

# Supporting Information

## Two 3D cobalt(II) metal–organic frameworks with micropores for selective dye adsorption

Ming Ze Wu,<sup>†,‡</sup> Jian Yun Shi,<sup>†,‡</sup> Peng Yun Chen,<sup>†,‡</sup> Li Tian,<sup>\*,†,‡</sup> and Jing Chen<sup>\*,†,‡</sup>

<sup>†</sup>Tianjin Key Laboratory of Structure and Performance for Functional Molecules

<sup>‡</sup>Key Laboratory of Inorganic-Organic Hybrid Functional Materials Chemistry, Ministry of Education, College of Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China. E-mail: [lilytianli@hotmail.com](mailto:lilytianli@hotmail.com) and [hxyycj@mail.tjnu.edu.cn](mailto:hxyycj@mail.tjnu.edu.cn).

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## 1 Crystallographic Data

**X-Ray crystallography.** Crystallographic data were collected at 129 K (for **1**) or 150 K (for **2**) on an Agilent SuperNova (Dual, Cu at zero, AtlasS2, CCD) diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 1.54184$  Å), using the  $\varphi$ - $\omega$  scan technique. Semiempirical multiscan absorption corrections were applied by SCALE3 ABSPACK, and the programs CrysAlisPro were used for integration of the diffraction profiles.<sup>1</sup> The structures were solved by direct methods with the ShelXT-2015 structure solution program and refined using least squares minimization by with the ShelXL-2015 refinement package.<sup>2-3</sup> Some restraints are employed, such as ISOR (anisotropic parameter), DFIX (restricting the distance between two atoms) to solve the disorder of the O atom in CH<sub>3</sub>OH. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located geometrically and refined isotropically. For complex **2**, after many times experiment, the highly disordered solvents and Cl<sup>-</sup> ions could not be finely made out in the refinement, so the cif data is not very good. The chemical formulas were determined by the combination of the crystal data, TGA, and elemental analysis. Crystallographic data are listed in Table S1.

Table S1. Crystallographic Data and Structure Refinement Details for **1-2**

	<b>1</b>	<b>2</b>
formula	C <sub>17</sub> H <sub>21</sub> Co <sub>0.5</sub> N <sub>8</sub> O <sub>4</sub>	C <sub>12</sub> H <sub>11</sub> ClCoN <sub>6</sub> O <sub>3</sub>
Mr	430.88	381.65
crystal system	monoclinic	tetragonal
space group	<i>P2<sub>1</sub>/n</i>	<i>P4<sub>2</sub>/mnm</i>
<i>a</i> (Å)	10.6493(9)	16.6991(6)
<i>b</i> (Å)	14.9679(13)	16.6991(6)
<i>c</i> (Å)	12.6966(13)	17.5671(8)
$\alpha$ (°)	90	90.00
$\beta$ (°)	104.300(9)	90.00
$\gamma$ (°)	90	90.00
<i>V</i> (Å <sup>3</sup> )	1961.1(3)	4898.7(4)
<i>Z</i>	4	8
$\rho$ calc (Mg/m <sup>3</sup> )	1.459	0.987
$\mu$ (mm <sup>-1</sup> )	0.510	0.769
<i>F</i> (000)	898	1476
$\theta$ range(°)	2.143~25.006	1.683~25.005
limiting indices	-11 ≤ <i>h</i> ≤ 12 -15 ≤ <i>k</i> ≤ 17 -15 ≤ <i>l</i> ≤ 12	-19 ≤ <i>h</i> ≤ 14 -17 ≤ <i>k</i> ≤ 19 -20 ≤ <i>l</i> ≤ 18
Reflns collected	9252	12098
GOF on <i>F</i> <sup>2</sup>	1.095	1.118
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0483, <i>wR</i> <sub>2</sub> = 0.1067	<i>R</i> <sub>1</sub> = 0.0694, <i>wR</i> <sub>2</sub> = 0.2036
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	<i>R</i> <sub>1</sub> = 0.0801, <i>wR</i> <sub>2</sub> = 0.1306	<i>R</i> <sub>1</sub> = 0.0860, <i>wR</i> <sub>2</sub> = 0.2280

