

## Supporting Information

### **Rare metal-ion metathesis of tetrahedral Zn(II) core of a noncentrosymmetric (3,4)-connected 3D MOF**

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## Experimental section

### Materials and methods

Chemical reagents were purchased commercially and were used as received without further purification. 4-Amino-3,5-bis(4-pyridyl)-1,2,4-triazole (4-abpt) was prepared according to the literature method.<sup>1</sup> Infrared spectra were recorded in the solid state (KBr pellets) on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in the 4000–400  $\text{cm}^{-1}$  range. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer. Thermogravimetric analyses (TGA) were performed under nitrogen with a Perkin-Elmer TGA-7 TG analyzer. Powder X-ray diffraction patterns (PXRD) were recorded on a Bruker D8 Advance X-ray diffractometer at 40 kV, 40 mA for Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Metal ion ratio was analyzed using ICP-OES on an Agilent 720 analyzer. The second-order nonlinear optical intensities were estimated by measuring microcrystalline samples relative to quartz by a digital oscilloscope (LeCroy WR64xi) equipment. Brunauer–Emmett–Teller (BET) analyses were carried out with a Micromeritics ASAP 2020 system using nitrogen and hydrogen as adsorbate at 77 K and carbon dioxide at 195 K.

### Synthesis of $\{[\text{Zn}_2(4\text{-abpt})(3,4\text{-pydc})_2]\cdot 2\text{DMAc}\cdot 3\text{MeOH}\cdot \text{H}_2\text{O}\}_n$ (1-Zn)

A mixture of  $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (15.1 mg, 0.05 mmol), 4-abpt (12.1 mg, 0.05 mmol), and 3,4- $\text{H}_2\text{pydc}$  (8.3 mg, 0.05 mmol) were dissolved in solution of DMAc (7 mL) and MeOH (1 mL). The mixture was sealed in a glass vial and heated at 50 °C in a water bath for 5 days. The colorless, plate-shaped crystals that were produced were isolated on a filter, washed with water and ethanol, and dried in air. Yield: 39% (18.9 mg, based on 3,4- $\text{H}_2\text{pydc}$ ). FT-IR (KBr pellets,  $\text{cm}^{-1}$ ): 3485 (m), 3304 (m), 2937 (m), 1642 (s), 1627 (s), 1485 (m), 1384 (s), 1365 (s), 1264 (w), 1222 (w), 1191 (w), 1161 (m), 1124 (w), 1021 (m), 941 (w), 869 (m), 836 (m), 783 (w), 734 (m), 715 (m), 679 (m), 608 (w),

568 (w), 562 (w), 512 (w). Elemental Analysis Calcd (%) for  $C_{37}H_{48}Zn_2N_{10}O_{14}$ : C, 44.99; H, 4.89; N, 14.18%; Found: C, 44.61; H, 5.26; N, 14.41%.

### **Metal ion exchange**

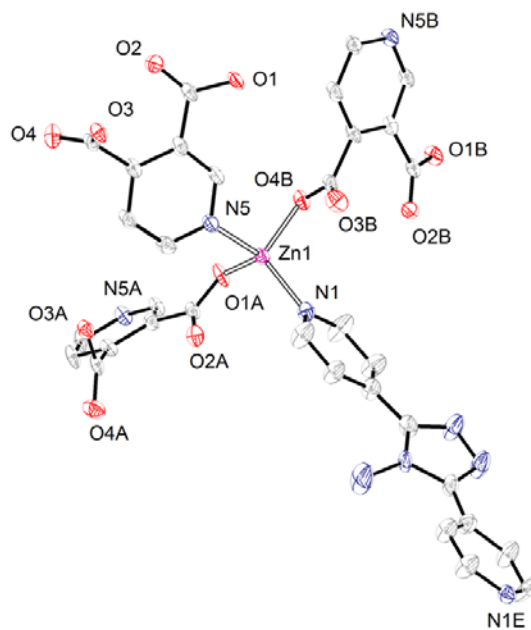
In a typical ion-exchange experiment, crystals of **1-Zn** (100 mg) were immersed in a DMAc solution of  $Cu(NO_3)_2 \cdot 3H_2O$  (0.1 M, 30 mL) for 10 days. During this period, the DMAc solution of  $Cu(NO_3)_2 \cdot 3H_2O$  was exchanged with fresh solution at least five times. After decanting the solution, the ion-exchanged products **1-Cu** were washed thoroughly with DMAc and then allowed to stand in fresh DMAc at room temperature for five days.

