3.08 mmol, 1eq) in 15 mL acetone, $KMnO_4$ 1.22g (7.69 mmol, 2.5eq) was slowly added at room temperature. The resulting mixture was stirred at 65 °C overnight and cooled down to room temperature. After evaporation of acetone under reduced pressure, the precipitate washed with dichloromethane three times, combined the organic layers and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give white solid powder intermediate in 53.5% yield (533 mg, 0.82mmol).

(2) Synthesis of 3,3',6,6'-tetrakis(pyridin-4-ylethynyl)-9,9'-bicarbazole (ligand)

The intermediate 1.5g (2.31 mmol, 1eq), 4-ethynylpyridine hydrochloride 2.58g (18.5 mmol, 8eq), diisopropylamine 12ml, tert-butylphosphane 705ul (3.00 mmol, 1.3eq), CuI 26.4mg (0.139 mmol, 0.06eq), $PdCl_2(PhCN)_2$ 88.6mg (0.231 mmol, 0.1eq) were dissolved in dry THF (40 mL). The reaction was stirred at 50 °C under N_2 for 48 h. After cooling down to room temperature, the reaction was diluted with water and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 for three times. The combined organic layers were washed with brine and dried over Na_2SO_4. After evaporation of CH_2Cl_2, the residue was purified by flash column chromatography on silica gel (CH_2Cl_2: CH_3OH = 60: 1) to give light yellow ligand in 79.2% yield (1.35 g, 1.83mmol).

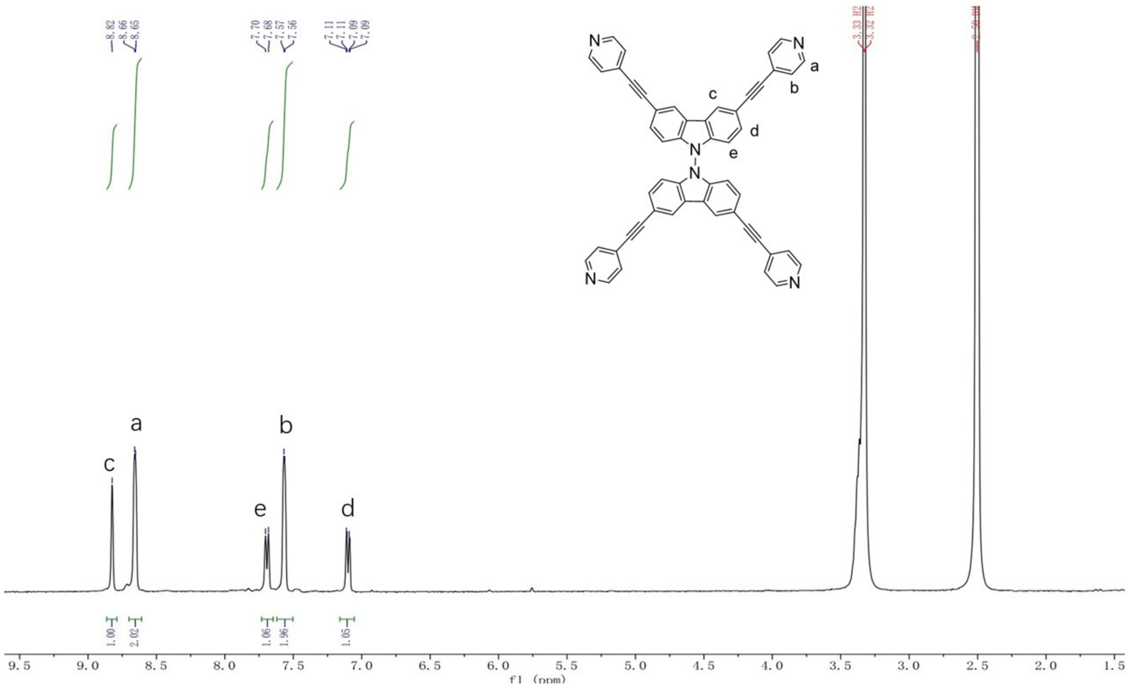


Fig. S1a ^{1}H-NMR spectrum of the ligand (400 MHz, DMSO-d_6).

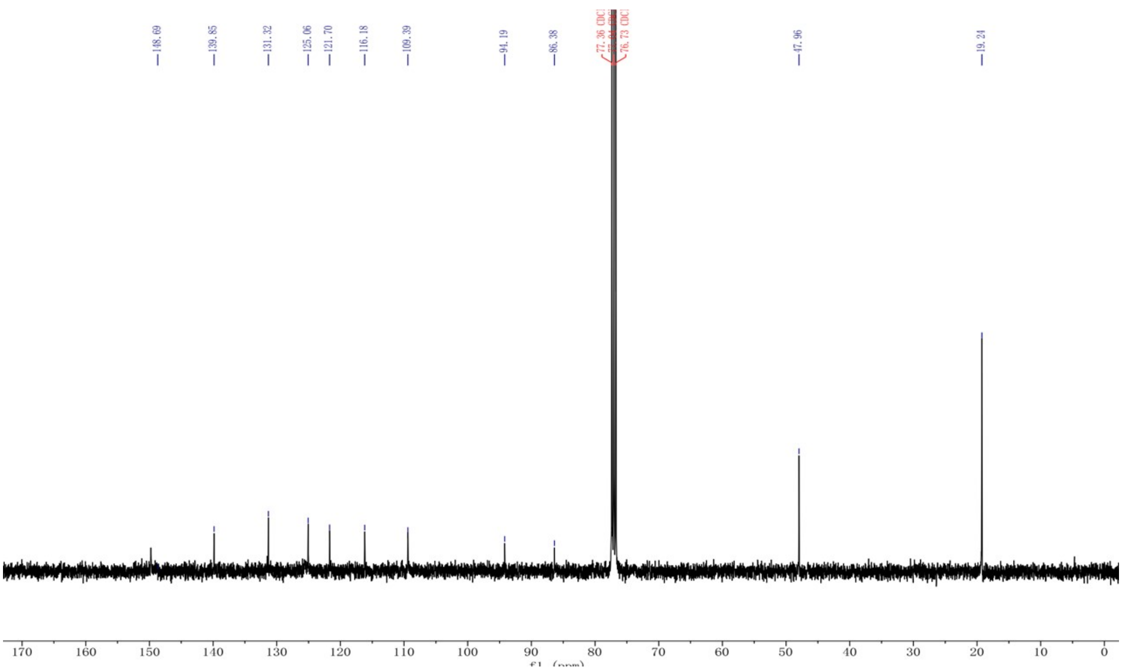
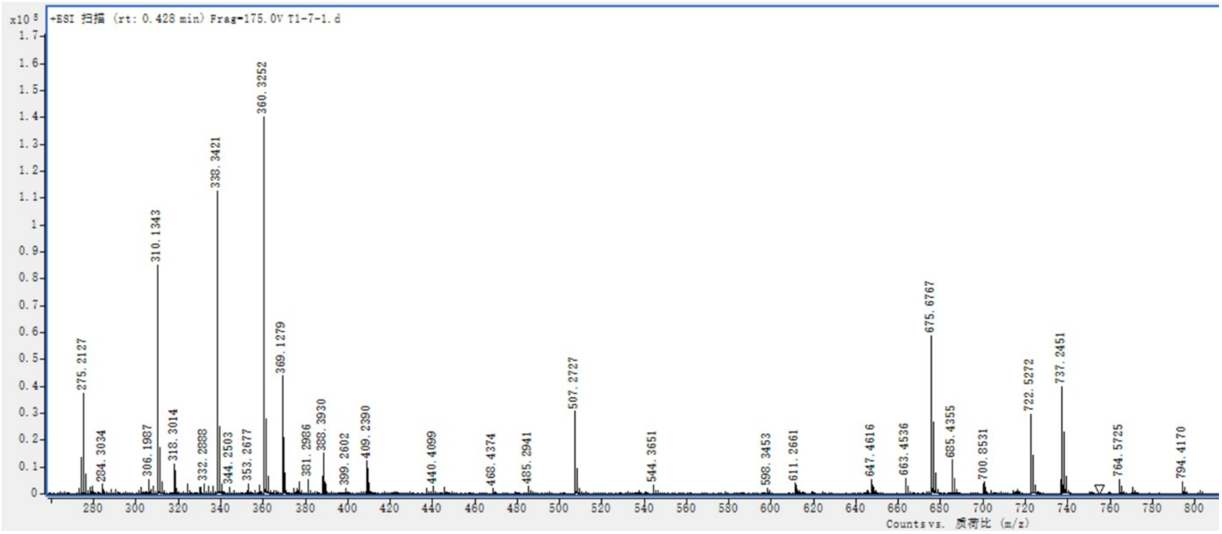


Fig. S1b ^{13}C-NMR spectrum of the ligand (400 MHz, $CDCl_3$).



HR-MS

Fig. S1c HRESI-MS of the ligand showing the molecular ion peak: $[M+H]^{+}$=737.2451, $[M+2H]^{2+}$=369.1279

S2 Synthesis of CMOF (crystal sponge)

CMOF was prepared by a layer-by-layer method in a test tube (diameter = 12 mm). A two-layered solution was prepared from a tetrahydrofuran solution of ligand (0.015 mmol/4 ml; bottom), and an acetonitrile solution of CuI (0.01 mmol /3ml; top) in a capped test tube and kept at 25°C in an incubator. Upon slow diffusion, high quality single crystals began to grow after two days. The yield of the crystals was 20 % after 10 days incubation.

We prepared a 25 mg/L rhodamine in THF. Then, CMOF (5 mg) was added to rhodamine solution, 12h and 24 h later, photos were taken separately. We also used UV-visible spectrophotometer to monitor the spectrum (Fig. S2a).

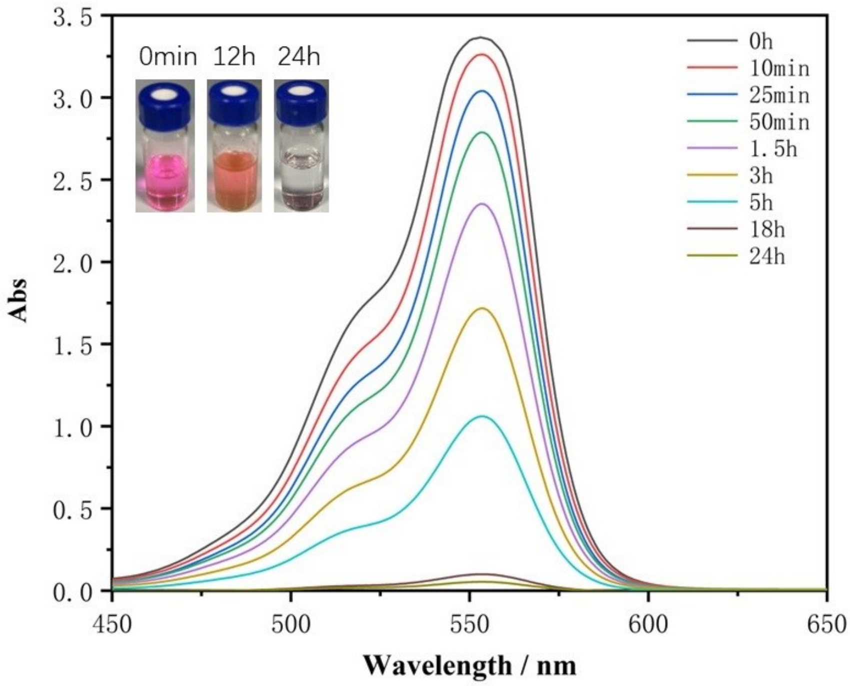


Fig. S2a Adsorption of rhodamine (25 mg/L) by CMOF (5 mg). The solution color was changed to pink to colorless and the absorption from the UV spectrum was decreased.

