

Supporting Information for

**Thermodynamic parameters of cation exchange in MOF-5 and MFU-4l**

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**Materials**

Fuming nitric acid (EMD), trifluoroacetic acid anhydride (99%, Alfa), dibenzo[1,4]dioxin (99.0%, TCI), acetic acid (Mallinckrodt), sodium nitrite (97%, Alfa), anhydrous zinc chloride (98%, Sigma), terephthalic acid (Sigma), nickel nitrate hydrate (99.9%, Strem), cobalt nitrate hydrate (99%, Alfa) and zinc nitrate hydrate (99%, Alfa) were used as received. Anhydrous cobalt chloride was prepared by placing cobalt chloride hydrate (99.9% Alfa) under high vacuum for 24 h. Dry, deaerated acetonitrile (MeCN, HPLC grade, Sigma), dichloromethane (DCM, HPLC grade, Honeywell), *N,N*-dimethylformamide (DMF, 99.8%, VWR), and methanol (MeOH, 99.9%, VWR), were obtained by degassing with a flow of argon gas for 30 min and by passing the solvent through two silica columns in a Glass Contour Solvent System. MFU-4l<sup>1</sup> and MOF-5<sup>2</sup> were prepared according to literature procedure.

*The following synthetic procedures were performed under an inert atmosphere using either a N<sub>2</sub>-filled glovebox or standard Schlenk technique.*

**Synthesis of Co-MFU-4l**

Anhydrous CoCl<sub>2</sub> (0.0649 g, 0.5 mmol) was dissolved in 5 mL of solvent and another 5 mL were added to freshly activated MFU-4l (16.5 mg, 0.013 mmol). For the exchange reactions conducted at 40 °C and 22 °C, the contents were combined at room temperature and left to sit for 4 months. For the exchange reactions conducted at -35 °C and 8 °C, the contents were first cooled in a -35 °C freezer before combining. The -35 °C exchange reaction was left in the -35 °C freezer for 4 months, whereas the 8 °C exchange reaction mixture was kept in a 8 °C freezer for 4 months. Afterwards, the crystals were collected by gravity filtration and soaked in fresh solvent. The solvent was replaced until UV-vis spectra of the mother liquor no longer displayed absorptions characteristic of Co<sup>2+</sup>.

### **Synthesis of Ni-MOF-5 Using DMF or MeCN**

Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1454 g, 0.500 mmol) was dissolved in 10 mL of either DMF or MeCN. Another 10 mL of solvent were added to Zn<sub>4</sub>O<sub>13</sub>C<sub>24</sub>H<sub>12</sub> (MOF-5) (20 mg, 0.026 mmol). For the exchange reactions conducted at 40 °C and 22 °C, the contents were combined at room temperature and left to sit for 4 months. For the exchange reactions conducted at –35 °C and 8 °C, the contents were first cooled in a –35 °C freezer before combining. The –35 °C exchange reaction was left in the –35 °C freezer for 4 months, whereas the 8 °C exchange reaction mixture was kept in a 8 °C freezer for 4 months. Afterwards, the crystals were collected by gravity filtration and soaked in fresh solvent. The solvent was replaced until UV-vis spectra of the mother liquor no longer displayed absorptions characteristic of Ni<sup>2+</sup>.

### **Synthesis of Co-MOF-5**

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1455 g, 0.500 mmol) was dissolved in 10 mL of DMF. Another 10 mL of solvent were added to Zn<sub>4</sub>O<sub>13</sub>C<sub>24</sub>H<sub>12</sub> (MOF-5) (20 mg, 0.026 mmol). For the exchange reactions conducted at 40 °C and 22 °C, the contents were combined at room temperature and left to sit for 4 months. For the exchange reactions conducted at –35 °C and 8 °C, the contents were first cooled in a –35 °C freezer before combining. The –35 °C exchange reaction was left in the –35 °C freezer for 4 months, whereas the 8 °C exchange reaction mixture was kept in a 8 °C freezer for 4 months. Afterwards, the crystals were collected by gravity filtration and soaked in fresh solvent. The solvent was replaced until UV-vis spectra of the mother liquor no longer displayed absorptions characteristic of Co<sup>2+</sup>.

### **Inductively Coupled Plasma Atomic Emission Spectroscopy**

Cobalt, nickel and zinc analyses were conducted at the MIT Center for Materials Science and Engineering Shared Experimental Facility (CSME-SEF) using a HORIBA Jobin ACTIVA inductively coupled plasma atomic emission spectrometer (ICP-AES). Standards were prepared from solutions purchased from ULTRA Scientific®, designated suitable for ICP analysis.

1. D. Denysenko, M. Grzywa, M. Tonigold, B. Streppel, I. Krkljus, M. Hirscher, E. Mugnaioli, U. Kolb, J. Hanss, and D. Volkmer, *Chem.—Eur. J.*, 2011, **17**, 1837.
2. S. S. Kaye, A. Dailly, O. M. Yaghi, and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176.