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Supporting Information for

Cage-like Crystal Packings through Metallocavitands within Cobalt Cluster-based Supramolecular Assembly

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General Methods

All the glassware is oven-dried prior to use. Powder X-ray diffraction (PXRD) analyses are performed using synchrotron radiation (wavelength 1.0 Å) in the focused beam configuration with a continuous scan rate of 2° min^{-1} in the 3–50° range at 100 K. Simulated PXRD patterns are calculated from single crystal X-ray diffraction (XRD) data using the Mercury 3.3 program. Thermogravimetric analysis (TGA) is performed using a TA Instruments SDT Q600 analyzer under a nitrogen atmosphere from 18 to 600 °C at a heating rate of 2 °C/min. Magnetic measurements are performed using a Quantum Design MPMS-5XL magnetometer for temperatures $3\ \text{K} \leq T \leq 300\ \text{K}$ with a 1,000 Oe applied fields. Gas adsorption isotherms are obtained using BELSORP-mini II (BEL Japan, Inc.). The gases used throughout adsorption experiments are highly pure (99.999%). Prior to the adsorption experiments, all the samples are activated as follows: First, the as-synthesized sample is thoroughly rinsed with DMF (3 × 10 mL) and immersed in 10 mL acetone for 24 h for solvent exchange; the acetone is decanted and replenished with fresh solvent. This procedure is repeated three times. Finally, the sample is dried under vacuum for 36 h prior to the gas sorption measurements. Adsorption experiments are carried out at 273 K, attained using a mixture of ice and water.

Materials

Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 98 %, Sigma-Aldrich), 2,6-pyridinedicarboxylic acid ($C_7H_5NO_4$, 99%, Sigma-Aldrich), 5-bromoisophthalic acid ($C_8H_{54}O_4Br$, 97%, Sigma-Aldrich), and N,N-dimethylformamide (DMF, 99.99%, Burdick & Jackson) are used as received. 5-iodoisophthalic acid ($C_8H_{54}O_4I$) is synthesized following a reported method with a slight modification.[1] Abbreviations used: OAc = acetate, PDA = 2,6-

pyridinedicarboxylate, H_2PDA = 2,6-pyridinedicarboxylic acid, Br-PTA = 5-bromoisophthalate, H_2Br-PTA = 5-bromoisophthalic acid, I-PTA = 5-iodoisophthalate, H_2I-PTA = 5-iodoisophthalic acid.

Synthesis of 5-iodoisophthalate (*I*-PTA) ligand

5-iodoisophthalate is synthesized with the modified protocol according to the literature.[1] The 10 mL of an aqueous solution of $NaNO_2$ (2.05 g, 29.5 mmol) is slowly added into a suspension of 5-aminoisophthalic acid (5 g, 27.6 mmol) in 100 mL of 6 M HCl solution, and the mixture is stirred for 1 h at 4 ºC. Upon slowly adding 40 mL of a potassium iodide solution (15 g, 90.3 mmol) into the above mixture, the color of the reaction mixture is turned to yellowish red. The reaction mixture is refluxed and stirred for 1 h. Afterwards, the reaction is cooled and 5-iodoisophthalate (*I*-PTA) ligand is obtained as precipitated powder. Yield: 1.93 mg, 23.91 %.

Synthesis of a cobalt supramolecular triple-stranded helicate, $[Co_8(PDA)_6(Br\text{-}PTA)_3(DMF)_4(H_2O)_2]$ (1)

To a mixed-ligand DMF solution (0.9 mL) of H_2PDA (5.0 mg, 0.030 mmol) and H_2Br-PTA (3.7 mg, 0.015 mmol) is added a DMF solution (0.3 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (4.4 mg, 0.015 mmol) in a 4 mL glass vial at room temperature. The vial is sealed tightly, and heated to 100 °C (increasing rate; 2.67 °C/min), and maintained at this temperature for 8 h. Afterward, the mixture is gradually cooled to 30 °C with a cooling rate of –0.25 °C/min. Purple rectangular crystals are collected, washed sequentially with DMF (3 × 10 mL) and acetone (3 × 10 mL), and dried under vacuum at room temperature. Yield: 3.81 mg, 30.5 % (based on H_2PDA).

Synthesis of a molecular cage with Br-PTAs, $\{[Co_8(PDA)_6(Br\text{-}PTA)_3(DMF)_6]_6\text{-}[Co(H_2O)_3]_4\}$ (2)

To a mixed-ligand DMF solution (0.9 mL) of H_2PDA (5.0 mg, 0.030 mmol) and H_2Br-PTA (3.7 mg, 0.015 mmol) is added a DMF solution (0.3 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (13.1 mg, 0.045 mmol) in a 4 mL glass vial at room temperature. The vial is sealed tightly, and heated to 100 °C (increasing rate; 2.67 °C/min), and maintained at this temperature for 8 h. Afterward, the mixture is gradually cooled to 30 °C with a cooling rate of –0.25 °C/min. Purple rectangular crystals are collected, washed sequentially with DMF (3 × 10 mL) and acetone (3 × 10 mL), and dried under vacuum at room temperature. Yield: 5.6 mg, 41.4 % (based on H_2PDA).

Synthesis of a molecular cage with I-PTAs, $\{[Co_8(PDA)_6(I\text{-}PTA)_3(DMF)_6]_6\text{-}[Co(H_2O)_3]_4\}$ (3)

To a mixed-ligand DMF solution (0.9 mL) of H_2PDA (5.0 mg, 0.030 mmol) and H_2I-PTA (4.4 mg, 0.015 mmol) is added a DMF solution (0.3 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (13.1 mg, 0.045 mmol) in a 4 mL glass vial at room temperature. The vial is sealed tightly, and heated to 100 °C (increasing rate; 2.67 °C/min), and maintained at this temperature for 8 h. Afterward, the mixture is gradually cooled to 30 °C with a cooling rate of –0.25 °C/min. Purple rectangular crystals are collected, washed sequentially with DMF (3 × 10 mL) and acetone (3 × 10 mL), and dried under vacuum at room temperature. Yield: 7.1 mg, 49.9 % (based on H_2PDA).

