

Electronic Supporting Information for

Hitherto unknown eight-connected frameworks formed from $A_4B_4O_{12}$ metal organophosphate heterocubanes

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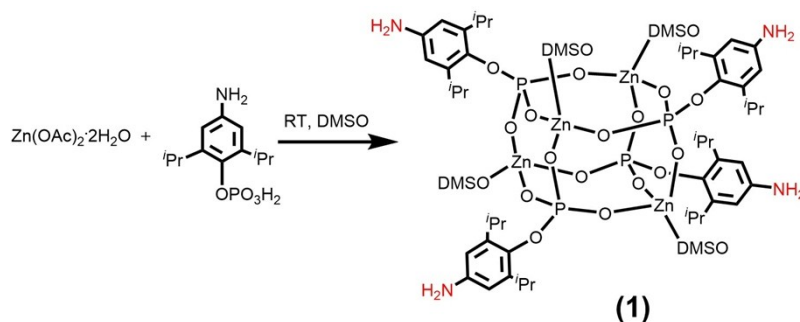
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Experimental Section

Instruments and methods: The starting materials used in the present study and the products formed were found to be stable towards moisture and air, and hence no specific precaution was taken to rigorously exclude air or moisture during all manipulations. The melting points were measured in glass capillaries and are reported uncorrected. Infrared spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer as KBr diluted discs. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. ^{31}P CP-MAS NMR spectra were recorded on a Bruker Advance spectrometer. For CP-MAS NMR measurements, a 4.0 mm zirconia rotor with a spin rate of $\sim 10\,000$ Hz at 295–300 K has been employed. Thermogravimetric analysis was carried out on a Perkin Elmer Pyris Diamond TG/DTA, under a stream of nitrogen gas at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Commercial grade solvents were purified and freshly distilled prior to use. Powder X-ray diffraction measurements were recorded on a Philips X'pert Pro (PANalytical) diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54190\text{ \AA}$). Gas sorption and uptake measurements were performed on a Quantachrome Autosorb-1C analyzer using UHP-grade gases. N_2 adsorption measurements were evaluated at 77 K and 1 bar. Prior to gas adsorption measurements, the samples were dried under air for 24 h, solvent exchanged with dichloromethane and evacuated at RT for 6-8 h under ultrahigh vacuum. Other starting materials such as $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (S.d.Fine-Chem.) were used as received. 4-amino-2,6-diisopropylphenyl phosphate (adippH₂ or H_2L^1),^[1] 4-acetylamino-2,6-di-iso-propylphenyl phosphate (acdippH₂ or H_2L^2)^[2] and 3,6-di-2-pyridyl-1,2,4,5-tetrazine (dptz)^[3] were prepared according to an earlier published procedure.