Although the large pore size of CMOF should allow N_2 adsorption, because the CMOF sample was put in a vacuum chamber before testing, loss of solvent and collapse of CMOF occurred. Obvious color changes from yellow to black was observed after the vacuum process (Fig. S2b) and no adsorption of N_2 at 77 K with negligible BET area (-0.0040 m²/g) was found (Fig. S2c).

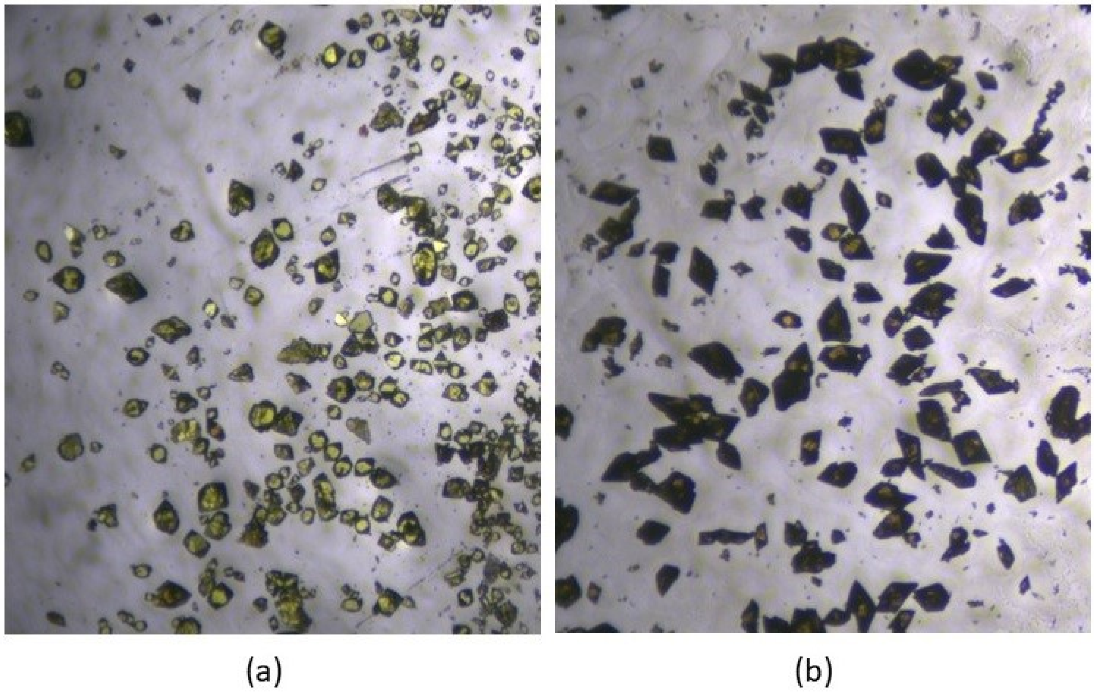


Fig. S2b Stability of CMOF in vacuum chamber. (a) original CMOF crystals; (b) CMOF crystals were put in the vacuum chamber for 10 minutes.

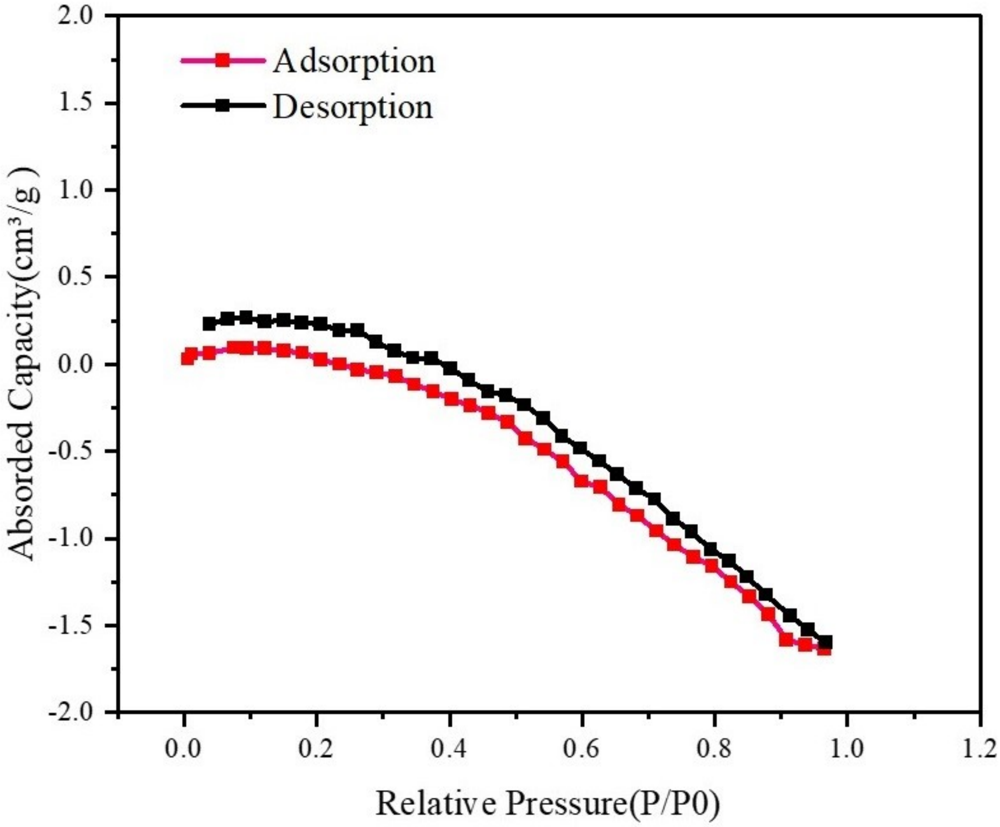


Fig. S2c The N_2 adsorption isotherms at 77 K

S3 Stability of the CMOF crystal sponge

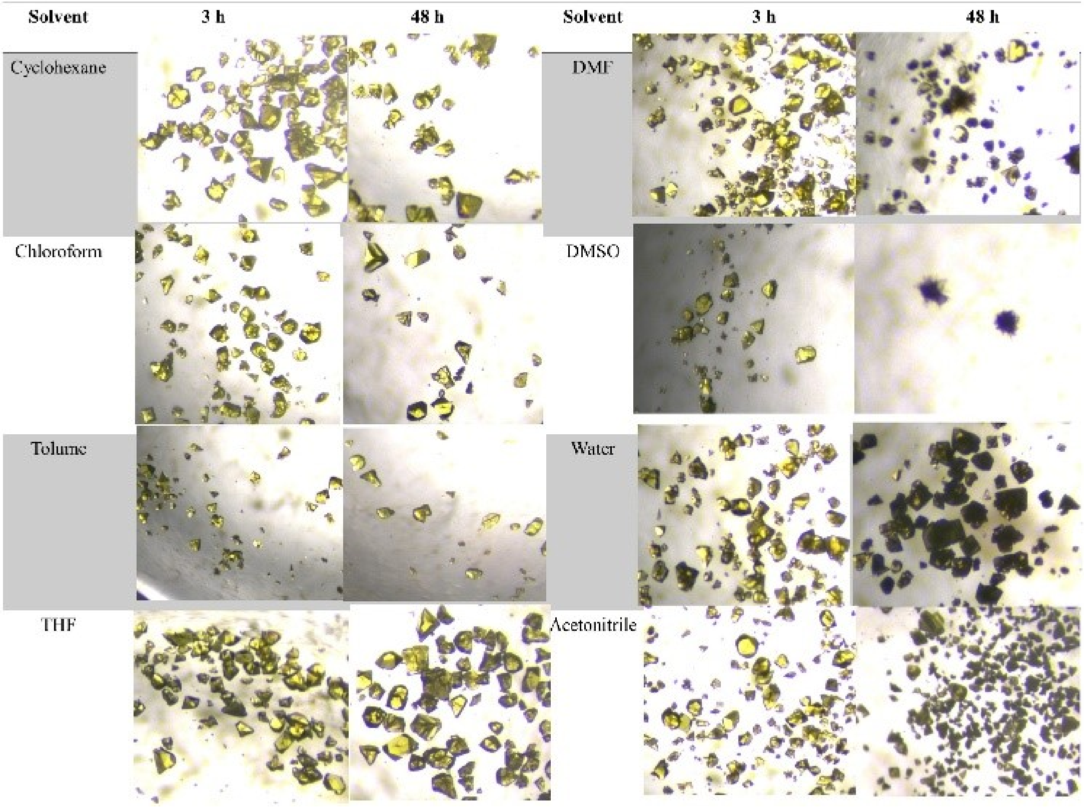


Fig. S3a Stability of the CMOF crystal sponge in different solvents and time points.

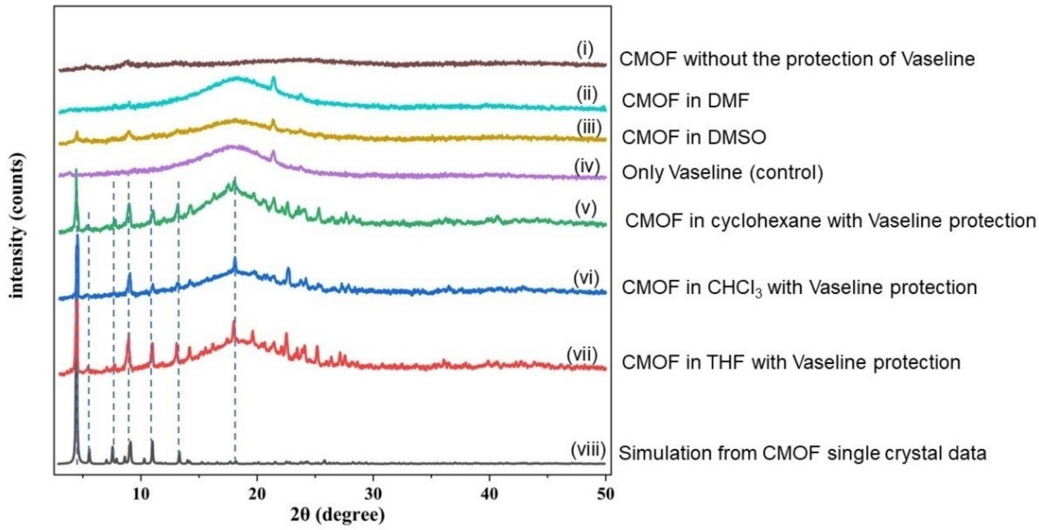


Fig. S3b Powder X-ray diffraction patterns of CMOF in different solvents (Rigaku X-ray diffractometer miniflex600, CuKa radiation, 40kV, 15mA, scanning range 3°-50°, speed: 5°/min). It could be seen that CMOF was also not stable in DMF (Fig. S3b-ii and DMSO (Fig. S3b-iii). Surprisingly, we found that CMOF could be protected by Vaseline. The PXRD patterns of CMOF in cyclohexane (Fig. S3b-v), chloroform (Fig. S3b-vi) and tetrahydrofuran (Fig. S3b-vii) were consistent with the simulated pattern from single crystal data (Fig. S3b-viii) except for the un-flat baseline due to the presence of Vaseline.

