

Supporting Information for

A heterobimetallic metal-organic framework with tunable reactive metal sites: synthesis, characterization, and reactivity

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General Methods: All reagents were of commercial origin and used as received. Product identity and purity were verified by comparison of the observed X-ray powder diffraction pattern with a calculated pattern generated from the single-crystal results. The solvent content of each compound was determined by elemental and thermogravimetric analysis. CHN analysis was performed by Ecology Analytical Lab in the Department of Biology at SDSU.

Preparation of $(\text{Et}_2\text{NH}_2)[\text{Cd}(\text{H}_2\text{O})][\text{H}_2\text{TCPP}]\cdot 4\text{DEF}\cdot \text{H}_2\text{O}$ (1). A 1.3 cm o.d. \times 23 cm length pyrex tube was charged with CdCl_2 (27 mg, 0.15 mmol), H_2TCPP (40 mg, 0.05 mmol), and DEF (3 mL) under anhydrous conditions. An aliquot of water (0.150 mL) was added, the sample frozen with liquid N_2 , and the tube sealed under vacuum. The tube was heated to 150 °C for 48 h followed by slow cooling to room temperature over 4 h. The solid was collected by filtration, washed by successive aliquots of DEF (3×10 mL), and dried in air to afford 52 mg (73.03%) of dark purple block-shaped crystals. IR (solid, ATR): Anal. Calc. for $\text{C}_{72}\text{H}_{86}\text{N}_9\text{O}_{14}\text{Cd}_{1.1}$: C, 60.72; H, 8.84; N, 6.01%. Found: C, 57.34; H, 8.67; N, 5.63%. UV-vis (solid): $\lambda_{\text{max}}/\text{nm} = 422, 527, 574, 623, 659$. IR (solid, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 2975 (CH), 1642 (CO), 1584 (conj. CC), 1535, 1380, 990.

Preparation of $(\text{Et}_2\text{NH}_2)[\text{Cd}(\text{H}_2\text{O})][\text{FeTCPP}]\cdot 2\text{DEF}\cdot \text{H}_2\text{O}$ (1-Fe). A 1.3 cm o.d. \times 23 cm length pyrex tube was charged with CdCl_2 (27 mg, 0.15 mmol), H_2TCPP (40 mg, 0.05 mmol), FeCl_2 (6.3 mg, 0.05 mmol) and DEF (3 mL) under anhydrous conditions. An aliquot of water (0.150 mL) was added, the sample frozen with liquid N_2 , and the tube sealed under vacuum. The tube was heated to 150 °C for 48 h followed by slow cooling to room temperature over 4 h. The solid was collected by filtration, washed by successive aliquots of DEF (3×10 mL), and dried in

air to afford 46 mg. Anal. Calc. for $C_{62}H_{64}N_7O_{12}CdFe$: C, 58.67; H, 5.00; N, 7.73%. Found: C, 54.86; H, 4.60; N, 7.07%. UV-vis (solid): $\lambda_{max}/nm = 428, 524, 566, 606, 654$. Metals analysis (Fe:Cd ratio): Calc. 1.0, Found 0.93. IR (solid, ATR) ν_{max}/cm^{-1} : 2975 (CH), 1647 (CO), 1582 (conj. CC), 1534, 1376, 997.

Preparation of $(Et_2NH_2)[Cd(H_2O)][CoTCPP] \cdot 4DEF \cdot H_2O$ (1-Co). A 1.3 cm o.d. \times 23 cm length pyrex tube was charged with $CdCl_2$ (27 mg, 0.15 mmol), H_2TCPP (40 mg, 0.05 mmol), $CoCl_2$ (6.5 mg, 0.05 mmol) and DEF (3 mL) under anhydrous conditions. An aliquot of water (0.150 mL) was added, the sample frozen with liquid N_2 , and the tube sealed under vacuum. The tube was heated to 150 °C for 48 h followed by slow cooling to room temperature over 4 h. The solid was collected by filtration, washed by successive aliquots of DEF (3×10 mL), and dried in air to afford 61 mg (83%). Anal Calc. for $C_{72}H_{86}N_9O_{14}CdCo$: C, 58.84; H, 5.82; N, 8.58%. Found: C, 59.46; H, 5.39; N, 7.94%. UV-vis (solid): $\lambda_{max}/nm = 410, 540$. Metals analysis (Co:Cd ratio): Calc. 1.0, Found 0.92. IR (solid, ATR) ν_{max}/cm^{-1} : 2979 (CH), 16511 (CO), 1586 (conj. CC), 1541, 1396, 1345, 1000.