Single crystal X-ray diffraction analysis of $[Co_8(PDA)_6(Br\text{-}PTA)_3(DMF)_4(H_2O)_2]$ (1)

Diffraction data from the dark purple crystals of **1** ($0.04\times 0.035 \times 0.03$ mm^3) mounted on a MiTeGen MicroMount© are collected at 100 K on a ADSC Quantum 210 CCD diffractometer equipped with a synchrotron radiation source (0.70000 Å) at the Supramolecular Crystallography beamline 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The ADSC Q210 ADX program[2] is used for data collection (detector distance is 63 mm, omega scan; $\Delta\omega = 1°$, exposure time is 1 sec/frame for **1**, and HKL3000sm (Ver. 703r)[3] is used for cell refinement, reduction, and absorption correction. The crystal structure of **1** is solved using the direct method with SHELX-XT (Ver. 2014/5)[4] and refined using full-matrix least-squares calculations with the SHELX-XL (Ver. 2014/7)[5] program package.

The systematic absences in the diffraction data are uniquely consistent with the cubic, *Fd-3* space group, yielding chemically reasonable and computationally stable refinement results.[5, 6]

The successful solution of the structure by direct methods provides most of the non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms are located through an alternating series of least-squares cycles and difference Fourier maps. All the non-hydrogen atoms are refined with anisotropic displacement coefficients. All the hydrogen atoms are included in the structure factor calculation at idealized positions, and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 643 parameters against 33519 data results in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all of the data) of 0.0643 and 0.2685 respectively. The final difference Fourier map was featureless.

Single crystal X-ray diffraction analysis of $\{[Co_8(PDA)_6(Br\text{-}PTA)_3(DMF)_6]_6\text{-}[Co(H_2O)_3]_4\}$ (2)

Diffraction data from the dark purple crystals of **2** (0.175 × 0.116 × 0.107 mm3) mounted on a MiTeGen MicroMount© are collected at 100 K on a ADSC Quantum 210 CCD diffractometer equipped with a synchrotron radiation source (0.70000 Å) at the Supramolecular

Crystallography beamline 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The ADSC Q210 ADX program[2] is used for data collection (detector distance is 63 mm, omega scan; $\Delta\omega = 1°$, exposure time is 1 sec/frame for 1, and HKL3000sm (Ver. 703r)[3] is used for cell refinement, reduction, and absorption correction. The crystal structure of **2** is solved using the direct method with SHELX-XT (Ver. 2014/5)[4] and refined using full-matrix least-squares calculations with the SHELX-XL (Ver. 2014/7)[5] program package.

The systematic absences in the diffraction data are uniquely consistent with the cubic, Fd-3 space group, yielding chemically reasonable and computationally stable refinement results.[5, 6]

The successful solution of the structure by direct methods provides most of the non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms are located through an alternating series of least-squares cycles and difference Fourier maps. All the non-hydrogen atoms are refined with anisotropic displacement coefficients. All the hydrogen atoms are included in the structure factor calculation at idealized positions, and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 696 parameters against 32405 data results in residuals R (based on F2 for $I \geq 2\sigma$) and wR (based on F2 for all of the data) of 0.0643 and 0.2278 respectively. The final difference Fourier map was featureless..

Single crystal X-ray diffraction analysis of $\{[Co_8(PDA)_6(I\text{-}PTA)_3(DMF)_6]_6\text{-}[Co(H_2O)_3]_4\}$ (3)

Diffraction data from the dark purple crystals of **1** ($0.164 \times 0.114 \times 0.105$ mm^3) mounted on a MiTeGen MicroMount© are collected at 100 K on a ADSC Quantum 210 CCD diffractometer equipped with a synchrotron radiation source (0.70000 Å) at the Supramolecular Crystallography beamline 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The ADSC Q210 ADX program[2] is used for data collection (detector distance is 63 mm, omega scan; Δω = 1°, exposure time is 1 sec/frame for **1**, and HKL3000sm (Ver. 703r)[3] is used for cell refinement, reduction, and absorption correction. The crystal structure of **1** is solved using the direct method with SHELX-XT (Ver. 2014/5)[3] and refined using full-matrix least-squares calculations with the SHELX-XL (Ver. 2014/7)[5] program package.

The systematic absences in the diffraction data are uniquely consistent with the cubic, *Fd-3* space group, yielding chemically reasonable and computationally stable refinement results.[5, 6]

The successful solution of the structure by direct methods provides most of the non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms are located through an alternating series of least-squares cycles and difference Fourier maps. All the non-hydrogen atoms are refined with anisotropic displacement coefficients. All the hydrogen atoms are included in the structure factor calculation at idealized positions, and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 642 parameters against 20868 data results in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all of the data) of 0.0652 and 0.2201 respectively. The final difference Fourier map was featureless.

Table S1. Crystal data and structure refinement for **1**; atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths, and angles shown in the CIF.

Empirical formula	$C_{78}H_{59}Br_3Co_8N_{10}O_{42}$
Formula weight	2519.52
Temperature/K	100
Crystal system	cubic
Space group	Fd-3
a/Å	59.303(7)
b/Å	59.303(7)
c/Å	59.303(7)
α/°	90
β/°	90
γ/°	90
Volume/Å3	208565(73)
Z	48
ρcalcg/cm3	0.963
μ/mm-1	1.427
F(000)	60192
Crystal size/mm3	0.04 × 0.035 × 0.03
Radiation	synchrotron (λ = 0.700)
2Θ range for data collection/°	3.514 to 66.854
Index ranges	-84 ≤ h ≤ 84, -82 ≤ k ≤ 81, -89 ≤ l ≤ 88
Reflections collected	496509
Independent reflections	33519 [Rint = 0.0771, Rsigma = 0.0329]
Data/restraints/parameters	33519/8/643
Goodness-of-fit on F2	1.089
Final R indexes [I>=2σ (I)]	R1 = 0.0643, wR2 = 0.2369
Final R indexes [all data]	R1 = 0.1109, wR2 = 0.2685
Largest diff. peak/hole / e Å-3	0.78/-0.39

Table S2. Crystal data and structure refinement for **2**; atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths, and angles shown in the CIF.

Empirical formula	$C_{486}H_{396}Br_{18}Co_{52}N_{66}O_{264}$
Formula weight	15888.04
Temperature/K	100
Crystal system	cubic
Space group	Fd-3
a/Å	58.368(7)
b/Å	58.368(7)
c/Å	58.368(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	198849(68)
Z	7.99968
ρ_{calc}g/cm^3	1.061
μ/mm^{-1}	1.562
F(000)	63360
Crystal size/mm^3	0.175 × 0.116 × 0.107
Radiation	synchrotron (λ = 0.700)
2Θ range for data collection/°	2.996 to 66.906
Index ranges	$-91 \leq h \leq 91$, $-63 \leq k \leq 64$, $-62 \leq l \leq 63$
Reflections collected	62970
Independent reflections	32405 [Rint = 0.0412, Rsigma = 0.0749]
Data/restraints/parameters	32405/12/696
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R1 = 0.0643, wR2 = 0.2058
Final R indexes [all data]	R1 = 0.1260, wR2 = 0.2278
Largest diff. peak/hole / e Å^{-3}	1.48/-1.48

Table S3. Crystal data and structure refinement for **3**; atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths, and angles shown in the CIF.