Table S3a The cell parameters after immersion in different solvents

Items	Cyclohexane	Toluene	Chloroform	Tetrahydrofuran
shape	unchange	unchange	unchange	unchange
Color	unchange	unchange	unchange	unchange
System	tetragonal	tetragonal	tetragonal	tetragonal
Space group	$I4_1$	$I4_1$	$I4_1$	$I4_1$
a(Å)	22.0341(6)	21.7143(3)	21.6640(6)	21.8272(4)
b(Å)	22.0341(6)	21.7143(3)	21.6640(6)	21.8272(4)
c(Å)	40.3722(2)	41.3410(5)	41.4120(7)	40.7299(8)
α(°)	90	90	90	90
β(°)	90	90	90	90
γ(°)	90	90	90	90
V(Å)	19600.8(16)	19492.7(6)	19435.8(7)	19404.8(8)

S4 Guest encapsulation by crystal sponge

CMOF ⊃ G**1** (diphenyl ether). The freshly prepared single crystals of CMOF (2 mg) were soaked in oxydibenzene (200ul) in a 2ml vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**2** (1,3-dimethoxybenzene). The freshly prepared single crystals of CMOF (2 mg) were soaked in 1,3-dimethoxybenzene (200ul) in a 2ml vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**3** (1,3-dibromobenzene). The freshly prepared single crystals of CMOF (2 mg) were soaked in 1,3-Dibromobenzene (200ul) in a 2ml vial. The vial was kept in 25 °C for 5 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**4** (3,4-dimethoxyphenol). The freshly prepared single crystals of CMOF (2 mg) were soaked in 3,4-dimethoxyphenol solution (10 mg 3,4-dimethoxyphenol dissolved in 200ul tetrahydrofuran) in a 2ml vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**5** (1,4-dimethoxybenzene). The freshly prepared single crystals of CMOF (2 mg) were soaked in 1,4-dimethoxybenzene solution (10 mg 1,4-dimethoxybenzene dissolved in 200 μl tetrahydrofuran) in a 2ml vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**6** [(1*R*)-(-)-menthyl acetate]. The freshly prepared single crystals of CMOF (2 mg) soaked in 6 (200ul) in a 2ml vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**7** [(1*S*)-(+)-menthyl acetate]. The freshly prepared single crystals of CMOF (2 mg) were soaked in 7 (200ul) in a 2ml vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ **ent1** (**6**&**7**) [(1*R*)-(-)-menthyl acetate & (1*S*)-(+)-menthyl acetate]. The freshly prepared (without activated) single crystals of CMOF (2 mg) were soaked in mixed solution [(1*R*)-(-)-menthyl acetate (100ul) and (1*S*)-(+)-menthyl acetate (100 µl)] in a 2ml vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**8** (4*R*(-)-carvone). The freshly prepared single crystals of CMOF (2 mg) were soaked in 4*R*(-)-carvone (200 µl) in a 2ml vial. The vial was kept in 25 °C for 5 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**9** (4*S*(+)-carvone). The freshly prepared single crystals of CMOF (2 mg) were soaked in (4*S*(+)-carvone) (200µl) in a 2ml vial. The vial was kept in 25 °C for 5 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ **ent2** (**8**&**9**) [4R(-)-carvone & 4S(+)-carvone]. The freshly prepared single crystals of CMOF (2 mg) were soaked in mixed solution [4R(-)-carvone (100ul) and 4S(+)-carvone (100ul)]in a 2ml vial. The vial was kept in 25 °C for 5 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ (G**2**&G**5**) (1,3-dimethoxybenzene &1,4-dimethoxybenzene). The freshly prepared single crystals of CMOF (2 mg) were soaked in mixed solution [100mg 1,3-dimethoxybenzen and 100mg 1,4-dimethoxybenzene dissolved in 100 ul tetrahydrofuran]in a 2ml vial. The vial was kept in 25 °C for 5 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ **G10** (cinnamaldehyde). The freshly prepared single crystals of CMOF (2 mg) were soaked in cinnamaldehyde (200ul) in a 2ml vial. The vial was kept in 25 °C for 5 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**11** (benzyl 2-hydroxybenzoate). The freshly prepared single crystals of CMOF (2 mg) were soaked in benzyl 2-hydroxybenzoate (200ul) in a 2ml vial. The vial was kept in 25 °C for 5 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**12** [(3,4-dimethoxyphenyl)methanol]. The freshly prepared single crystals of CMOF (2 mg) were soaked in (3,4-dimethoxyphenyl)methanol (200ul) in a 2ml vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**13** (4-allyl-2-methoxyphenol). The freshly prepared single crystals of CMOF (2 mg) were soaked in 4-allyl-2-methoxyphenol (200ul) in a 2ml vial. The vial was kept in 25

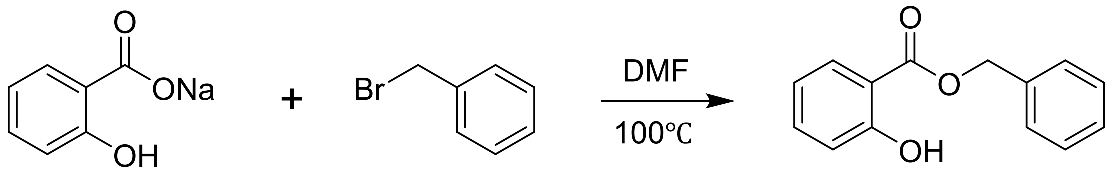
°C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

CMOF ⊃ G**14** (4-allyl-2-methoxyphenyl acetate). The freshly prepared single crystals of CMOF (2 mg) were soaked in 4-allyl-2-methoxyphenyl acetate (200ul) in a 2ml vial, The sample is formed by the reaction of eugenol and acetyl chloride. The vial was kept in 25 °C for 5 days. After the reaction, one of the single crystals was used for SXRD analysis.

S5 Identification of *trans*-cinnamaldehyde (G10) in natural product isolation

The bark of Cinnamomum cassia (10g) was cut into small species. After extraction with ethanol (3 x 100ml), the solutions were combined and condensed under reduced pressure to afford a crude extract (0.8 g). The crude extract was subjected to column chromatography and eluted with gradient petroleum ether-ethyl acetate (100:1, 10:1, 5:1 and 1:1). The 10:1 eluted fraction showed the strongest antibacterial activity (*Staphylococcus aureus*). Crystalline sponge CMOF was put into the neat oil of this fraction. Three days later, one of crystalline sponges was analyzed by X-ray diffraction.

S6 Synthesis of benzyl salicylate (G11)

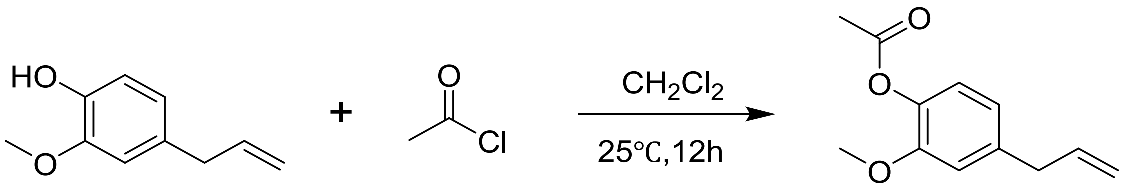


Sodium salicylate 0.50g (3.12 mmol, 1eq) and benzylbromobenzene 0.53g (3.12 mmol,1eq) were dissolved in 2ml of anhydrous DMF solution, the reaction solution was stirred at 100 ℃ for 4h. Poured the reaction solution into 20ml water, added dichloromethane to extract three times (10ml*3), combined the organic phases and washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to obtain a colorless liquid benzyl salicylate 0.68 g (3.00 mmol), yield 96%.

S7 Biosynthesis of veratryl alcohol (G12)

The Fungus *Phanerochaete chrysosporium* purchased from China Center of Industrial Culture Collection) was cultured in a PDA broth (100ml, potato dip powder) for 48 hours. Then the cuture both was extracted with ethyl acetate (100ml). The solvent was removed under reduced pressure to afford a oil like residue (55 mg). Crystalline spone CMOF was put into the residue. Three days later, one of crystalline sponges was analyzed by X-ray diffraction.

S8 Synthesis of acetyleugenol (G14) from eugenol (G13)



Eugenol 0.50g (3.04 mmol, 1eq) and triethylamine (1ml), were dissolved in 2ml dichloromethane solution, then add acetyl chloride 0.24g (3.04 mmol,1eq), the reaction solution was stirred at 25 °C for 12h. A small part of the reaction mixture (50 μl) was selected and crystalline sponge CMOF was put into it. After the appearance of strong carbonyl peak in IR spectrum, one of crystalline sponges was analyzed by X-ray diffraction. The other part of the reaction mixture was concentrated under reduced pressure, the crude product was separated by column chromatography (petroleum ether: ethyl acetate = 3:1), to obtain a white liquid eugenol acetate 0.52g (2.52 mmol) with a yield of 83 %.

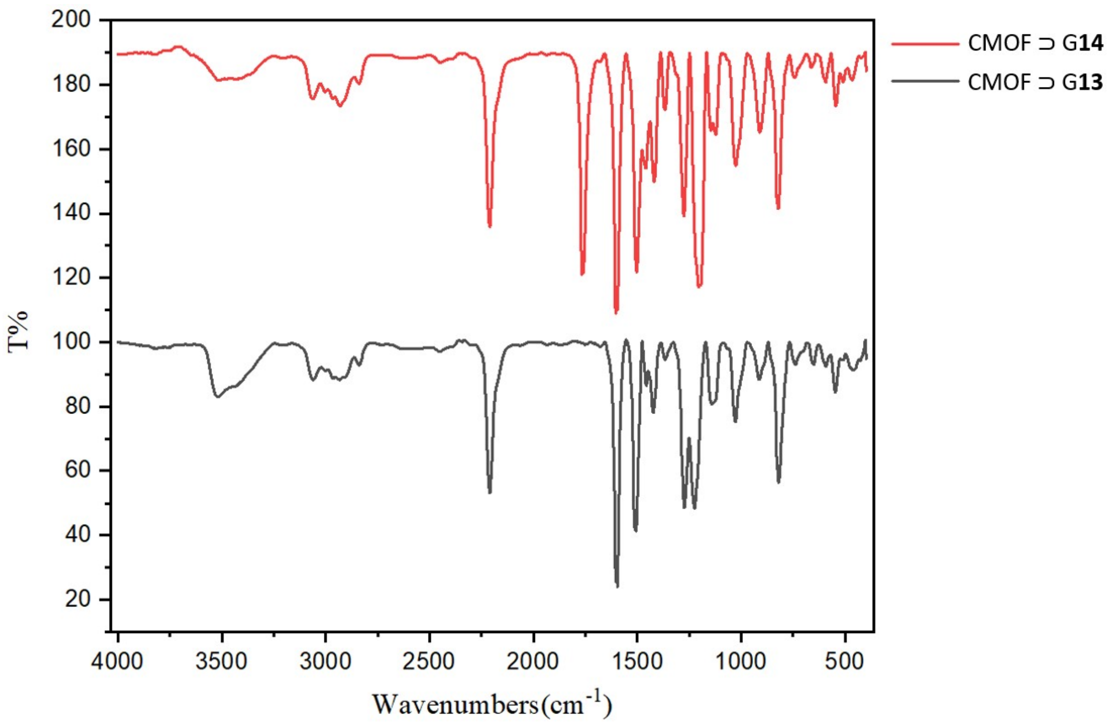


Fig. S8 IR of (Eugenol, G**13**) and (acetylated eugenol, G**14**). About 1 mg crystal sponge containing either G**13** or G**14** were ground together with dry potassium bromide using a mortar and pestle to form a transparent disk. Then the disk was analyzed on JASCO FT/IR-480 Plus spectrometer.

S9 ^{1}H-NMR

The crystal sponge CMOF (2 mg) after soaking in guest solution was washed with THF (0.5 ml for two times). Then, it was transferred to a 2 mL vial, where deuterated dimethyl sulfoxide (DMSO-d_6, 600 μL) and H_2SO_4 (20 μL, 1 M in D_2O) were added. The vial was sonicated for 10 minutes and then placed in an oven at 80 °C for 30 minutes to completely dissolve the crystals. The final clear solution was used for ^{1}H NMR experiments.