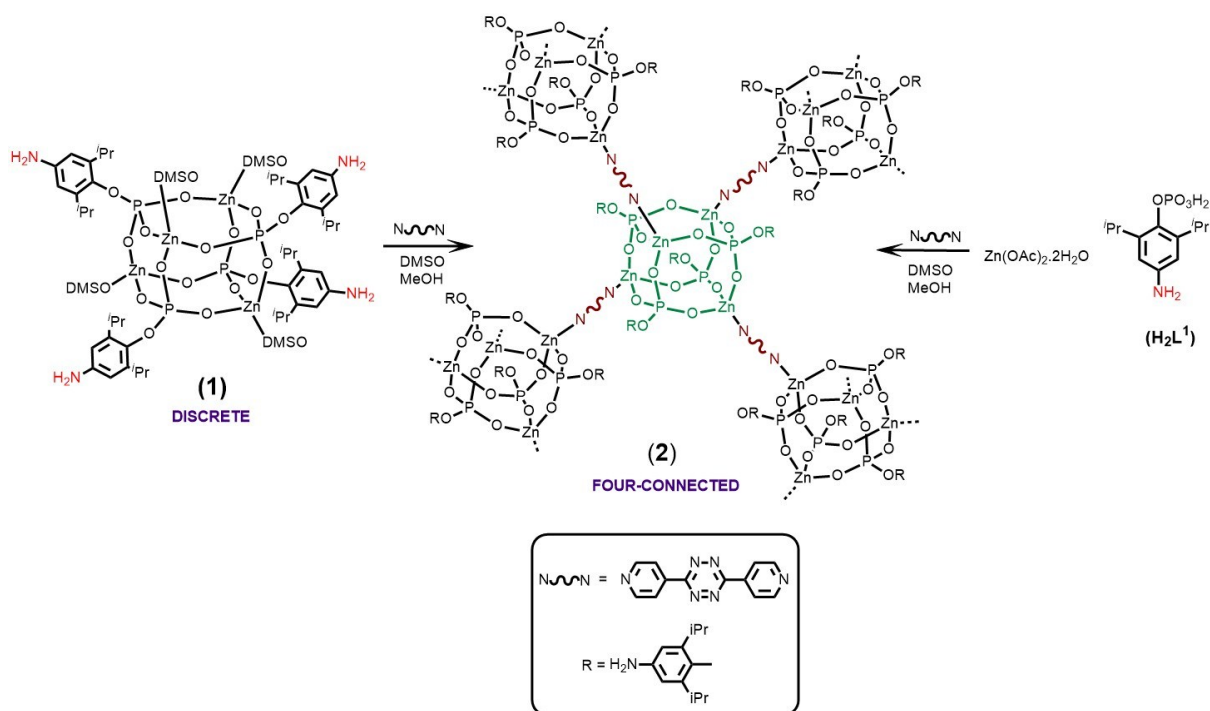
X-ray Crystallography. Suitable single crystals of each of the compounds were selected and mounted on a Rigaku Saturn 724+ CCD diffractometer for unit cell determination and intensity data collection. Single crystals of **1** slowly lose transparency when kept outside the mother liquor at ambient conditions. Hence, they were transferred from the solvent to Paratone oil for data collection. Thin needle like single crystals of **2** diffracted weakly. Single crystal of **3** were directly transferred from the mother liquor to Paratone oil and mounted on a loop. Single crystals of **3** when kept outside the mother liquor for few hours under ambient atmospheric conditions transformed in to a pseudo-polymorphic form **3'** where the methanol solvates in the voids are replaced by water molecules. Data integration and

indexing were carried out using the Rigaku CrystalClear-SM Expert^[4] and finally solved by direct methods (SIR-97)^[5] programs in WinGX module^[6]. The final refinement of the structure was carried out using full least-squares methods on F^2 using SHELXL-2014^[7] resulted in the structure determination for all the compounds (details in Table S1). The diffuse electron density in the lattice/voids that couldn't be modeled was refined with routine PLATON SQUEEZE program.^[8] The electron count of 226.9 in the solvent accessible void of **3** accounts for one methanol and one water molecule per asymmetric unit while the squeezed electron count for **3'** approximately corresponds to 1.5 molecule of water per asymmetric unit (considering the H-atoms that could not be refined).



