Surfactant-thermal method to prepare four new three-dimensional heterometal-organic frameworks

Junkuo Gao,^[a] Mi He,^[b] Zhi Yi Lee,^[a] Wenfang Cao,^[a] Wei-Wei Xiong,^[a] Yongxin Li,^[b] Ganguly Rakesh,^[b] Tom Wu^[c] and Qichun Zhang^{*[a]}

^[a] School of Materials Science & Engineering, Nanyang Technological University, Singapore 639798,

Singapore

^[b] School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

^[c] Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

Supporting Information:

Experimental Section

Materials. All chemicals were purchased from Alfa Aesar, TCI chemical and Aldrich and used without further purification. Polyethylene glycol 400 (PEG 400) were purchased from Alfa Aesar.

Characterization. Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized Cu *Ka* radiation. FTIR spectra were recorded from KBr pellets by using a Perkin Elmer FTIR SpectrumGX spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 °C/min up to 800 °C under N₂ atmosphere. The elemental analyses of Co, Mn, Ni, Zn and Cu have been examined with the aid of an EDX-equipped JEOL/JSM-6360A SEM using the Al substrate. The DC magnetic susceptibility measurements were made on an MPMS magnetometer at temperatures between 2.0 and 300 K.

Synthesis of Co(BTC)Cu(py)₂ (**NTU-Z7a**). A mixture of cobalt acetate tetrahydrate (0.8 mmol, 0.20 g), H_3BTC (1 mmol, 0.21 g), copper(II) nitrate trihydrate (0.8 mmol, 193 mg) and pyridine (0.5 mL) were mixture with 3 mL of PEG 400 in a 25 mL Teflon-lined stainless-steel autoclave was heated to 160 °C for 6 days. The resulting mixture was naturally cooled to room temperature and washed with methanol to get red crystals of **NTU-Z7a**. Yield: 68 % (based on Cu(NO₃)₂). IR data (in KBR, cm⁻¹): 3065 (w), 1622 (s), 1582 (m), 1447 (m), 1375 (s), 765 (s), 723 (m), 694 (s).

Synthesis of Mn(BTC)Cu(py)₂ (NTU-Z7b). A mixture of manganese acetate tetrahydrate (0.8 mmol, 0.20 g), H_3BTC (1 mmol, 0.21 g), copper(II) nitrate trihydrate (0.8 mmol, 193 mg) and pyridine (0.5 mL) were mixture with 3 mL of PEG 400 in a 25 mL Teflon-lined stainless-steel autoclave was heated to 160 °C for 6 days. The resulting mixture was naturally cooled to room temperature and washed with methanol to get green crystals of **NTU-Z7b.** Yield: 63 % (based on Cu(NO₃)₂). IR data (in KBR, cm⁻¹): 3066 (w), 1621 (s), 1579 (m), 1444 (m), 1374 (s), 767 (s), 720 (m), 694 (s).

Synthesis of Ni(BTC)Cu(py)₂ (**NTU-Z7c).** A mixture of nickel acetate tetrahydrate (0.8 mmol, 0.20 g), H₃BTC (1 mmol, 0.21 g), copper(II) nitrate trihydrate (0.8 mmol, 193 mg) and pyridine (0.5 mL) were mixture with 3 mL of PEG 400 in a 25 mL Teflon-lined stainless-steel autoclave was heated to 160 °C for 6 days. The resulting mixture was naturally cooled to room temperature and washed with methanol to get green crystals of **NTU-Z7c**. Yield: 56 % (based on Cu(NO₃)₂). IR data (in KBR, cm⁻¹): 3072 (w), 1667 (s), 1610 (m), 1449 (m), 1379 (s), 761 (s), 723 (m), 696 (s).

Synthesis of $Zn(BTC)Cu(py)_2$ (NTU-Z7d). A mixture of zinc acetate (1 mmol, 0.18 g), H₃BTC (1 mmol, 0.21 g), copper(II) nitrate trihydrate (0.8 mmol, 193 mg) and pyridine (0.5 mL) were mixture with 3 mL of PEG 400 in a 25 mL Teflon-lined stainless-steel autoclave was heated to 160 °C for 6 days. The resulting mixture was naturally cooled to room temperature and washed with methanol to get light-green block crystals of NTU-Z7d and another light-yellow rod crystal phase. Pure NTU-Z7d crystals were separated by hand. Yield: 30 % (based on Zn(OAc)₂). IR data (in KBR, cm⁻¹): 3067 (w), 1626 (s), 1583 (m), 1449 (m), 1375 (s), 767 (s), 722 (m), 698 (s).

Crystallographic measurements. Data collection of crystals was carried out on Bruker APEX II CCD diffractometer equipped with a graphite-monohromatized Mo-K α radiation source (λ =0.71073 Å). Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of a SHELXTL program package. All hydrogen atoms were calculated and refined using a riding model. The **CCDC** number for **NTU-Z7a** and **NTU-Z7c** are 932108 and 932109, respectively.

Magnetic susceptibility. The DC magnetic susceptibility measurements were made on an MPMS magnetometer at temperatures between 2.0 and 300K. The X-ray pure polycrystalline sample was ground to a fine powder to minimize possible anisotropic effects and loaded into a gelatin capsule. The sample was cooled in a constant magnetic field of 50 Oe for measurements of magnetization versus temperature. The data were corrected for the susceptibility of the container and for the diamagnetic contribution from the ion core.

Compound	NTU-Z7a	NTU-Z7c
Empirical formula	C ₁₉ H ₁₃ N ₂ O ₆ CoCu	C ₁₉ H ₁₃ N ₂ O ₆ NiCu
Formula weight	487.78	487.56
T (K)	103(2)	103(2)
λ	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	C222(1)	C222(1)
a	12.3843(6)	12.419(3)
b	15.8374(7)	15.579(3)
с	19.3284(10)	19.680(4)
α	90	90
β	90	90
γ	90	90
v	3791.0(3)	3807.5(13)
Z	8	8
Dc (g/cm3)	1.709	1.670

Table 1. Summary of crystal and structure refinement data for NTU-Z7a and NTU-Z7c.

GOF on F2	1.177	0.985
R1a [I>2σ(I)]	0.0266	0.0694
$\omega R2b[I>2\sigma(I)]$	0.0740	0.1728



Figure S1. The IR spectra of HMOFs NTU-Z7a, NTU-Z7b, NTU-Z7c and NTU-Z7d.



Figure S2. a) The3-D structures of NTU-Z7a viewed along the b-axis. b) The3-D structures of NTU-Z7a viewed along the a-axis. C, N, O, Co and Cu atoms are shown in gray, blue, red, cyan and yellow, respectively. H atoms were removed for clarity.



Figure S3. The energy dispersive X-ray spectroscopy (EDX) spectra of HMOF

NTU-Z7a.



Figure S4. EDX spectra of HMOF NTU-Z7b.



Figure S5. EDX spectra of HMOF NTU-Z7c.



Figure S6. EDX spectra of HMOF NTU-Z7d.

Figure S7. The TGA spectra of HMOFs NTU-Z7a, NTU-Z7b, NTU-Z7c and NTU-Z7d.