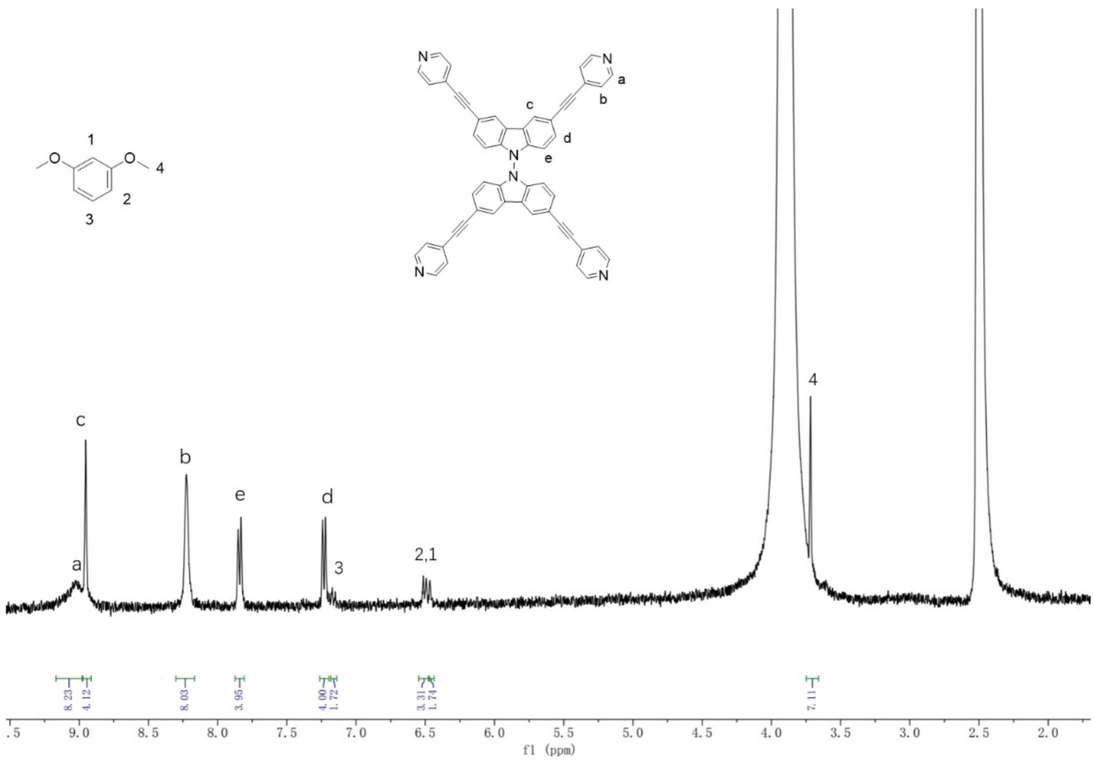


Fig. S9a ^{1}H NMR spectrum of digested CMOF ⊃ G**2** in DMSO-d_6.

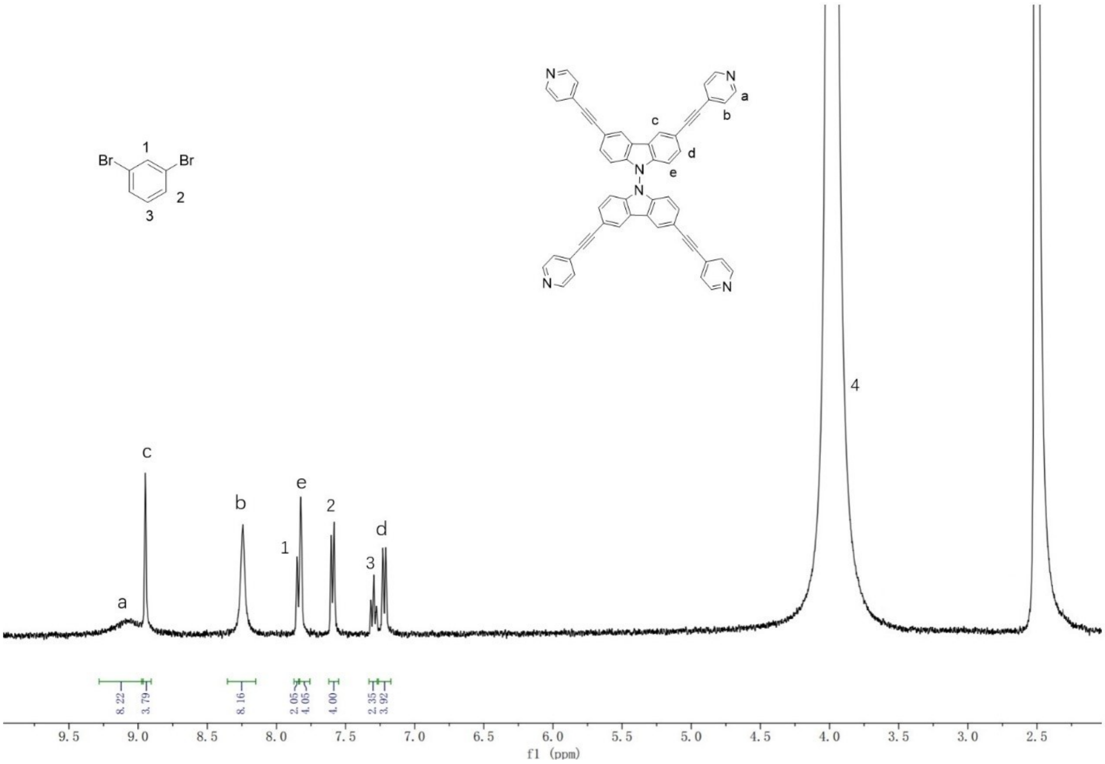


Fig. S9b [1]H NMR spectrum of digested CMOF⊃ G**3** in DMSO-d_6.

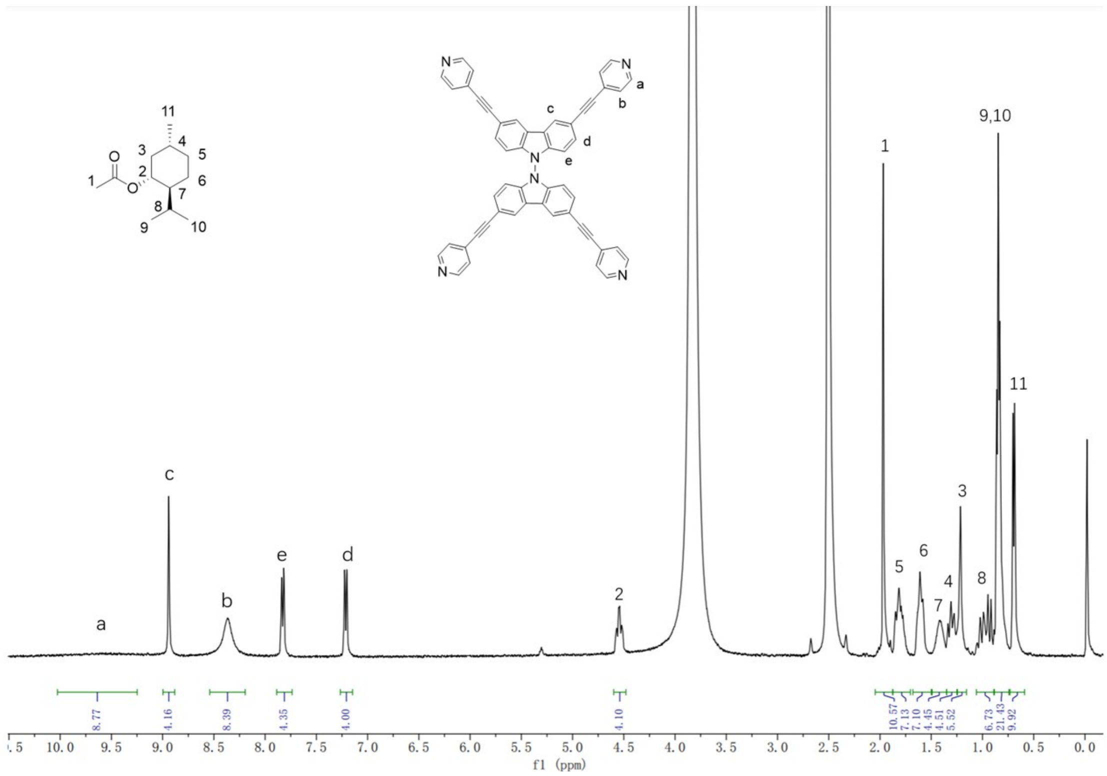


Fig. S9c [1]H NMR spectrum of digested CMOF ⊃ G**6** in DMSO-d_6.

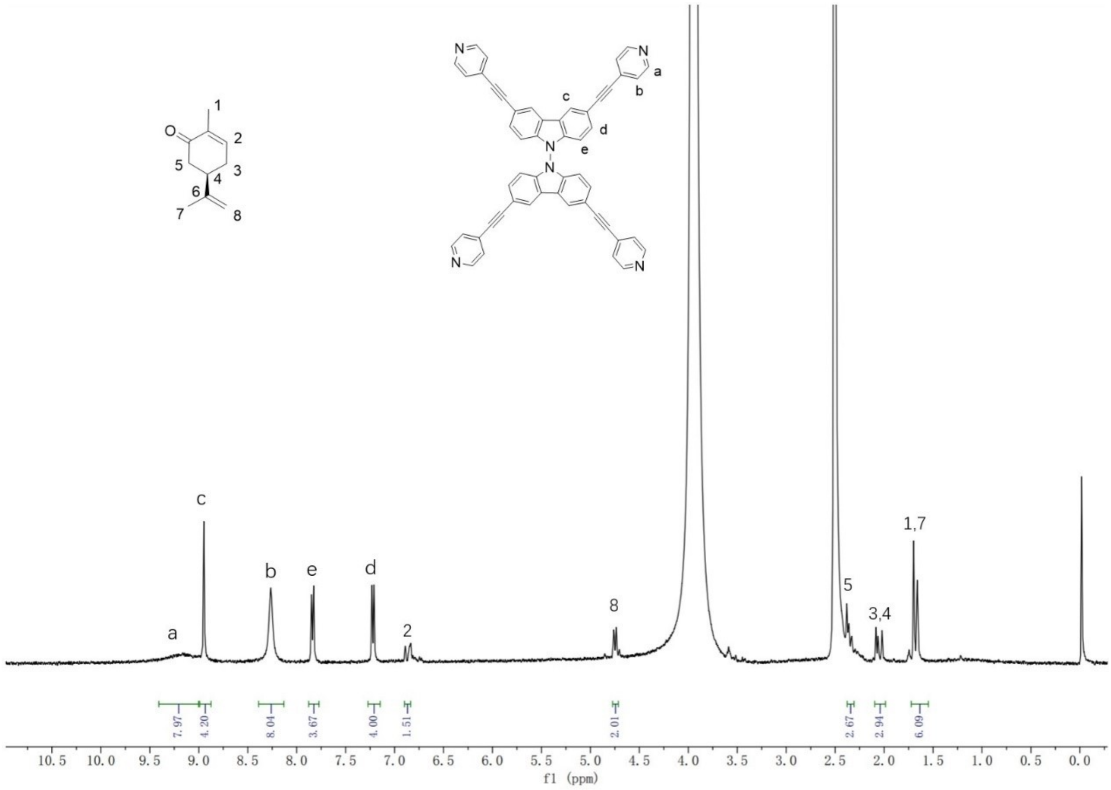


Fig. S9d ^{1}H NMR spectrum of digested CMOF⊃ G**8** in DMSO-d_6.

