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Supporting Information

Controlling the Secondary Assembly of Porous Anionic Uranyl-organic Polyhedra through Organic Cationic Templates

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Table of contents

Section S1. Materials and instrumentations

Materials

Caution! The uranyl nitrate hexahydrate $UO_2(NO_3)_2$•$6H_2O$ is a radioactive and chemically toxic reactant, precautions with suitable care and protection for handling such substances should be followed. All the reagents and solvents used were purchased and used without further purification except for the H_3BTPCA ligand, which was synthesized by following a literature report.[1]

Synthesis of complex 1($(NH_2(CH_3)_2)_4(UO_2)_4$(BTPCA)$_4$•16DMF**):** $UO_2(NO_3)_2$•$6H_2O$ (0.5 M, 120 μL), H_3BTPCA (13.89 mg, 0.04 mmol), DMF (2.0 mL) was loaded into a 12 mL autoclave. The autoclave was sealed and heated to 90 ºC in an oven for 2 days, then cooled to room temperature naturally. Colorless flake crystals of complex 1 were produced as well as amorphous yellow solid.

Synthesis of complex 2 ($(NH_2(CH_3)_2)_2$(Bmim)$_2(UO_2)_4$(BTPCA)$_4$•8DMF**):** $UO_2(NO_3)_2$•$6H_2O$ (0.5 M, 120 μL), H_3BTPCA (13.89 mg, 0.04 mmol), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl, 6.98 mg, 0.04 mmol), DMF (2.0 mL) was loaded into a 12 mL autoclave. The autoclave was sealed and heated to 90 ºC in an oven for 2 days, then cooled to room temperature naturally. Yellow block crystals of complex 2 were produced. Yield: 34.6% based on H_3BTPCA.

Contrast experiments

1、$UO_2(NO_3)_2$•$6H_2O$ (0.06 mmol), H_3BTPCA (0.04 mmol), 1-butyl-3-methylimidazolium perchlorate ([Bmim][ClO_4], 0.04 mmol), DMF (2.0 mL) was loaded into a 12 mL autoclave. The autoclave was sealed and heated to 90 ºC in an oven for 2 days, then cooled to room temperature naturally. Yellow block crystals of complex **2** were produced.

2、$UO_2(NO_3)_2$•$6H_2O$ (0.06 mmol), H_3BTPCA (0.04 mmol), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6], 0.04 mmol), DMF (2.0 mL) was loaded into a 12 mL autoclave. The autoclave was sealed and heated to 90 ºC in an oven for 2 days, then cooled to room temperature naturally. Yellow block crystals of complex **2** were produced.

3、$UO_2(NO_3)_2$•$6H_2O$ (0.06 mmol), H_3BTPCA (0.04 mmol), 1-hexyl-3-methylimidazolium chloride ([Hmim]Cl, 0.04 mmol), DMF (2.0 mL) was loaded into a 12 mL autoclave. The autoclave was sealed and heated to 90 ºC in an oven for 2 days, then cooled to room temperature naturally. Colorless flake crystals of complex **1** were produced as well as amorphous yellow solid.

4、$UO_2(NO_3)_2$•$6H_2O$ (0.06 mmol), H_3BTPCA (0.04 mmol), 1-octyl-3-methylimidazolium chloride ([Omim]Cl, 0.04 mmol), DMF (2.0 mL) was loaded into a 12 mL autoclave. The autoclave was sealed and heated to 90 ºC in an oven for 2 days, then cooled to room temperature naturally. Colorless flake crystals of complex **1** were produced as well as amorphous yellow solid.

5、$UO_2(NO_3)_2$•$6H_2O$ (0.06 mmol), H_3BTPCA (0.04 mmol), 1-hexyl-3-methylimidazolium chloride ([Hmim]Cl, 0.04 mmol), DMF (2.0 mL) was loaded into a 12 mL autoclave. The autoclave was sealed and heated to 90 ºC in an oven for 2 days, then cooled to room temperature naturally. Then 0.04 mmol [Bmim]Cl was added into the autoclave, which was sealed and heated to 90 ºC in an oven for one day. Then the autoclave cooled to room temperature naturally. The colorless flake crystals of complex 1 were completely transformed into yellow microcrystals of complex **2**.

Instrumentations

The IR tests were carried out on a Bruker Tensor 27 infrared spectrometer. The sample was diluted and mixed with KBr and pressed into a pellet. The measured wavenumber is between 700 and 4000 cm^{-1}. Powder X-ray diffraction (PXRD, Bruker, D8-Advance X-ray Diffractometer) with Cu Kα radiation (λ = 1.5406 Å). Thermogravimetry (TGA, TA Instruments, Q500) was employed in air atmosphere with a heating rate of 5 ºC•min^{-1}. Single crystal X-ray data were collected on a Bruker APEXII X-ray diffractometer equipped with a CMOS PHOTON 100 detector with a Cu Kα X-ray source (Kα = 1.54178 Å). Data were indexed, integrated and scaled SAINT v8.37A (Bruker, 2015). The structures were solved by direct method (SHELXS-97, Sheldrick 2008) and refined by full-matrix least-squares (SHELXL 2018/3, Sheldrick, 2015) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. The SQUEEZE routine of PLATON was used to remove the diffraction contribution from disordered solvents of complex 1 and complex 2.[2] Pertinent crystal parameters and structure refinement is summarized in Table S1. Selected bond distances are listed in Tables S2 and S3.

Section S2. Chemical Analysis

Infrared Spectroscopy (IR)

Complex 2 was characterized by IR spectroscopy (Fig. S1). The broad peak between 3280-3700 cm^{-1} is due to the presence of dissociative water molecule. The characteristic absorption peaks of the 1,3,5-triazine ring can be observed at 1674, 1539, and 1441 cm^{-1}, respectively. And two peaks appearing near 1374 and 1666 cm^{-1} are attributed to the symmetrical and asymmetrical stretching vibration absorption of C-O bond. The sharp and intense peak near 912 cm^{-1} is due to the U=O stretching vibration.

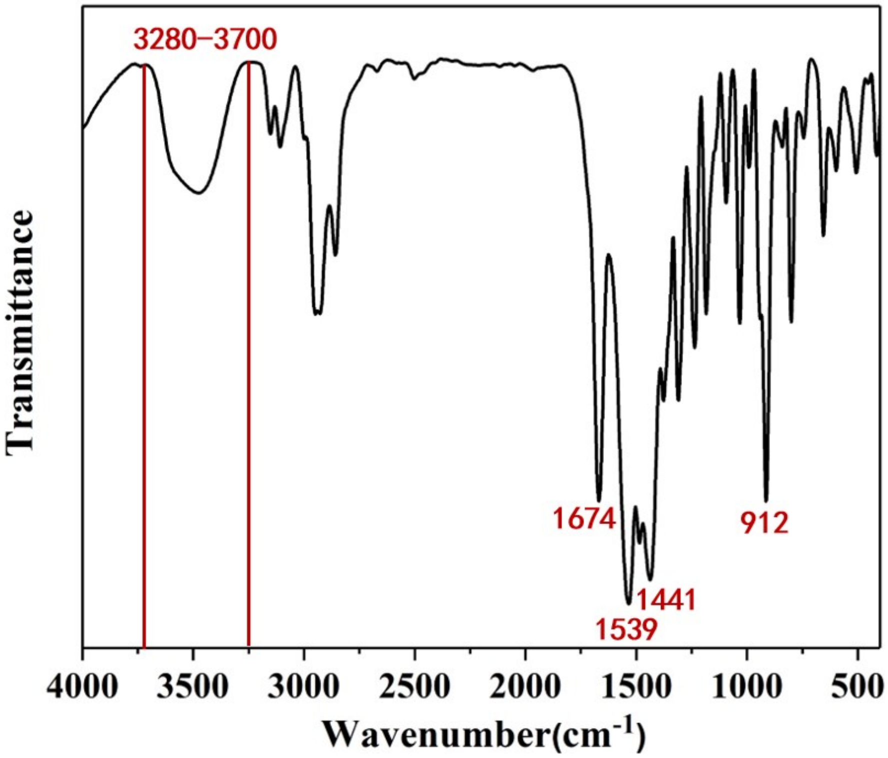

Fig. S1. The IR spectrum of complex 2.

Thermo gravimetric Analysis (TGA)

The thermogravimetric experiment was carried out to check the thermal stability of complex 2, and the result was shown in Fig. S2. The experiment was performed in a constant air atmosphere with a heating rate of 5 ºC•min^{-1} in the temperature range of 25-800 ºC. The TG curve of complex 2 exhibits three weight loss stages. The solid sample reduces about 10.11% weight before 140 ºC. With the temperature increases to 275 ºC, the second weight loss stage finishes with mass decrement about 5.96%. The following weight loss till 560 ºC reveals completely decomposed of skeleton structure and the total weight loss is 69.75%.