## 2 Powder X-ray Diffraction

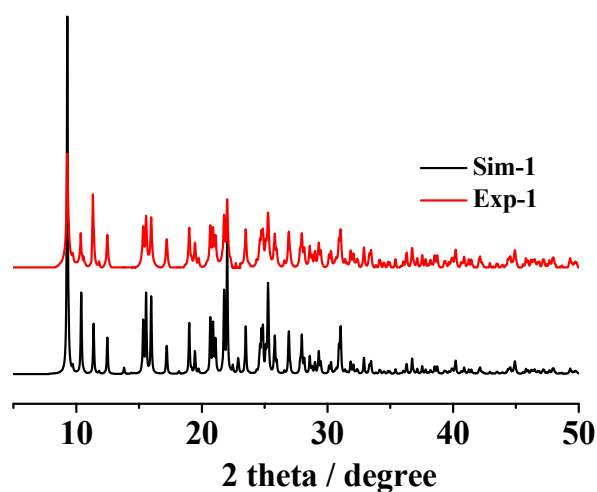
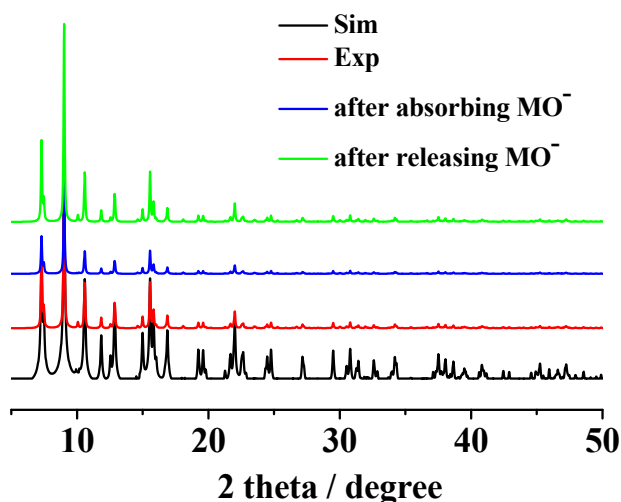
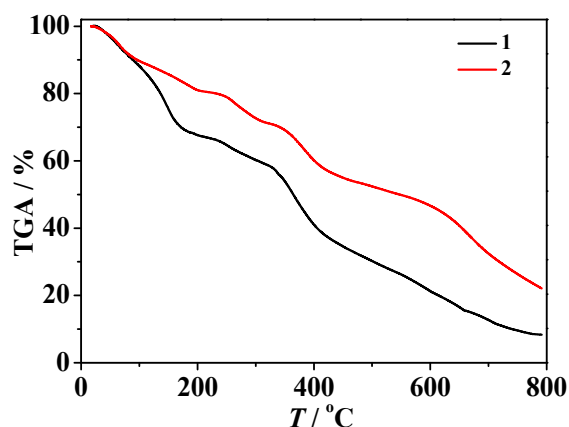


Figure S1. XRD patterns of complex 1.



**Figure S2.** XRD patterns of complex **2** simulated (black), experimented of the samples as-synthesized (red), after adsorbing  $\text{MO}^-$  molecules (blue), and after releasing  $\text{MO}^-$  in NaCl saturated solution (green), respectively.

### 3 Thermal Gravimetric Analysis Curves



**Figure S3.** TGA curves of complexes **1-2**.

Thermogravimetric analysis (TGA) for the as-synthesized **1** shows a continuous weight loss of 33.2 % upon heating because of the strong interaction between the solvent molecules and the framework, as well as the high boiling point of DMF (calcd 33.88%). Further weight loss indicates the collapse of whole framework. **2** shows a weight loss of 8.5% from 25 to 83 °C, corresponding to the loss of coordinated MeOH molecules (calcd 8.38%). Further weight loss occurred continuously, indicating the collapse of whole framework.

