

Supporting Information

Bridging different Co₄-calix[4]arene building blocks into grids, cages and 2D polymers with chiral camphoric acid

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Experimental section

Materials and Measurements. Starting materials, *p*-tert-butylthiacalix[4]arene, *p*-phenylthiacalix[4]arene and *p*-tert-butylsulfonylcalix[4]arene, were prepared according to literature method,^{S1} while other chemicals and solvents were of reagent grade and purchased from commercial sources and used as received. Elemental analyses (C, H, N) were performed on a German Elementary Varil EL III service. Powder X-ray diffraction (PXRD) measurements were recorded at room temperature by a RIGAKU-DMAX2500 X-ray diffractometer for Cu_{K α} radiation ($\lambda = 0.154 \text{ \AA}$). Thermogravimetric analysis (TGA) curves were performed under a N₂ flow by using a NETZSCH STA 449C thermal analyzer. Temperature dependence of solid-state direct current (dc) magnetic susceptibilities data were collected from 300 K down to 2 K on microcrystalline sample with a Quantum Design PPMS-9T and MPMS-XL magnetometers. All experimental magnetic data were applied for the diamagnetic corrections of the sample holders and of the constituent atoms according to the Pascal's constants. Moreover, gas adsorption measurements of **7** were carried out in an ASAP 2020 surface area analyzer.

Syntheses of Complexes 1-3

Complex 1: H₄BSC4A (0.1 mmol, 85 mg), CoCl₂•6H₂O (0.4 mmol, 100 mg), and H₂CAM (0.2 mmol, 40 mg) were taken in 10 mL of CH₃OH. The mixture was sealed in a 25 mL Teflon-lined autoclave at 160°C for 72 h and then cooled slowly to room temperature for 24 h. X-ray quality crystals were isolated by filtration, washed with CH₃OH and air dried. Elemental analysis (%) calculated for **1**: C, 43.90; H, 4.42. Found (dried in vacuum): C, 44.32; H, 4.59. The phase purity of the sample was determined by PXRD (Figure S9).

Complex 2. H₄BTC4A (0.1 mmol, 72 mg), CoCl₂•6H₂O (0.4 mmol, 100 mg), and H₂CAM (0.2 mmol, 40 mg) were taken in 10 mL of DMA-CH₃OH (v/v 1:1) and concentrated HCl (0.25 ml). This mixture was sealed in a 25 mL Teflon-lined autoclave at 120°C for 72 h and then cooled slowly to room temperature for 24 h. X-ray quality crystals were isolated by filtration, washed with DMA/CH₃OH (1:1, v/v) and air dried. Yield 66% based on ligand. Elemental analysis (%) calculated for **2**: C, 51.12; H, 5.62; N, 1.03. Found (dried in vacuum): C, 50.02; H, 5.48; N, 1.07. The phase purity of the sample was determined by PXRD (Figure S10).

Complex 3. H₄PTC4A (0.1 mmol, 80 mg), CoCl₂•6H₂O (0.4 mmol, 100 mg), and H₂CAM (0.2 mmol, 40 mg) were taken in 10 mL of DMA-CH₃OH (v/v 1:1) and concentrated HCl (0.25 ml). This mixture was sealed in a 25 mL Teflon-lined autoclave at 160°C for 72 h and then cooled slowly to room temperature for 24 h. X-ray quality crystals were isolated by filtration, washed with DMA/CH₃OH (1:1, v/v) and air dried. Yield 66% based on ligand. Elemental analysis (%) calculated for **3**: C, 52.54; H, 5.20; N, 1.27. Found (dried in vacuum): C, 51.76; H, 5.38; N, 1.18. The phase purity of the sample was determined by PXRD (Figure S11).