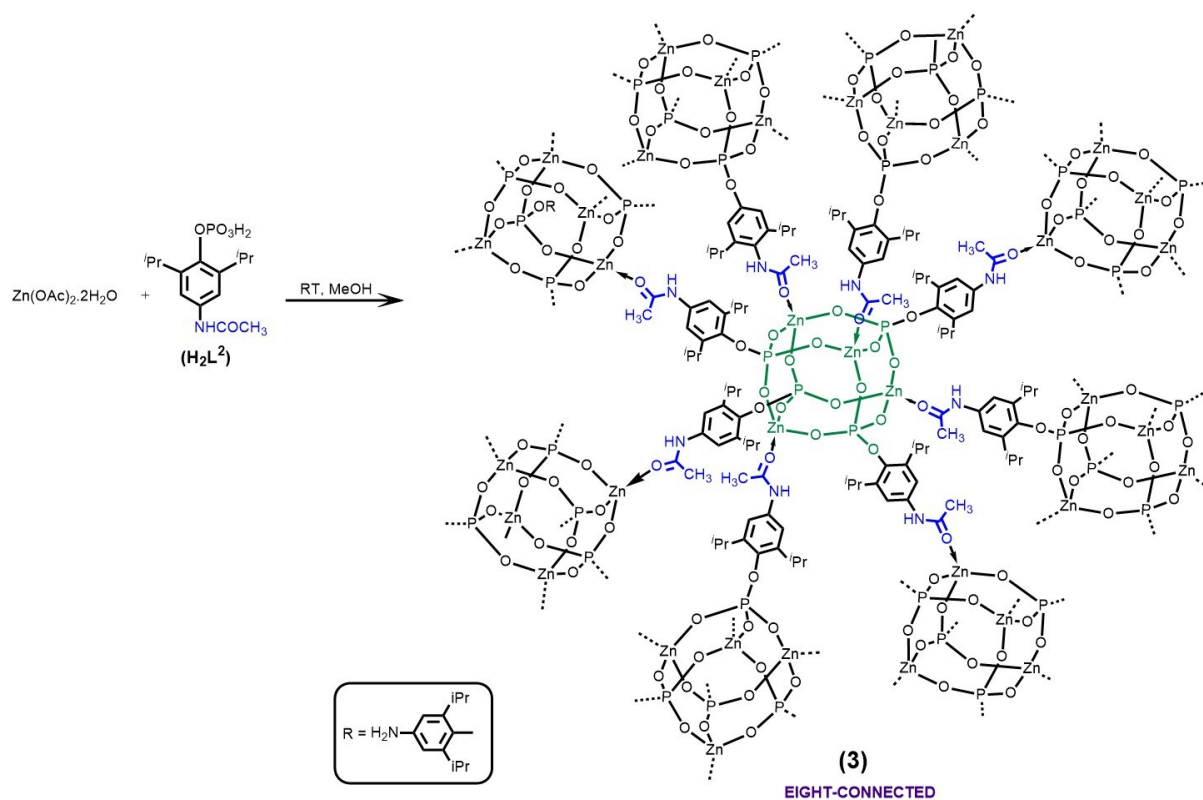
Scheme S1. Synthesis of discrete D4R SBU **1**.

*Synthesis of $[Zn(L^1)(DMSO)]_4$ (**1**).* A solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.220 g, 1.0 mmol) in DMSO (10 mL) was added to a solution of H_2L^1 (0.273 g, 1.0 mmol) in DMSO (10 mL) at room temperature. The resultant reaction mixture was stirred, filtered and kept at room temperature undisturbed for crystallization. Block shape crystals of **1** formed over a period of twenty days. Yield: 180 mg (43.4 %). Mp: > 250 °C. Anal. Calcd. for $C_{56}H_{96}N_4O_{20}P_4S_4Zn_4$ (%): C, 40.54; H, 5.83; N, 3.38; S, 7.73. Found: C, 39.95; H, 6.19; N, 2.75; S, 8.19. FT-IR (KBr/ cm^{-1}): 3400 (br), 3241 (m), 3016 (w), 2961 (s), 2868 (m), 1606 (m), 1470 (m), 1381 (w), 1347 (w), 1315 (w), 1272 (w), 1246 (w), 1175 (vs), 1019 (vs), 949 (m), 908 (s), 834 (m), 769 (w), 706 (w), 531 (w). ^{31}P CP-MAS NMR (202 MHz): δ -6.16 ppm. TGA: Temp. range °C (% weight loss): 30-330 (24.4); 330-550 (34.7).



Scheme S2. Synthetic route for supramolecular assembly of 4-connected 3D network of D4R zinc phosphate **2**.

*Synthesis of $[Zn_4(L^1)_4(dptz)_2]_n$ (**2**).* A solution of 3,6-di-2-pyridyl-1,2,4,5-tetrazine (0.118 g, 0.5 mmol) in MeOH (100 mL) was slowly layered over a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.220 g, 1.0 mmol) and H_2L^1 (0.273 g, 1.0 mmol) in DMSO (30 mL). It was then kept undisturbed at ambient condition for crystallization. Thin needle shaped dark red crystals of **2** were obtained over a period of four weeks from this solution. Yield: 160 mg (35.2 %). Mp: > 250 °C. Anal. Calcd. for $C_{36}H_{44}N_8O_8P_2Zn_2$ (%): C, 47.54; H, 4.88; N, 12.32. Found: C, 48.68; H, 4.99; N, 13.13. FT-IR (KBr/ cm^{-1}): 3426 (br), 2965 (s), 2869 (m), 1608 (vs), 1467 (m), 1404 (m), 1384 (m), 1342 (w), 1247 (w), 1152 (s), 1066 (m), 1019 (vs), 911 (m), 834 (m), 713 (m), 612 (w), 529 (m). ^{31}P CP-MAS NMR (202 MHz): δ -4.4 ppm. TGA: Temp. range °C (% weight loss): 30-100 (3.2); 100-220 (13.6); 220-550 (44.6).