Empirical formula	$C_{504}H_{450}Co_{52}I_{18}N_{72}O_{264}$
Formula weight	17088.58
Temperature/K	100
Crystal system	cubic
Space group	Fd-3
a/Å	58.465(7)
b/Å	58.465(7)
c/Å	58.465(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	199843(70)
Z	7.99968
ρ_{calc}g/cm^3	1.136
μ/mm^{-1}	1.402
F(000)	67584
Crystal size/mm^3	0.164 × 0.114 × 0.105
Radiation	synchrotron (λ = 0.700)
2Θ range for data collection/°	2.99 to 55.99
Index ranges	$-78 \leq h \leq 78$, $-55 \leq k \leq 55$, $-54 \leq l \leq 54$
Reflections collected	40033
Independent reflections	20868 [Rint = 0.0532, Rsigma = 0.1041]
Data/restraints/parameters	20868/30/695
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R1 = 0.0652, wR2 = 0.1994
Final R indexes [all data]	R1 = 0.1277, wR2 = 0.2201
Largest diff. peak/hole / e Å^{-3}	0.87/-1.09

Table S4. The calculated values through the bond valence sum analysis for cobalt ions in **1**, **2**, and **3**.[7, 8]

Compounds		**Bond valence sum**
1	Co1	1.98
	Co2	2.08
	Co3	2.09
	Co4	2.07
2	Co1	2.02
	Co2	2.11
	Co3	2.08
	Co4	2.07
	Co5	2.04
3	Co1	2.00
	Co2	2.06
	Co3	2.10
	Co4	2.11
	Co5	1.76

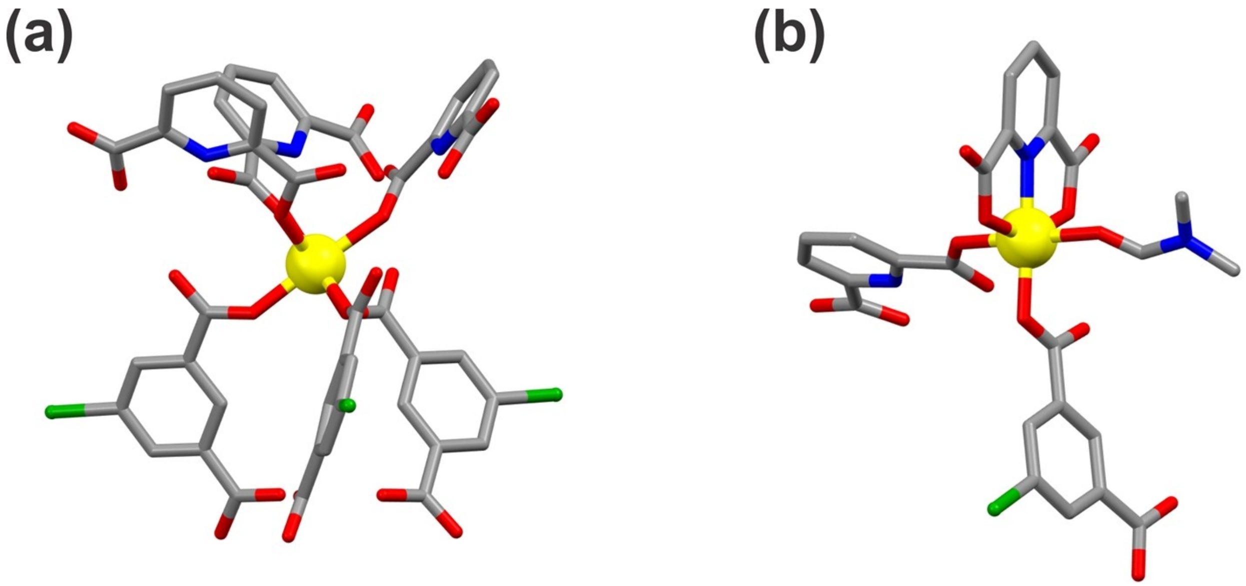

Figure S1. Coordination mode of (a) the central (Co1) and (b) surrounding (Co2─Co4) cobalt atoms in a tetranuclear cobalt cluster of **1**. Colors: C gray; N blue; O red; Co yellow; Br green.