### **X-ray Crystallography**

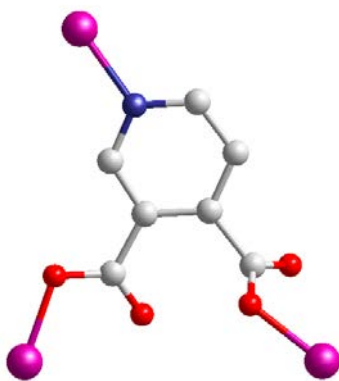
A single crystal of **1-Zn** suitable for crystallographic analysis was measured for intensity data collection on Bruker Nonius Kappa CCD diffractometer fitted with graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Data reduction included absorption corrections by the MULTI-SCAN method, using SAINT and SADABS.<sup>2</sup> The X-ray structure was determined by direct methods and difference Fourier techniques and were refined by full-matrix least squares, using SHELXL97.<sup>3</sup> Non-hydrogen atoms were refined with independent anisotropic displacement parameters. The hydrogen atoms of the carbon atoms were geometrically calculated, while the hydrogen atoms of the imidazole nitrogen atoms were located from difference Fourier maps. The pyridyl group of the 4-adpt ligand was disordered over two occupied sites with site occupancy factors refined to be 0.65 and 0.35. The crystal data and structure refinement results are listed in Table S2, and the selected bond lengths and angles are given in Table S3.

## References

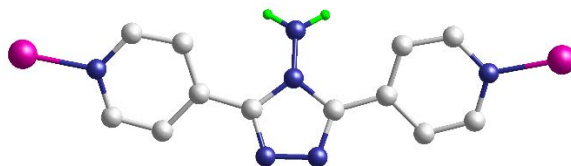
1. F. Bentiss and M. Lagrenée, *J. Heterocyclic Chem.*, 1999, **36**, 149.
2. (a) SAINT, Bruker (2003), Bruker AXS Inc., Madison Wisconsin, USA; (b) SADABS, Bruker (2002), Bruker AXS Inc, Madison Wisconsin, USA.
3. (a) G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64** 112; (b) G. M. Sheldrick, SHELX-97 (including SHELXS and SHELXL); University of Göttingen: Göttingen, Germany, 1997.



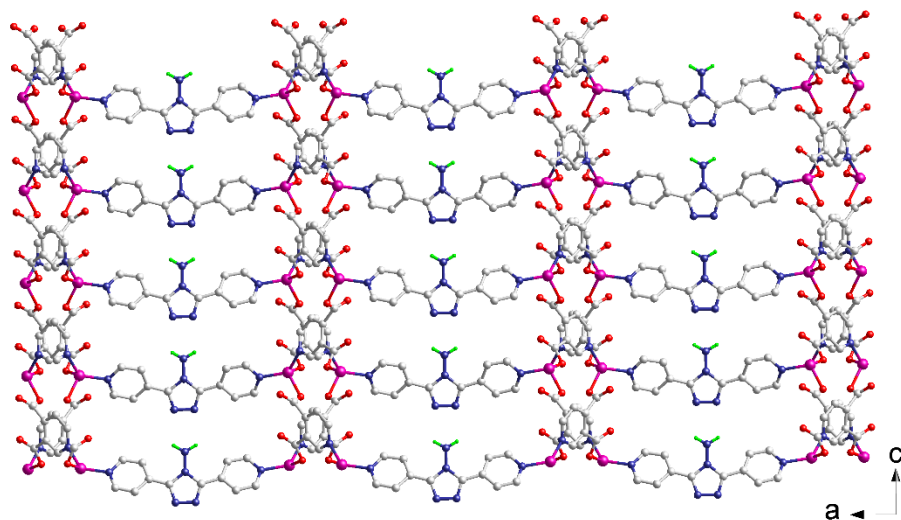
**Fig. S1** Coordination environment of the Zn<sup>II</sup> ion in **1-Zn**. Symmetry code: (A)  $-x + 1.5, y + 1/2, z$ ; (B)  $-x + 1.5, -y + 1/2, z - 1/2$ ; (E)  $x - 1, y, z$ .



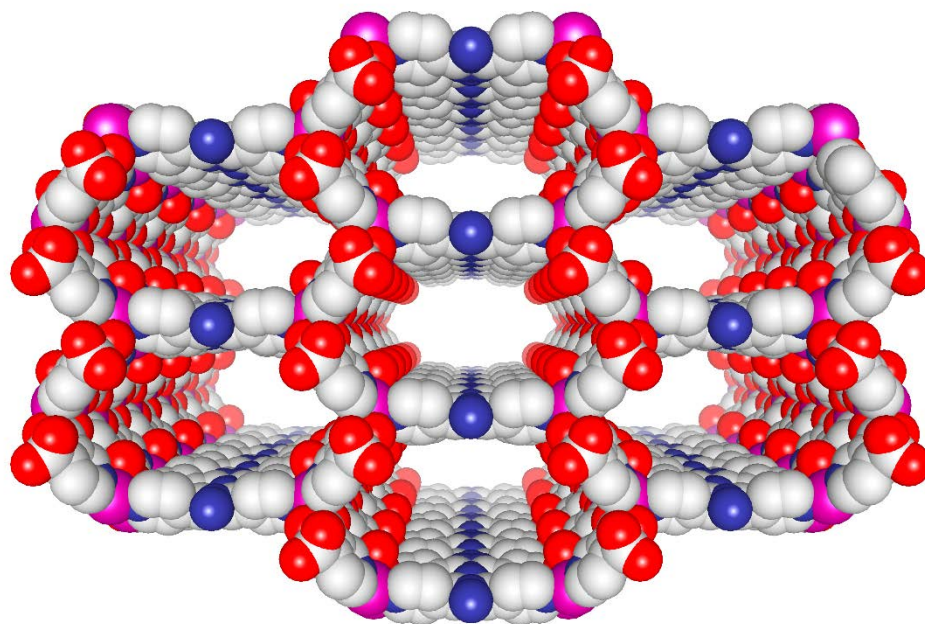
**Fig. S2** The coordination mode of the 3,4-pydc<sup>2-</sup> ligand in **1-Zn**.