## 4 Dye Absorption, Separation, and Release

**Dye absorption.** Freshly prepared crystals of **1** (~5 mg) were solvent exchanged with methyl alcohol for 48 h, then transferred into CH<sub>3</sub>OH solutions of MO<sup>-</sup>, DY, MB<sup>+</sup>, and JGB<sup>+</sup> (5 mL, 2×10<sup>-5</sup> M), respectively. UV-vis spectra of the dye solution were used to record the dye adsorption ability of **1** along with the soaking time.

Freshly prepared crystals of **2** (~5 mg) were solvent exchanged with methyl alcohol for 48 h, then transferred into aqueous solutions of MO<sup>-</sup>, CR<sup>-</sup>, MB<sup>+</sup>, and RB<sup>+</sup> (5 mL, 2×10<sup>-5</sup> M), respectively. UV-vis spectra of the dye solution were used to record the dye adsorption ability of **2** along with the soaking time.

**Dye separation.** Methyl alcohol exchanged **2** (~5 mg) were transferred into aqueous solutions of an equimolar concentration of MB<sup>+</sup> and MO<sup>-</sup> (2×10<sup>-5</sup> M), and then the adsorption process was monitored by UV-Vis spectroscopy.

**Dye release.** The materials MO<sup>-</sup>@**2** were transferred into pure water or saturated aqueous solution of NaCl, respectively. UV-vis spectra of the extraction solution were used to record the dye release ability of **2** along with the soaking time (Fig. S4-S5).

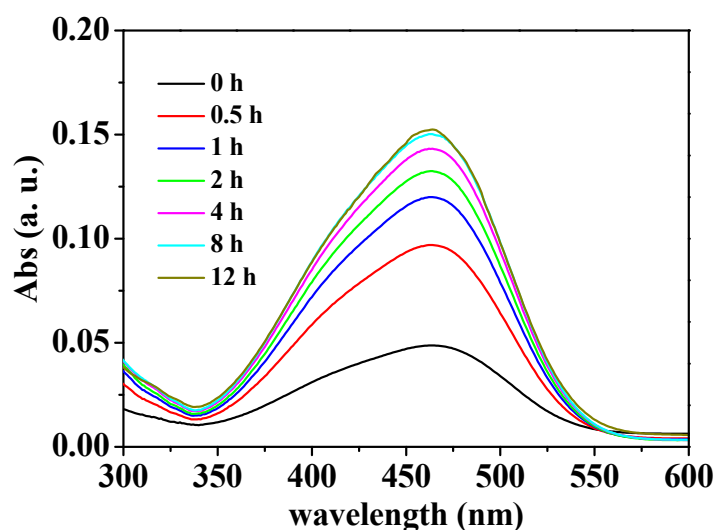


Figure S4. The MO<sup>-</sup> release ability from MO<sup>-</sup>@**2** in pure water.