Single-Crystal X-ray Crystallography

All X-ray single crystal data for complexes **1-3** were measured on a SuperNova diffractometer which are equipped with a copper micro-focus X-ray sources ($\lambda = 1.5406 \text{ \AA}$) at 100(2) K. The CrystalClear program was applied for the absorption correction.^{S2} All crystal structures were solved by direct methods and refined using full-matrix least-squares on F^2 by the *SHELXTL-97* program package.¹⁷ All the non-hydrogen atoms were refined anisotropically except some badly disordered atoms and the lattice solvent molecules. Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Moreover, hydrogen atoms on some coordinated water and H₂CAM ligands cannot be generated due to disorder and weak crystal diffraction, but they were directly added into the molecular formulas. It should be noted that disorders were found in all CAM²⁻ ligands for complexes **1-3**. The C43, C45 and C48 showed disordered with its symmetrical equivalent position with the occupancies of 0.5 for **1**; the C47, C49 and C50 with the occupancies of 0.5, and C60A and C60B with the occupancy factor of 40:60 for **2**; the C33, C34, C36, C37 and C38 with the occupancies of 0.5 for **3**. Because the crystals do not diffract very well owing to the weak crystal diffractions, the R_1 and wR_2 factors in the final structure refinement are relatively high, but typical in such system. Therefore, the “SQUEEZE” method routine in PLATON^{S3} was applied for the crystal structures of complexes **1** and **2**, which had dramatically improved the agreement indices. The summary of crystallographic data and structure refinement details for complexes **1-3** are summarized in Table 1.

Solvent assignment for HMONCs:

SQUEEZE results for these five compounds are as follows:

(1) Complex 1

loop_

_platon_squeeze_void_nr

_platon_squeeze_void_average_x

_platon_squeeze_void_average_y

_platon_squeeze_void_average_z

_platon_squeeze_void_volume

_platon_squeeze_void_count_electrons

1	-0.002	0.000	0.500	650.3	120.4
2	0.500	0.500	0.000	252.4	34.2

_platon_squeeze_details

;

PLATON/SQUEEZE gives 154.2 electrons/unit cell for the voids of complex **1**. The electron densities were tentatively modeled as CH₃OH (18 e⁻), so there are 9 CH₃OH molecules in per unit cell. The final chemical formula of **1** was calculated from the SQUEEZE results combined with the TG analysis data.^{S4}

(2) Complex 2

loop_

_platon_squeeze_void_nr

_platon_squeeze_void_average_x

_platon_squeeze_void_average_y

_platon_squeeze_void_average_z

_platon_squeeze_void_volume

_platon_squeeze_void_count_electrons

1	-0.008	0.555	0.000	887.0	77.8
2	-0.025	0.055	0.500	887.0	77.8
3	-0.001	0.779	0.500	14.2	-1.6
4	0.499	0.278	0.000	14.2	-1.6

_platon_squeeze_details

;

PLATON/SQUEEZE gives 152.4 electrons/unit cell for the voids of complex **2**. The electron densities were tentatively modeled as one DMA and six CH₃OH molecules ($z = 2$; half dma and three CH₃OH molecules per asymmetric unit) which account for (48+18+18+18+18+18+18) electrons. The final chemical formula of **2** was calculated from the SQUEEZE results combined with the TG analysis data.

Table S1. Crystal Data and Structure Refinement for complexes **1–3**.

complexes	1	2	3
chemical formula	C ₁₀₉ H ₁₅₆ O ₄₃ Cl ₄ S ₈ Co ₈	C ₁₂₁ H _{168.5} N _{2.5} O _{25.5} Cl ₂ S ₈ Co ₈	C _{62.6} H _{69.9} N _{1.3} O ₁₂ ClS ₄ Co ₄
formula mass	3024.21	2865.06	1431.89
crystal system	Triclinic	Monoclinic	Orthorhombic
space group	<i>P</i> -1	<i>I</i> 2	<i>Cmca</i>
<i>a</i> (Å)	12.6110(3)	11.7307(6)	20.4878(9)
<i>b</i> (Å)	13.0901(6)	21.7103(11)	15.1811(6)
<i>c</i> (Å)	23.1334(11)	27.7720(13)	39.3306(11)
α (°)	86.751(4)	90.00	90.00
β (°)	89.566(3)	89.317(5)	90.00
γ (°)	66.489(4)	90.00	90.00
unit cell volume (Å ³)	3495.7(2)	7072.4(6)	12232.9(8)
temperature (K)	100(2)	100(2)	100(2)
<i>Z</i>	1	2	8
F(000)	1566	2988	5702
no. of reflections measured	26472	14926	15591
no. of independent reflections	12438	10287	6003
R _{int}	0.0592	0.0645	0.0327
final R1 values (I>2σ(I))	0.0629	0.0771	0.0869
final wR (F ²) values (I>2σ(I))	0.1564	0.2223	0.2359
goodness of fit on F ²	0.978	1.095	1.071