**Fig. S3** The coordination mode of the 4-adpt ligand in **1-Zn**.



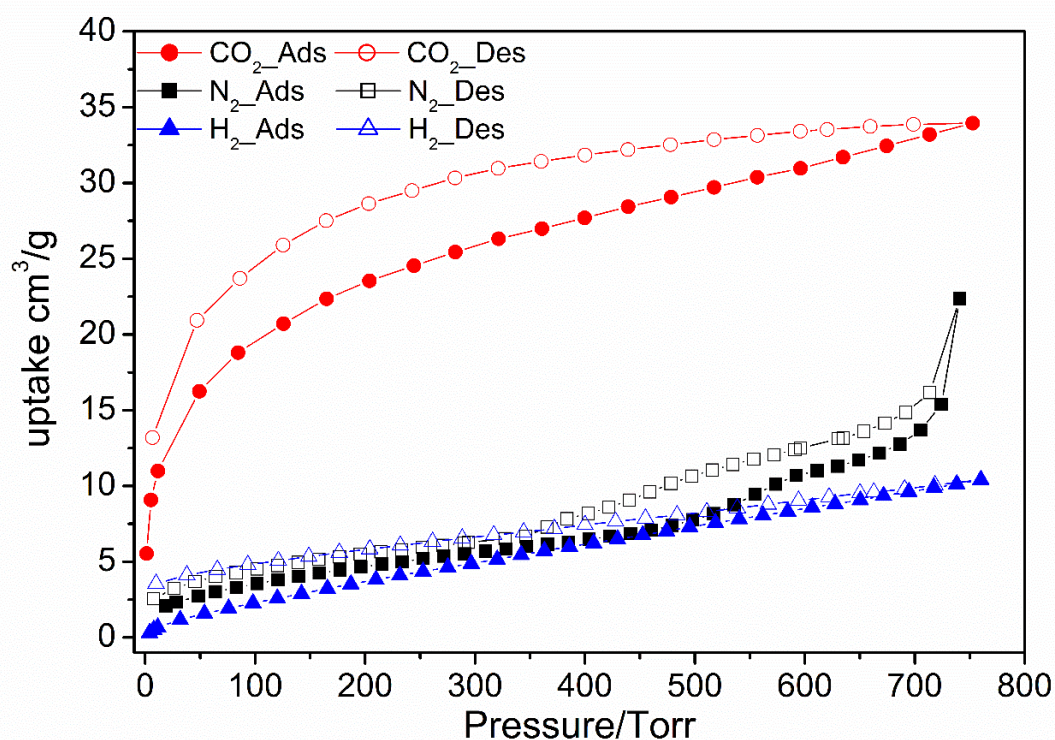
**Fig. S4** A perspective view of **1-Zn** along the  $b$  axis.



