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. 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 1succ (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.

Fourier-transform infrared (FT-IR) spectra were collected using 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.

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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 1succ 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 x 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.