Preparation of $(Et_2NH_2)[Cd(H_2O)][NiTCPP] \cdot 2DEF \cdot H_2O$ (1-Ni). A 1.3 cm o.d. \times 23 cm length pyrex tube was charged with $CdCl_2$ (27 mg, 0.15 mmol), H_2TCPP (40 mg, 0.05 mmol), $NiCl_2$ (6.5 mg, 0.05 mmol) and DEF (3 mL) under anhydrous conditions. An aliquot of water (0.150 mL) was added, the sample frozen with liquid N_2 , and the tube sealed under vacuum. The tube was heated to 150 °C for 48 h followed by slow cooling to room temperature over 4 h. The solid was collected by filtration, washed by successive aliquots of DEF (3×10 mL), and dried in air to afford 46 mg (72.5 %). Anal. Calc.. for $C_{62}H_{64}N_7O_{12}CdNi$: C, 58.67; H, 5.01; N, 7.72%.

Found: C, 58.83; H, 5.47; N, 8.07%. UV-vis (solid): $\lambda_{\max}/\text{nm} = 413, 533, 651$. Metals analysis (Ni: Cd ratio): Calc. 1.0, Found 1.0. IR (solid, ATR) $\nu_{\max}/\text{cm}^{-1}$: 2974 (CH), 1636 (CO), 1605 (conj. CC) 1540, 1388, 1349, 1000.

Preparation of $(\text{Et}_2\text{NH}_2)[\text{Cd}(\text{H}_2\text{O})][\text{CuTCPP}]\cdot 2\text{DEF}\cdot \text{H}_2\text{O}$ (1-Cu). A 1.3 cm o.d. \times 23 cm length pyrex tube was charged with CdCl_2 (27 mg, 0.15 mmol), H_2TCPP (40 mg, 0.05 mmol), CuCl_2 (6.7 mg, 0.05 mmol) and DEF (3 mL) under anhydrous conditions. An aliquot of water (0.150 mL) was added, the sample frozen with liquid N_2 , and the tube sealed under vacuum. The tube was heated to 150 °C for 48 h followed by slow cooling to room temperature over 4 h. The solid was collected by filtration, washed by successive aliquots of DEF (3×10 mL), and dried in air to afford 43 mg, (66.9%). Anal. Calc. for $\text{C}_{62}\text{H}_{64}\text{N}_7\text{O}_{12}\text{CdCu}$: C, 57.86; H, 4.90; N, 7.62%. Found: C, 56.38; H, 5.12; N, 8.06%. UV-vis (solid): $\lambda_{\max}/\text{nm} = 411, 550, 590, 633, 662$. Metals analysis (Cu: Cd ratio): Calc. 1.0, Found 0.94. IR (solid, ATR) $\nu_{\max}/\text{cm}^{-1}$: 2976 (CH), 1650 (CO), 1586 (conj. CC) 1537, 1392, 1345, 1000.

Preparation of $(\text{Et}_2\text{NH}_2)[\text{Cd}(\text{H}_2\text{O})][\text{ZnTCPP}]\cdot 2\text{DEF}\cdot \text{H}_2\text{O}$ (1-Zn). A 1.3 cm o.d. \times 23 cm length pyrex tube was charged with CdCl_2 (27 mg, 0.15 mmol), H_2TCPP (40 mg, 0.05 mmol), ZnCl_2 (6.8 mg, 0.05 mmol) and DEF (3 mL) under anhydrous conditions. An aliquot of water (0.150 mL) was added, the sample frozen with liquid N_2 , and the tube sealed under vacuum. The tube was heated to 150 °C for 48 h followed by slow cooling to room temperature over 4 h. The solid was collected by filtration, washed by successive aliquots of DEF (3×10 mL), and dried in air to afford 43 mg (67.5%). Anal. Calc. for $\text{C}_{62}\text{H}_{64}\text{N}_7\text{O}_{12}\text{CdZn}$: C, 58.36; H, 4.97; N, 7.68%. Found: C, 56.25; H, 5.35; N, 8.15%. UV-vis (solid): $\lambda_{\max}/\text{nm} = 428, 524, 566, 606, 654$. Metals

analysis (Zn:Cd ratio): Calc. 1.0, Found 0.92. IR (solid, ATR) $\nu_{\max}/\text{cm}^{-1}$: 2976 (CH), 1647 (CO), 1584 (conj. CC) 1540, 1376, 994.