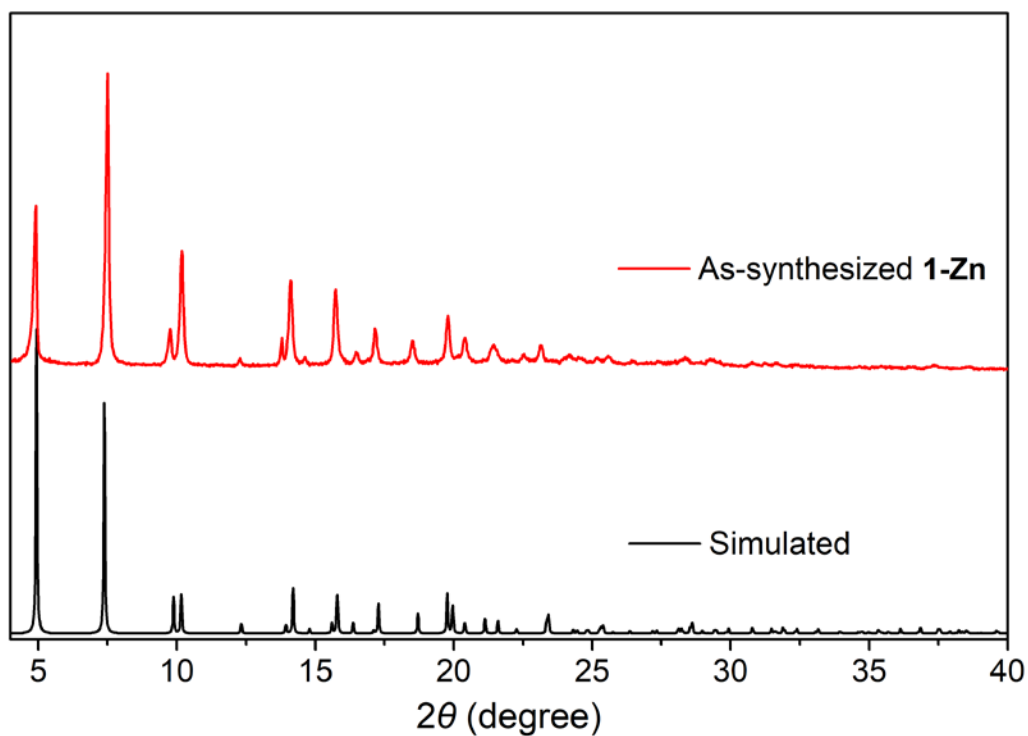
**Fig. S5** A space-filling model representation showing the one-dimensional honeycomb-shape channels along the  $[001]$  direction.

## Gas adsorption studies

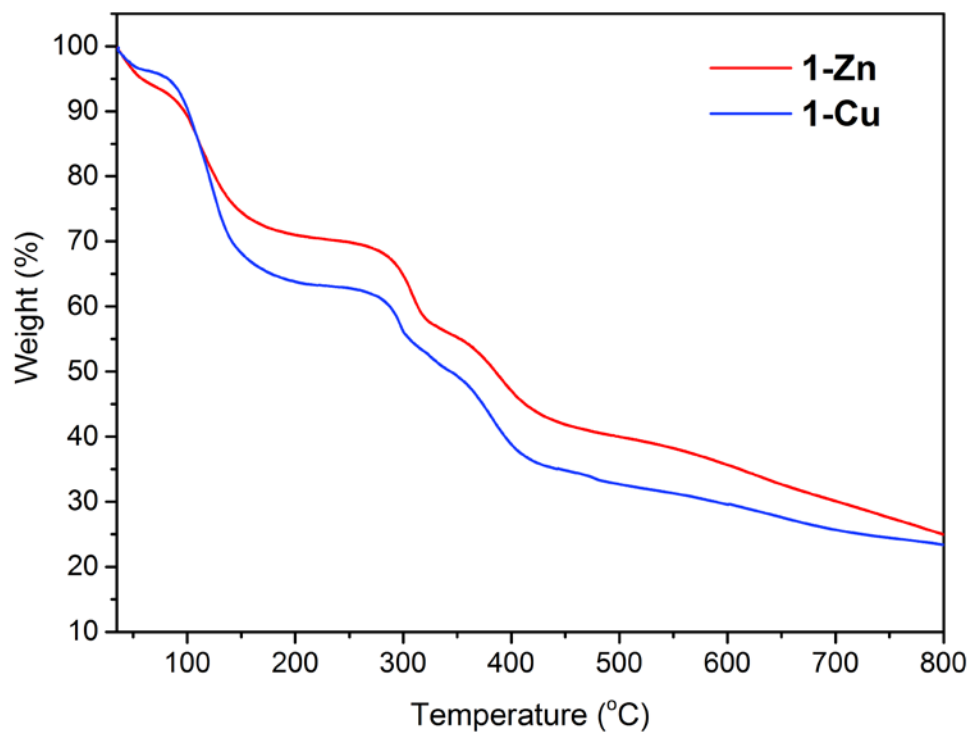
Adsorption experiments for CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> were performed on **1-Zn** (Fig. S6). Freshly prepared samples were activated at 150 °C under a vacuum for 12 h to remove the guest molecules. The results indicated that the activated sample adsorbed only minor amounts of N<sub>2</sub> and H<sub>2</sub> at 77 K and 1 atm. The N<sub>2</sub> and H<sub>2</sub> molecules did not diffuse into the channels and only surface adsorption was observed (22.3 cm<sup>3</sup> g<sup>-1</sup> for N<sub>2</sub> and 10.4 cm<sup>3</sup> g<sup>-1</sup> for H<sub>2</sub>, respectively). However, the CO<sub>2</sub> gas sorption isotherm for **1-Zn** at 195 K displayed type I adsorption behavior, which is characteristic of microporous materials. Adsorption measurements indicated that the total amount CO<sub>2</sub> taken up was 33.9 cm<sup>3</sup> g<sup>-1</sup> with an apparent Brunauer–Emmett–Teller (BET) surface area of 110 m<sup>2</sup> g<sup>-1</sup> (Langmuir surface area of 157 m<sup>2</sup> g<sup>-1</sup>).



