

Supporting Information

**A permanently porous van der Waals solid by using
phosphonate monoester linkers in a metal organic framework.**

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Experimental

Synthesis of Tetraethyl 1,4-benzenediphosphonate (TEtBDP)

1,4-dibromo benzene 9.44 g (40 mmol) and anhydrous NiBr₂ 4.34 g (33 mmol) were dried with mild heating (50 °C) under vacuum in a two neck round bottom flask. The flask was backfilled with argon and 1,3-diisopropylbenzene (100 ml) added. The solution was brought to reflux and P(OEt)₃ (53.15 g, 320 mmol) in 1,3-diisopropylbenzene (30 ml) was added dropwise over 10 hours, followed by a further refluxing for 48 hours. After cooling the solvent was distilled off under vacuum at 30 °C to give a brown solid residue. The solid was washed with hexanes (2×100 mL) before being dissolved in diethyl ether and filtered. The resulting yellow filtrate was taken to dryness to give pale yellow solid. Column chromatography of the residue on silica gel using ethyl estate-methanol-acetic acid (100:5:1) as eluent (*R_f*:0.38) gave **TEtBDP** as a crystalline white solid. Yield: 9.67g, 69%. Anal. Calc. for TEtBDP: C, 48.00; H, 6.91. Found: 47.90; H, 6.83; ¹H NMR (400 MHz CDCl₃) δ (ppm): 1.32 (td, 12H, CH₃); 4.13 (m, 8H, CH₂); 7.89 (m, 4H, CH); ³¹P NMR (400 MHz CDCl₃/(CH₃O)₃PO) δ (ppm): 16.87; ¹³C NMR (100 MHz CDCl₃) δ (ppm): 16.46 (CH₃), 62.57 (CH₂), 131.73 (CH), 133.96 (CP).

Synthesis of Sodium diethyl 1,4-benzenediphosphonate (Na₂DEtBDP)

TEtBDP (5.95 g, 17 mmol) in a mixture of concentrated ammonia (30 %) solution (20 mL), and ethanol (10 mL) was refluxed for 16 h. The solvents were removed *in vacuo* to give white solid. This was dissolved in distilled water (5 mL) and passed through a 50W-X8 cation exchange column (Na⁺ form) using distilled water as eluent. The clear solution was collected and was taken to dryness *in vacuo*. The resulting white solid, was then recrystallized twice from an H₂O/methanol mixture to yield **Na₂DEtBDP** as a white crystalline solid. Yield: 4.73 g, 82%. Anal. Calc. for Na₂DEtBDP.0.5H₂O: C, 34.60; H, 4.36. Found: C, 34.31; H, 4.17.; ¹H NMR (400 MHz D₂O/(CH₃)₂CO) δ (ppm): 1.26 (td, 6H, CH₃); 3.84 (m, 4H), 7.78 (m, 4H, CH). ³¹P NMR (400 MHz D₂O/(CH₃O)₃PO) δ (ppm): 15.61; ¹³C NMR (100 MHz D₂O/(CH₃)₂CO) δ (ppm): 16.32 (CH₃), 61.93 (CH₂), 131.30 (CH), 136.51 (CP).

Synthesis of ZnDEtBDP (1)

Tetrahydrofuran was slowly diffused into a solution of **Na₂DEtBDP** (0.200 g, 0.59 mmol) and Zn(NO₃)₂·6H₂O (0.176 g, 0.59 mmol) in water (8 ml). Single crystals of **ZnDEtBDP** formed after the period of 1 week. The crystals were then filtered off and washed with 5×20 ml THF before

being dried *in vacuo*. Yield: 4.73 g, 53%. Anal. Calc. for **ZnDEtBDP**: C, 33.59; H, 3.95. Found: C, 33.73; H, 4.01.

Single crystal data collection

Single crystals were mounted by freezing to the tip of a glass loop using Paratone oil. Experiments were conducted at 173K on a Nonius kappa diffractometer with a graphite monochromated Mo K α radiation (λ = 0.71073 Å) and equipped with a APEX II CCD detector. The intensity data collection was performed in the scanning mode with the goniometer and detector angular settings optimized using the program COSMOS. The unit cell and the orientation matrix were refined using the entire data set of reflections. The diffraction spots were measured in full with a high accuracy, scaled, corrected for Lorentz-polarization correction, and integrated using HKL Denzo and Scalepack (Otwinowski & Minor 1997). Absorption effects were empirically corrected by using SADABS (Sheldrick, G. M., SADABS; Universitat Gottingen, 1997). Full-matrix least-squares refinement on F² was carried out using SHELXL97. The crystallographic data and conditions for structure analysis are listed below. The solvent water molecules could not be located. All the hydrogens were fixed by placing them in a riding mode.