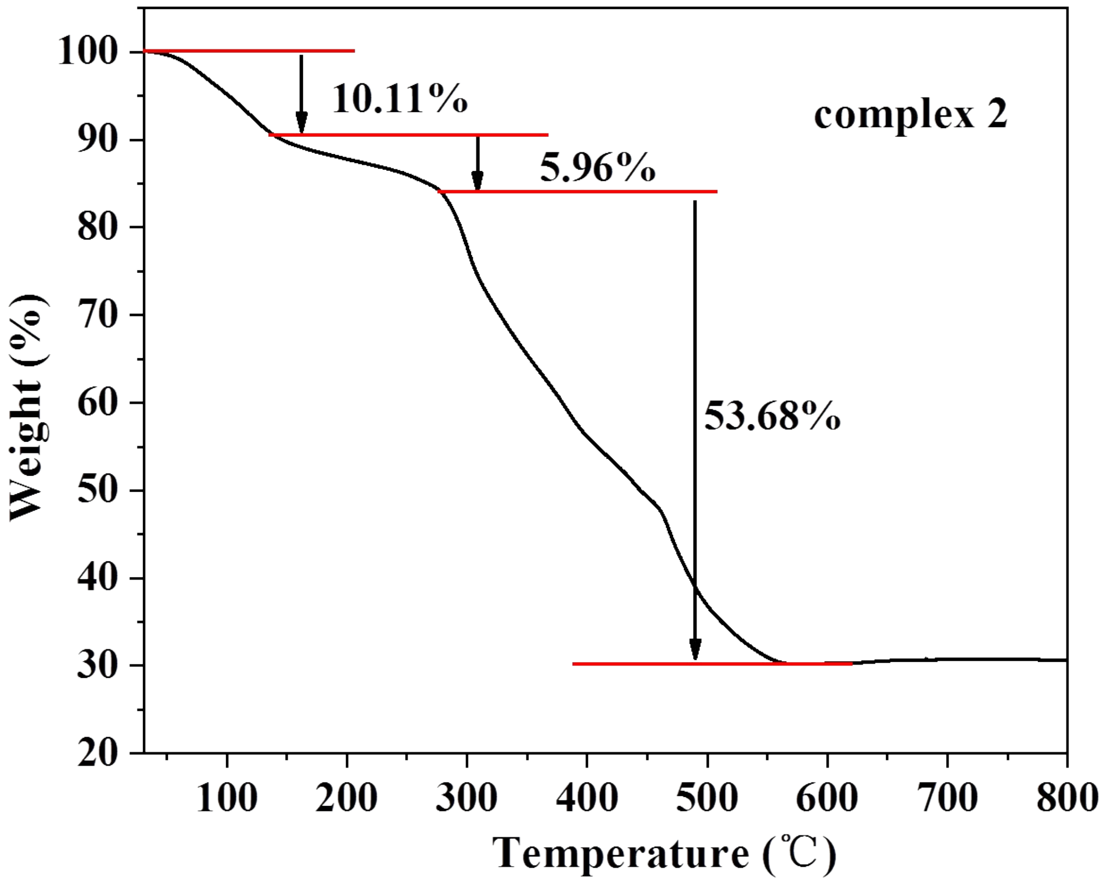

Fig. S2. TGA of complex 2 measured under air atmosphere with a heating rate of 5 ºC•min^{-1}.

Powder X-ray Diffraction (PXRD)

In order to confirm the phase purity of complex 2 and structure stability in ethanol solution, the powder X-ray diffraction (PXRD) patterns were recorded. As shown in Fig. S3, the predominant diffraction peaks of complex 2 are comparable with the simulated results. During the dyes adsorption process, the complex 2 sample remains intact after soaked in C_2H_5OH for 36 hours.

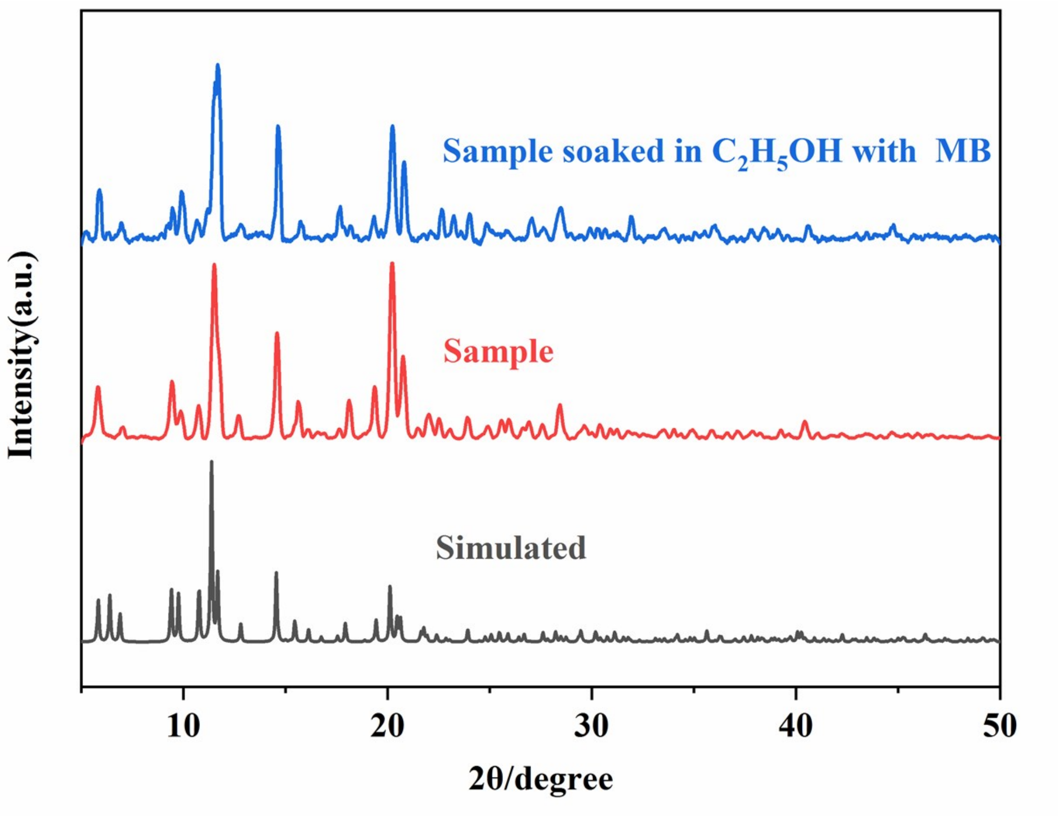

Fig. S3. The PXRD patterns of complex 2 and soaking in C_2H_5OH with MB for 36 hours.

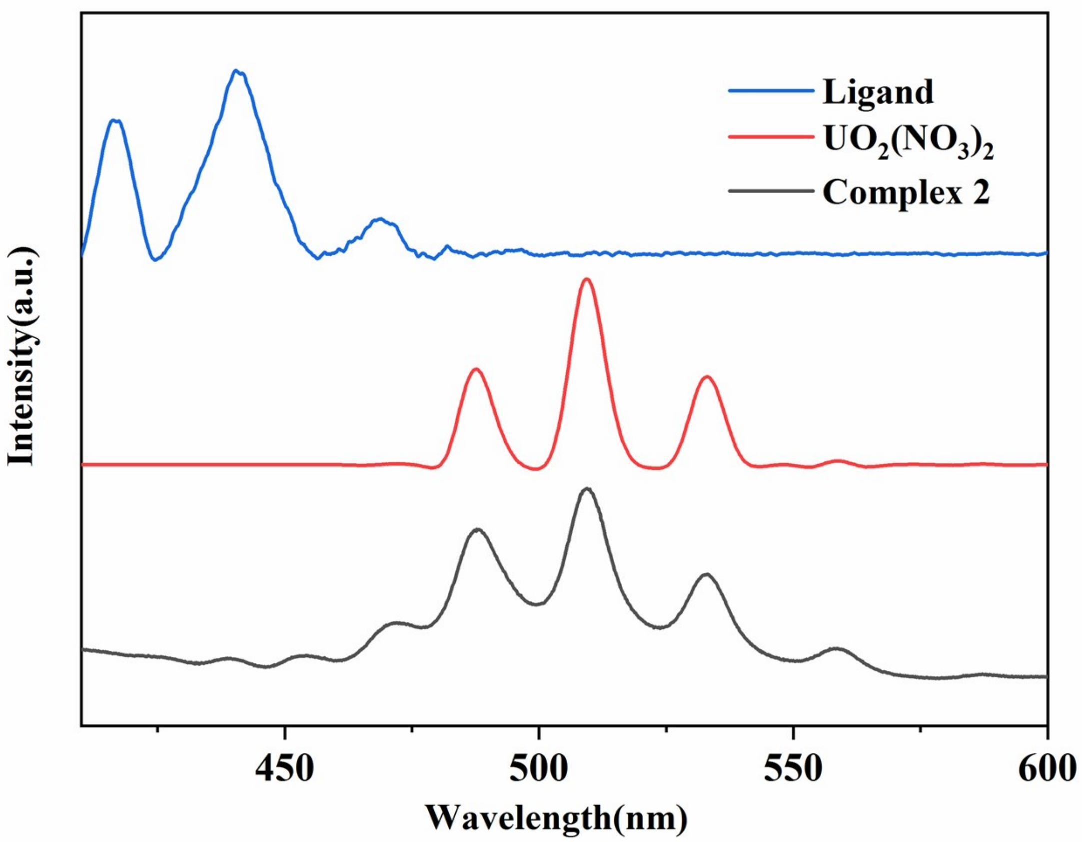

Fig. S4. Fluorescence spectra of complex 2, uranyl nitrate and ligand.