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

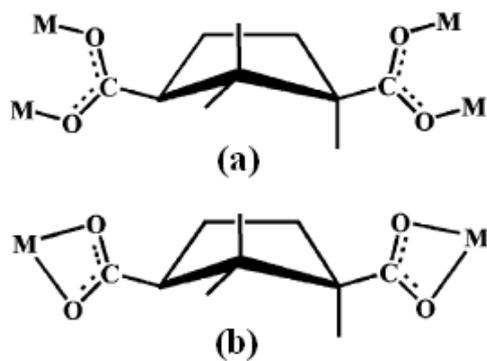


Figure. S1. Two Coordination Modes of the CAM^{2-} Ligands Observed in **1** (a), **2** (a, b) and **3**(a).

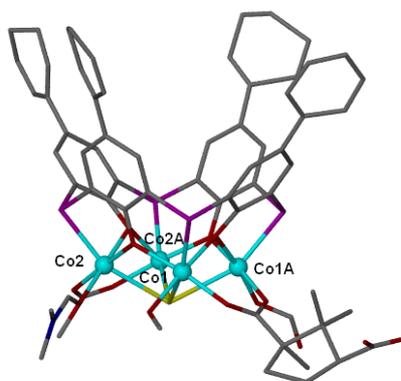


Figure. S2. Co_4 -PTC4A MBBs and its coordination environment. Symmetry code: X, 2-Y, Z.

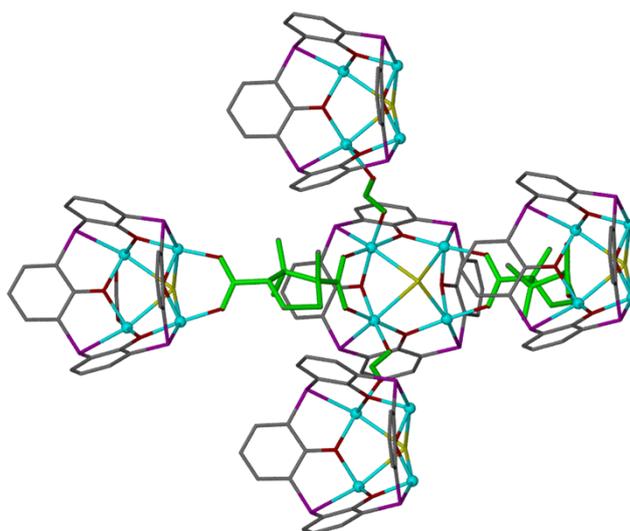


Figure. S3. Co_4 -PTC4A MBBs and the bridging CAM^{2-} and HCOO^- ligands labeled in green color. The phenyl groups are deleted for clarity.