**Fig. S6** Gas adsorption isotherms of **1-Zn** (black, for N<sub>2</sub>-77 K; blue, for H<sub>2</sub>-77 K; red, for CO<sub>2</sub>-195 K).

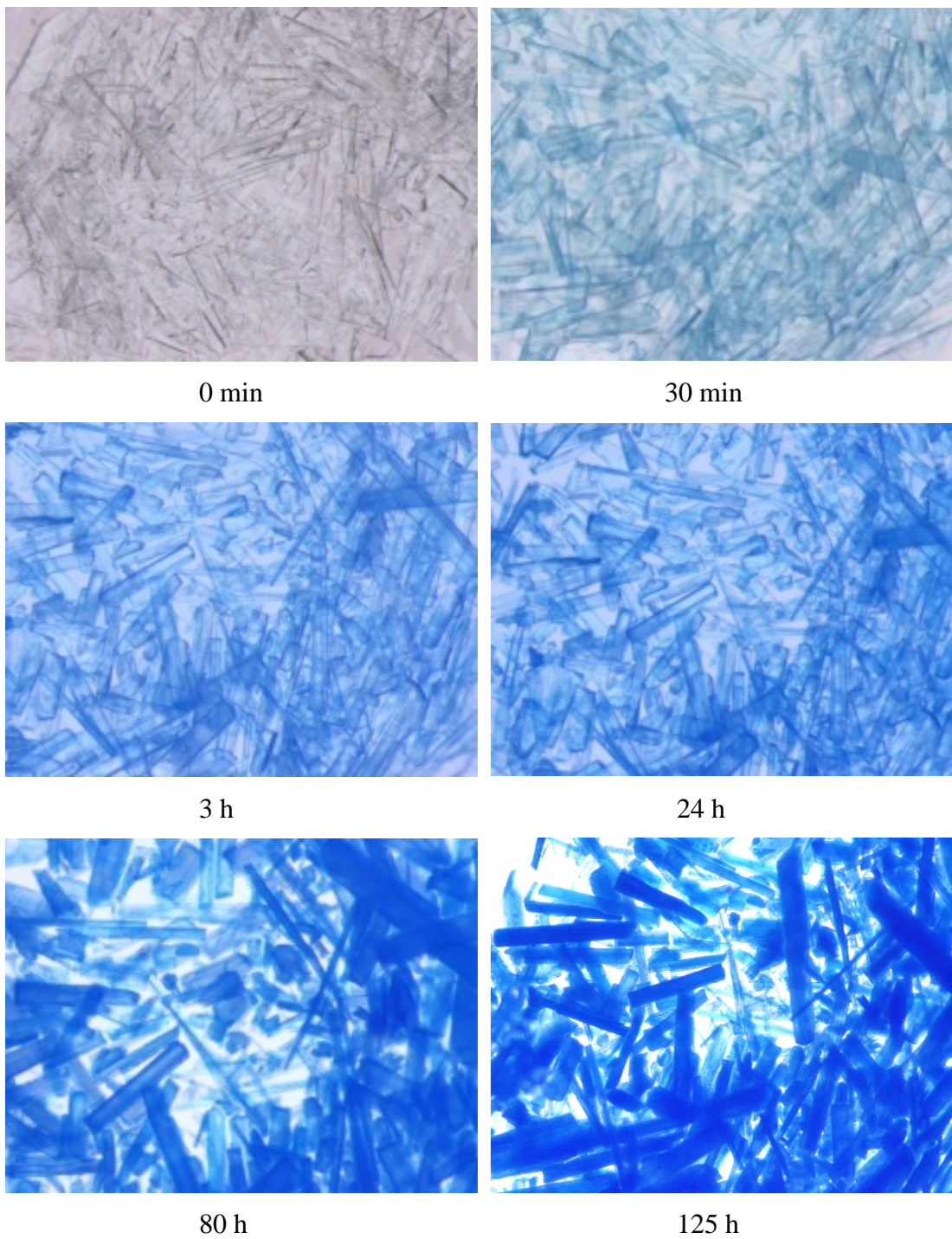