Section S3. Typical Figures and Tables

Table S1. X-ray crystallographic parameters for complex 1 and complex 2.

compound	complex 1	complex 2
formula	$C_{140}H_{252}N_{44}O_{48}U_4$	$C_{118}H_{184}N_{34}O_{38}U_4$
Fw	4271.96	3639.10
T/K	170	170
crystal system	monoclinic	tetragonal
space group	$C2$	$I\bar{4}$
a/Å	22.7224(11)	18.1058(4)
b/Å	27.2567(13)	18.1058(4)
c/Å	28.5054(14)	27.6190(6)
α /°	90	90
β/°	103.334(3)	90
γ /°	90	90
V /Å^3	17178.5(15)	9054.1(4)
Z	4	2
ρ_{calcd}/g cm^{-3}	1.652	1.335
λ(Å)	1.54178	1.54178
μ(MoKa)/ mm^{-1}	11.246	10.518
F(000)	8608	3604
GOF	1.048	0.995
R1[I > 2σ(I)]^a	0.0482	0.0383
wR2 (all data)^b	0.1281	0.1004

^{a} $R1=\Sigma \| F_o| - |F_c \| / \Sigma |F_o|$. ^{b} $wR2=\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Selected bond distances (Å) for complex 1

	complex 1		complex 1
U(1)–O(1)	1.76(3)	U(1)–O(5)	2.50(2)
U(1)–O(2)	1.750(11)	U(1)–O(6)	2.49(2)
U(1)–O(3)	2.45(2)	U(1)–O(7)	2.41(2)
U(1)–O(4)	2.56(2)	U(1)–O(8)	2.48(2)
U(2)–O(25)	1.741(15)	U(2)–O(26)	1.742(15)
U(2)–O(27)	2.45(2)	U(2)–O(28)	2.48(2)
U(2)–O(29)	2.43(2)	U(2)–O(30)	2.49(2)

U(2)–O(31)	2.46(2)	U(2)–O(32)	2.48(2)
U(3)–O(9)	1.761(15)	U(3)–O(10)	1.771(15)
U(3)–O(11)	2.49(2)	U(3)–O(12)	2.45(3)
U(3)–O(13)	2.49(3)	U(3)–O(14)	2.42(2)
U(3)–O(15)	2.52(3)	U(3)–O(16)	2.47(3)
U(4)–O(17)	1.74(3)	U(4)–O(18)	1.749(12)
U(4)–O(19)	2.49(2)	U(4)–O(20)	2.47(2)
U(4)–O(21)	2.48(2)	U(4)–O(34)	2.44(2)
U(4)–O(23)	2.47(2)	U(4)–O(24)	2.49(2)

Table S3. Selected bond distances (Å) for complex 2

	complex 2		complex 2
U(1)–O(1)	1.780(9)	U(1)–O(5)	2.456(7)
U(1)–O(2)	1.753(10)	U(1)–O(6)	2.469(9)
U(1)–O(3)	2.463(6)	U(1)–O(7)	2.458(7)
U(1)–O(4)	2.455(8)	U(1)–O(8)	2.465(7)

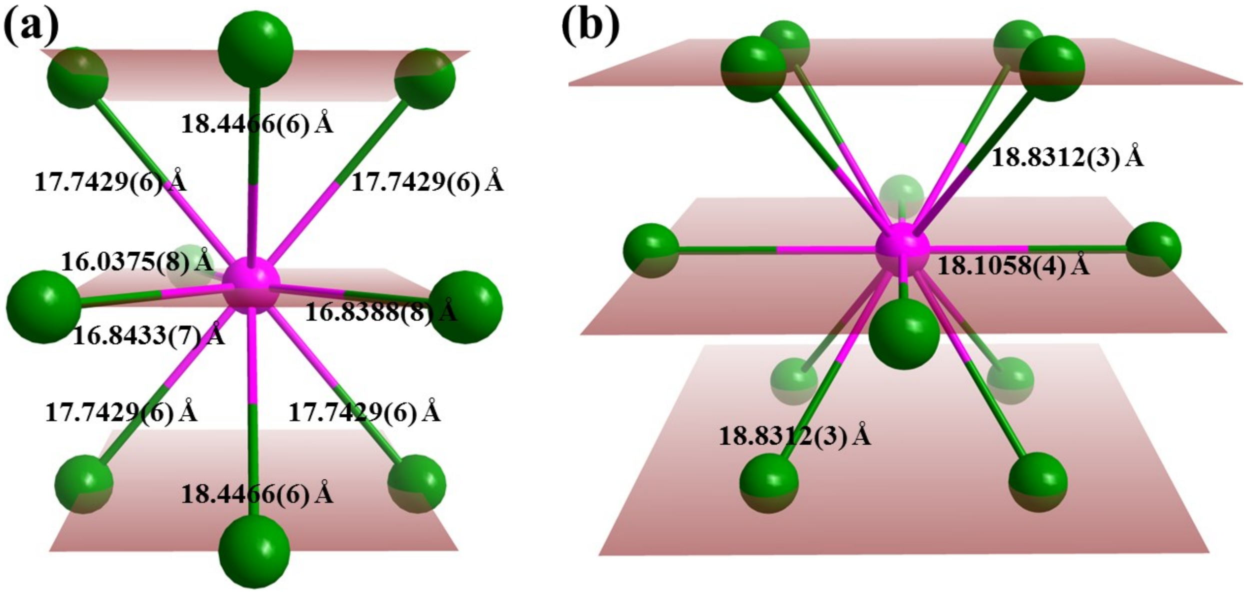

Fig. S5. (a) The surrounded situation of U_4L_4 cage in complex 1 with cage-cage distances ranging from 16.0375(8) to 18.4466(6) Å. (b) The surrounded situation of U_4L_4 cage in complex 2 with cage-cage distances ranging from 18.1058(4) to 18.8312(3) Å.

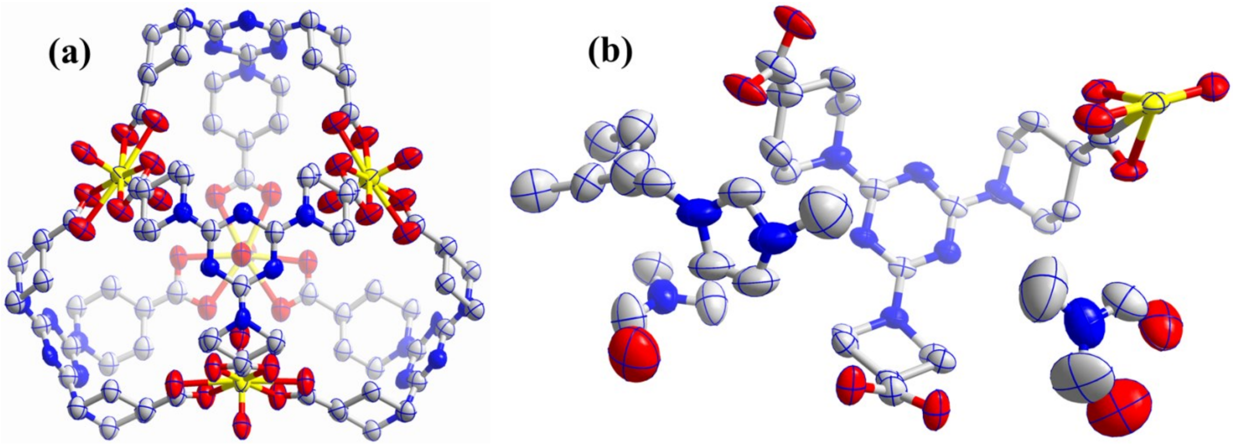

Fig. S6. ORTEP view of the asymmetric units of complex 1 (a) and complex 2 (b) with thermal ellipsoids at 50% probability. Color scheme: U, yellow; C, gray; O, red; N, blue. H atoms were omitted for clarity.