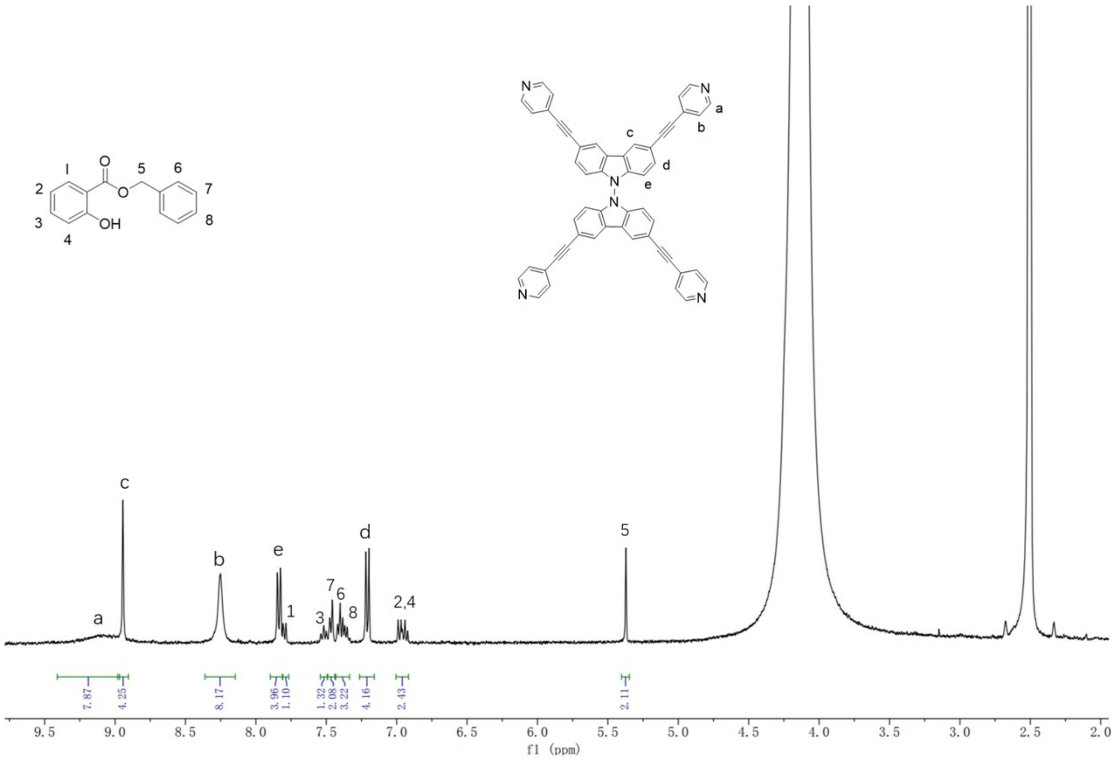


Fig. S9e ^{1}H NMR spectrum of digested CMOF ⊃ G**11** in DMSO-d_6.

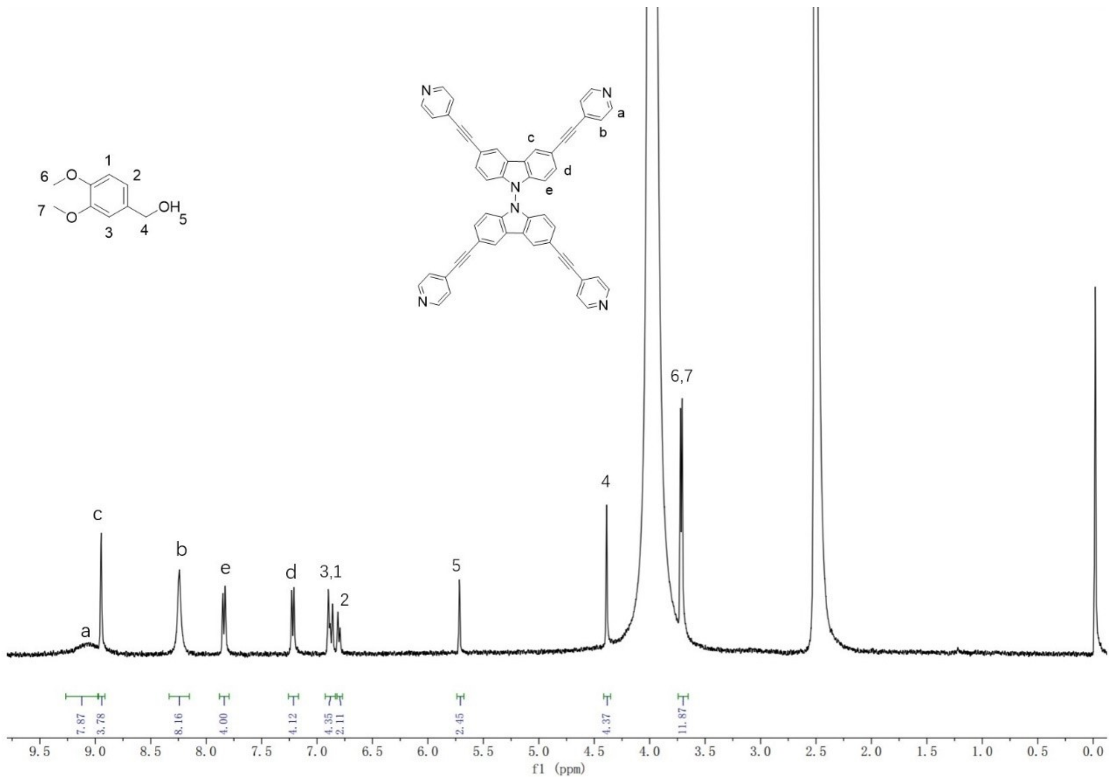


Fig. S9f [1]H NMR spectrum of digested CMOF ⊃ G**12** in DMSO-d_6.

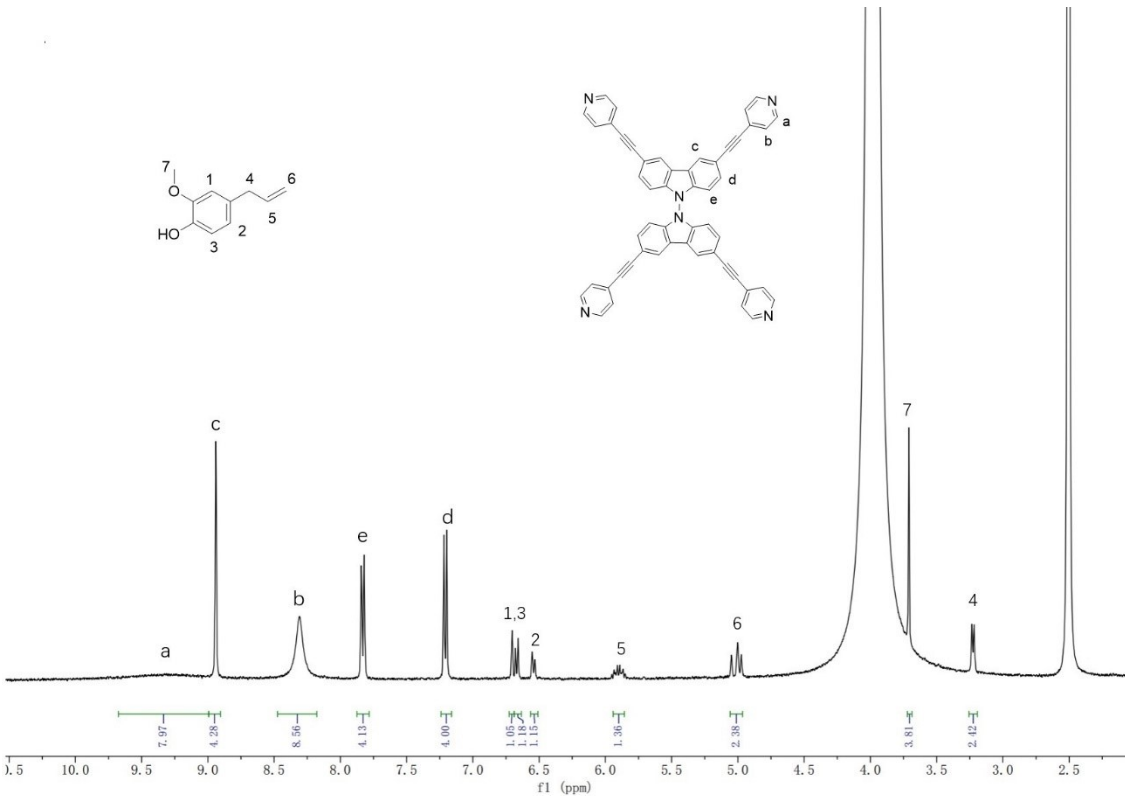


Fig. S9g [1]H NMR spectrum of digested CMOF ⊃ G**13** in DMSO-d_6.

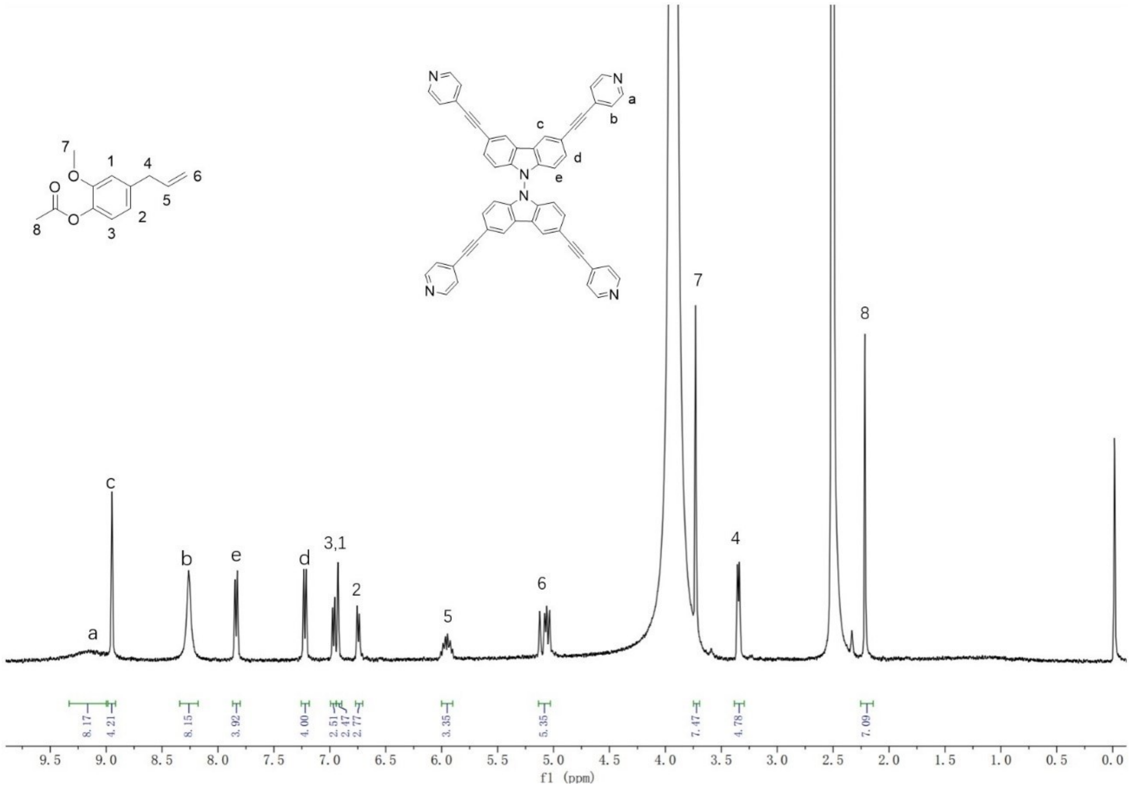
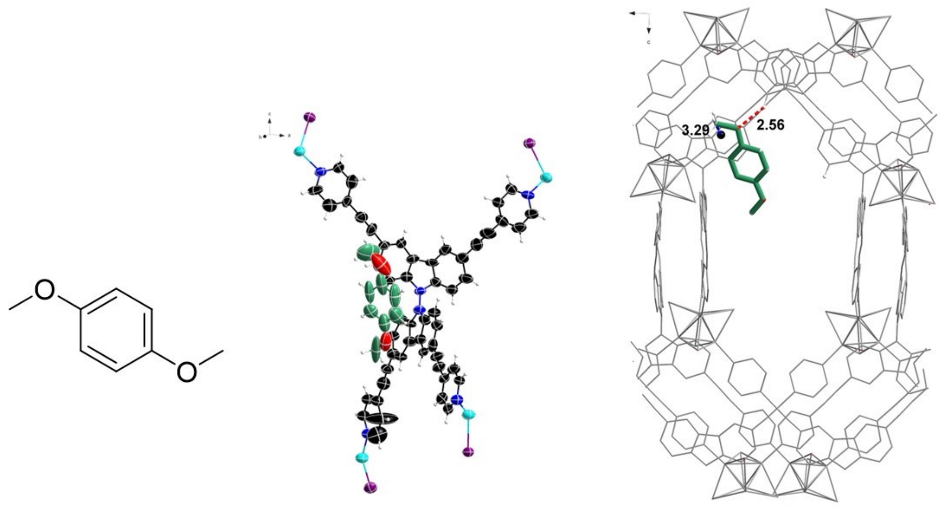


Fig. S9h ^{1}H NMR spectrum of digested CMOF⊃ G**14** in DMSO-d_6.

