

# Sulfate separation by selective crystallization of a urea-functionalized metal-organic framework

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## Electronic Supplementary Information

FT-IR spectra were recorded in KBr pellets with a Digilab FTS 7000 spectrometer. Powder X-ray diffraction patterns were obtained with a Bruker D5005 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ); step size  $0.02^\circ$ ;  $0.5 \text{ s / step}$ .

**Synthesis of EDPU:** Nicotinyln azide<sup>1</sup> (1.106 g, 7.4 mmol) was refluxed under argon in 23 mL of anhydrous benzene for 5.5 h. Ethylenediamine (0.223 g, 3.7 mmol) was subsequently added, which resulted in the formation of a white precipitate. The solution was refluxed for 15 minutes with stirring under argon, then it was cooled to room temperature, filtered, and washed three times with 15 mL diethyl ether. Yield 1.049 g, 94%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, 25 °C):  $\delta = 8.86$  (s, 2H; NH), 8.58 (d,  $J(\text{H,H}) = 2.30 \text{ Hz}$ , 2H; CH), 8.14 (d,  $J(\text{H,H}) = 4.58 \text{ Hz}$ , 2H, CH), 7.92 (d,  $J(\text{H,H}) = 7.67 \text{ Hz}$ , 2H, CH), 7.28 (dd,  $J(\text{H,H}) = 8.27, 4.64 \text{ Hz}$ , 2H, CH), 6.42 (s, 2H, NH), 3.25 ppm (s, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>, 25 °C):  $\delta = 39.6, 123.5, 124.5, 137.1, 139.6, 142.1, 155.3 \text{ ppm}$ ; Elemental analysis found: C, 56.24; H, 5.28; N, 27.48. Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>6</sub>O<sub>2</sub>: C, 55.99; H, 5.37; N, 27.98.

**Synthesis of 1:** A solution of 30 mg (0.1 mmol) of EDPU in 2 mL of EtOH/DMF (3:1) was added to 2 mL of a 0.025 M aqueous solution of NiSO<sub>4</sub>. The resulting solution was stirred at room temperature for 16 h, and the blue precipitate formed was collected and washed with water, DMF, and ethanol. Yield 34 mg, 79%; FT-IR (KBr):  $\nu_{\max}/\text{cm}^{-1}$  3299 (s, br), 3138 (m), 3090 (m), 1675 (m), 1565 (s), 1489 (m), 1428 (m), 1330 (w), 1268 (m), 1233 (w), 1108 (s), 805 (w), 700 (w), 619 (w); Elemental analysis found: C, 37.77; H, 5.10; N, 18.26. Calc. for [Ni(EDPU)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O)<sub>3.5</sub>(EtOH)<sub>0.4</sub>: C, 38.06; H, 5.48; N, 18.49.

**Competitive crystallization experiments:** a) A solution of 30 mg (0.1 mmol) of EDPU in 2 mL of EtOH/DMF (3:1) was added to 2 mL of an aqueous solution containing NiSO<sub>4</sub> (0.05 mmol), NaF (0.1 mmol), NaCl (0.1 mmol), NaBr (0.1 mmol), NaI (0.1 mmol), NaNO<sub>3</sub> (0.1 mmol), and NaClO<sub>4</sub> (0.1 mmol). The resulting solution was stirred at room temperature for 16 h, and the blue precipitate formed was collected and washed with water, DMF, and ethanol. Yield 29 mg, 67%; Elemental analysis found: C, 38.22; H, 5.18; N, 18.49. Calc. for [Ni(EDPU)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O)<sub>3.5</sub>(EtOH)<sub>0.4</sub>: C, 38.06; H, 5.48; N, 18.49.

b) A solution of 60 mg (0.2 mmol) of EDPU in 2.5 mL of EtOH/DMF (3:1) was added to 2 mL of an aqueous solution containing NiSO<sub>4</sub> (15.5 mg, 0.1 mmol) and NaNO<sub>3</sub> (170.0 mg, 2 mmol). The mixed solution was stirred occasionally and the resulting blue precipitate was collected after 2 weeks and washed with water, DMF, and ethanol. Yield 24 mg, 27%. The FT-IR spectrum and powder X-ray diffraction pattern were identical with those of **1**.

**X-Ray Crystallography:** Single crystals of **1** were obtained by slow diffusion of a solution of EDPU in EtOH/DMF (3:1) into an aqueous solution of NiSO<sub>4</sub>. Single-crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer with fine-focus Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), operated at 50 kV and 30 mA. The structure was solved by direct methods and refined on  $F^2$  using the SHELXTL software package.<sup>2</sup> Absorption corrections were applied using SADABS, part of the SHELXTL package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined with a riding model, except for hydrogen atoms on the water and ethanol solvent molecules, which were not included in the model.

**Table 1.** Hydrogen bonding parameters ( $\text{\AA}$ ,  $^\circ$ ) for SO<sub>4</sub><sup>2-</sup> binding by the urea groups in **1**.

D-H---A	H---A	D---A	<D-H-A
N2-H2N---O7	2.00	2.850(8)	163
N3-H3N---O9*	2.41	3.207(9)	150
N4-H4N---O9	2.16	3.019(9)	166
N5-H5N---O8	1.99	2.814(8)	155
N8-H8N---O10	2.03	2.908(7)	172
N9-H9N---O7	2.04	2.895(8)	163
N10-H10N---O8	2.05	2.872(8)	156
N11-H11N---O10	2.06	2.880(8)	155
N3-H3N---O7*	2.29	3.060(9)	145

\* bifurcated hydrogen bonds

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<sup>1</sup> R. Custelcean, B. A. Moyer, V. S. Bryantsev, B. P. Hay, *Cryst. Growth Des.*, 2006, **6**, 555.

<sup>2</sup> SHELXTL 6.12, Bruker AXS, Inc., Madison, WI, 1997.