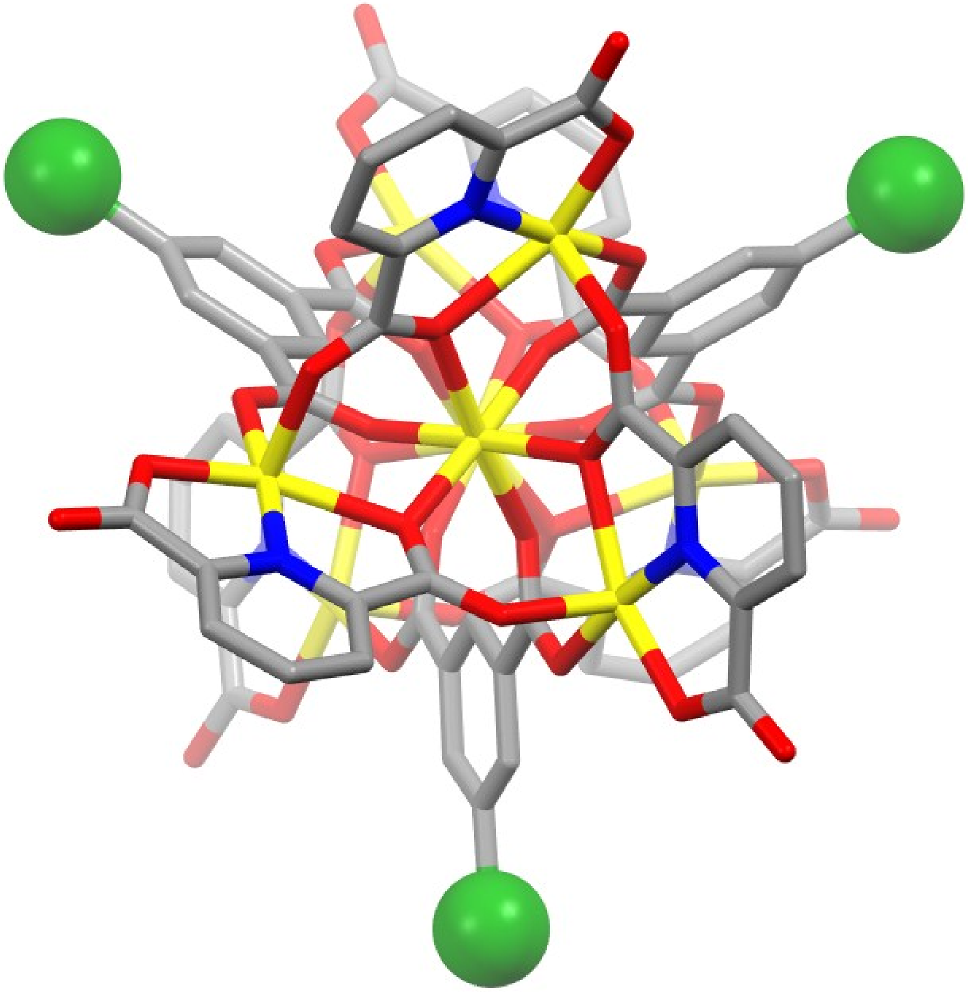

Figure S2. A top-view projection shows the orientation of bromo groups in **1**. All the coordinated and free solvent molecules, and hydrogen atoms have been omitted for clarity. Colors: C gray; N blue; O red; Co yellow; Br green.

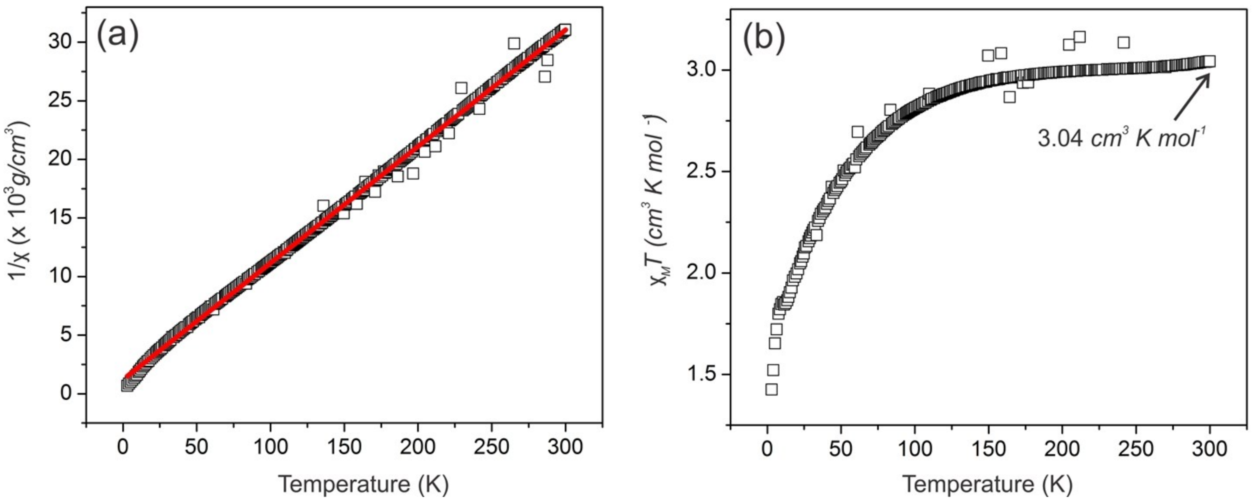

Figure S3. (a) Curie-Weiss fitting (red line) of the inverse mass susceptibility ($1/\chi$) versus temperature, and (b) plot of $\chi_M T$ versus T of **1**.

The magnetic behavior of **1** is described by Curie-Weiss law:[9, 10]

$$\chi = \frac{C}{T - \theta} \qquad \text{(eq. 1)}$$

where χ is mass susceptibility (cm^3 g^{-1}); C is the Curie-Weiss constant (cm^3 K g^{-1}); T is temperature (K); θ is the Weiss constant (K). The mass susceptibility of the compound is related to the molar susceptibility (cm^3 mol^{-1}), χ_M:

$$\chi_M = \chi \,.\, MW/Z \qquad \text{(eq.2)}$$

where ***MW*** is the molecular weight of the compound and ***Z*** is the number of moles of magnetic ions per formula weight of the compound (for the calculation, the ***MW*** and ***Z*** for **1** are 2519 g/mol and 8 moles, respectively).

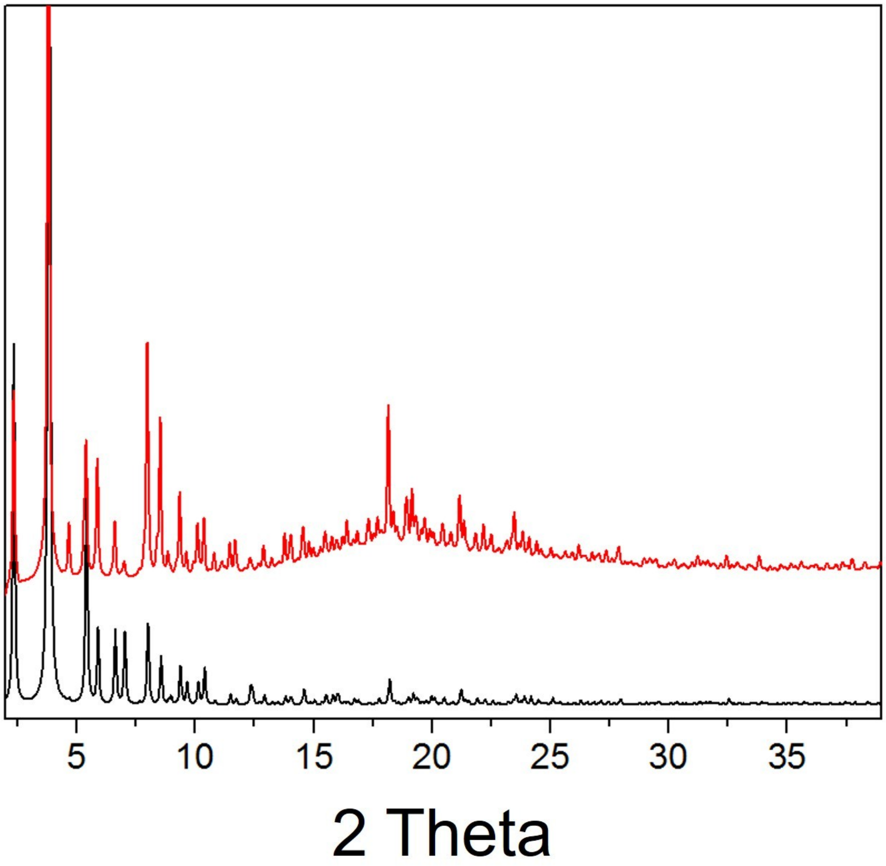

Figure S4. PXRD patterns for **1** using synchrotron radiation (wavelength 1.4 Å). Pattern simulated from single-crystal structure is shown in black; experimental patterns for as-synthesized in red obtained.