Preparation of $(\text{Et}_2\text{NH}_2)[\text{Cd}(\text{H}_2\text{O})][\text{PdTCPP}]\cdot 2\text{DEF}\cdot \text{H}_2\text{O}$ (1-Pd**).** A 1.3 cm o.d. \times 23 cm length pyrex tube was charged with CdCl_2 (27 mg, 0.15 mmol), H_2TCPP (40 mg, 0.05 mmol), PdCl_2 (8.5 mg, 0.05 mmol) and DEF (3 mL) under anhydrous conditions. An aliquot of water (0.150 mL) was added, the sample frozen with liquid N_2 , and the tube sealed under vacuum. The tube was heated to 150 °C for 48 h followed by slow cooling to room temperature over 4 h. The solid was collected by filtration, washed by successive aliquots of DEF (3×10 mL), and dried in air to afford 38 mg (57.7%). Anal. Calc. for $\text{C}_{62}\text{H}_{64}\text{N}_7\text{O}_{12}\text{CdPd}$: C, 56.45; H, 4.82; N, 7.45%. Found: C, 57.74; H, 5.44; N, 8.11%. UV-vis (solid): $\lambda_{\max}/\text{nm} = 413, 530, 565, 612, 660$. Metals analysis (Pd:Cd ratio): Calc. 1.0, Found 0.62. IR (solid, ATR) $\nu_{\max}/\text{cm}^{-1}$: 2976 (CH), 1651 (CO), 1585 (conj. CC), 1537, 1392, 1011.

Preparation of $(\text{Et}_2\text{NH}_2)_2\text{Cd}_2[\text{TCPPFe-O-FeTCPP}]$ (2**).** A 20 ml vial was loaded with CdCl_2 (27 mg, 0.15 mmol), H_2TCPP (40 mg, 0.05 mmol), FeCl_2 (6.3 mg, 0.05 mmol) and DEF (3 mL) under anhydrous conditions. An aliquot of water (0.150 mL) was added and the solution was oxygenated. The vial was sealed with a Teflon-lined cap and heated to 150 °C for 48 h followed by a slow cooling to room temperature over 4 h. Crystals suitable for single crystal X-ray diffraction were collected from the gelatinous reaction mixture.

Reaction of **1-Fe with peroxides.** For UV-vis measurements, freshly prepared samples of **1-Fe** were ground to fine powder and diluted with CaO (5 mass % **1-Fe**). The samples were treated

with either 30% H₂O₂ or 30% TBHP to afford a pale green solid mixture. For elemental analysis, **1-Fe** crystals were treated with 30% TBHP and air-dried. Anal. Calcd for 1282.184: C, 58.67; H, 5.00; N, 67.74%. Found: C, 58.35; H, 5.01; N, 7.72%. UV-vis (nm): $\lambda = 402, 580.4, 623.2$.

X-ray Structure Determinations

Single crystals of compounds **1**, **1-M**, and **2** were extracted from the product mixture, mounted on Cryoloops coated in Paratone oil, transferred to a diffractometer, and cooled in a dinitrogen stream. The single crystal X-ray diffraction studies were performed on a Bruker D8 Smart Apex II CCD diffractometer equipped with Mo K _{α} radiation ($\lambda = 0.71073$) (Compounds **1**, **1-Zn**, **1-Pd**, **2**) or a Bruker D8 Smart 6000 CCD diffractometer equipped with Cu K _{α} radiation ($\lambda = 1.54178$) (Compounds **1-Fe**, **1-Co**, **1-Ni**, **1-Cu**). Data were collected in a nitrogen gas stream at 100(2) K, using ϕ and ω scans. Lattice parameters were initially determined from a least squares refinement of more than 200 carefully centered reflections. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXS) produced a complete phasing model consistent with the proposed structures. Using Olex2, the structures were then refined with the XL refinement package using Least Squares minimization. Lattice solvent molecules and Et₂NH₂⁺ cations were disordered and could not be located in the structures. Unless noted, all atoms except hydrogen were refined anisotropically. Contributions to scattering from all solvent molecules and cations were removed using the SQUEEZE routine of PLATON, and the structures were refined against this data.

Note that several PLATON A-level alerts are found with these structures. Some of these errors are expected because MOF structures typically have a large amount of void space. For all of these compounds, several data sets were collected from several crystals and the best data set was

used for the refinement. The large residual electron density arises due to disordered solvent molecules or occur near a heavy atom (Cd). Full explanations and refinement details are available in the CIF files.

