

Electronic Supplementary Information for:

A tetrapyridine ligand with a rigid tetrahedral core forms metal-organic frameworks with PtS type architecture

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General Methods

4-Pyridineboronic acid, $[\text{Cu}(\text{H}_2\text{O})_6][\text{CF}_3\text{SO}_3]_2$ and $[\text{Cu}(\text{H}_2\text{O})_6][\text{BF}_4]_2$ were purchased from Aldrich and used as received. Tetraphenylmethane,¹ tetrakis(4-bromophenyl)methane² and 2,6-dimethyl-4-pyridine boronic ester³ were prepared using literature procedures. All reactions were carried out under an atmosphere of $\text{N}_2(\text{g})$. Solvents were dried using an Innovative Technology Solvent Purification System. ^1H NMR spectra were obtained on a Bruker Avance 500 instrument operating at 500 MHz. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. High-resolution mass spectra were recorded in 50/50 MeCN/ H_2O on a Micromass LCT Electrospray TOF mass spectrometer.

1. D. Su, F. M. Menger, *Tetrahedron Letters*, **1997**, 38, 1485-1488
2. R. Rathore, *et al.*, *J. Org. Chem.* **2004**, 69, 1524-1530
3. P. Harrisson, J. Morris, T. B. Marder, P. G. Steel, *Organic Letters*, **2009**, 11, 3586-3589.

Tetra-(4-(4-pyridyl)phenyl)methane, TPPM

Tetrakis(4-bromophenyl)methane (1.000 g, 0.00157 mol) and 4-pyridineboronic acid (0.928 g, 0.00755 mol) were added to a 250 mL Schlenk flask. The contents of the flask were dissolved in DMF and sodium carbonate (1.660 g, 0.0157 mol) dissolved in degassed water added to the reaction flask. Tetrakis(triphenylphosphine)palladium(0) (0.182 g, 1.572×10^{-4} mol) was added to the reaction and the mixture refluxed for 5 days with stirring. The reaction was then cooled to room temperature, filtered and the solvent removed under high vacuum. The resulting residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (50 mL). The organic layer was separated and the H_2O layer washed three more times with CH_2Cl_2 (100 mL) and the combined organic extracts dried over anhydrous MgSO_4 . The product was further purified by flash column chromatography using Teledyne Ultra Pure Silica with a solvent gradient of CH_2Cl_2 and MeOH (0 - 7 %). Yield of white crystalline solid; 0.440 g, 45 %. X-ray quality crystals of **TPPM** were grown from the slow cooling of a solution of **TPPM** dissolved in hot DMF. Crystals were colourless rods. MP = 323 °C (dec.) **HR-ESMS**: calculated for $\text{C}_{49}\text{H}_{32}\text{N}_4$ 629.2627; found 629.2675.

Table S-1. ^1H NMR Spectrum of **TPPM** in CDCl_3 at 500 MHz.

Proton	δ (ppm)	Multiplicity	# of Protons	J (Hz)
a	8.67	d	8	$^3J_{ab} = 6.0$
b	7.57	d	8	$^3J_{ba} = 6.1$
c	7.65	d	8	$^3J_{cd} = 8.5$
d	7.47	d	8	$^3J_{dc} = 8.5$

^{13}C NMR (CD_2Cl_2) δ : 149.08, 148.44, 147.35, 135.72, 131.61, 121.60, 66.63

MOF {[CuCl₂(TPPM)].(DMF)_{6.5}}_x

The metal salt (5.0 mg of either [Cu(H₂O)₆][CF₃SO₃]₂ or [Cu(H₂O)₆][BF₄]₂) was dissolved in DMF (1mL). Dilute HCl(aq) was added dropwise to a heated mixture of **TPPM** (1 equivalent) in DMF (1 mL) until the solution was clear. The metal solution was then added slowly to the hot ligand solution. The mixture was sealed in a 20 mL scintillation vial and placed in a temperature controlled oven at 110 °C until crystal growth began at which point heating was ceased to allow the solution to slowly cool to room temperature. Yield of blue-green crystals; 40 – 50% based on the amount of **TPPM** used.

PXRD (see Figure S-1) is consistent with maintenance of the structural integrity of the crystalline material following soaking with MeOH then CH₂Cl₂ prior to drying at room temperature and pressure.

MOF {[Cu₃Cl₆(TPPM)₂].(DMF)₆}_x

The metal salt (5.0 mg of either [Cu(H₂O)₆][CF₃SO₃]₂ or [Cu(H₂O)₆][BF₄]₂) was dissolved in DMF (1mL). Dilute HCl(aq) was added dropwise to a heated mixture of **TPPM** (2 equivalents) in DMF (1 mL) until the solution was clear. The metal solution was then added slowly to the hot ligand solution. The mixture was sealed in a 20 mL scintillation vial and placed in a temperature controlled oven at 110 °C for 24 hours. The solution was then cooled slowly to room temperature. After 1 week, a small amount of greenish-blue crystals were isolated. Yield; 10 – 15% based on the amount of **TPPM** used.

The material desolvates rapidly upon removal of the crystals from the mother liquor resulting in collapse of the framework observed in the single crystal structure. Inspection of a crop of the as-synthesized crystals bathed in mother liquor with a polarizing microscope shows a uniform morphology throughout consistent with the single crystal data being representative of the bulk sample.

Single Crystal X-ray Diffraction

Crystals were frozen in paratone oil inside a cryoloop. Reflection data were integrated from frame data obtained from hemisphere scans on a Bruker APEX diffractometer using MoK α radiation and a CCD detector. Decay was monitored using 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined using full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined using a riding model. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL program library¹ and figures drawn with DIAMOND software.² For details of the final solutions see CCDC 822537-822539.

