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Supporting information

Formation of a Non-Porous Cobalt-Phosphonate Framework by small pH Change in the Preparation of the Microporous STA-16(Co)

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S1. Instrumentation

A purple crystal of CoMOF was mounted on an OXFORD Gemini Ultra CCD diffractometer equipped with an Oxford Cryosystems 700 Cryostream and cooled to -150 °C. The data were collected with Cu K_a radiation (λ =1.5418 Å). The structure was solved by Direct Methods and refined using full matrix Least Squares with the SHELX-97 program suite.¹ Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon were placed in calculated positions using a riding model with d(C-H) = 0.99 Å and $U_{iso}(H)=1.2\times U_{eq}(C)$. Hydrogen atoms attached to oxygen were refined with the O-H distance restrained to 0.84(1) Å and the H-O-H angle approximately 109 degrees. The data was treated as a pseudo-merohedral twin (twin law:-1 0 -1 0 -1 0 0 0 1, corresponding to a 180 degree rotation about *a*, BASF 0.03) which reduced *R*1 by approximately 2%. However, there remained an electron density maxima of 3.3 e.Å⁻³ in the final difference Fourier map, located *ca* 1.95 Å from O(8) and is presumed to be a consequence of further unaccounted for twinning. Attempts to model the electron density peak as a disordered water molecule were unstable and were not pursued further.

The phase purities of the bulk samples were identified by X-ray powder diffraction on a Bruker D8 Focus powder diffractometer using Cu K α radiation. The PXRD pattern was simulated using the module "Reflex Tools" in Materials Studio 6.0.

The C, H, N and P contents were determined by elemental analysis in the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.

SEM images and EDX were obtained using a JEOL 7001F Field Emission Scanning Electron Microscope. The accelerating voltage was set to 15 kV.

The FT-IR spectra were recorded on KBr pellets in a Perkin-Elmer Spectrum RXI Fouriertransform infrared spectrometer in the spectral range 4000 to 400 cm⁻¹.

Thermogravimetric analysis was performed using a Setaram TAG 24 symmetrical thermoanalyzer from room temperature to 900 °C at a ramp of 2 °C min⁻¹ under an air and argon mixture.

Argon physisorption at -186 °C was measured on a ASAP 2020 porosimeter. Prior to analysis the MOF was degassed at 150 °C.

S2. Single-crystal X-ray structure determination and refinement details

Compound	CoMOF
Empirical formula	$Co_2C_{12}H_{26}N_2O_8P_2$
Formula weight/ g mol ⁻¹	506.15
Crystal system	Monoclinic
Space group	P 21/c
a / Å	15.0954(6)
b / Å	11.5689(4)
c / Å	10.6232(4)
β/°	110.192(4)
V / Å ³	1741.19(11)
Ζ	4
$D_{calcd} / g cm^{-3}$	1.931
μ / mm^{-1}	2.135
F(000)	1040
Measured reflection/unique	18166/3992
Observed reflection	3699
R _{int}	0.0333
Goodness-of fit on F ²	1.037
R_1, wR_2 (obs. data)	0.0356, 0.0853
R_1, wR_2 (all data)	0.0405, 0.0892

 Table S1 Details for structural analysis of CoMOF.

S3 PXRD



Figure S1: Effect of different pH values on the formation of STA-16(Co) and CoMOF.

S4 Thermal decomposition



Figure S2: Thermal decomposition of CoMOF.



S5 Argon physisorption and pore size distribution

Figure S3.1: Adsorption (■) and desorption (□) isotherms of Ar uptake on CoMOF at -186 °C.



Figure S3.2: Nonlinear DFT-calculated pore size distribution, assuming cylindrical pores.

S6 FTIR spectrum



Figure S4: FTIR spectrum of CoMOF.

References

1 G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.