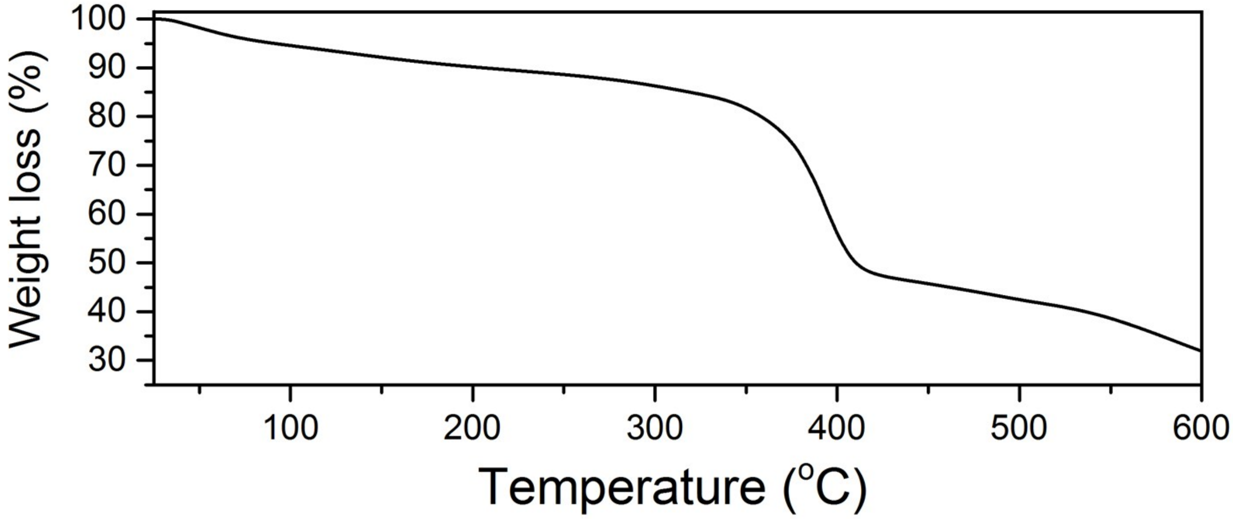

Figure S5. Thermogravimetric analysis (TGA) for **1**.

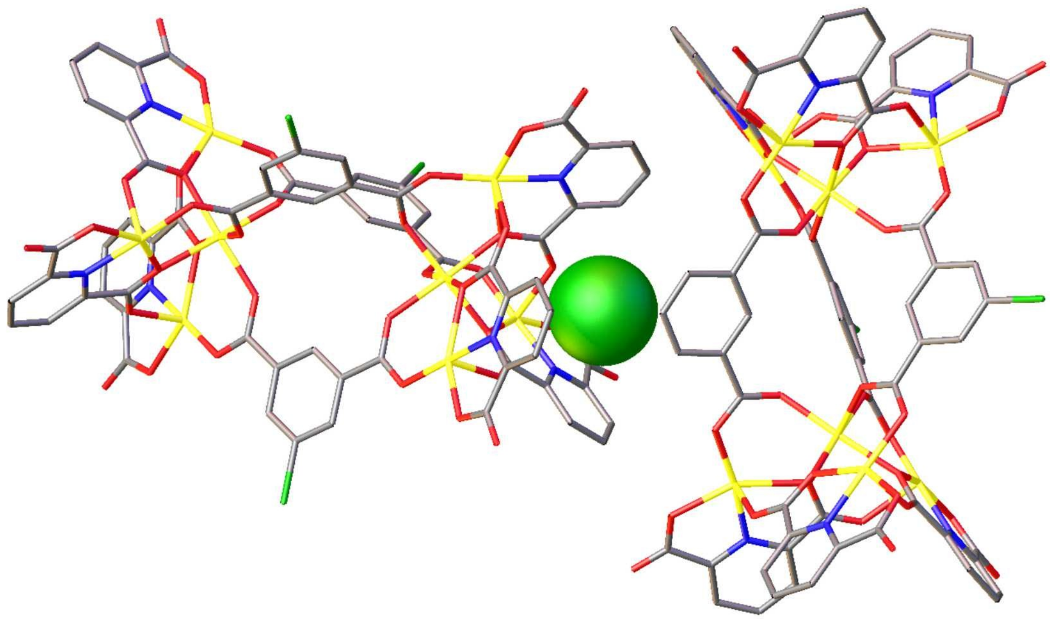

Figure S6. Metallocavitand-induced crystal packing of two neighboring structures of **1**. All the coordinated and free solvent molecules, and hydrogen atoms have been omitted for clarity. Colors: C gray; N blue; O red; Co yellow; Br green.