Other Physical Measurements. Routine X-ray powder diffraction data were collected using Cu K_{α} ($\lambda = 1.5406 \text{ \AA}$) radiation with a PANalytical Xpert diffractometer. Diffuse reflectance UV-vis spectra were acquired on a JASCO V670 spectrophotometer equipped with a 60 mm integrating sphere. Thermogravimetric analyses were performed in a dinitrogen atmosphere at a ramp rate of 5 °C/min using a TA Instruments TGA 2950. Infrared spectra were recorded on a Perkin Elmer Spectrum RX FTIR spectrometer equipped with an attenuated total reflectance accessory. Metals analysis was performed with a Perkin Elmer AAnalyst 100 atomic absorption spectrometer.

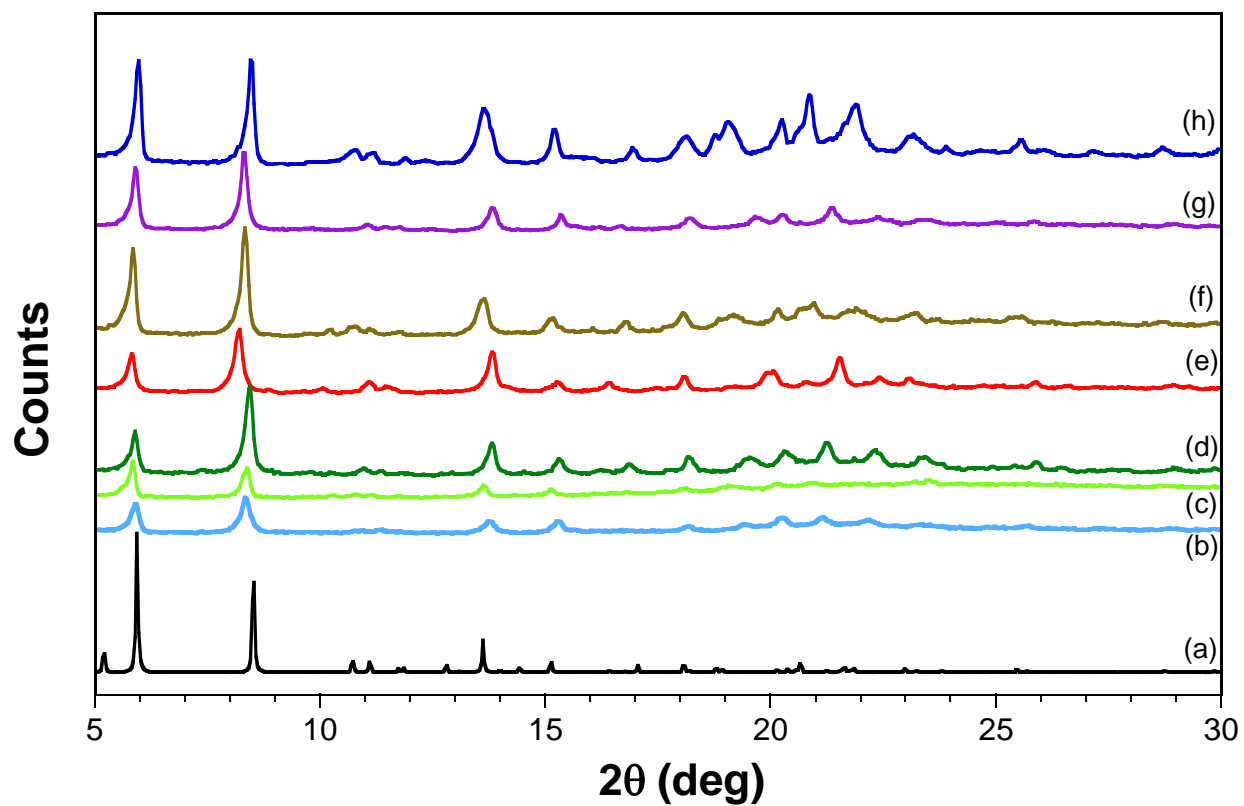


Fig. S1 X-ray powder diffraction data for (a) simulation using the crystal structure of **1** compared to bulk samples of (b) **1**, (c) **1-Fe**, (d) **1-Co**, (e) **1-Ni**, (f) **1-Cu**, (g) **1-Zn**, and (h) **1-Pd**.