S10 Rapid capture of guest molecule in one minute

A tiny crystal of CMOF (~100 × 100 × 100 μm^3) was placed in the insert of a HPLC vial with 50μL tetrahydrofuran solution of *p*-dimethoxybenzene (500 μg). After soaking for 1 minute at room temperature, the crystal sponge was selected and directly tested on an in-house X-ray diffractometer. The crystal structure was fully determined from the diffraction data and showed that *p*-dimethoxybenzene molecule was trapped in the cavity of CMOF.



(1) (2) (3)

Fig. S10 Rapid Structure determination of 1,4-dimethoxybenzene.

(1) Chemical structure of 1,4-dimethoxybenzene, (2) the asymmetric unit of CMOF⊃1,4-dimethoxybenzene, (3) 1,4-dimethoxybenzene was captured in the cavity of CMOF. The solvent molecules were omited for clarity.

S11 **Reusability of CMOF.**

IR spectrum was used to monitor the presence and disappearance of G**8** signal. IR spectra was measured on a Shimadzu IRSpirit FTIR spectrophotometers.

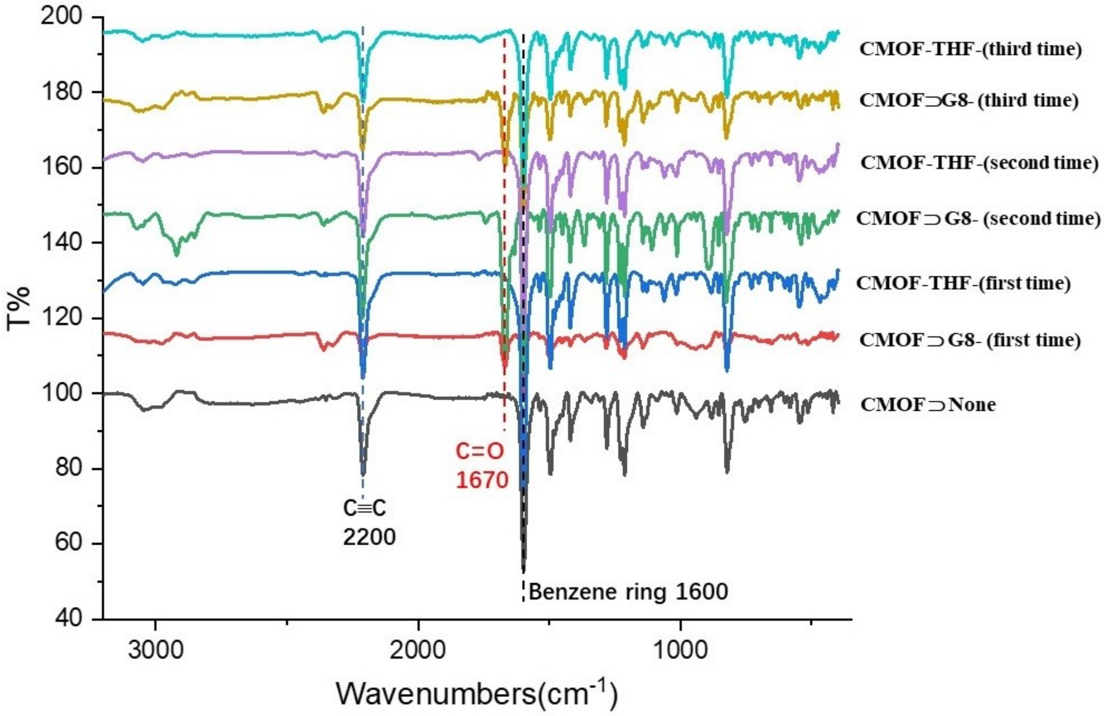
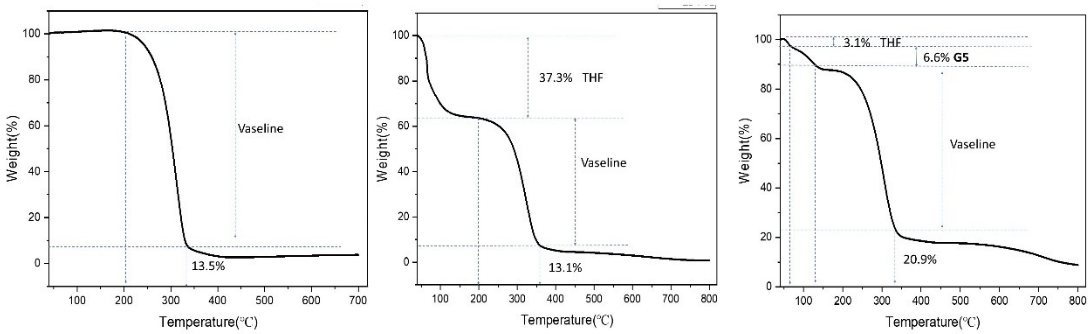


Fig. S11 Reusability of CMOF. IR spectrum was used to monitor the presence and disappearance of G**8** signal.

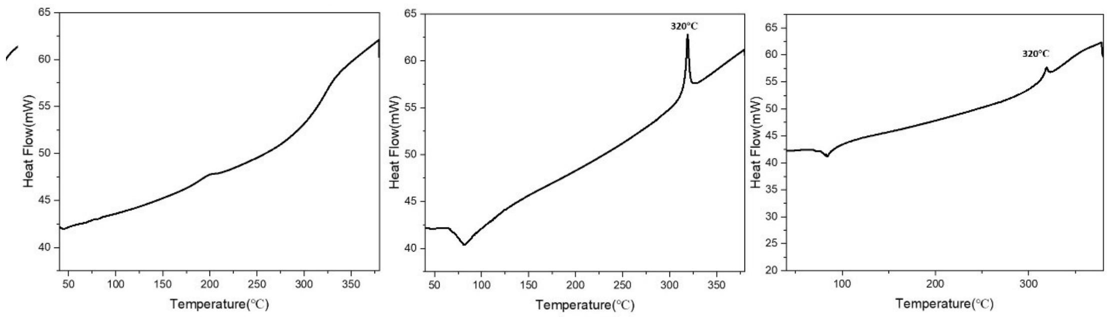
S12 **Thermogravimetric analyses and differential scanning calorimetry**

Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed on a Thermogravimetric Analyzer (TGA2, Mettler-Toledo) and Q20, (TA instruments), respectively.



(a) (b) (c)

Fig. S12a Thermogravimetric analysis. (a) Vaseline; (b) Vaseline+CMOF; (c) Vaseline+CMOF+G5



(a) (b) (c)

Fig. S12b Differential scanning calorimetry. (a) Vaseline; (b) Vaseline+CMOF showing an exothermal transition temperature at 320°C; (c) Vaseline+CMOF+G5 showing an exothermal transition temperature at 320°C

S13 **Details for the crystal structure elucidation and refinements**

All single-crystal X-ray measurements were performed on a Rigaku Oxford Atals-CCD diffractometer using CuKα (λ= 1.54056 Å) radiation. The diffraction data were collected in the ω-scanning mode (resolution 0.80-0.85Å). All crystal structures were solved by direct methods (SHELXTL-2014) and refined by full-matrix least-squares on F^2 using the Olex2 software package. In the structure refinements, non-H atoms were refined anisotropically. H-atoms bonded to carbons were placed on the geometrically ideal positions by the riding model. Due to high symmetries and high pore volumes, the solvent molecule (tetrahydrofuran) was extremely disordered, and could not be located for refinement. Thus, the residual electrons were squeezed by using the "solvent mask" function of Olex2 software. The numbers of masked solvent molecules were calculated based on the masked electron using Platon software. For these host-guest complexes, disorders were also found in the guest molecules, and thus proper restrains or constrains (Table S6) were applied.

Table S1 Crystal data and refinement details of CMOF⊃guests

Items	CMOF	CMOF ⊃G**1**	CMOF ⊃G**2**	CMOF ⊃G**3**	CMOF ⊃G**4**	CMOF ⊃G**5**	CMOF ⊃G**6**	CMOF ⊃G**7**	CMOF ⊃**ent1**
Formula	$Cu_4I_4C_{52}H_{28}N_6$ $2.33(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $1^* (C_{12}H_{10}O)$ $0.16(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $2^* (C_8H_{10}O_2)$ $6.5(C_4H_8O)$	$Cu_{16}I_{16}C_{208}H_{112}N_{24}$ $2.5^* (C_6H_4Br_2)$ $14.625(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $0.5^* (C_8H_{10}O_3)$ $7(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $3^* (C_8H_{10}O_2)$ $0.8(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $1^*1(C_{12}H_{22}O_2)$ $1.3(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $1^*1(C_{12}H_{22}O_2)$ $13.5(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ 1* (*R*-$C_{12}H_{22}O_2$) 0.5* (*S*-$C_{12}H_{22}O_2$) $5.8(C_4H_8O)$
Mw [gmol−1]	1666.56	1668.76	2243.55	7638.79	2080.37	1970.72	1790.59	2670.34	2214.20
System	tetragonal	tetragonal	tetragonal	triclinic	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
Space group	$I4_1$	$I4_1$	$I4_1$	P1	$I4_1$	$I4_1$	$I4_1$	$I4_1$	$I4_1$
a(Å)	21.8232(5)	22.1406(5)	21.7043(2)	21.8801(3)	22.1118(4)	21.6214(9)	22.1908(2)	22.1489(5)	22.2780(3)
b(Å)	21.8232(5)	22.1406(5)	21.7043(2)	22.0969(3)	22.1118(4)	21.6214(9)	22.1908(2)	22.1489(5)	22.2780(3)
c(Å)	41.096(3)	40.3041(18)	41.2270(6)	24.3319(4)	40.2666(10)	41.405(4)	40.2740(6)	40.3009(18)	40.0457(7)
α(°)	90	90	90	109.0950(10)	90	90	90	90	90
β(°)	90	90	90	114.5340(10)	90	90	90	90	90
γ(°)	90	90	90	96.3860(10)	90	90	90	90	90
V(Å)	19572.2(15)	19757.3(13)	19421.1(5)	9686.4(3)	19687.6(9)	19356(2)	19832.2(5)	19770.6(13)	19875.1(6)
Z	8	8	8	1	8	8	8	8	8
Resolution(Å)	0.80	0.85	0.81	0.80	0.84	0.83	0.80	0.81	0.81
ρ(calcg/cm³)	1.131	1.122	1.535	1.129	1.404	1.353	1.199	1.795	1.480
R_{int}	0.0415	0.0478	0.0311	0.0595	0.0560	0.0546	0.0637	0.0791	0.0353
GOOF	0.971	1.089	1.046	0.948	1.064	0.987	1.117	0.962	1.084
Flack	0.128(8)	0.25(2)	0.164(8)	0.464(3)	0.503(11)	0.061(12)	0.287(9)	0.277(9)	0.298(11)
Temp. (K)	99.99(13)	100.00(10)	99.97(13)	150.00(10)	99.98(10)	99.98(10)	149.99(10)	100.00(10)	130.00(11)
R1 [I >2σ(I)]	0.0898	0.1349	0.0663	0.0671	0.1348	0.1106	0.0887	0.1126	0.0886
wR2(all data)	0.1909	0.2977	0.1602	0.1667	0.2431	0.2237	0.2455	0.2097	0.2247
F(000)	6426.0	6400.0	8944.0	3115.0	8248.0	7712.0	6976.0	10888.0	8856.0
CCDC No.	2309572	2309573	2309575	2309587	2309579	2309576	2309577	2309581	2309585