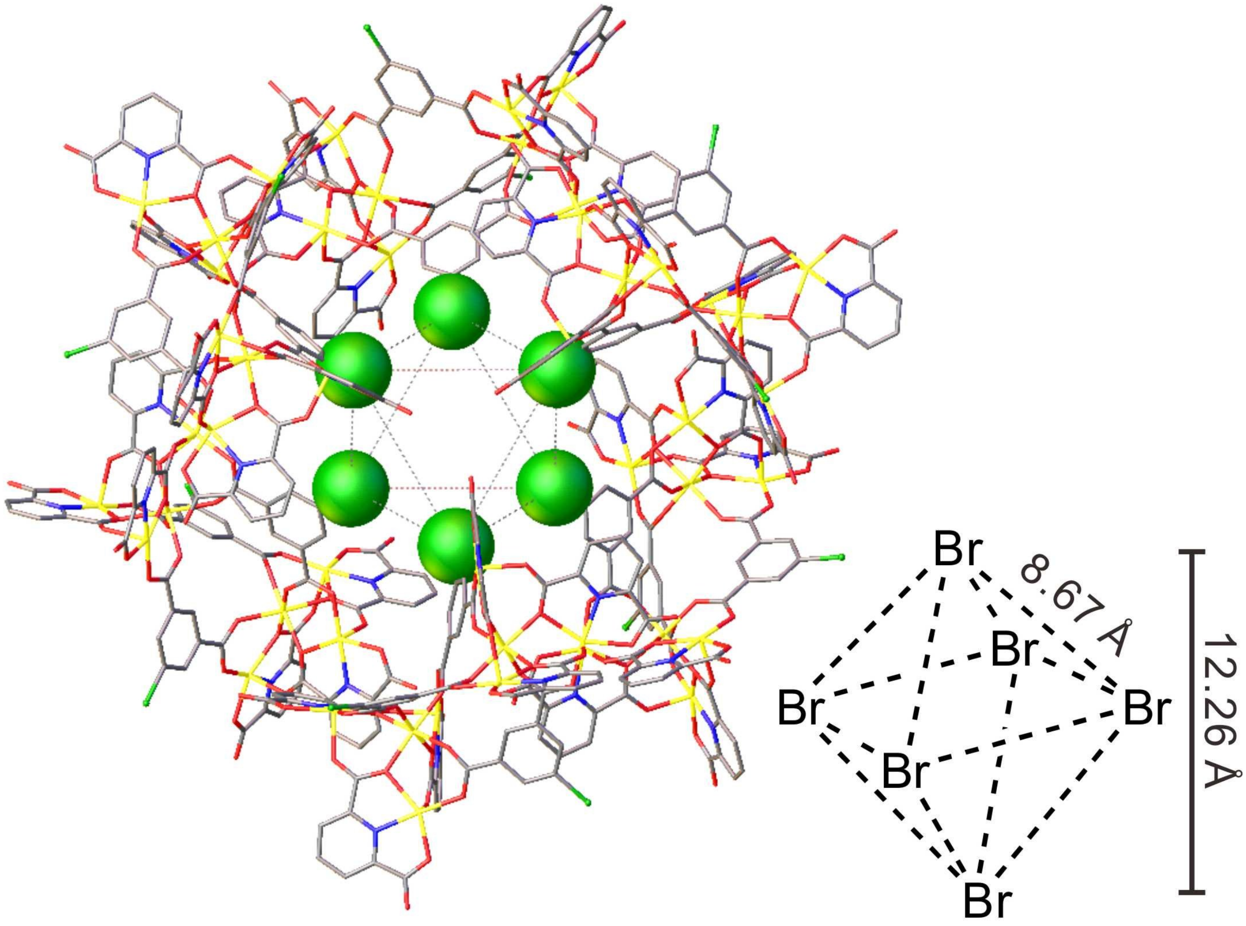

Figure S7. A cage-like crystal packing of six TSHs of **1** in solid state, in which the six bromo groups (inset) form an octahedral arrangement. All the coordinated and free solvent molecules, and hydrogen atoms have been omitted for clarity. Colors: C gray; N blue; O red; Co yellow; Br green.

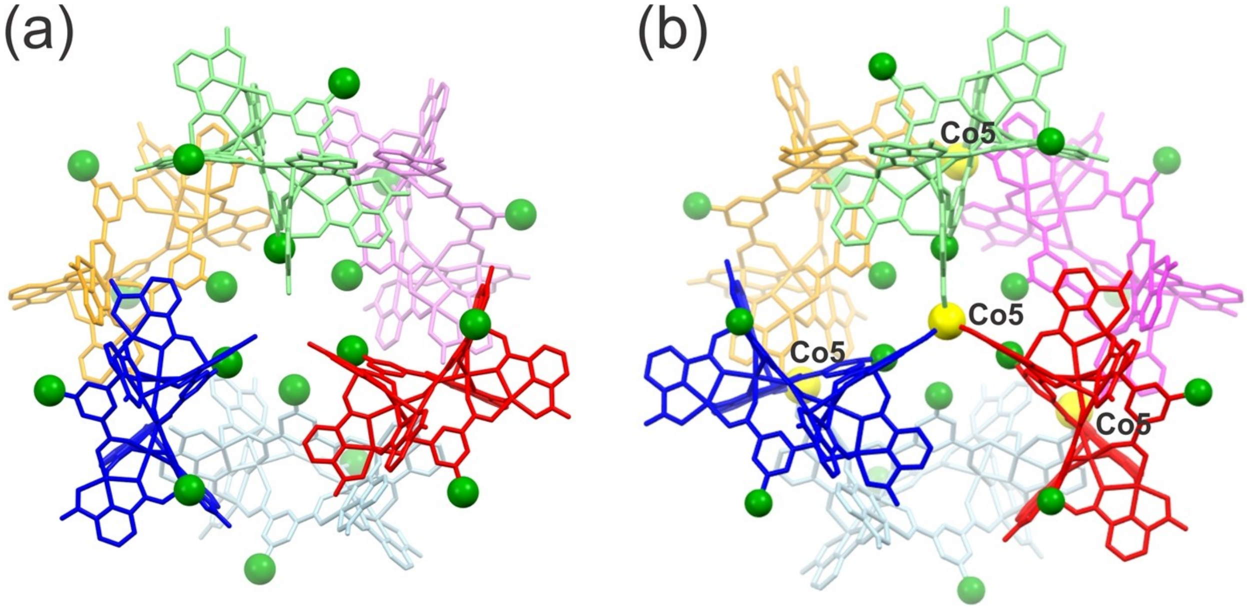

Figure S8. Structural comparison of (a) the cage-like crystal packing of six TSHs of **1** in solid state and (b) the cage structure of **2** displayed in the same manner reveals the absence of connecting cobalt sites (Co5) in the cage-like crystal packing of **1** . TSHs in **1** and **2** are portrayed in different colors. All the coordinated and free solvent molecules, hydrogen atoms, and disordered components have been omitted for clarity.