**Fig. S7** Powder X-ray diffraction patterns of **1-Zn** (simulated) and **1-Zn** (as-synthesized).

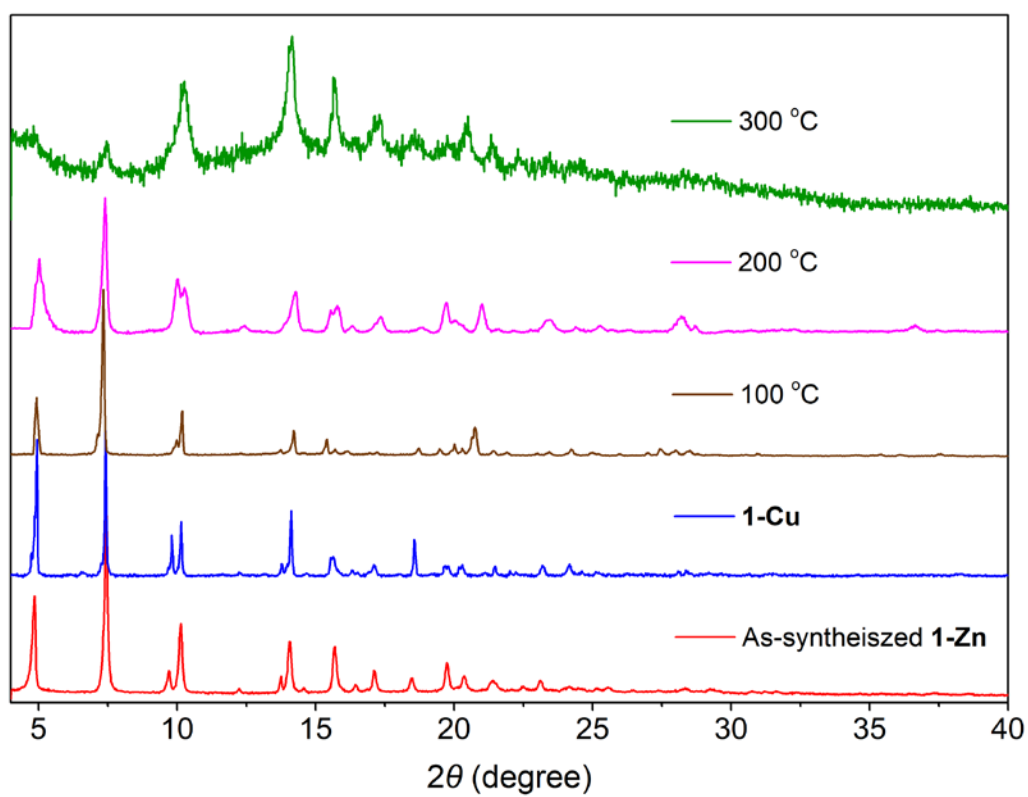
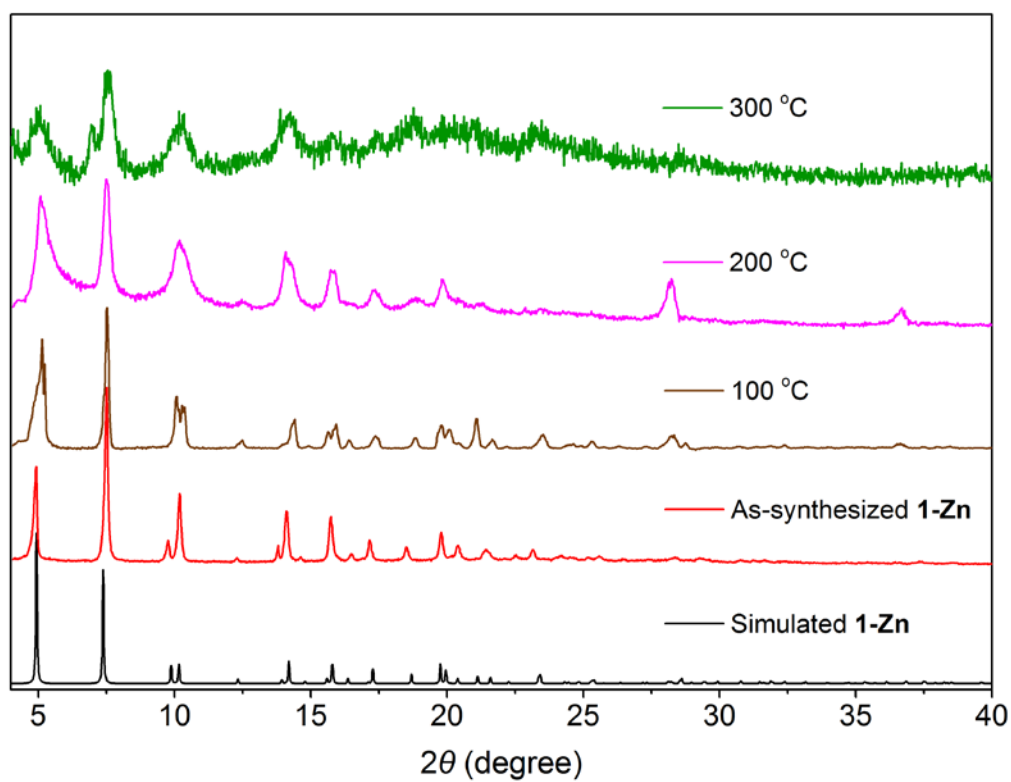