Crystallographic data for **1**: Crystal data for Zn(C₆H₄)(PO₃C₂H₅)₂, **1**: M = 357.57, orthorhombic, *Ibam*, a = 15.729(3), b = 23.170(5), c = 9.737(2) Å, V = 3548.6(12) Å³, Z = 8, D_c = 1.391 g cm⁻³, T = 173(2) K, μ (Mo K α) = 1.581 mm⁻¹, crystal size 0.09 x 0.05 x 0.03 mm. A total of 1612 reflections were processed of which 1241 were unique and considered significant with $I_{\text{net}} > 2\sigma(I_{\text{net}})$. Final residuals for $I_{\text{net}} > 2\sigma(I_{\text{net}})$ were R = .0610 and R_w = .1555 (GoF = 0.977) for 107 parameters. Final data are deposited with the Cambridge Structural Database with registry number CCDC 798055.

Powder X-ray data collection

To study the pore stability, samples were heated, in air for 1 hr and 24 hrs at 120°C and 24 hrs at 200 °C. In the absence of a VT-PXRD, the samples were heated in the Al PXRD sample holder and rapidly transferred from the oven to the adjacent PXRD. An infrared thermal sensor measured the temperature of the sample holder as 80°C after 2 min and 50°C after 6 min. The scan rate for the PXRD was 5 deg/min so the major peaks (below 15 deg in 2 theta) were scanned while the temperature was above 80 C. Also, the relative humidity in our Calgary lab is ~10% which, coupled with the heat of the holder, gives us high confidence no water vapour sorbed into the hydrophobic pores of **1** prior to measurement.

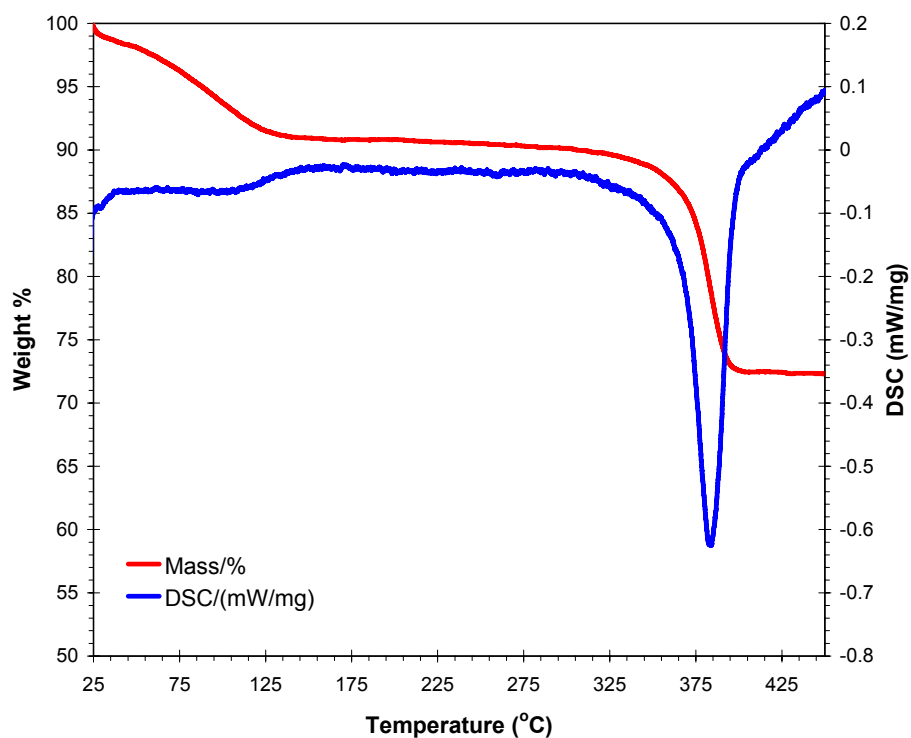


Figure S1. TGA of **ZnDEtBDP·THF**. Thermal analysis (TGA-DSC) data were recorded on a Netzsch STA 449C apparatus with a heating rate of 2°C /min in the temperature range of 25 to 450°C under N₂ atmosphere.