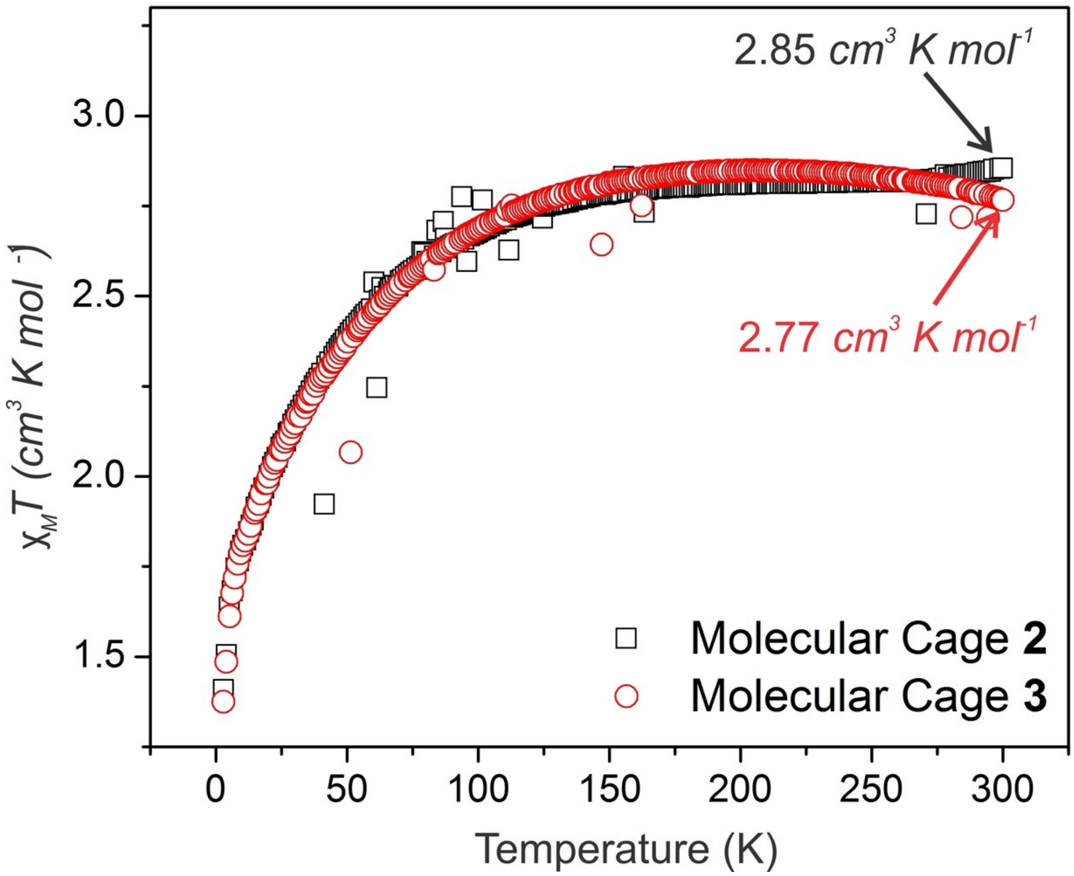

Figure S9. Plot of $\chi_M T$ versus T of **2** and **3** obtained from their respective temperature-dependent magnetic measurements. For the calculation, ***MW* and *Z*** for **2** are 16230.6 g/mol and 52 moles, respectively, and for **3** are 17076.6) g/mol and 52 moles, respectively.

The values $\chi_M T$ at 300 K for **2** and **3** are estimated to be ~2.85 and 2.77 cm^3 K mol^{-1}, which can be assigned for high-spin octahedral Co(II) ions.[11-13]

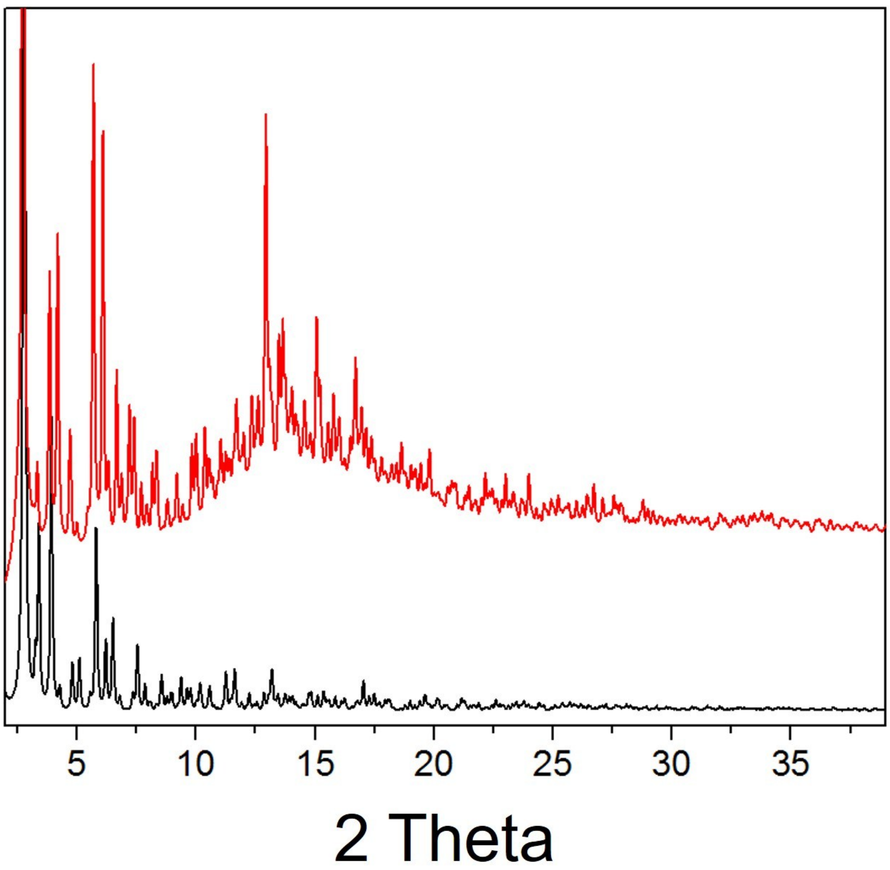

Figure S10. PXRD patterns for **2** using synchrotron radiation (wavelength 1.0 Å). Pattern simulated from single-crystal structure is shown in black; experimental patterns for as-synthesized in red.