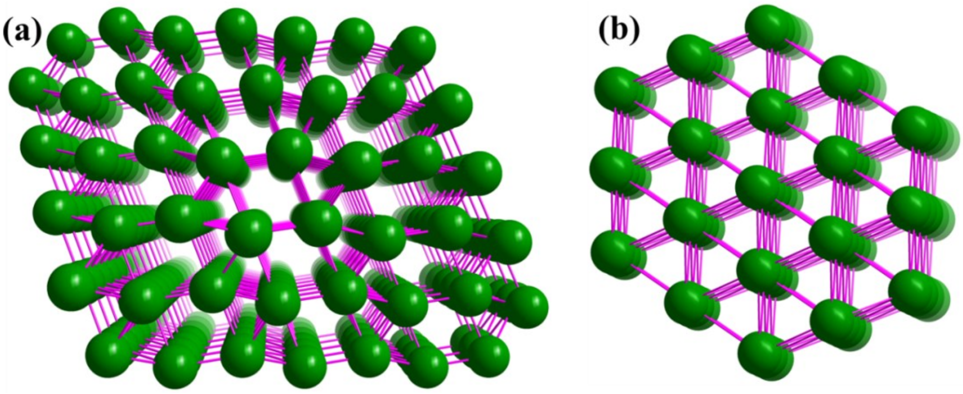

Fig. S7. (a) The 3D framework of complex 1. (b) The 3D framework of complex 2.

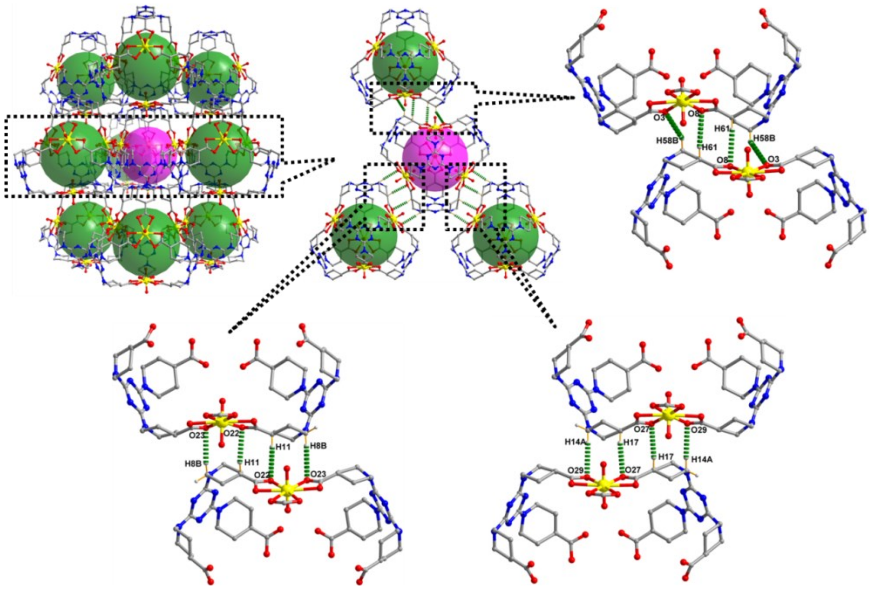

Fig. S8. Each U_4L_4 cage is surrounded by nine equivalent cages via hydrogen bonds to form 3D structure of complex 1. The three cages closest to the center cage are connected to it through four hydrogen bonds between piperidine rings and carboxyl groups, respectively. Color scheme: U, yellow; C, gray; O, red; N, blue.

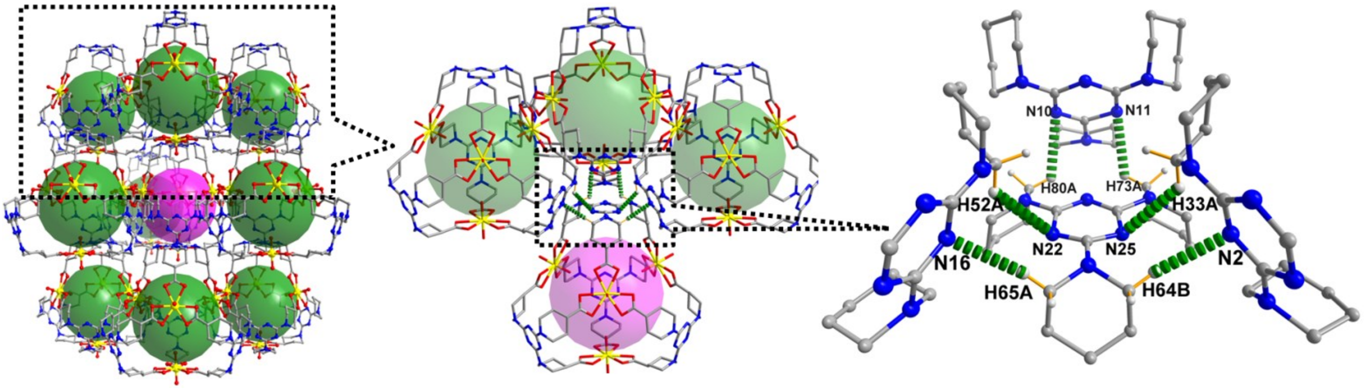

Fig. S9. Each U_4L_4 cage is surrounded by nine equivalent cages via hydrogen bonds to form 3D structure of complex 1. The three cages above the center cage are connected to it through hydrogen bonds between piperidine rings and triazine rings. Color scheme: U, yellow; C, gray; O, red; N, blue.

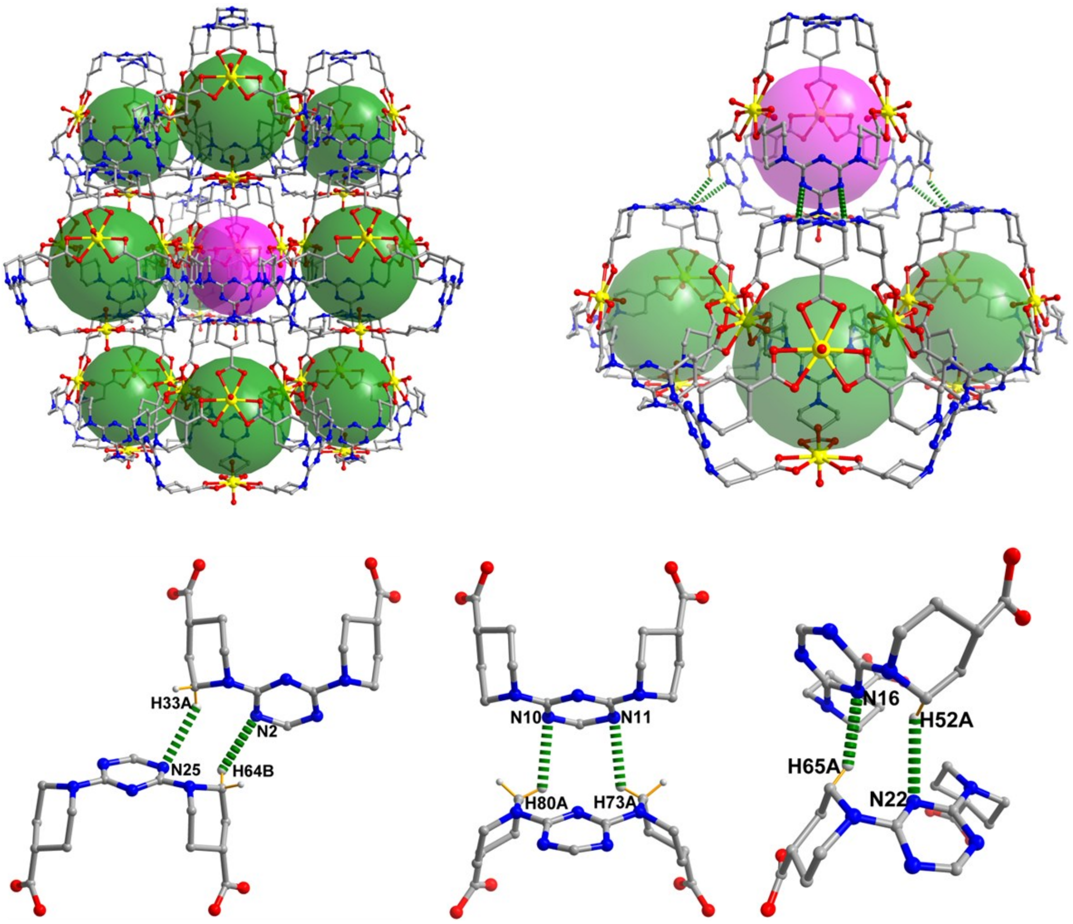

Fig. S10. Each U_4L_4 cage is surrounded by nine equivalent cages via hydrogen bonds to form 3D structure of complex 1. The three cages below the center cage are connected to it through hydrogen bonds between piperidine rings and triazine rings. Color scheme: U, yellow; C, gray; O, red; N, blue.