**Fig. S8** Thermogravimetric analyses (TGA) curves of **1-Zn** and **1-Cu**.

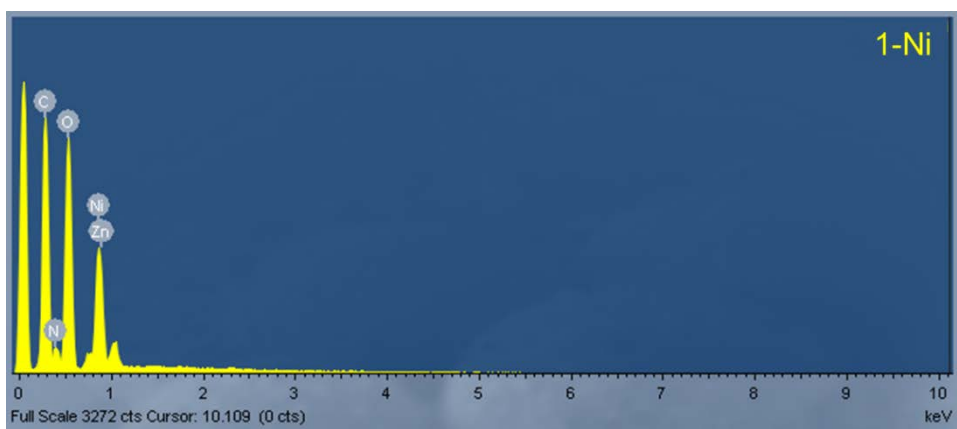
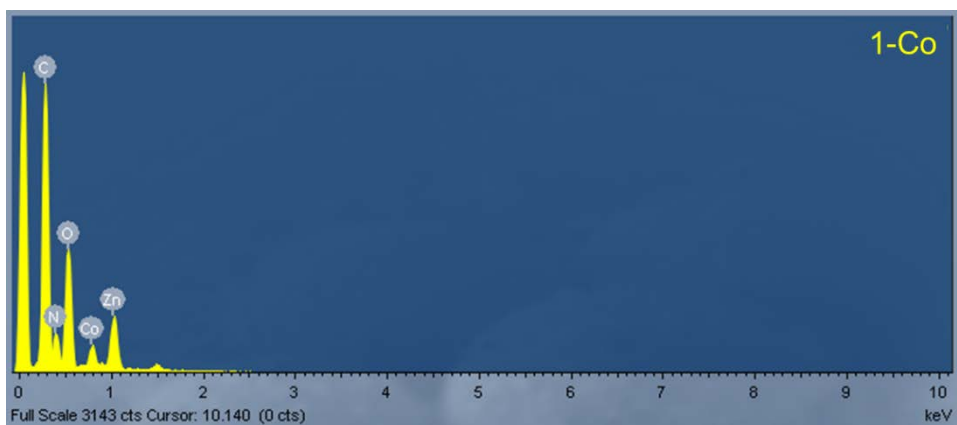
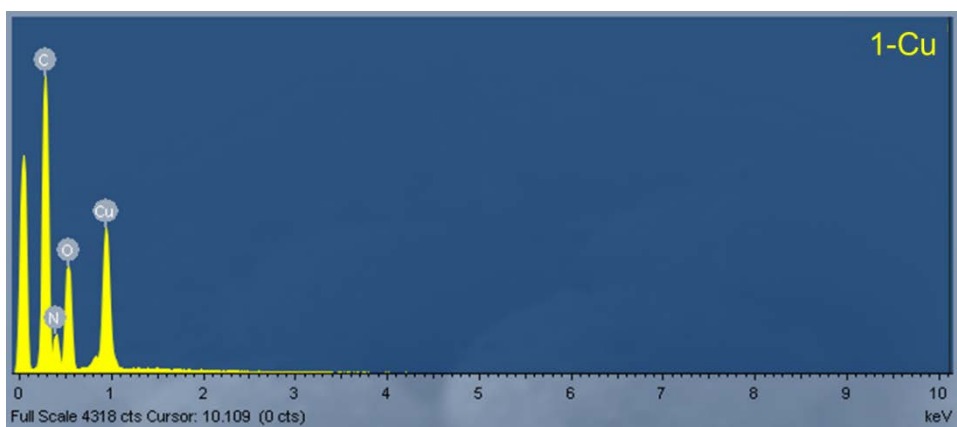
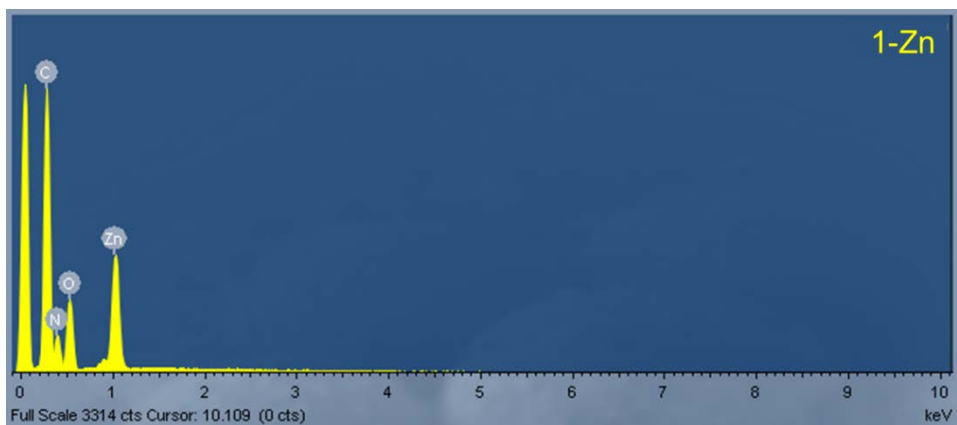