Exceptional Features of X-ray Crystal Structure Solutions

TPPM: A disordered molecule of DMF was modeled with a 50% site occupancy factor for both sites. SADI, SIMU and DELU commands were required to restrain the DMF to a chemically reasonable geometry.

MOF $\{[\text{CuCl}_2(\text{TPPM})] \cdot (\text{DMF})_{6.5}\}_x$: The unit cell contains an estimated 26 molecules of DMF which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. There was evidence of disorder at the Cu2-Cl2-N13 coordination environment. The largest residual peak is close to Cu2 and there is evidence for splitting peaks N13 - C18. All attempts to model this disorder with two sets of CuCl(py) fragments resulted in unstable refinement and/or NPD atoms.

MOF $\{[\text{Cu}_3\text{Cl}_6(\text{TPPM})_2] \cdot (\text{DMF})_6\}_x$: The unit cell contains an estimated 24 molecules of DMF which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. Separate SIMU commands were employed to restraints displacement parameters on individual aromatic rings. It was also

necessary to employ the ISOR command to restrain the displacement parameters for C14, C22, C36 and C43.

1. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
2. DIAMOND 3.2 - CRYSTAL IMPACT, Postfach 1251, D-53002, Bonn, Germany 2009.
3. PLATON/SQUEEZE, P. v. d. Sluis and A. L. Spek, *Acta Cryst.*, 1990, **A46**, 194.

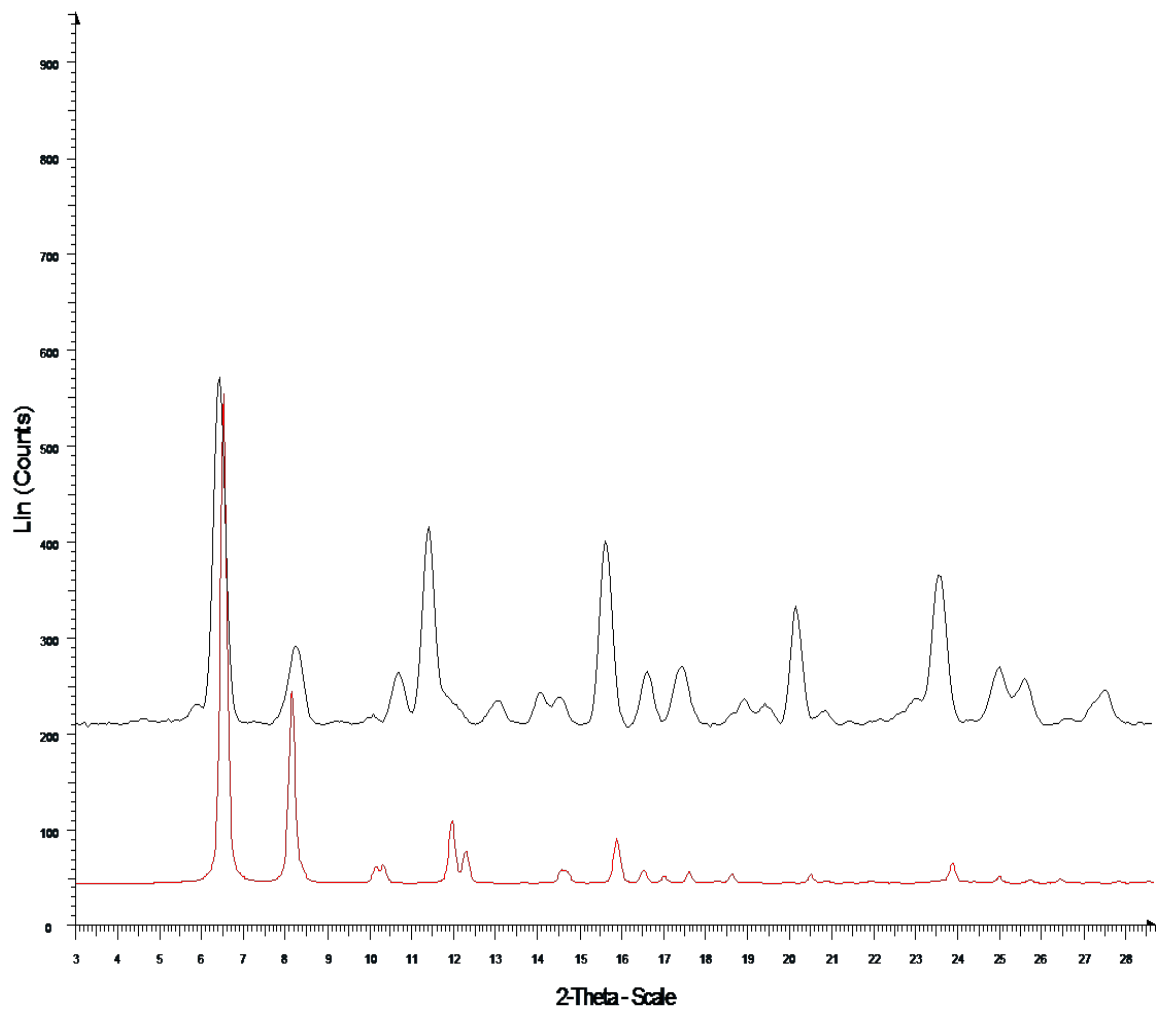


Figure S-1. Powder X-ray diffraction pattern for MOF $\{[\text{CuCl}_2(\text{TPPM})]\}_x$; the bottom (red) spectrum is simulated from the single crystal data and the (black) top spectrum is the experimental spectrum. The sample was washed with MeOH then CH_2Cl_2 and allowed to air dry prior to the measurement.