Items	CMOF ⊃G**8**	CMOF ⊃G**9**	CMOF ⊃**ent2**	CMOF ⊃G**10**	CMOF ⊃G**11**	CMOF ⊃G**12**	CMOF ⊃G**13**	CMOF ⊃G**14**	CMOF ⊃G**2**&G**5**
Formula	$Cu_4I_4C_{52}H_{28}N_6$ $2.5^* (C_{10}H_{14}O)$ $2.23(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $3^* (C_{10}H_{14}O)$	$Cu_4I_4C_{52}H_{28}N_6$ 1.58*(*R*-$C_{10}H_{14}O$) 1.42* (*S*-$C_{10}H_{14}O$)	$Cu_4I_4C_{52}H_{28}N_6$ $1^* (C_9H_8O)$ $0.45(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $0.5^* (C_{14}H_{12}O_3)$ $8.6(C_4H_8O)$	$Cu_8I_8C_{104}H_{56}N_{12}$ $6^* (C_9H_{12}O_3)$ $7.5(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ $1^* (C_{10}H_{12}O_2)$	$Cu_4I_4C_{52}H_{28}N_6$ $0.5^* (C_{12}H_{14}O_3)$ $0.45(C_4H_8O)$	$Cu_4I_4C_{52}H_{28}N_6$ 1* (*m*-$C_8H_{10}O_2$) 0.75* (*p*-$C_8H_{10}O_2$) 0.25* (*p*-$C_8H_{10}O_2$) $1.6(C_4H_8O)$
Mw [gmol−1]	2034.88	1949.20	1949.27	1663.16	2232.77	4547.01	1662.76	1634.12	1890.25
System	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
Space group	$I4_1$	$I4_1$	$I4_1$	$I4_1$	$I4_1$	$P4_3$	$I4_1$	$I4_1$	$I4_1$
a(Å)	21.9275(4)	21.9870(3)	21.7043(2)	21.9255(4)	22.1250(3)	22.11620(10)	21.8628(2)	21.8699(3)	21.6573(3)
b(Å)	21.9275(4)	21.9870(3)	21.7043(2)	21.9255(4)	22.1250(3)	22.11620(10)	21.8628(2)	21.8699(3)	21.6573(3)
c(Å)	40.7399(10)	40.6983(7)	41.2270(6)	40.8385(11)	40.3563(8)	39.9270(3)	40.9305(8)	40.8331(7)	41.2291(9)
α(°)	90	90	90	90	90	90	90	90	90
β(°)	90	90	90	90	90	90	90	90	90
γ(°)	90	90	90	90	90	90	90	90	90
V(Å)	19588.4(8)	19674.7(6)	19421.1(5)	19632.2(9)	19755.0(7)	19529.3(2)	19564.0(5)	19530.2(6)	19338.0(7)
Resolution(Å)	0.81	0.81	0.81	0.80	0.81	0.81	0.81	0.81	0.81
Z	8	8	8	8	8	4	8	8	8
ρ(calcg/cm³)	1.380	1.316	1.315	1.125	1.501	1.546	1.129	1.112	1.299
R_{int}	0.0535	0.0511	0.0360	0.0396	0.0602	0.0689	0.0745	0.0361	0.0359
GOOF	0.937	1.018	1.030	0.980	0.874	1.065	1.024	0.915	1.112
Flack	0.090(11)	-0.003(4)	-0.011(4)	0.077(10)	0.121(9)	0.163(7)	0.462(15)	0.092(10)	0.117(8)
Temp. (K)	99.98(14)	129.99(11)	129.98(10)	150.00(10)	99.98(10)	100.00(10)	150.00(10)	99.99(10)	99.97(15)
R1 [I >2σ(I)]	0.1126	0.0614	0.0647	0.1011	0.0829	0.0943	0.1332	0.1043	0.0764
wR2(all data)	0.1866	0.1474	0.1482	0.2294	0.1468	0.2520	0.2962	0.2089	0.2087
F(000)	8034.0	7648.0	7636.0	6384.0	8912.0	7858.0	6384.0	6264.0	7376.0
CCDC No.	2309578	2309574	2309583	2309580	2309586	2309588	2309584	2309582	2320293

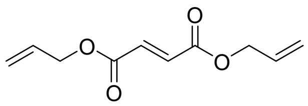
Table S2. The guest occupancy in CMOF⊃guests

Guest occupancy	CMOF ⊃None	CMOF ⊃G**1**	CMOF ⊃ G**2**	CMOF ⊃G**3**	CMOF ⊃G**4**	CMOF ⊃G**5**	CMOF ⊃G**6**	CMOF ⊃G**7**	CMOF ⊃ **ent1**
1	0	0	1	2	0	1	1	1	1
0.5	0	2	2	1	1	4	0	0	1

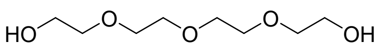
Guest occupancy	CMOF ⊃ G**8**	CMOF ⊃G**9**	CMOF ⊃**ent2**	CMOF ⊃G**10**	CMOF ⊃G**11**	CMOF ⊃G**12**	CMOF ⊃G**13**	CMOF ⊃G**14**	CMOF ⊃**G2&G5**
1	1	1	0	0		5	0	0	0
0.75									1
0.5	3	4	6	2	1	2	2	1	2
0.25									1

Table S3 The guest volume and three-dimensional values

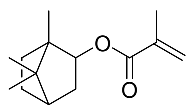
Guest	Length (Å)	Width (Å)	Height (Å)	Volume (Å3)	Standard Deviation (Å^3)
G**1**	7.974	9.869	4.257	335.006	12.632
G**2**	5.554	11.107	6.685	412.386	8.136
G**3**	9.521	8.046	4.247	325.346	13.255
G**4**	7.292	9.309	3.700	251.161	6.879
G**5**	6.624	11.583	4.246	325.778	5.466
G**6**	11.494	6.674	8.933	685.259	30.941
G**7**	10.330	9.972	5.896	607.351	16.458
G**8**	9.782	7.075	7.004	484.730	9.358
G**9**	10.606	7.016	5.817	432.853	18.457
G**10**	7.080	11.081	3.400	266.742	12.115
G**11**	13.860	7.760	4.229	454.844	8.756
G**12**	8.339	11.408	4.257	404.974	10.682
G**13**	8.867	11.041	4.246	415.486	15.332
G**14**	12.469	8.814	5.436	597.43	8.753
Diallyl fumarate	15.951	7.337	4.231	495.164	13.368
Tetraethylene glycol	18.129	4.616	4.221	353.228	8.452
Methyl jasmonate	11.001	9.800	6.814	734.616	28.352
Isobornyl methacrylate	11.852	7.965	7.797	736.046	32.535



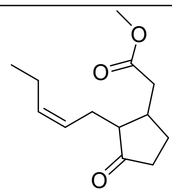
Diallyl fumarate



Tetraethylene glycol



Isobornyl methacrylate



Methyl jasmonate

Table S4. C-H···π intermolecular interactions in CMOF⊃guests

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**1**	C1A-H1A···Cg1 [a]	2.89(0)	134	3.61(7)
	C4-H4···Cg2 [b]	2.77(0)	139	3.54(3)
	C49-H49···Cg3 [c]	2.53(0)	167	3.47(2)

Symmetry codes: [a] -x, 2-y, 1+z; [b] 1/2-y, 1+x, 3/4+z; [c] 1/2-x, 5/2-y, 1/2+z ; Cg1 is the centroid of N1, C1, C2, C3, C4, C5. Cg2 is the centroid of C7A, C8A, C9A, C10A, C11A, C12A. Cg3 is the centroid of C7B, C8B, C9B, C10B, C11B, C12B.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**2**	None			

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**3**	C180-H180···Cg5 [a]	2.98(0)	122	3.58(2)
	C194-H194···Cg6 [b]	3.27(0)	146	4.10(1)
	C152-H152···Cg7 [c]	3.54(0)	138	4.30(2)

Symmetry codes: [a] x, y, z; [b] -1+x, y, -1+z; [c] -1+x, -1+y, z; Cg5 is the centroid of C085, C09N, C77 C0AH, C09X, C09B; Cg6 is the centroid of C09E, C058, C61, C088, C095, C097; Cg7 is the centroid of C0AE, C07X, C09A, C09D, C09H, C036.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**4**	C8A-H8AB···Cg8 [a]	3.48(0)	137	4.23(7)

Symmetry codes: [a] -3/2+x, 1/2+y, 1/2+z; Cg8 is the centroid of N5, C45, C44, C43, C47, C46.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**5**	C1E-H1EB···Cg9 [a]	3.01(0)	151	3.87(7)
	C3C-H3C···Cg10 [b]	2.81(0)	168	3.72(4)
	C8B-H8BB···Cg11 [c]	2.65(0)	115	3.17(5)

Symmetry codes: [a] -1+x, 1+y, 1+z; [b] -3/2+y, 2-x, 3/4+z; [c] -3/2+y, 2-x, 3/4+z; Cg9 is the centroid of N5, C27, C28, C29, C30, C31; Cg10 is the centroid of C2A, C3A, C4A, C5A, C6A, C7A; Cg11 is the centroid of C2C, C3C, C4C, C5C, C6C, C7C

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**6**	C53-H53A···Cg12 [a]	3.11(0)	137	3.86(4)

Symmetry codes: [a] -1+y, 3/2-x, 1/4+z; Cg12 is the centroid of N2, C22, C23, C24, C25, C26;

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**7**	C10A-H10C···Cg13 [a]	3.33(0)	132	4.06(3)

Symmetry codes: [a] -1/2-y, 1+x, 3/4+z; Cg13 is the centroid of N5, C27, C28, C29, C30, C31;

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃ **ent1**	C11B-H11D···Cg14 [a]	3.49(0)	134	4.22(5)
	C12A-H12C···Cg15 [b]	3.36(0)	135	4.12(3)

Symmetry codes: [a] -1/2-x, 5/2-y, 1/2+z; [b] -x, 2-y, 1+z; Cg14 is the centroid of C8, C9, C10, C11, C13, C14; Cg15 is the centroid of N6, C47, C48, C49, C50, C51;

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**8**	C3A-H3AB···Cg16 [a]	3.28(0)	128	3.95(4)

	C10C-H10CA···Cg17 [b]	2.81(0)	147	3.67(4)
	C2B-H2BC···Cg18 [c]	2.99(0)	133	3.72(4)

Symmetry codes: [a] -1/2-x, 3/2-y, 1/2+z; [b] -y, 3/2+x, 1/4+z; [c] -x, 2-y, z; Cg16 is the centroid of N5, C27, C28, C29, C30, C31; Cg17 is the centroid of C40, C41, C42, C43, C44, C45; Cg18 is the centroid of N2, C22, C23, C24, C25, C26;

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**9**	C1A-H1AA···Cg19 [a]	2.97(0)	131	3.69(7)