**Fig. S9** Photographs of a colorless crystal of **1-Zn** soaked in a DMAC solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  at different time periods.



**Fig. S10** Temperature-dependent powder X-ray diffraction patterns of **1-Zn** and **1-Cu**.



**Fig. S11** EDX spectra of **1-Zn**, **1-Cu**, **1-Co**, and **1-Ni**.

**Table S1.** Metal ion ratio during the ion exchange process analyzed by ICP-OES.

<b>Samples</b>	<b>Time</b>	<b>Metal molar ratio (%)</b>	
		<b>Zn</b>	<b>Cu</b>
<b>1-Zn</b> soaked in a DMAc solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.1 M)	0 min	100	0
	30 min	98	2
	1 h	95	5
	3 h	89	11
	5 h	85	15
	10 h	81	19
	20 h	70	30
	30 h	61	39
	40 h	50	50
	50 h	45	55
	62 h	37	63
	76 h	30	70
	90 h	25	75
	105 h	21	79
	125 h	15	85
	150 h	8	92
180 h	2	98	
250 h	1	99	
		<b>Zn</b>	<b>Co</b>
<b>1-Zn</b> soaked in a DMAc solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 M)	30 d	88	12
		<b>Zn</b>	<b>Ni</b>
<b>1-Zn</b> soaked in a DMAc solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 M)	30 d	49	51

**Table S2.** Crystal data and structure refinement data for compound **1-Zn**.

Compound	1-Zn
Empirical formula	C <sub>37</sub> H <sub>48</sub> Zn <sub>2</sub> N <sub>10</sub> O <sub>14</sub>
Formula weight	987.59
Crystal system	Orthorhombic
Space group	<i>Cmc</i> 2 <sub>1</sub>
<i>a</i> , Å	35.7794(16)
<i>b</i> , Å	12.6929(5)
<i>c</i> , Å	12.7024(5)
$\alpha$ , deg	90
$\beta$ , deg	90
$\gamma$ , deg	90
<i>V</i> , Å <sup>3</sup>	5768.7(4)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.137
$\mu$ , mm <sup>-1</sup>	0.889
<i>F</i> (000)	6723
Reflections collected	21838
<i>R</i> <sub>int</sub>	0.0633
GOF	1.107
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0691
<i>wR</i> <sub>2</sub> <sup>b</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.1888
<i>R</i> <sub>1</sub> <sup>a</sup> (all data)	0.0806
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.1970

$$^a R_1 = (\sum ||F_O| - |F_C||) / \sum |F_O|, \quad ^b wR = [\sum [w(F_O^2 - F_C^2)^2] / \sum [w(F_O^2)^2]]^{1/2}$$

**Table S3.** Selected bond lengths [Å] and angles [°] for **1-Zn**.

Zn(1)–O(1)#1	1.968(4)	Zn(1)–O(3)#2	1.973(4)
Zn(1)–N(1)	1.989 (4)	Zn(1)–N(5)	2.026(4)
O(1)#1–Zn(1)–O(3)#2	102.54(15)	O(1)#1–Zn(1)–N(51)	110.42(17)
O(1)#1–Zn(1)–N(5)	101.54(17)	O(3)#2–Zn(1)–N(1)	109.81(16)
O(3)#2–Zn(1)–N(5)	104.40(17)	N(1)–Zn(1)–N(5)	125.62(18)

Symmetry transformations used to generate equivalent atoms: #1  $-x + 3/2, y + 1/2, z$ ; #2  $-x + 3/2, -y + 1/2, z - 1/2$ ; #3  $-x + 3/2, y - 1/2, z$ ; #4  $-x + 3/2, -y + 1/2, z + 1/2$ ; #5  $-x + 1, y, z$ .