

## SUPPORTING INFORMATION

### ***In situ* large-scale construction of sulfur-functionalized metal-organic framework and its efficient removal of Hg(II) from water\*\***

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## S1. Materials and Methods

### 1.1. Materials and Instruments.

Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich, Merck and Acros) and used without further purification. The power X-ray diffraction patterns (PXRD) were collected by a Rigaku D using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). Single component gas adsorption measurements were performed in the Accelerated Surface Area and Porosimetry 2020 System (ASAP2020). Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. The ratios of the metal ions were determined by using JY ULTIMA 2 ICP instrument. FT-IR spectra were obtained using a Bruker Optics VERTEX 70 FT-IR spectrophotometer. Laser light-scattering size distribution analysis was performed on a Brook haven BI-200SM instrument.

#### 1.2.1 Preparation of [Co<sub>3</sub>(Timt)<sub>4</sub>(SCN)<sub>6</sub>(H<sub>2</sub>O)<sub>12</sub>(EtOH)<sub>0.5</sub>]<sub>n</sub> (FJI-H12) single crystal

A solution of 2,4,6-tris(3-imidazole)-1,3,5-triazine (Timt, 11.2 mg, 0.04 mmol) in 1 mL pure ethanol was placed in a 5 ml vial (inner diameter 1 cm, height 5 cm). ethanol/water 3/1 (v/v) (0.5 mL) was layered onto the top of the solution as a buffer. Then, a solution of K<sub>2</sub>Co(NCS)<sub>4</sub> (1.0 mL, 0.03 mol/L) was carefully layered on the top of the resultant solution, and the test tube was allowed to stand at room temperature for 3 days. The titled network crystallized on the glass surface of the test tube was collected by filtration. The resultant framework formula is defined as a [Co<sub>3</sub>(Timt)<sub>4</sub>(SCN)<sub>6</sub>(H<sub>2</sub>O)<sub>14</sub>(EtOH)]<sub>n</sub> which is calculated from the combination of elemental analysis (EA) data after the SQUEEZE process. (Elemental analysis: calculated C, 34.48%; H, 3.62%; N, 30.07%; Found: C, 34.11%; H, 3.70%; N, 30.19%)

#### 1.2.2 Synthesis of microcrystal of FJI-H12:

Addition of a high concentration water solution (1 mol/L, 0.3 mL) of K<sub>2</sub>Co(SCN)<sub>4</sub> to a vigorously stirred ethanol solution (0.02 mol/L, 20 mL) of Timt could immediately produce a uniform microcrystalline powder of **FJI-H12** (48% yield). And this method can be enlarged to 10g-scale (Figure S8). The titled network microcrystals was collected by filtration and the powder was fully washed with EtOH/H<sub>2</sub>O 3/1 (v/v) and then exchanged with ethanol and activated in a vacuum box 80 °C overnight.

### 1.3. Single-Crystal X-ray Crystallography

The structure data of **FJI-H12** was collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 99.99(16) K during data collection. By using Olex2<sup>S1</sup>, the structure was solved with the ShelXS<sup>S2</sup> structure solution program using Direct Methods and refined with the ShelXL<sup>S3</sup> refinement package using Least Squares minimisation. Crystallographic data and structure refinement parameters for this crystal is summarized in Table S1. We employed PLATON/SQUEEZE<sup>S4</sup> to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. The final formula was calculated from the SQUEEZE results. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF files. Crystallographic data for the structure reported in this paper has been deposited. The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number (CCDC No. 1474064) for **FJI-H12**. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1. Summary of Crystal Data and Refinement Results**

Items	FJI-H12
formula	[Co <sub>3</sub> (Timt) <sub>4</sub> (SCN) <sub>6</sub> ]
Mass	1642.40
crystal system	<i>Tetragonal</i>
space group	<i>I41/a (#88)</i>
<i>a</i> (Å)	23.3588(3)
<i>b</i> (Å)	23.3588(3)
<i>c</i> (Å)	31.3531(1)
$\alpha$ (°)	90.00
$\beta$ (°)	90.00
$\gamma$ (°)	90.00
<i>V</i> (Å <sup>3</sup> )	17107.3(6)
<i>T</i> (K)	103
<i>Z</i>	8
F(000)	6648
R <sub>int</sub>	0.0376
R <sub>1</sub> ( <i>I</i> >2σ( <i>I</i> ))	0.0839
wR <sub>2</sub> (all reflections)	0.2598