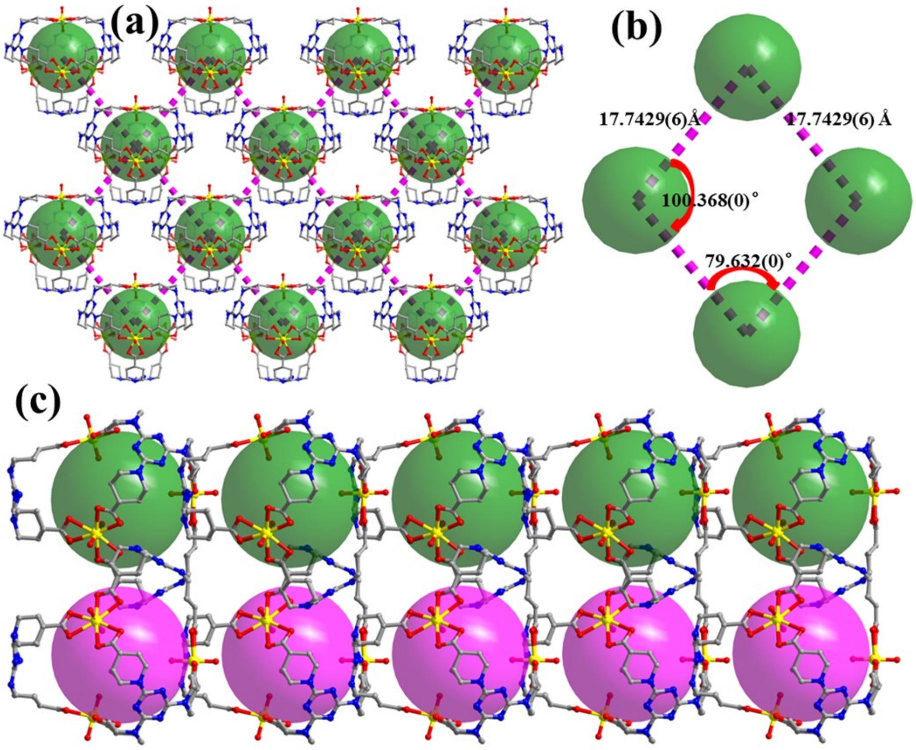

Fig. S11. (a) The 2D grid-like network of complex 1 formed by U_4L_4 cages. (b) The smallest grid in the network, in which the side length is 17.7429(6) Å and the two included angles are 100.368(0) degree and 79.632(0) degree, respectively. (c) The adjacent two equivalent 2D grid-like networks form a composite 2D planar structure. Color scheme: U, yellow; C, gray; O, red; N, blue.

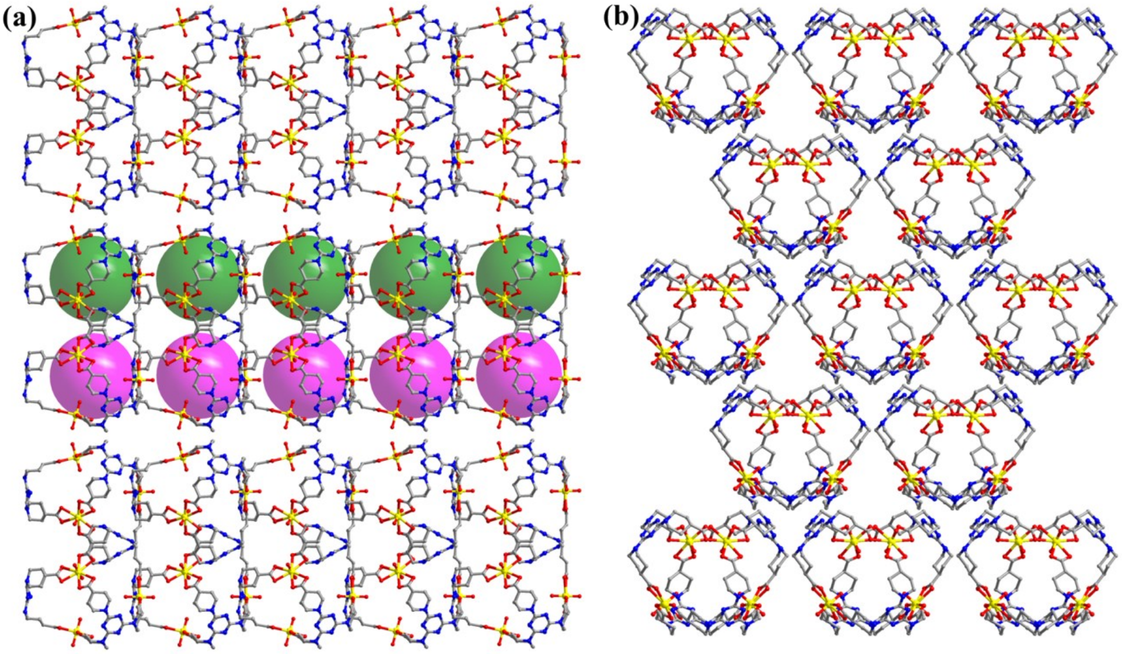

Fig. S12. (a) 3D structure of complex 1. The neighboring 2D composite planes interconnect via hydrogen bonds to form 3D structure. (b) 3D structure of complex 2. Color scheme: U, yellow; C, gray; O, red; N, blue.

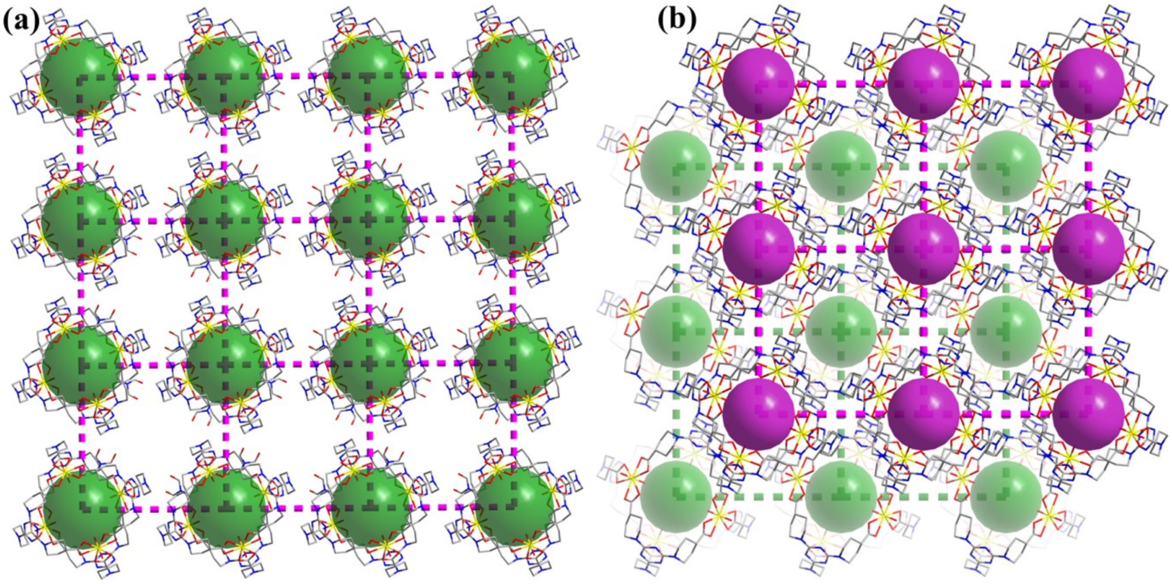

Fig. S13. (a) A series of U_4L_4 cages are regularly arranged to form a 2D grid-like network of complex 2 on the a×b plane. (b) The neighboring 2D grid-like networks interconnect arranged in ABAB stacking mode in complex 2. Color scheme: U, yellow; C, gray; O, red; N, blue.