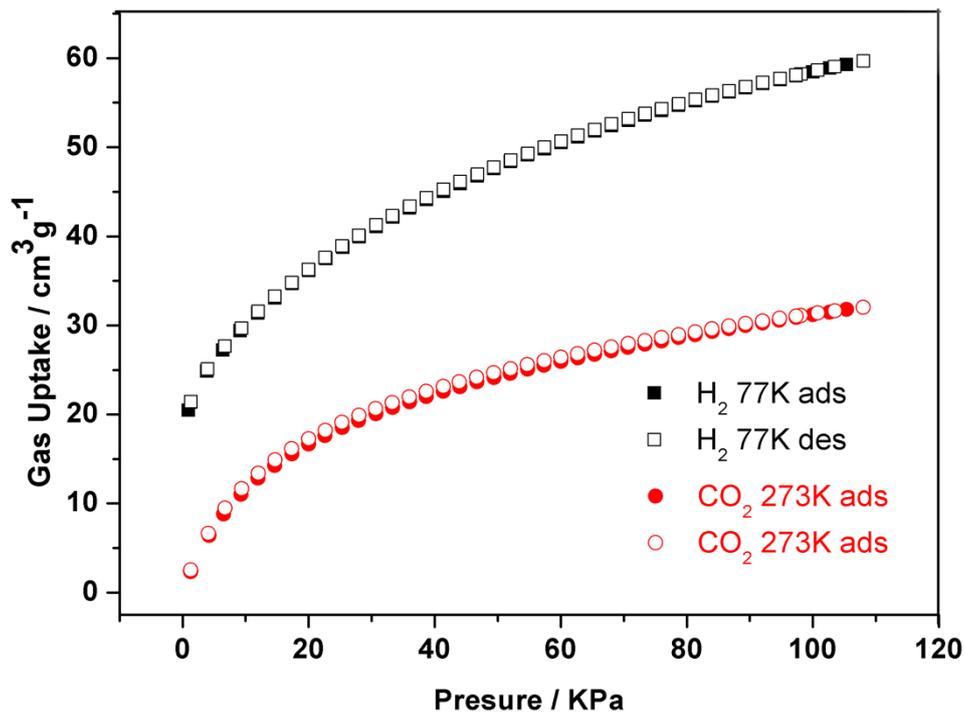


Figure. S4. The CO₂ and H₂ uptakes for complex **2**. Solid and open circles represent adsorption and desorption data.

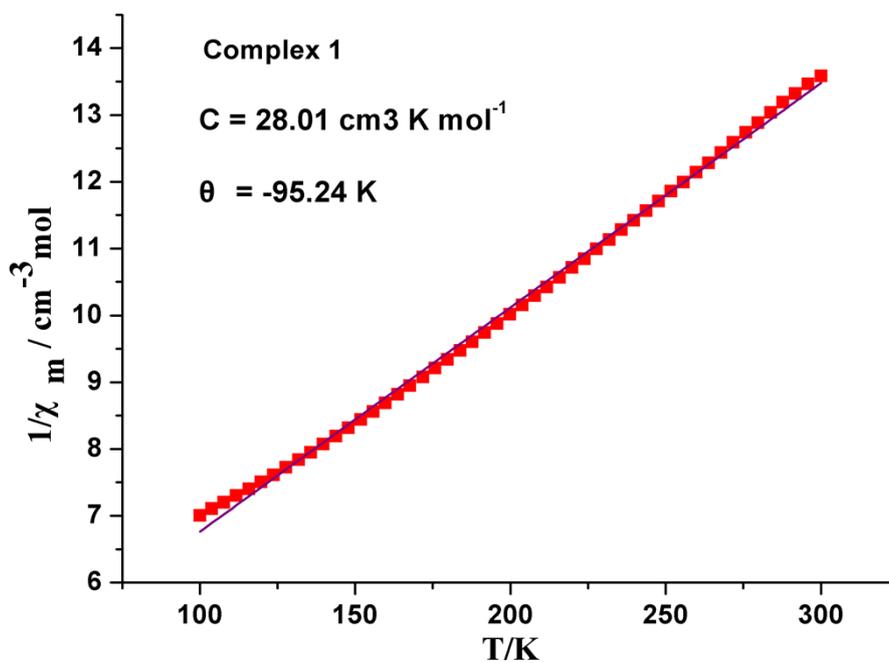


Figure. S5. Plots of $1/\chi_m$ against T for complex **1**.