*More details see CIF files.*

## S2. Gas Sorption Analysis

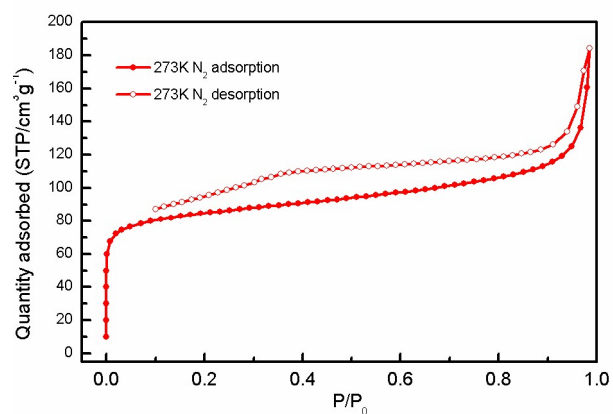


Figure S1. N<sub>2</sub> adsorption isotherm at 273K for activated FJI-H12

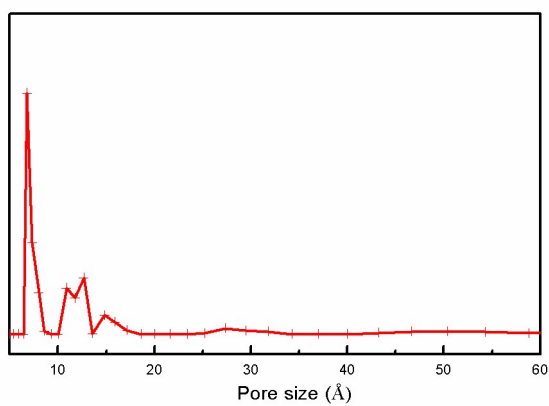


Figure S2. Pore size distribution of FJI-H12.

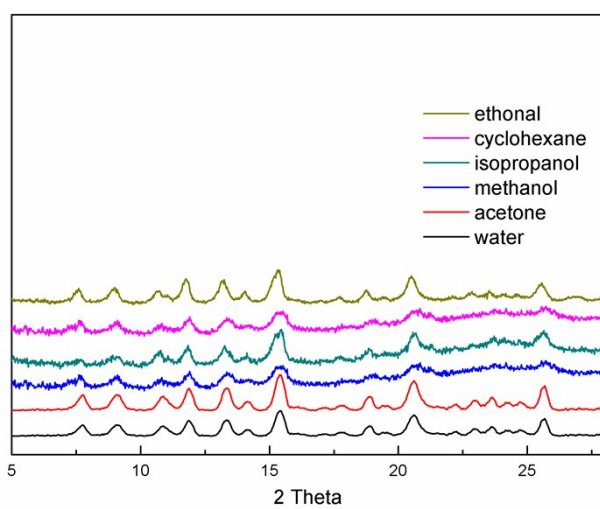


Figure S3. PXRD patterns of FJI-H12 after immersion in different solvents

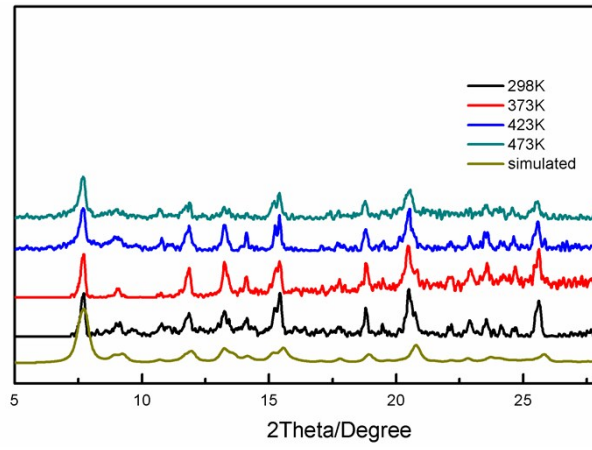
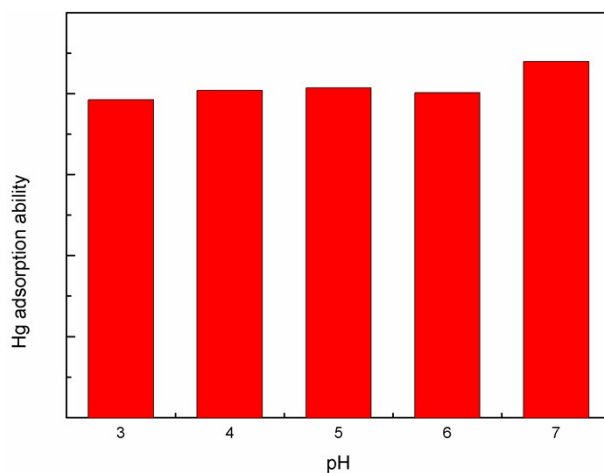