Scheme S3. Room temperature assembly of a rare 8-connected 3D network of D4R zinc phosphates **3**.

*Synthesis of $\{[\text{Zn}_4(\text{L}^2)_4] \cdot 4\text{CH}_3\text{OH}\}_n$ (**3**).* A methanol solution (20 mL) of $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ (0.220 g, 1.0 mmol) was slowly added to a methanol (30 mL) solution of H_2L^2 (0.315 g, 1.0 mmol) at room temperature and the resultant solution was stirred for 10 minutes and filtered to give a clear solution. Colourless crystals of **3** formed over a period of fifteen days at room temperature. Yield: 140 mg (34.1 %). Mp: > 250 °C. Anal. Calcd. for $\text{C}_{15}\text{H}_{24}\text{NO}_6\text{PZn}$ (%): C, 43.87; H, 5.89; N, 3.41. Found: C, 42.46; H, 5.26; N, 3.28. FT-IR ($\text{KBr}/\text{cm}^{-1}$): 3423 (br), 3295 (br), 2967 (s), 2870 (m), 1660 (s), 1602 (s), 1557 (m), 1470 (s), 1421 (m), 1380 (m), 1342 (m), 1280 (m), 1185 (vs), 1021 (vs), 953 (m), 907 (s), 782 (w), 738 (m), 688 (w), 565 (m), 539 (m). ^{31}P CP-MAS NMR (202 MHz): δ -5.9 ppm. TGA: Temp. range °C (% weight loss): 30-350 (5.0); 350-500 (45.3).

Table S1. Crystal data and structure refinement details for **1-3'**.

Compound	1	2	3	3'
Empirical formula	C ₅₆ H ₉₆ N ₄ O ₂₀ P ₄ S ₄ Zn ₄	C ₃₆ H ₄₃ N ₈ O ₈ P ₂ Zn ₂	C ₁₅ H ₂₄ N ₁ O ₆ P ₁ Zn ₁	C ₁₄ H ₂₆ N ₁ O ₈ P ₁ Zn ₁
Formula weight	1658.96	908.46	410.69	432.69
Temperature (K)	100(2)	150(2)	120(2)	150(2)
Crystal system	Orthorhombic	Tetragonal	Tetragonal	Tetragonal
Space group	<i>Iba2</i>	<i>P4/nnc</i>	<i>I-4</i>	<i>I-4</i>
a (Å)	21.231(8)	18.2767(4)	16.942(5)	16.7211(2)
b (Å)	21.328(8)	18.2767(4)	16.942(5)	16.7211(2)
c (Å)	20.064(7)	30.7812(9)	15.489(5)	15.5352(4)
Volume (Å ³)	9085(6)	10282.1(5)	4446(3)	4343.6(2)
Z	4	8	8	8
Reflections collected	34447	73345	16615	49457
Independent reflections	6093 [R(int) = 0.0596]	4541 [R(int) = 0.1350]	3890 [R(int) = 0.0347]	3810 [R(int) = 0.0860]
Completeness to θ	99.60%	99.80%	99.70%	99.80%
Data / restraints / parameters	6093 / 101 / 444	4541 / 34 / 279	3890 / 0 / 225	3810 / 0 / 232
Goodness-of-fit on F ²	1.092	1.07	1.042	1.08
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.0726, wR2 = 0.1700	R1 = 0.0955, wR2 = 0.2324	R1 = 0.0285, wR2 = 0.0708	R1 = 0.0393, wR2 = 0.1041
R indices (all data)	R1 = 0.0741, wR2 = 0.1710	R1 = 0.1491, wR2 = 0.2683	R1 = 0.0297, wR2 = 0.0715	R1 = 0.0415, wR2 = 0.1067
Largest diff. peak and hole e.Å ⁻³	1.009 and -0.731	0.706 and -0.399	0.340 and -0.259	0.385 and -0.352

Table S2. Selected bond distances [Å] and angles [°] for **1**.