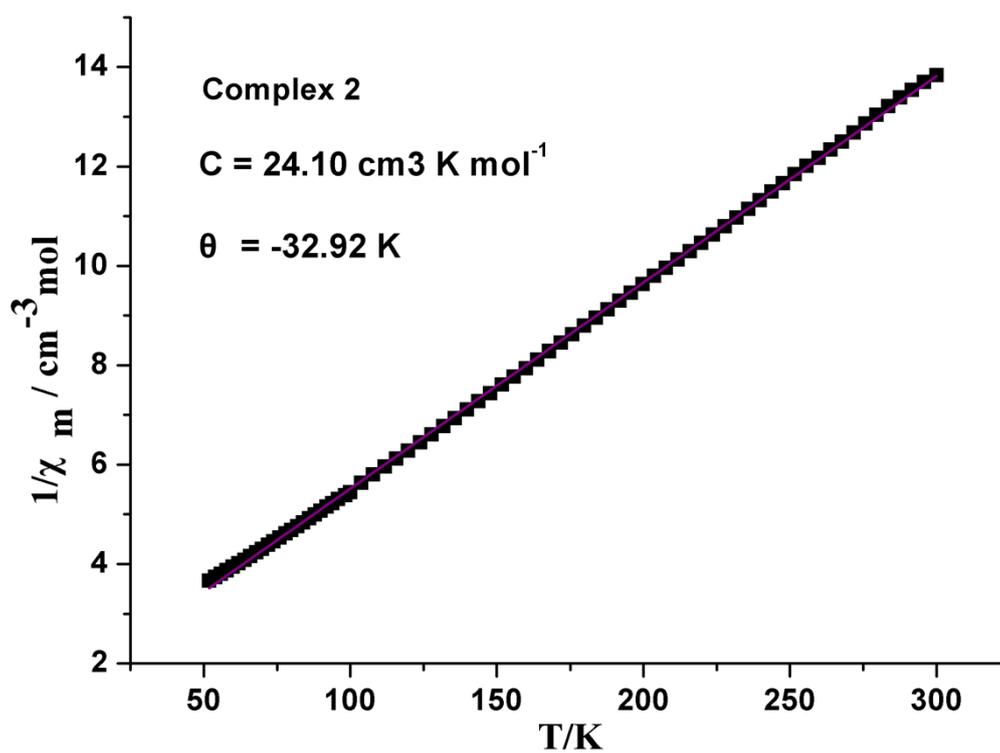


Figure. S6. Plots of $1/\chi_m$ against T for complex 2.

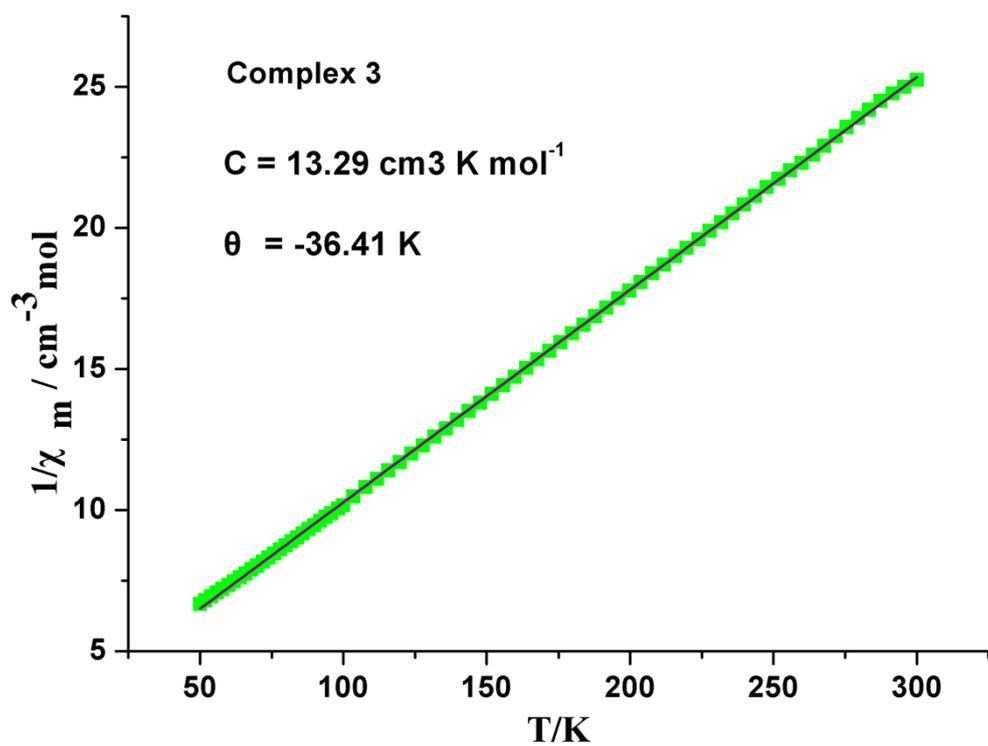


Figure. S7. Plots of $1/\chi_m$ against T for complex 3.