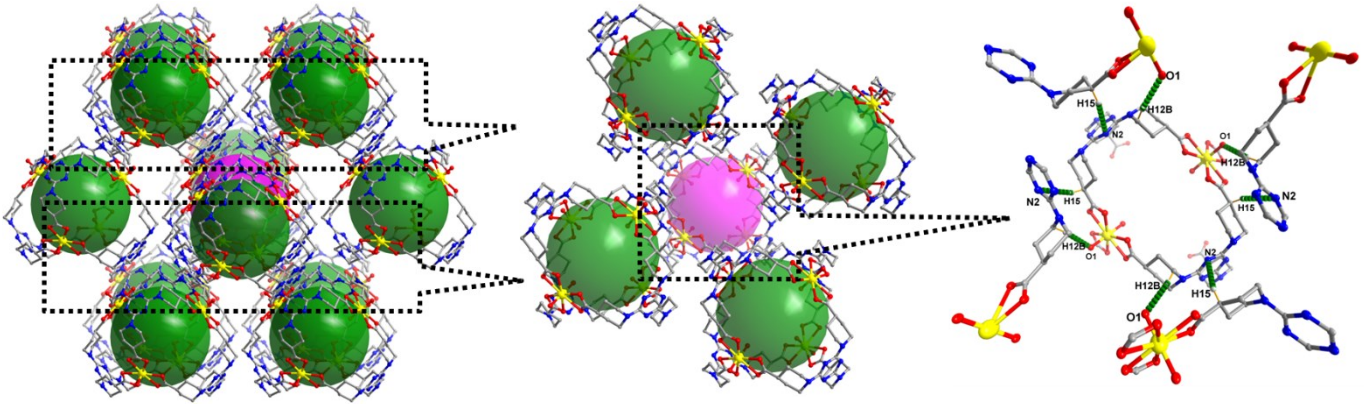

Fig. S14. Each U_4L_4 cage is surrounded by twelve equivalent cages via hydrogen bonds to form 3D structure of complex 2. The hydrogen bonds are between the piperidine rings and triazine rings or acyl-oxygens. Color scheme: U, yellow; C, gray; O, red; N, blue.

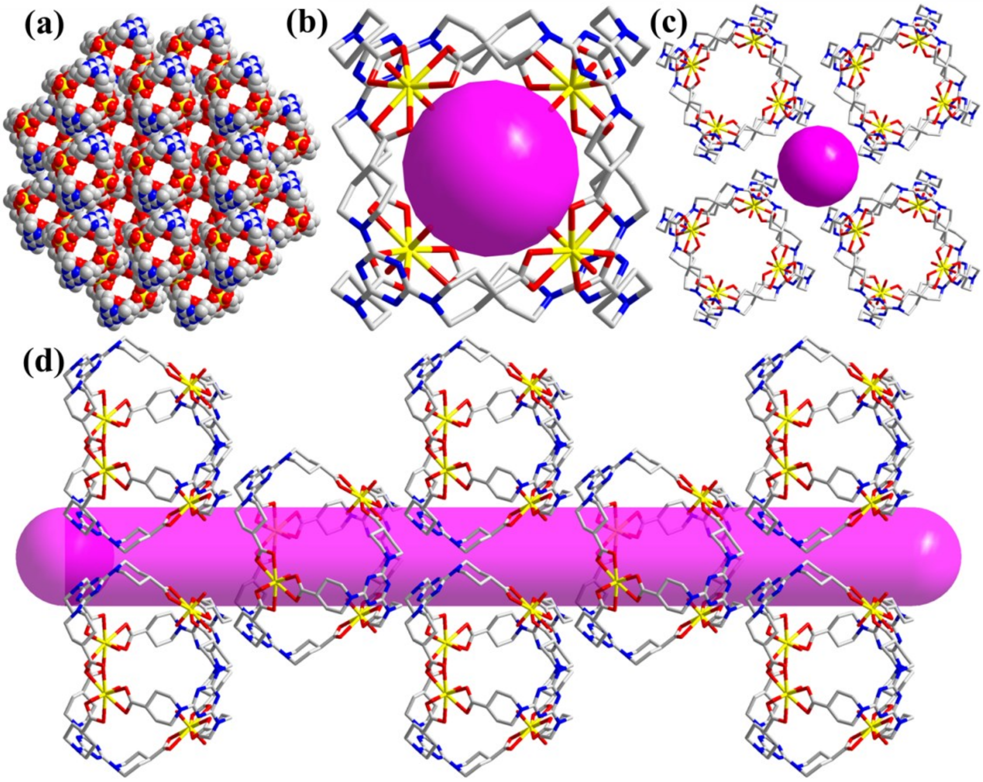

Fig. S15. (a) Along the c axis, a series of 1D channels with diameter of about 8 Å in the 3D skeleton of complex 2. (b) The hole in the U_4L_4 cage itself. (c) The void surrounded by four U_4L_4 cages. (d) The holes and voids are alternately connected to form a final 1D channel structure in complex 2. Color scheme: U, yellow; C, gray; O, red; N, blue.

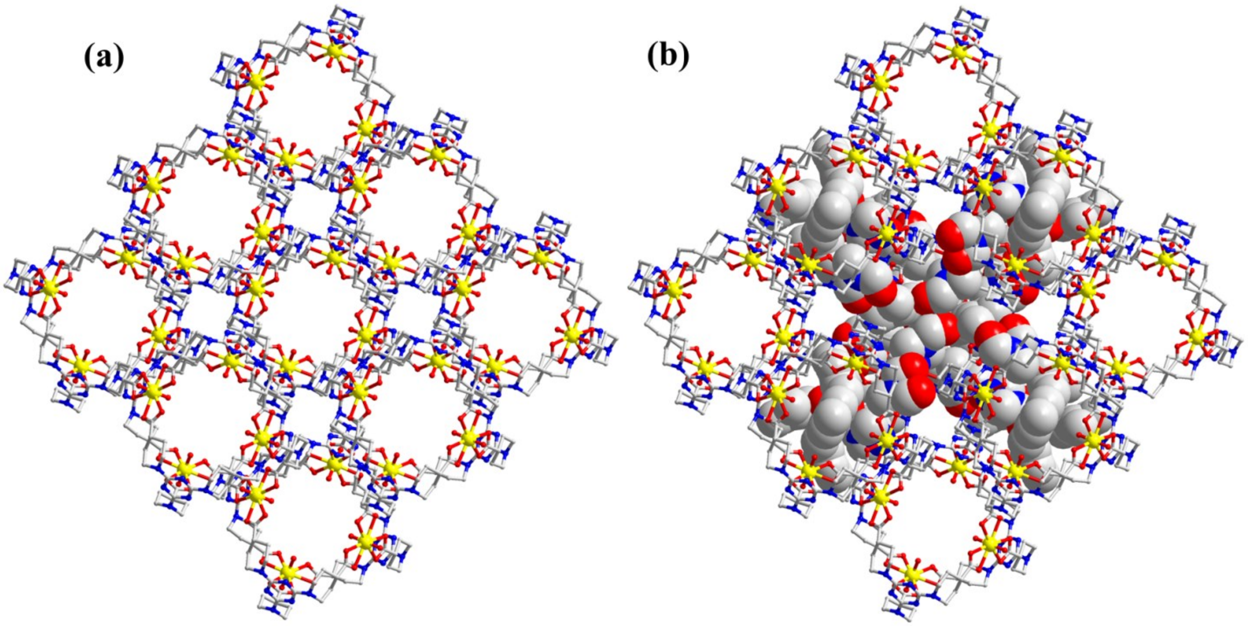

Fig. S16. The 1D channel structures of complex 2 are filled by guest molecules, including solvent molecules DMF, H_2O and charge balanced cations dimethylamine, 1-butyl-3-methylimidazolium. Color scheme: U, yellow; C, gray; O, red; N, blue.