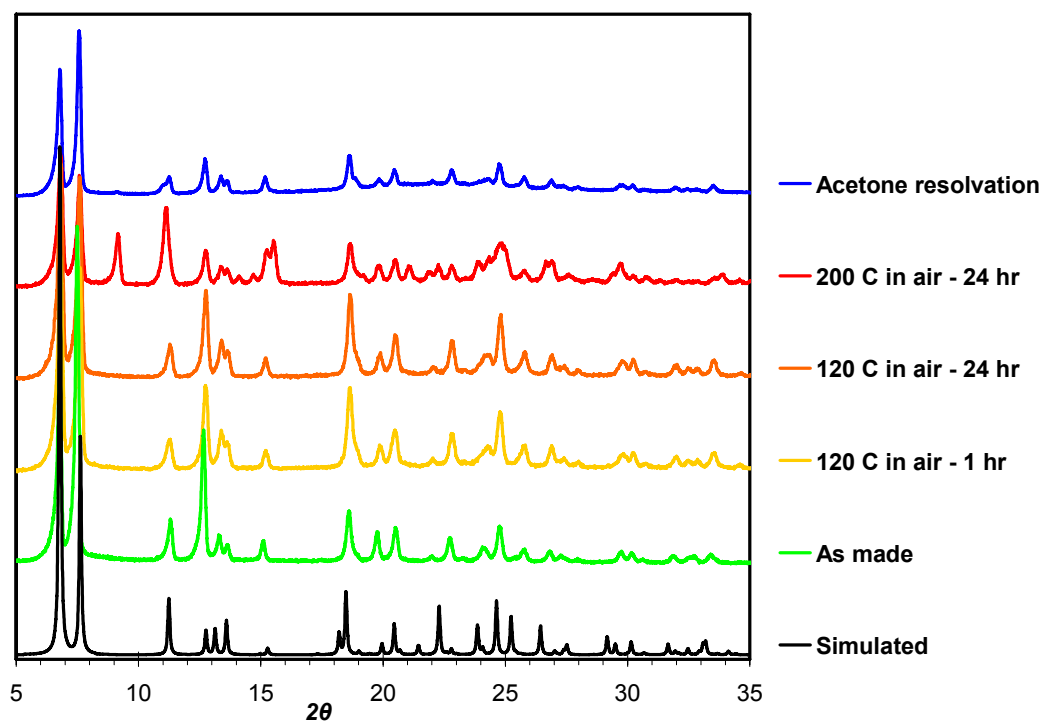


Figure S2. PXRD of the as made **ZnDEtBDP·THF** and post adsorption in comparison to the simulated pattern.

Adsorption Measurements

The adsorption isotherms for CO₂ (99.998%), N₂ (99.999%) and H₂ (99.999%) were conducted using an Accelerated Surface Area & Porosimetry System (ASAP) 2020 supplied by Micromeritics Instruments Inc. In a general procedure, the dry sample (~100 mg) was loaded into the glass analysis tube. The sample was heated under vacuum ($\sim 10^{-3}$ mbar) 40 °C for 18 hrs. No increase in surface area was observed at higher activation temperatures. After this the outgas rate was less than 1 $\mu\text{bar hr}^{-1}$. The sample was then backfilled with N₂ before being transferred to the analysis port where it was evacuated for at least a further 240 min before the analysis was started.