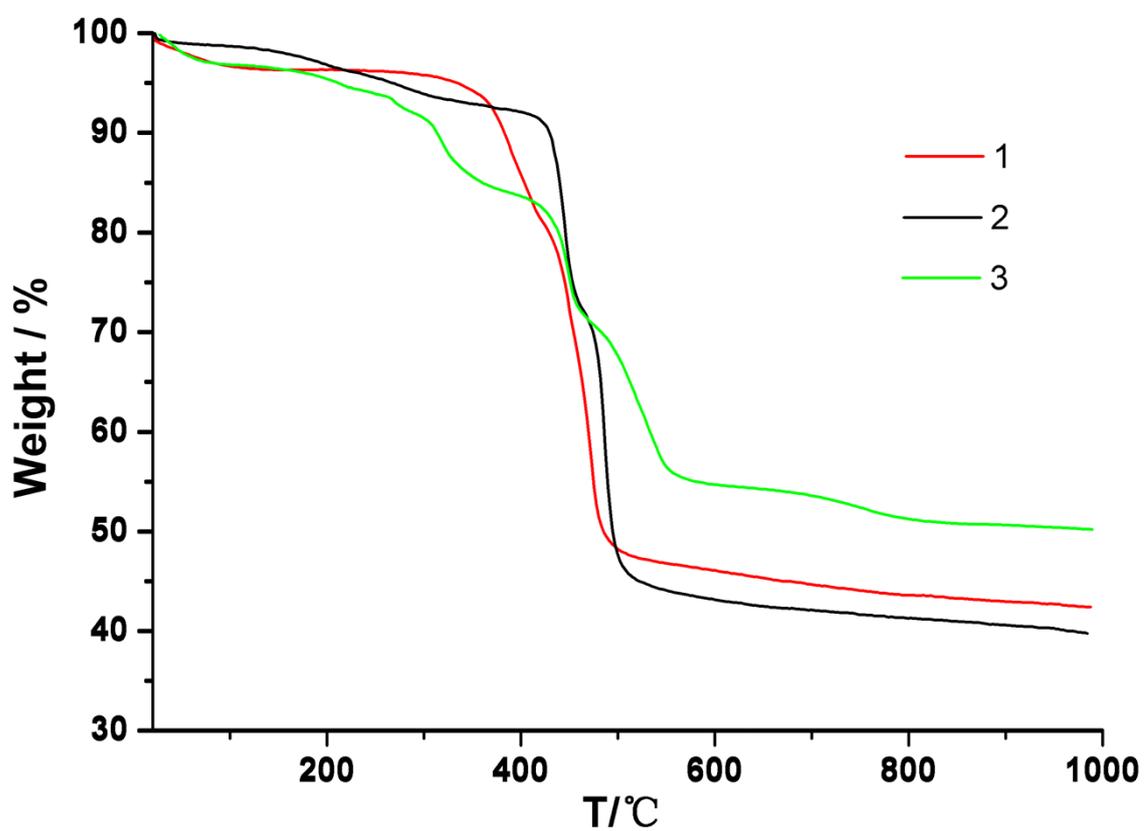


Figure. S8. The TG curves of complexes 1-3.

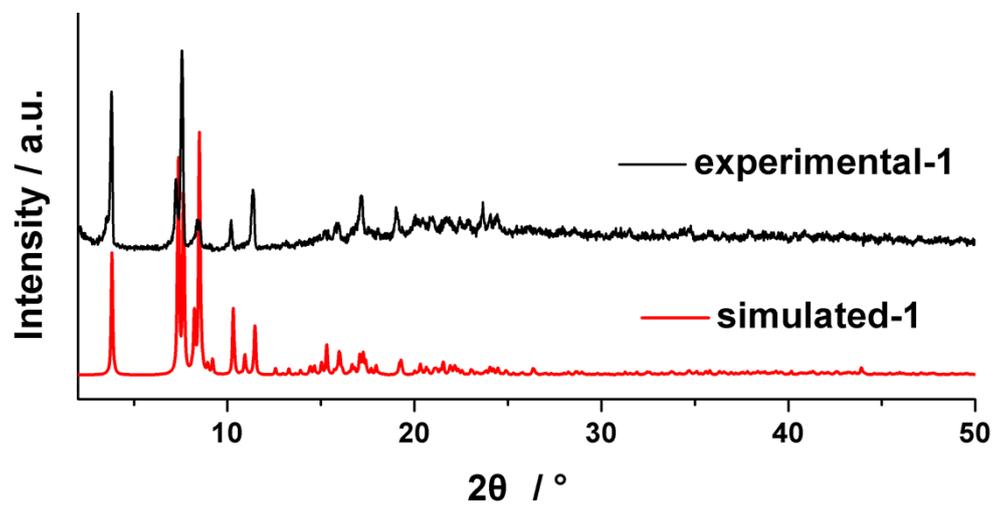


Figure. S9. PXRD of complex 1.