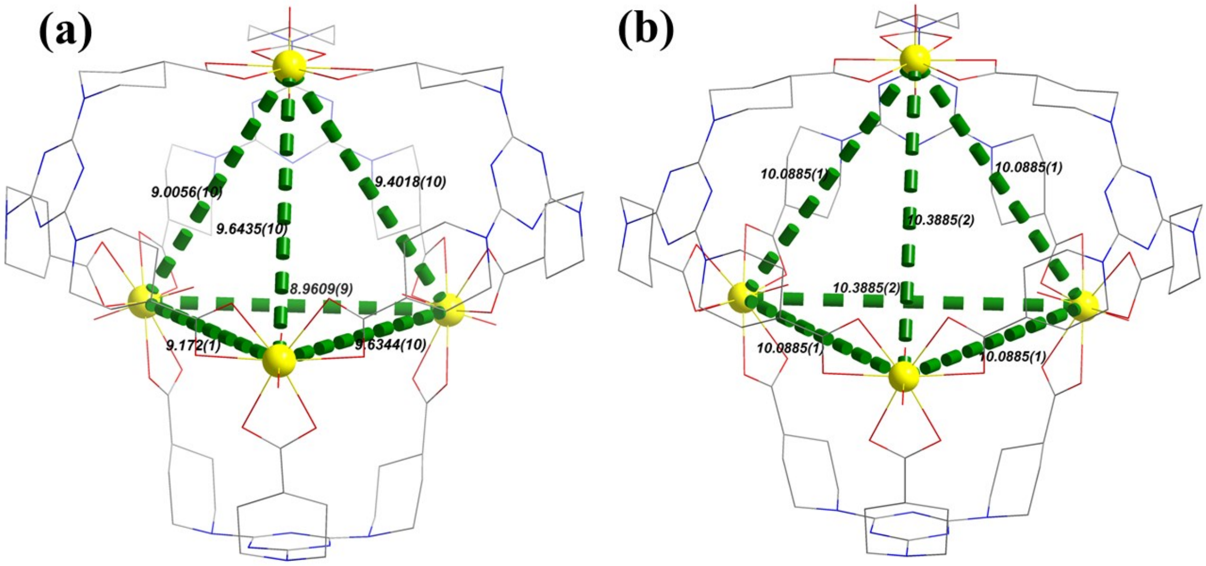

Fig. S17. The tetrahedron simulated within four vertices of the cage structure in (a) complex 1 (b) complex 2. Color scheme: U, yellow; C, gray; O, red; N, blue.

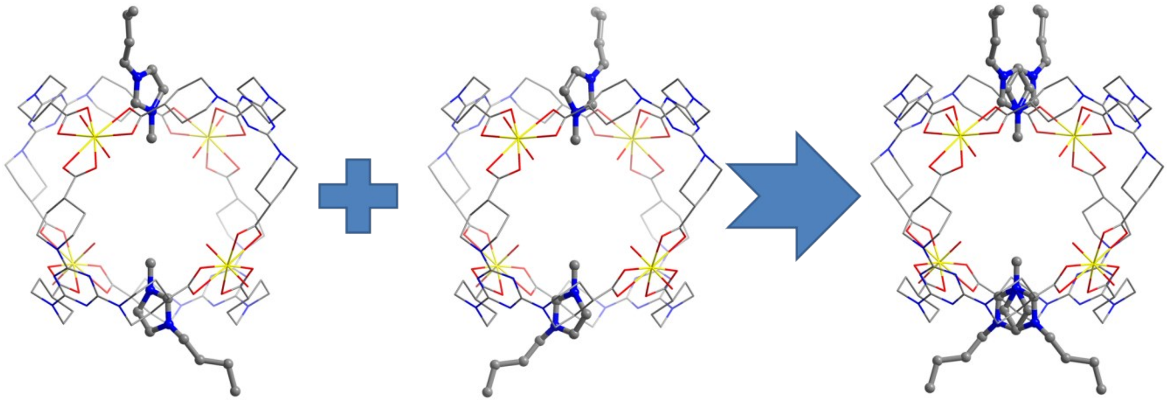

Fig. S18. The two windows along the 1D channel of U_4L_4 cage in complex 2 are occupied by two disordered $[Bmim]^+$ cations. Color scheme: U, yellow; C, gray; O, red; N, blue.

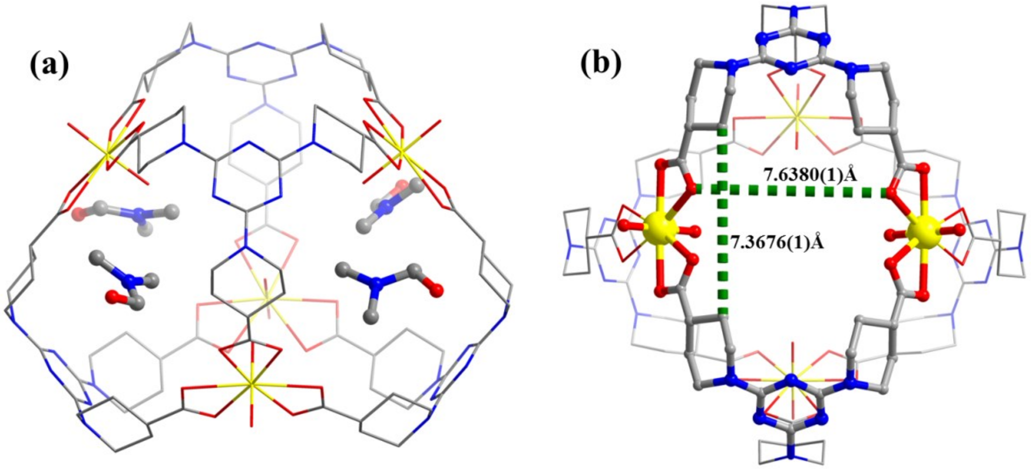

Fig. S19. (a) Four DMF molecules occupied the remaining four windows of U_4L_4 cage in complex 2. (b) Six open windows with the size of 7.3676(1) Å × 7.6380(1) Å in the U_4L_4 cage of complex 2. Color scheme: U, yellow; C, gray; O, red; N, blue.

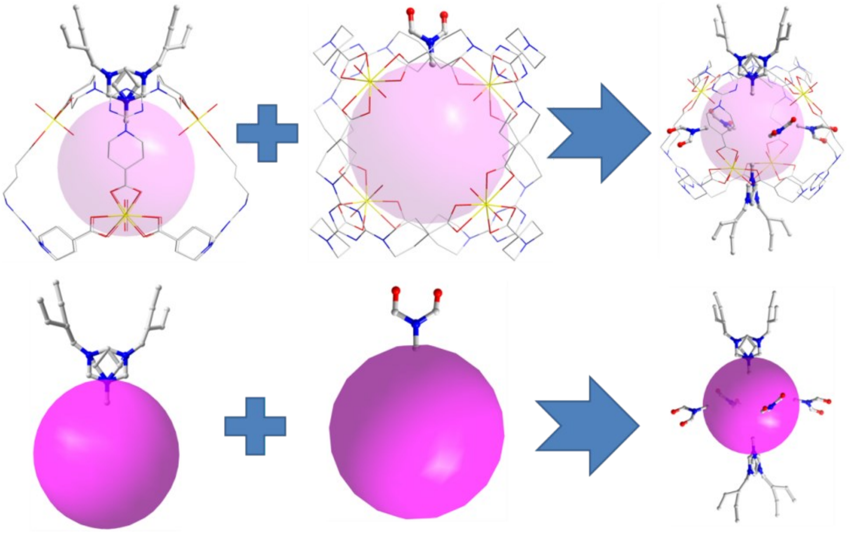

Fig. S20. In complex 2, a U_4L_4 cage is modified by six guest molecules. Color scheme: U, yellow; C, gray; O, red; N, blue.

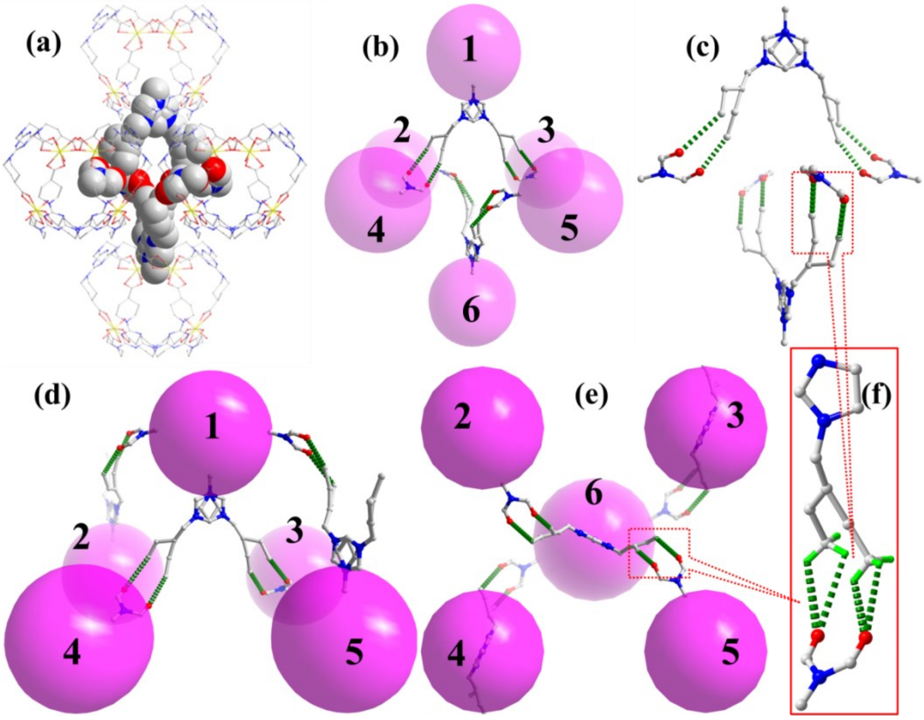

Fig. S21. In complex 2, (a) six U_4L_4 cages are assembled into a regular octahedral supramolecular cage $(U_4L_4)_6$ through weak interactions between their respective guest molecules. (b, c) The terminal methyl group of disordered $[Bmim]^+$ cation of cage 1 forms hydrogen bonds with the oxygen atoms of DMF molecules of cage 3 and cage 4, respectively. The terminal methyl group of disordered $[Bmim]^+$ cation of cage 6 forms hydrogen bonds with the oxygen atoms of DMF molecules of cage 2 and cage 5, respectively. (d) The oxygen atoms of two DMF molecules of cage 1 form hydrogen bonds with the terminal methyl groups of $[Bmim]^+$ cations of cage 2 and cage 5, respectively. (e) The oxygen atoms of two DMF molecules of cage 6 form hydrogen bonds with the terminal methyl groups of $[Bmim]^+$ cations of cage 3 and cage 4, respectively. (f) The hydrogen bonds between DMF of one U_4L_4 cage and $[Bmim]^+$ cation of another U_4L_4 cage. Color scheme: U, yellow; C, gray; O, red; N, blue.