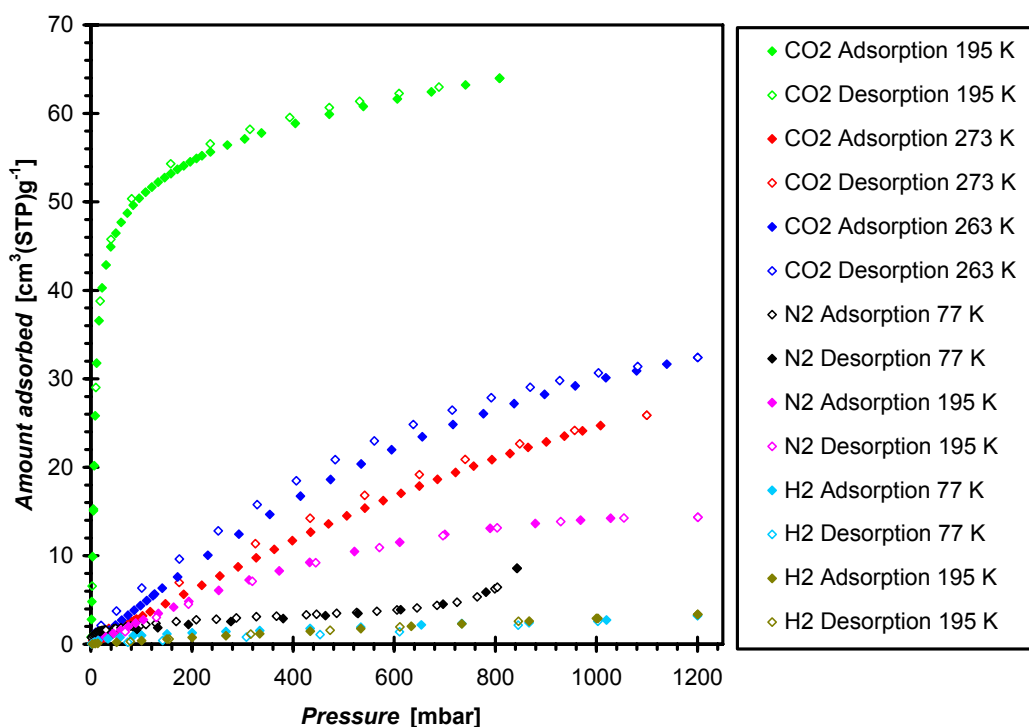
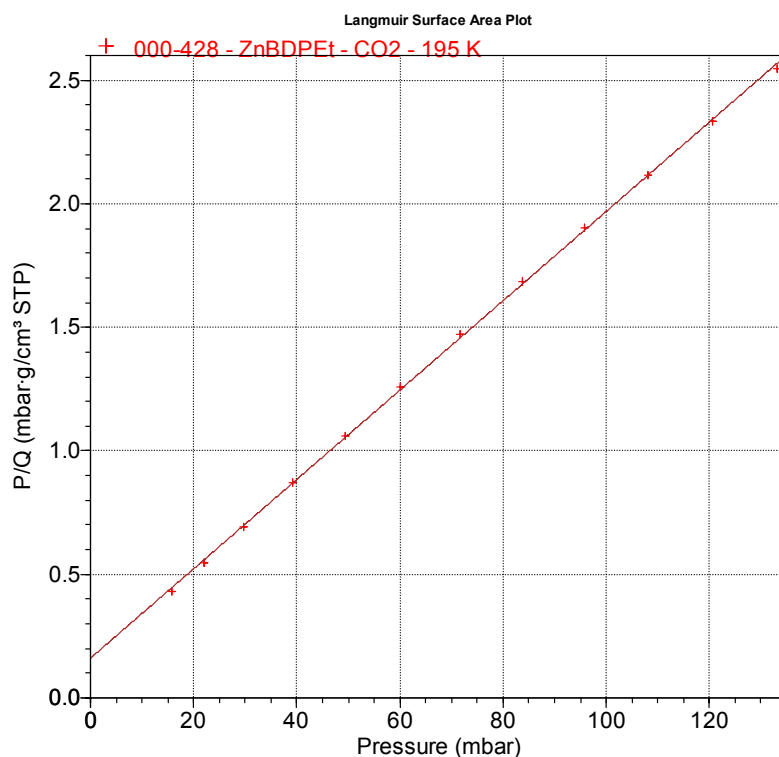


Figure S3. Gas sorption isotherms for 1: CO₂ at 195, 263, 273 K and N₂ and H₂ at 77 and 195 K.

Temperature (K)	Amount of gas adsorbed [cm ³ (STP)/g]		
	N ₂	H ₂	CO ₂
77	4.52 [†]	3.24	-
195	14.35	3.36	63.98
263	-	-	32.41
273	-	-	25.89

[†]Taken at 0.77 P/P₀ to avoid contributions from condensation between particles.