Figure S4. Temperature-dependent X-ray powder diffraction data

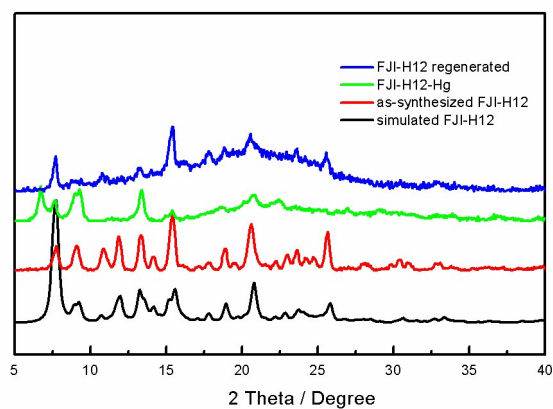
### S3. Hg(II) adsorption kinetic parameter and PXRD data



**Figure S5** Hg adsorption capacity under different pH conditions.

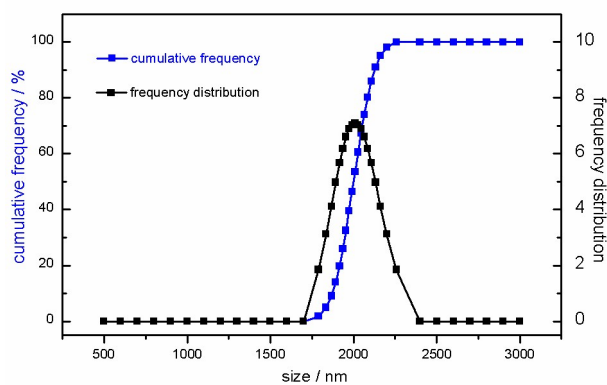
**Table S2** Kinetic parameters for adsorption of Hg(II)

$q_{e,exp}$	$k_2$	$q_{e,cal}$	$R_2$
49.865	0.127	49.850	>0.9999

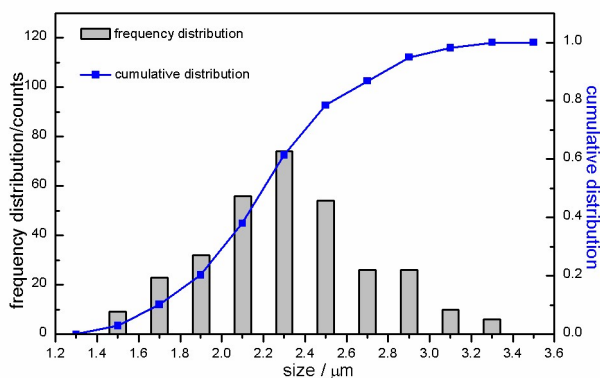


**Figure S6** PXRD patterns of **FJI-H12**: simulated from the crystallographic information file (black); from the as-synthesized sample (red); from the Hg(II) solution processed for 12h sample (green); from the KSCN solution processed FJI-H12-Hg for 1day sample (blue).

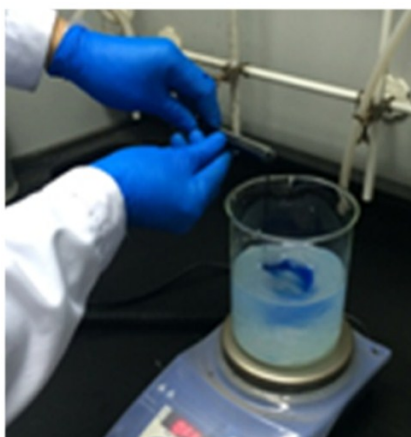
## S4. Size distribution analysis



**Figure S7.** Laser light-scattering size distribution analysis of **FJI-H12** microcrystal



**Figure S8.** Size distribution histogram of **FJI-H12** microcrystal obtained from microscopic measurement



**Figure S9.** The synthesis of **FJI-H12** microcrystal in 10g-scale in 10 minutes.

## S5. References.

- [S1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.
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- [S3] SHELXL, G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
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