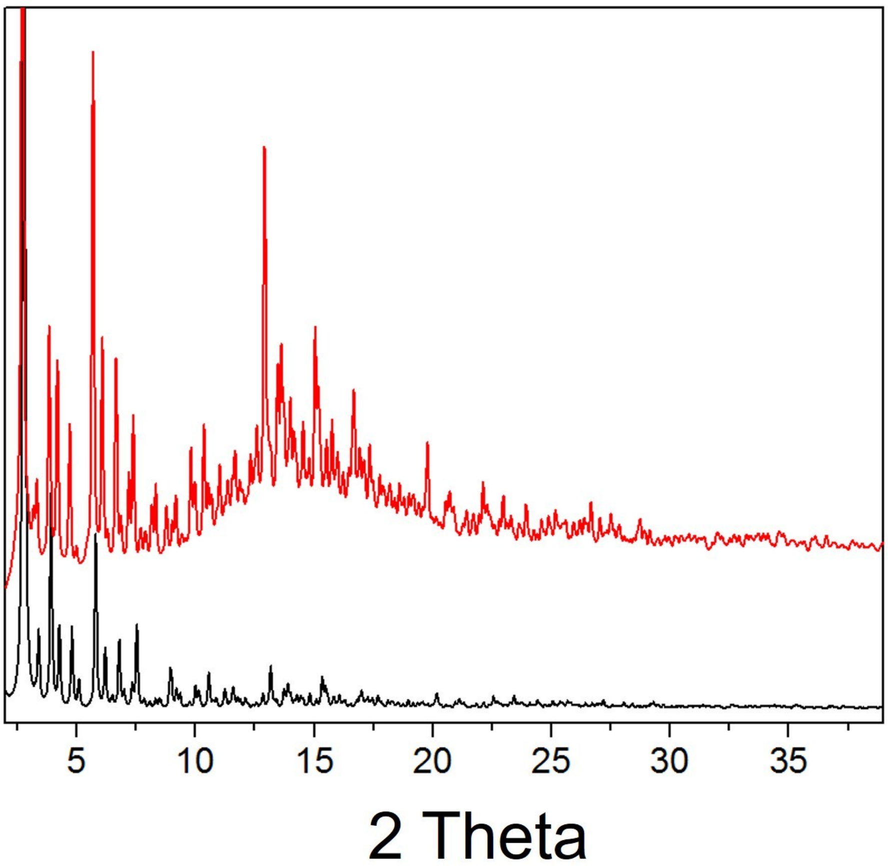

Figure S11. PXRD patterns for **3** using synchrotron radiation (wavelength 1.0 Å). Pattern simulated from single-crystal structure is shown in black; experimental patterns for as-synthesized in red.

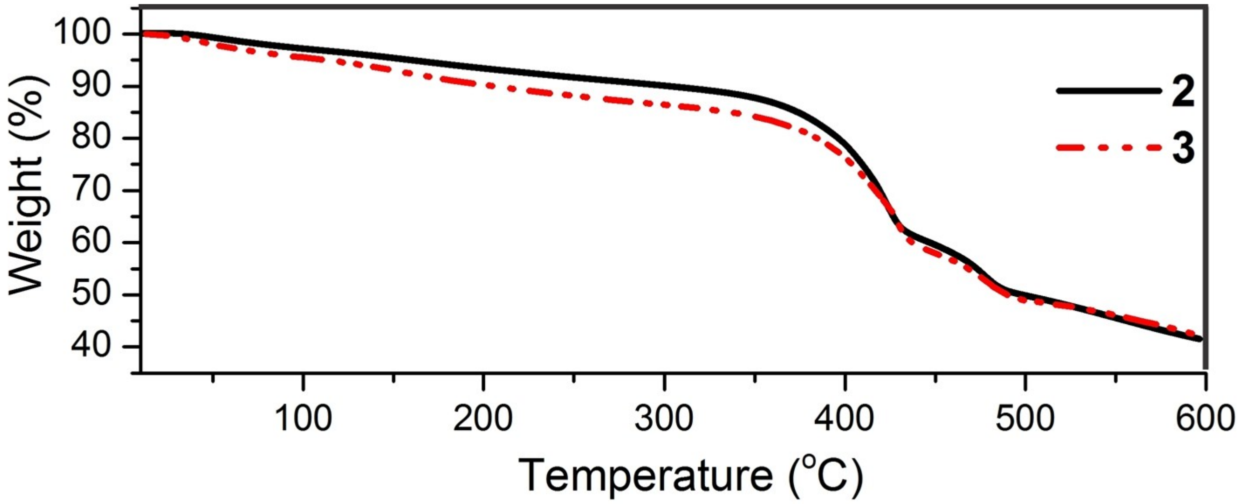

Figure S12. Thermogravimetric analysis (TGA) for **2** and **3**.

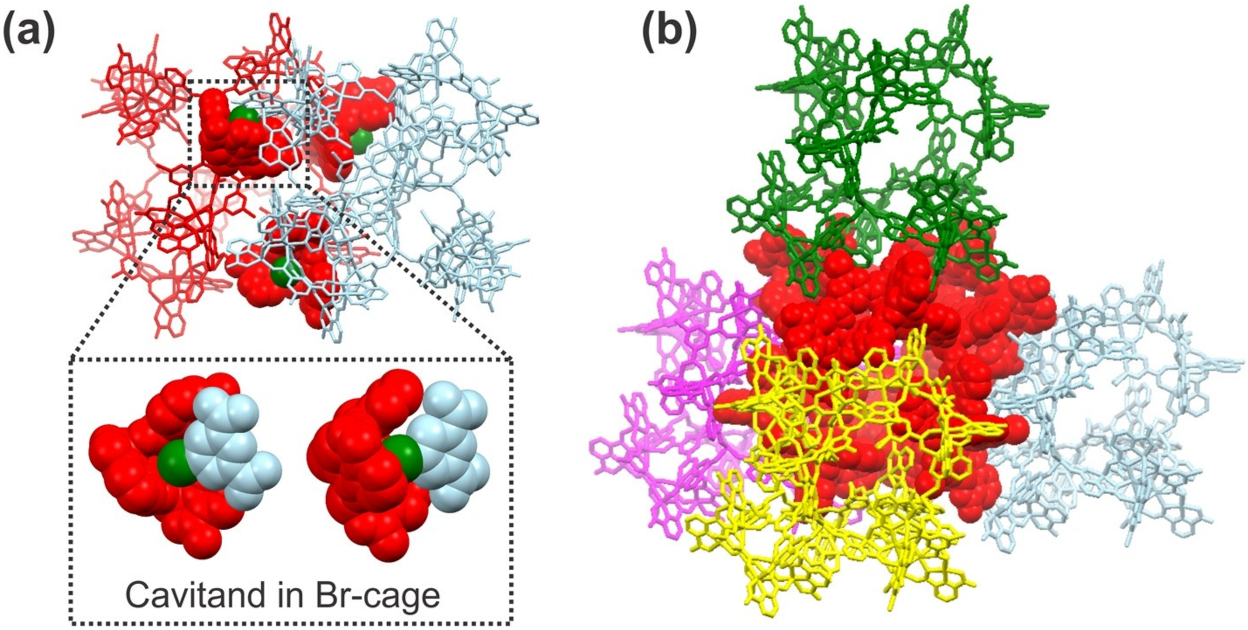

Figure S13. (a) The metallocavitands-induced crystal packing of two adjacent molecular cages of **2** (colored in red and light blue); cobalt clusters (portrayed in red space-filling) from one cage functioning as a cone-shaped cavity hosting a bromo group (portrayed in green sphere) belong to the neighboring cage; (b) In a typical packing, one molecular cage **2** (in red) is surrounded by four other adjacent cages (in different colors). All the coordinated and free solvents, hydrogen atoms, and disorder components of bromo groups are omitted for clarity.

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