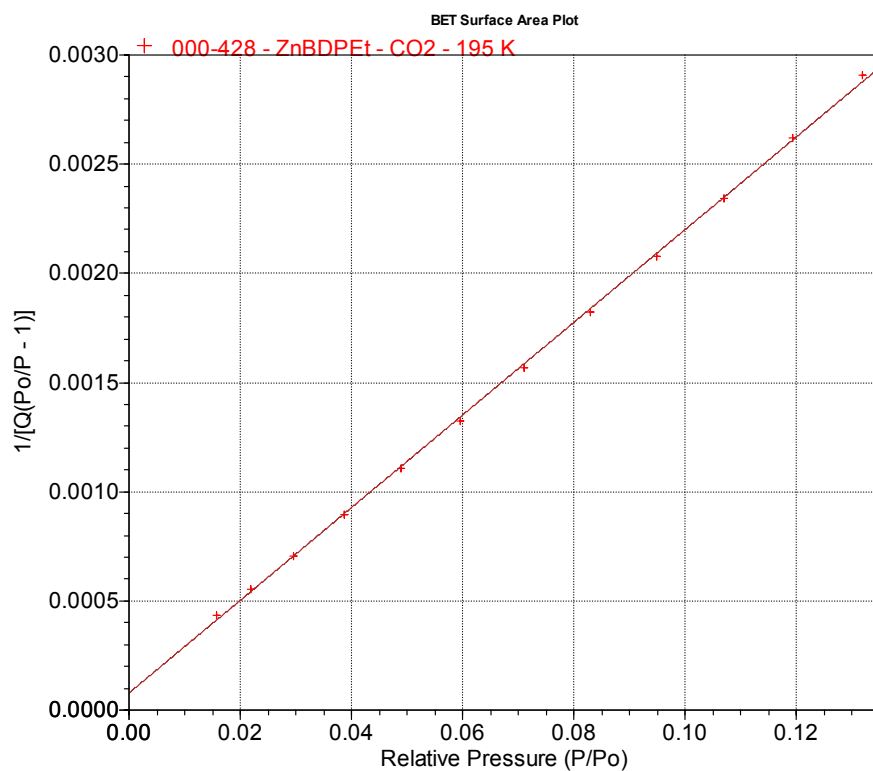
Table S1. Summary of gas adsorption of **ZnBDPEt**.



Langmuir Surface Area Report

Langmuir Surface Area:	312.1122 ± 1.5846 m ² /g
Slope:	0.018080 ± 0.000092 g/cm ³ STP
Y-Intercept:	0.161086 ± 0.007230 g/cm ³ STP
b:	0.112239 1/mbar
Qm:	55.3093 cm ³ /g STP
Correlation Coefficient:	0.999871
Molecular Cross-Sectional Area:	0.2100 nm ²

Figure S4. Langmuir Surface area analysis of CO₂ adsorption at 195 K in **ZnDEtBDP**



BET Surface Area Report

BET Surface Area:	264.7848 ± 1.6342 m ² /g
Slope:	0.021234 ± 0.000131 g/cm ³ STP
Y-Intercept:	0.000078 ± 0.000010 g/cm ³ STP
C:	272.327150
Qm:	46.9224 cm ³ /g STP
Correlation Coefficient:	0.9998093
Molecular Cross-Sectional Area:	0.2100 nm ²

Figure S5. BET Surface area analysis of CO₂ adsorption at 195 K in **ZnDEtBDP**

Determining the Enthalpy of Adsorption

To allow extrapolation between adsorption points the adsorption branches of the 273.37 and 293.46 K CO₂ isotherms were fitted via least-squares regression to the Virial model (equation 1).¹⁻⁷

$$\ln(n/p) = A_0 + A_1n + A_2n^2 \dots \text{(equation 1)}$$

Only equivalent adsorption values were fitted on both isotherms. The Virial plot and parameters are shown in figure S7 and table S1 respectively. The isosteric enthalpies of adsorption at zero loading were calculated from the A_0 parameters determined using equation 1 for adsorption data at 273.37 and 263.37 K. The enthalpies of adsorption of CO₂ for specific surface coverage's were calculated using the van't Hoff isochore.