Symmetry codes: [a] y, 3/2-x, 1/4+z; Cg19 is the centroid of C14, C15, C16, C17, C18, C19.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃ **ent2**	C1C-H1CA···Cg20 [a]	2.73(0)	153	3.61(3)

Symmetry codes: [a] -y, 1/2+x, 1/4+z; Cg20 is the centroid of C8, C9, C10, C11, C12, C13.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**10**	C9A-H9A···Cg21 [a]	2.74(0)	138	3.48(2)
	C4-H4···Cg22 [b]	3.02(0)	144	3.81(2)
	C43-H43···Cg22 [b]	2.97(0)	163	3.87(2)

Symmetry codes: [a] 1/2+x, 1/2+y, -1/2+z; [b] 1/2+x, 1/2+y, -1/2+z; Cg21 is the centroid of N1, C1, C2, C3, C4, C5. Cg22 is the centroid of C4B, C5B, C6B, C7B, C8B, C9B.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**11**	C4-H4···Cg23 [a]	2.63(0)	149	3.48(1)
	C5A-H5A···Cg24 [b]	2.89(0)	124	3.50(2)

Symmetry codes: [a] -1+x, y, 1+z; [b] -3/2+y, 1-x, 3/4+z; Cg23 is the centroid of C9A, C10A, C11A, C12A, C13A, C14A. Cg24 is the centroid of N1, C1, C2, C3, C4, C5.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**12**	C8E-H8EC···Cg25 [a]			

Symmetry codes: [a] -1+x, y, 1+z; Cg25 is the centroid of C2B, C3B, C4B, C5B, C6B, C7B.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**13**	C61-H61···Cg26 [a]	2.89(0)	116	3.55(4)
	C37-H37···Cg27 [b]	3.16(0)	117	3.69(3)

Symmetry codes: [a] -1+x, y, z; [b] -y, 1/2+x, 1/4+z; Cg26 is the centroid of N6, C27, C28, C29, C30, C31; Cg27 is the centroid of C2A, C3A, C4A, C5A, C6A, C7A.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃G**14**	C2-H2···Cg28 [a]	3.08(0)	119	3.64(2)

Symmetry codes: [a] -1+x, 1+y, 1+z; Cg28 is the centroid of C3A, C4A, C5A, C6A, C7A, C8A.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
CMOF ⊃ G**2** & G**5**	C76-H76···Cg29[a]	3.08(0)	143	3.91(3)
	C68-H68B···Cg30[b]	2.86(0)	166	3.80(3)

Symmetry codes: [a] -1/2-y, -1+x, 3/4+z; [b] -1+x, y, z; Cg29 is the centroid of N1, C1, C2, C3, C4, C5; Cg30 is the centroid of N2, C48, C49, C50, C51, C52;

Table S5. Geometric parameters of the O–H···O and C–H···O hydrogen bonding interactions in CMOF⊃guests

Host-Guest	Interactions	D–H (Å)	H···A (Å)	D···A (Å)	D-H···A (deg)	Symmetry code
CMOF ⊃G**1**	C28-H28--- O1A	0.95	2.59(7)	3.51(8)	162	1/2-y, 1+x, 3/4+z
	C17-H17---O1B	0.95	2.76(9)	3.62(10)	151	1/2-x, 5/2-y, 1/2+z
CMOF ⊃G**2**	C9-H9---O1B	0.93	3.01(2)	3.83(3)	148	-3/2+x, 1/2+y, 1/2+z
	C30-H30---O1B	0.93	2.73(2)	3.52(3)	143	-3/2+x, 1/2+y, 1/2+z
	C24-H24--- O2C	0.93	3.04(4)	3.78(5)	139	1/2-x, 3/2-y, 1/2+z
	C17-H17--O1A	0.93	2.65(2)	3.37(2)	134	-1/2+x, 1/2+y, 1/2+z
CMOF ⊃G**3**	None					
CMOF ⊃G**4**	C4-H4---O1A	0.93	2.55(5)	3.44(6)	160	3/2+y, 2-x, 3/4+z
	C5-H5---O1A	0.93	2.91(5)	3.47(6)	120	-3/2+y, 2-x, 3/4+z
CMOF ⊃G**5**	C23-H23--- O1E	0.93	2.62(5)	3.43(5)	146	-1/2+x, 1/2+y, 1/2+z
	C52-H52--- O2A	0.93	2.75(4)	3.41(5)	129	-3/2+y, 2-x, 3/4+z
	C49-H49--- O2B	0.93	2.53(3)	3.37(4)	151	-3/2+y, 2-x, 3/4+z
CMOF ⊃G**6**	C23-H23--- O1	0.93	2.63(3)	3.09(3)	111	-1/2-x, 3/2-y, 1/2+z
	C43-H43--- O2	0.93	2.63(4)	3.54(5)	165	-1/2-x, 3/2-y, 1/2+z
CMOF ⊃G**7**	C23-H23--- O1A	0.95	2.68(2)	3.19(3)	114	-1+y, 3/2-x, 1/4+z
	C35-H35--- O2A	0.95	2.60 (3)	3.52(4)	163	-1+y, 3/2-x, 1/4+z
CMOF⊃**ent1**	C17-H17--- O1A	0.95	2.35(2)	3.27(3)	164	-1/2-x, 5/2-y, 1/2+z
	C49-H49--- O2A	0.95	2.61(2)	3.08(2)	111	-1/2-x, 5/2-y, 1/2+z
	C30-H30--- O1B	0.95	2.83(4)	3.77(4)	171	-1/2+y, 2-x, 3/4+z
	C10-H10--- O2B	0.95	3.18(4)	3.62(4)	110	-1/2+y, 2-x, 3/4+z
CMOF ⊃G**8**	C4D-H4D--- O1C	0.98	2.51(3)	3.29(4)	134	-y, 3/2+x, 1/4+z
	C9A-H9AA--O1D	0.97	2.76(2)	3.69(4)	161	-1+y, 3/2-x, 1/4+z
CMOF ⊃G**9**	C6A-H6AA--- O1B	0.99	2.69(2)	3.66(4)	162	1/2+x, 1/2+y, 1/2+z
	C4C-H4CA--O1B	0.99	2.87(2)	3.79(3)	155	1/2-x, 5/2-y, 1/2+z
	C6C-H6CA--O1D	0.99	3.06(3)	3.65(5)	120	1-y, 1/2+x, 1/4+z
	C10E-H10J--O1C	0.99	3.15(4)	4.06(8)	154	1-x, 2-y, z
	C16-H16--- O1E	0.99	2.73(3)	3.59(4)	150	x, 1+y, z
CMOF⊃**ent2**	C28-H28--- O1D	0.93	3.03(2)	3.93(2)	163	-y, 1/2+x, 1/4+z
	C65-H65--- O1C	0.99	2.73(2)	3.51(6)	136	-y, 1/2+x, 1/4+z
	C4C-H4CB--O1A	0.96	3.09(4)	3.72(6)	124	1/2-x, 3/2-y, 1/2+z
	C51-H51--- O1A	0.93	2.99(5)	3.65(5)	129	1/2-x, 3/2-y, 1/2+z
	C4A-H4AA--O1B	0.96	2.74(4)	3.35(8)	122	-1+y, 5/2-x, 1/4+z
	C9B-H9BB--O1E	0.96	2.34(3)	3.21(5)	151	-1+y, 5/2-x, 1/4+z
CMOF ⊃G**10**	C6A-H6A--- O1B	0.93	2.94(5)	3.49(6)	120	1/2+x, 1/2+y, -1/2+z
CMOF ⊃G**11**	C50-H50--- O1A	0.95	3.16(3)	4.06(3)	158	-1+x, y, 1+z
	C50-H50--- O2A	0.95	3.39(4)	3.85(4)	112	-1+x, y, 1+z
CMOF ⊃G**12**	C65-H65---O1A	0.95	2.60 (2)	3.29 (2)	130	1-y, -1+x, -1/4+z
	C8D-H8DA--O3A	0.98	3.09 (2)	3.61 (5)	114	-1+x, y, z
	C8A-H8AB--O3D	0.98	2.71(3)	3.54 (5)	142	-x, 2-y, -1/2+z
	C56-H56---O2B	0.95	2.48(2)	3.40 (3)	162	1-y, -1+x, -1/4+z
	O1B-H1B --- O3E	0.83	2.28(3)	2.91(4)	132	(1+x, y, z)
	C101-H101--O2C	0.95	2.82(4)	3.69 (4)	152	1-y, x, -1/4+z
	C1C-H1CA ---O3G	0.99	2.79(3)	3.73 (5)	159	x, 1+y, z

	C13-H13--- O2D	0.95	2.62(3)	3.52 (3)	159	1-x, 1-y, 1/2+z
	C6G-H6G--- O3D	0.95	3.10 (3)	3.78 (4)	129	-y, 1+x, -1/4+z
	C7E-H7E--- O2G	0.95	2.68 (4)	3.52(4)	148	-y, x, -1/4+z
	C49-H49--- O3F	0.95	2.42 (2)	3.32 (4)	159	1+y, 1-x, 1/4+z
	O1F-H1F--- O1G	0.84	2.09 (3)	2.80 (4)	142	-x, 1-y, -1/2+z
CMOF ⊃G**13**	C43-H43--- O1B	0.95	2.61(6)	3.52(6)	161	-3/2+x, 1/2+y, 1/2+z
CMOF ⊃G**14**	None					
CMOF ⊃ G**2** &G**5**	C23-H23--- O6	0.95	2.59(2)	3.44(3)	150	-1+y, 1/2-x, 1/4+z
	C16-H16--- O4	0.95	2.39(3)	3.32(3)	164	-3/2+x, -1/2+y, 1/2+z
	C50-H50--- O8	0.95	2.63(3)	3.48(4)	148	-y, -1/2+x, 1/4+z
	C4-H4--- O2	0.95	2.48(2)	3.32(3)	147	1/2-x, -1/2-y, 1/2+z

Table S6 Details for the refinement restrain & constrain

Host-guest complex	Refinement restrains & constrains
CMOF	RIGU, DFIX
CMOF ⊃G**1**	RIGU, DFIX, ISOR, DANG, SADI, SIMU, FLAT
CMOF ⊃G**2**	RIGU, DFIX, SADI, DANG, ISOR, FLAT
CMOF ⊃G**3**	SIMU, FLAT, DFIX, DELU, RIGU
CMOF ⊃G**4**	ISOR, RIGU, DFIX, DELU, SIMU, EADP
CMOF ⊃G**5**	RIGU, DFIX, SIMU, DANG, EADP, ISOR, SADI, FLAT
CMOF ⊃G**6**	ISOR, SADI, DFIX, EADP, RIGU
CMOF ⊃G**7**	DFIX, RIGU, ISOR
CMOF ⊃**ent1**	DFIX, RIGU, EADP, DANG, SIMU, DELU, SADI, ISOR
CMOF ⊃G**8**	RIGU, DFIX, DANG, ISOR, DELU, SIMU, EADP
CMOF ⊃G**9**	DFIX, RIGU, ISOR, DANG, SADI
CMOF ⊃**ent2**	RIGU, SADI, DFIX, ISOR, EADP, DANG, SIMU, DELU
CMOF ⊃G**10**	RIGU, DFIX, DANG, EADP, SIMU, FLAT
CMOF ⊃G**11**	ISOR, RIGU, DANG, DFIX, DELU, SIMU, EADP, FLAT
CMOF ⊃G**12**	DFIX, DANG, RIGU, SIMU, DELU, ISOR, EADP
CMOF ⊃G**13**	DFIX, RIGU, SIMU, FLAT, ISOR, SADI
CMOF ⊃G**14**	DFIX, DANG, SADI, RIGU, ISOR, EADP
CMOF ⊃G**2**&G**5**	DFIX, RIGU, ISOR, RIGU, SADI