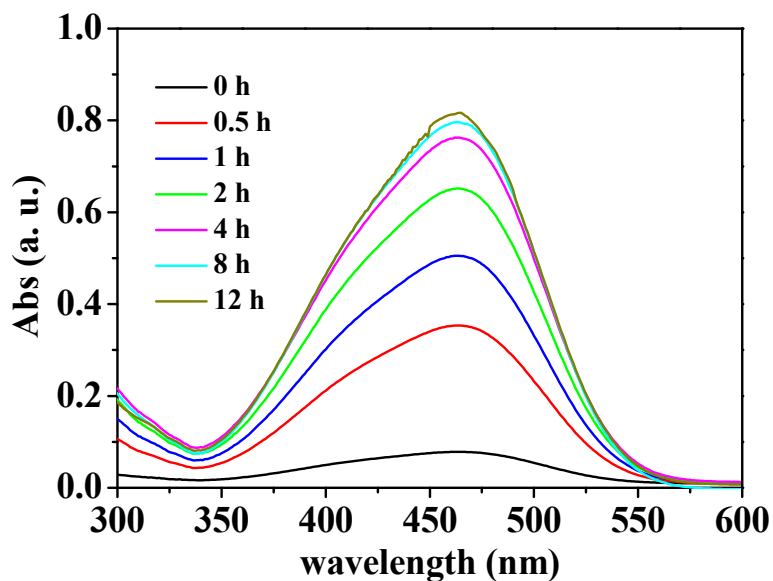


Figure S5. The MO<sup>-</sup> release ability from MO<sup>-</sup>@2 in saturated NaCl aqueous solution.

## 5 Tables of Crystal Data

Table S2. Selected bond lengths (Å) and bond angles (°) in complex 1.

Co(1)-O(1)	2.043(2)	N(6)#5-Co(1)-N(3)#3	91.91(10)
Co(1)-O(1)#1	2.043(2)	N(6)#4-Co(1)-N(3)#2	91.91(10)
Co(1)-N(3)#2	2.160(3)	N(6)#5-Co(1)-N(3)#2	88.09(10)
Co(1)-N(3)#3	2.160(3)	N(6)#4-Co(1)-N(3)#3	88.09(10)
Co(1)-N(6)#4	2.140(3)	N(6)#4-Co(1)-N(6)#5	180
Co(1)-N(6)#5	2.140(3)	O(1)-Co(1)-N(6)#4	87.29(11)
O(1)-Co(1)-O(1)#1	180.0	O(1)-Co(1)-N(6)#5	92.71(11)
O(1)#1-Co(1)-N(3)#2	85.22(10)	O(1)#1-Co(1)-N(6)#5	87.29(11)
O(1)-Co(1)-N(3)#2	94.78(10)	N(3)#2-Co(1)-N(3)#3	180

#1: 2-x, 1-y, -z; #2: 3/2-x, -1/2+y, 1/2-z; #3: 1/2+x, 3/2-y, -1/2+z; #4: -1/2+x, 3/2-y, -1/2+z;  
 #5: 5/2-x, -1/2+y, 1/2-z.

Table S3. Selected bond lengths (Å) and bond angles (°) in complex **2**.

Co(1)-O(1)	2.057(3)	O(1)-Co(1)-O(2)	81.2(3)
Co(1)-O(1)#1	2.057(3)	O(1)#1-Co(1)-O(2)	89.0(3)
Co(1)-Cl(1)	2.434(2)	N(3)#2-Co(1)-Cl(1)	88.79(13)
Co(1)-N(3)#2	2.135(5)	N(3)#3-Co(1)-Cl(1)	88.79(13)
Co(1)-N(3)#3	2.135(5)	N(3)#2-Co(1)-N(3)#3	93.3(3)
Co(1)-O(2)	2.136(6)	N(3)#3-Co(1)-O(2)	84.3(3)
Co(1)#4-Cl(1)	2.434(2)	N(3)#2-Co(1)-N(3)#3	92.1(3)
O(1)-Co(1)-Cl(1)	97.95(12)	Cl(1)-Co(1)-O(2)	173.0(3)
O(1)-Co(1)-N(3)#2	173.21(18)	Co(1)-Cl(1)-Co(1)#4	97.15(10)
O(1)-Co(1)-O(1)#1	93.7(2)	O(1)#1-Co(1)-N(3)#2	86.10(18)
O(1)-Co(1)-N(3)#3	86.10(18)	O(1)#1-Co(1)-N(3)#3	173.21(18)

#1:  $x, y, -z$ ; #2:  $-1/2+x, 1/2-y, 1/2-z$ ; #3:  $-1/2+x, 1/2-y, -1/2+z$ ; #4:  $x, y, -z$ .

## 6 References

- (1) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- (2) Sheldrick, G. M. SHELXT-Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3–8.
- (3) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3–8.