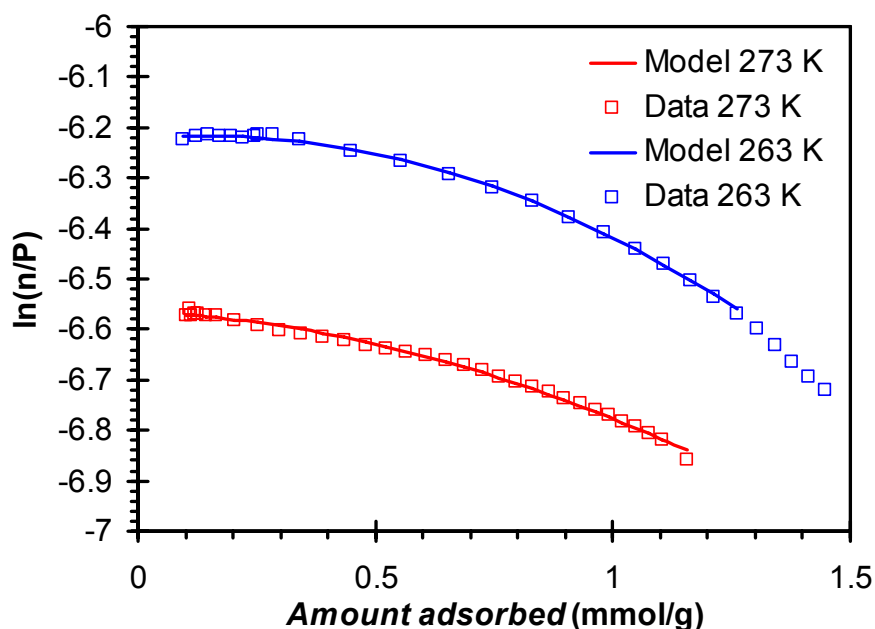


Figure S6. Virial plots

Table S2: Summary of the fitted Virial parameters

Virial Parameter	263 K	273 K
A_0	-6.56446	-6.22155
A_1	-0.04679	0.07484
A_2	-0.16571	-0.27189

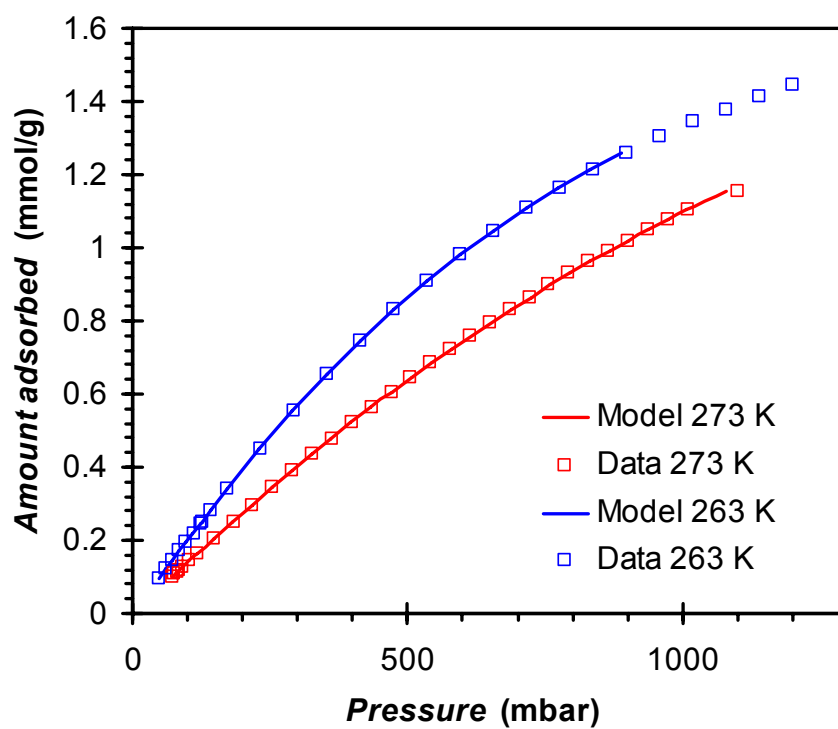


Figure S7. CO₂ sorption isotherms for 263 and 273 K showing the data and fit from the Virial model.

References

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