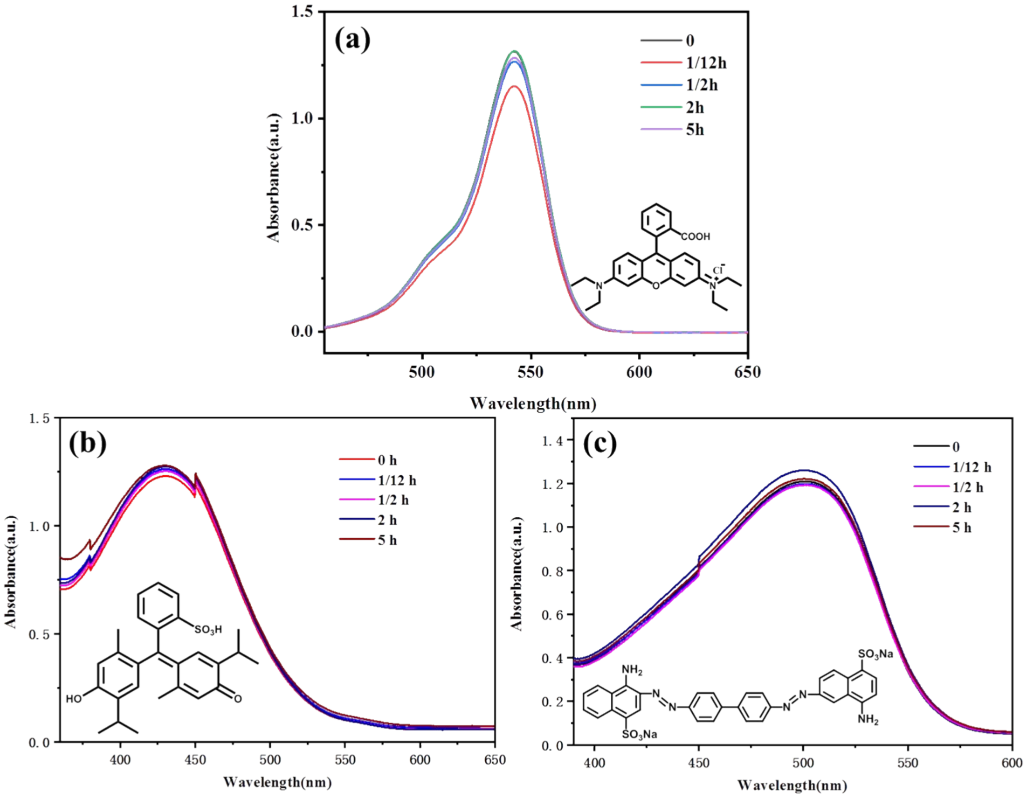

Fig. S22. UV/Vis spectra of C_2H_5OH solutions of RB (a), TB (b) and CR (c) in the presence of complex 2 monitored with time to check the adsorption ability of it towards these dyes.

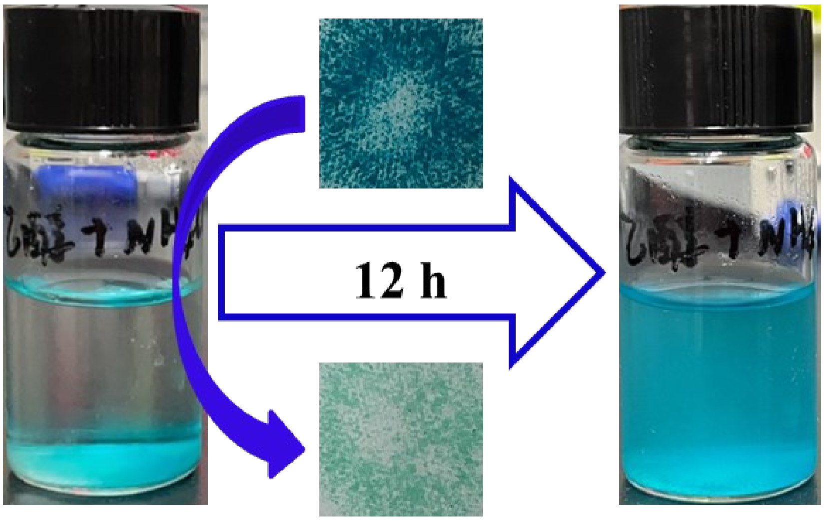

Fig. S23. The desorption experiment. 10 mg of MB@**2** with blue crystals was soaked in 6 mL NH_4Cl solution (0.1 M, C_2H_5OH). It was observed that the solution changed from colorless to blue, as well as crystals changed from blue to cyan.

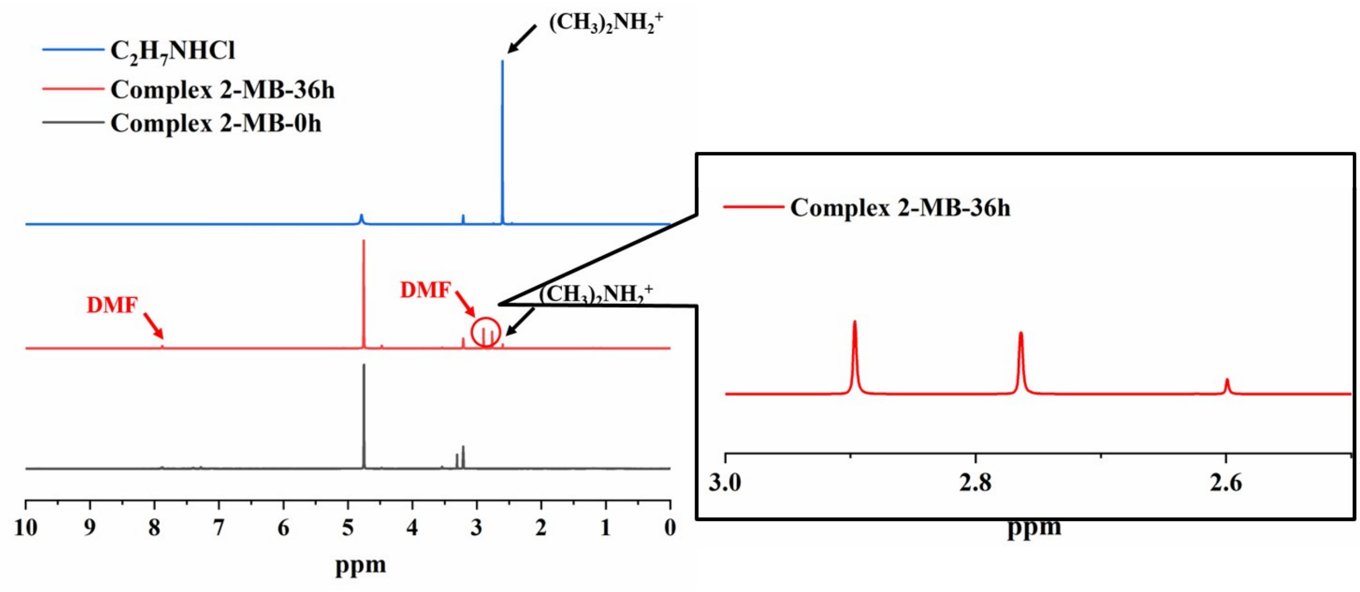

Fig. S24. ^1H NMR spectra of filtrates of complex 2-MB treated by CD_4O solution.

References

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2. A. L. Spek, *J Appl Crystallogr*, 2003, **36**, 7.