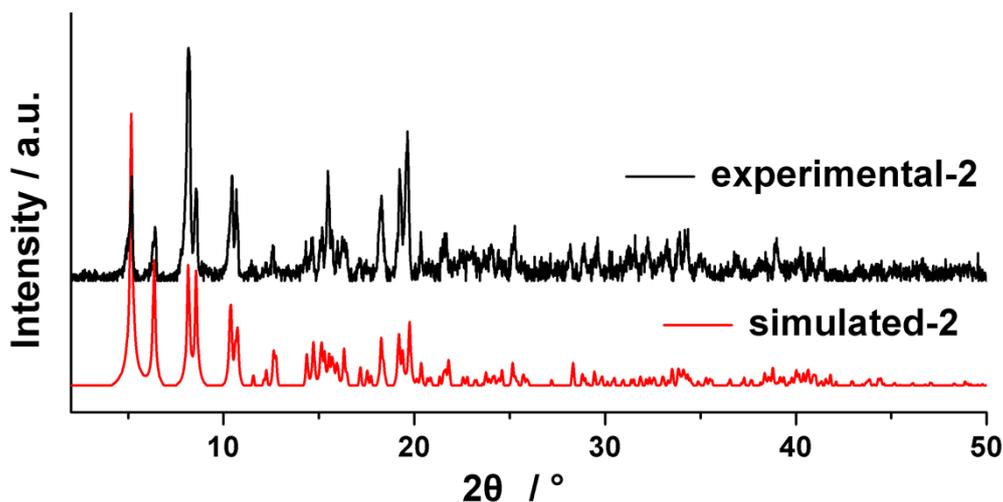


Figure. S10. PXRD of complex 2.

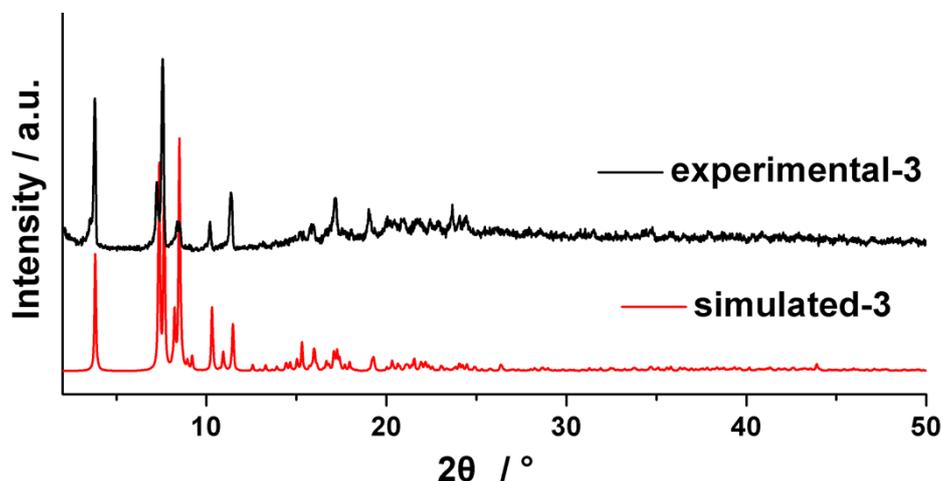


Figure. S11. PXRD of complex 3.

References.

- S1 (a) Iki, N.; Kabuto, C.; Fukushima, T.; Kumagai, H.; Takeya, H.; Miyanari, S.; Miyashi, T.; Miyano, S., *Tetrahedron*. 2000, **56**, 1437-1443. (b) Lhoták, P.; Šmejkal, T.; Stibor, I.; Havlíček, J.; Tkadlecová, M.; Petříčková, H., *Tetrahedron Lett.* 2003, **44**, 8093-8097. (c) Morohashi, N.; Iki, N.; Sugawara, A.; Miyano, S., *Tetrahedron* **2001**, **57**, 5557-5563.
- S2 Sheldrick, G. M. SHELXS 97, *Program for crystal Structure Solution and Program for crystal Structure Refinement*, 1997, University of Göttingen.
- S3 van der Sluis P.; and Spek, A. L.; *Acta Cryst. Sect. A.* 1990, **46**, 194-201.
- S4 (a) Bi, Y. F.; Wang, X. T.; Liao, W. P.; Wang, X. F.; Wang, X. W.; Zhang H. J.; and Gao, S.; *J. Am. Chem. Soc.* 2009, **131**, 11650; (b) Dolomanov, O. V.; Cordes, D. B.; Champness, N. R.; Blake, A. J.; Hanton, L. R.; Jameson, G. B.; Schröder M.; and Wilson, C.; *Chem. Commun.*, 2004, **40**, 642.