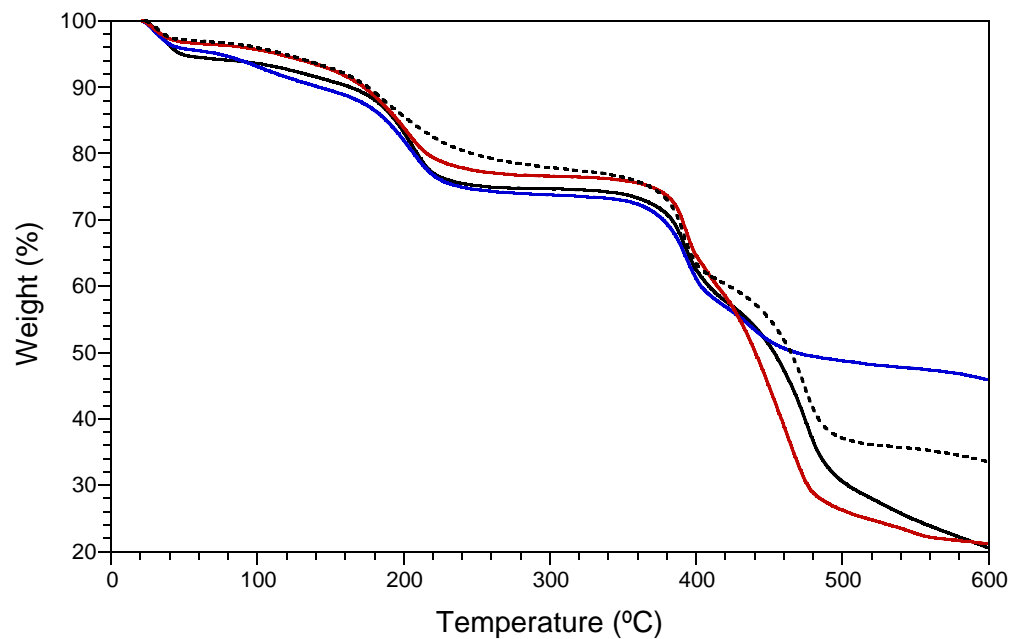


Fig. S2 Thermogravimetric analysis showing weight loss in compounds **1** (black), **1-Co** (blue), **1-Cu** (red), and **1-Ni** (black, dashed) with temperature increasing at a rate of 5 °C/min.

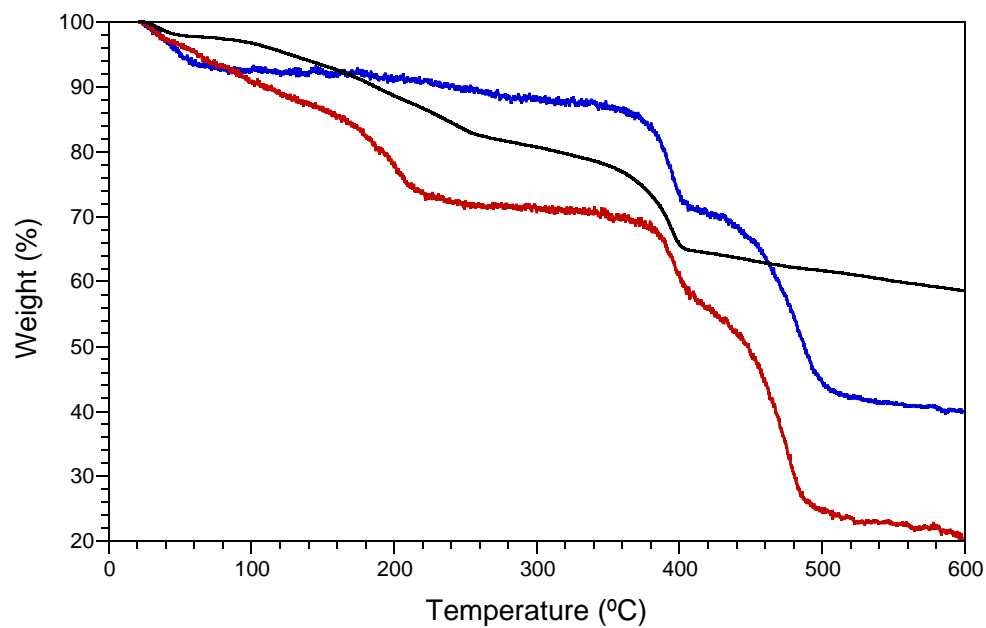


Fig. S3 Thermogravimetric analysis showing weight loss in compounds **1-Fe** (black), **1-Pd** (blue), and **1-Zn** (red) with temperature increasing at a rate of 5 °C/min.