

A Zn-based, pillared paddlewheel MOF containing free carboxylic acids via covalent post-synthesis elaboration

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Materials.

All chemicals were used as received from commercial sources unless otherwise noted. Tetrahydrofuran (THF), pyridine, H₂SO₄, HNO₃, and hydrogen peroxide were purchased from Fisher Scientific. Anhydrous *N,N'*-dimethylformamide (DMF) was obtained from Acros Organics. Succinic anhydride, sodium deuteroxide (NaOD), D₂O, 2-hydroxy-1-naphthoic acid, and copper chloride were purchased from Aldrich Chemicals. Deionized (DI) water was obtained from a Millipore system (18.2 MΩ•cm resistivity).

Synthetic Procedures.

Procedure for the modification of 1. MOF 1¹ (30 mg) was weighed into a 16-mL glass vial, to which succinic anhydride (5 mL of a 1.0 M solution in anhydrous DMF) was added. The reaction mixture was heated at 80 °C for 3 days, and the crude **1_{succ}** was isolated via vacuum filtration. This crude product was transferred to a Soxhlet thimble and rinsed with THF for 48 h using a Soxhlet extractor.

Procedure for the chelation of Cu²⁺. A 1-mg sample of the appropriate MOF was placed into a 1.5-mL polypropylene Eppendorf Safe-Lock centrifuge tube. CuCl₂ (1 mL of a 75-ppm solution) was then added. The tubes were capped and rocked continuously for an hour on a Thermolyne Maxi-mix III (Type 65800) shaker before the MOF suspension was removed and filtered. The MOF was rinsed with DI water until the filtrate was 5 mL. This solution was then analyzed to determine the Cu²⁺ content.

Characterization.

¹H NMR spectra were recorded on a Varian INOVA 500 NMR spectrometer (500 MHz for ¹H). NMR chemical shifts were reported in ppm against residual solvent resonance as the internal standard (δ(THF) = 1.85 ppm). Samples of **1_{succ}** (1-2 mg) were transferred into an NMR tube and NaOD (0.6 mL of a 0.1 N solution in D₂O) was added. The tubes were capped and sonicated until all the solid was dissolved (~ 5 min).

Matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectrometry was performed on a PE Voyager DE-Pro MALDI-TOF mass spectrometer in positive, reflector ionization mode, using 2-hydroxy-1-naphthoic acid as a matrix. In a typical procedure, a small sample of the MOF (~1 mg) and pyridine (~ 0.1 mL) was combined in a 0.5-mL polypropylene Eppendorf Safe-Lock microtube. The tube was then capped and sonicated for 15 minutes. After sonication, the mixture was left to settle. An aliquot of the supernatant solution, which contained dissolved MOF components, was spotted onto a MALDI plate, which was left in a fume hood until all the pyridine had evaporated. A saturated solution of the MALDI matrix in acetone was then spotted on top of the dissolved MOF spot and also allowed to dry in the fume hood prior to analysis.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted on a Varian VISTA-MPX ICP spectrometer equipped to cover the spectral range from 175 to 785 nm. MOF samples (3-5 mg) were first dissolved in concentrated HNO₃ and the acid was evaporated off at 110 °C. The remaining organic residue was subsequently digested in a hot (110°C) mixture of concentrated H₂SO₄:30% aqueous H₂O₂ (3:1 v/v) until the solution became clear. This solution was diluted to 5% (v/v) acid in DI water, and analyzed for Cu (λ = 324.754 nm) and Zn (λ = 206.200 nm) content.

Fourier-transform infrared (FT-IR) spectra were collected with a Thermo Nicolet Nexus 870 instrument. Samples of dry MOF (1 mg) were combined with anhydrous KBr (25 mg) and ground with a mortar and pestle to a fine powder. The powder was then pressed into a thin and transparent pellet and spectra were collected in transmission mode.

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku XDS 2000 diffractometer using nickel-filtered Cu Kα radiation (λ = 1.5418 Å) over a range of 5° < 2θ < 40° in 0.1° steps with a 1-s counting time per step. Samples were collected from the bottom of the reaction vial as a thick suspension in DMF and spread on a fritted glass slide immediately before PXRD measurements. Given the high boiling point of DMF, the crystals never dry out during the PXRD measurement.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA851 interfaced with a PC using Star software. Samples were heated at a rate of 10 °C/min under a nitrogen atmosphere. Samples of **1_{succ}** rinsed with THF were solvent exchanged with DMF prior to analysis.

Gas adsorption/desorption isotherms were measured volumetrically at 77 K for N₂, and at 273 K for CO₂ in the range 8.0 × 10⁻⁶ ≤ P/P₀ ≤ 1.0 using an Autosorb 1 instrument (Quantachrome Instruments) equipped with the ASWin software package. Ultra-high purity N₂ (99.999%) and CO₂ (99.999%) were purchased from Airgas, Inc. and used as received. All samples were solvent-exchanged with THF prior to measurements, following by outgassing at 100 °C at the outgas port of the Autosorb 1. For CO₂, surface areas were calculated by applying non-local density functional theory (NLDFT) for 0.005 ≤ P/P₀ ≤ 1.0.

1. K. L. Mulfort, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2008, **130**, submitted, attached to this manuscript for review purposes.