O(3)-Zn(1)	1.913(9)	O(3)-Zn(1)-O(6)	117.1(4)	P(2)-O(7)-Zn(2)	129.4(6)
O(4)-Zn(1)	1.941(7)	O(3)-Zn(1)-O(4)	114.8(4)	P(2)-O(8)-Zn(2)#1	162.7(7)
O(6)-Zn(1)	1.922(9)	O(6)-Zn(1)-O(4)	111.3(4)	S(1)-O(9)-Zn(1)	128.7(6)
O(9)-Zn(1)	2.014(10)	O(3)-Zn(1)-O(9)	100.7(4)	S(2)-O(10)-Zn(2)	128.5(6)
O(2)-Zn(2)	1.932(9)	O(6)-Zn(1)-O(9)	109.4(4)	O(2)-P(1)-O(4)#1	113.6(5)
O(7)-Zn(2)	1.911(10)	O(4)-Zn(1)-O(9)	101.6(4)	O(2)-P(1)-O(3)	115.5(5)
O(8)-Zn(2)#1	1.893(8)	O(8)#1-Zn(2)-O(7)	116.9(4)	O(4)#1-P(1)-O(3)	110.8(5)
O(10)-Zn(2)	1.990(9)	O(8)#1-Zn(2)-O(2)	113.9(4)	O(2)-P(1)-O(1)	107.5(5)
O(1)-P(1)	1.612(8)	O(7)-Zn(2)-O(2)	106.9(4)	O(4)#1-P(1)-O(1)	105.6(5)
O(2)-P(1)	1.501(9)	O(8)#1-Zn(2)-O(10)	103.1(4)	O(3)-P(1)-O(1)	102.7(5)
O(3)-P(1)	1.543(9)	O(7)-Zn(2)-O(10)	107.0(4)	O(7)-P(2)-O(8)	111.3(5)
O(4)-P(1)#1	1.513(9)	O(2)-Zn(2)-O(10)	108.4(4)	O(7)-P(2)-O(6)	112.9(5)
O(5)-P(2)	1.606(8)	P(1)-O(2)-Zn(2)	128.4(5)	O(8)-P(2)-O(6)	113.9(6)
O(6)-P(2)	1.520(10)	P(1)-O(3)-Zn(1)	141.9(6)	O(7)-P(2)-O(5)	104.2(5)
O(7)-P(2)	1.504(9)	P(1)#1-O(4)-Zn(1)	128.6(5)	O(8)-P(2)-O(5)	106.0(5)
O(8)-P(2)	1.505(9)	P(2)-O(6)-Zn(1)	125.8(6)	O(6)-P(2)-O(5)	107.8(5)

Table S3. Selected bond distances [Å] and angles [°] for **2**.

Zn(1)-O(3)	1.902(5)	O(3)-Zn(1)-O(1)	114.7(2)	O(2)#2-P(1)-O(1)	111.2(3)
Zn(1)-O(1)	1.906(5)	O(3)-Zn(1)-O(2)	119.0(3)	O(3)#1-P(1)-O(4)	107.7(3)
Zn(1)-O(2)	1.919(6)	O(1)-Zn(1)-O(2)	106.8(2)	O(2)#2-P(1)-O(4)	104.0(3)
Zn(1)-N(1)	2.033(6)	O(3)-Zn(1)-N(1)	98.8(3)	O(1)-P(1)-O(4)	103.9(3)
P(1)-O(3)#1	1.476(6)	O(1)-Zn(1)-N(1)	114.1(3)	P(1)-O(1)-Zn(1)	128.5(4)
P(1)-O(2)#2	1.488(6)	O(2)-Zn(1)-N(1)	102.8(2)	P(1)#2-O(2)-Zn(1)	140.3(4)
P(1)-O(1)	1.504(5)	O(3)#1-P(1)-O(2)#2	114.2(4)	P(1)#1-O(3)-Zn(1)	144.7(3)
P(1)-O(4)	1.608(5)	O(3)#1-P(1)-O(1)	114.6(3)	C(13)-N(1)-Zn(1)	121.8(6)
				C(17)-N(1)-Zn(1)	120.2(6)

Table S4. Selected bond distances [Å] and angles [°] for **3**.

O(2)-Zn(1)#1	1.895(3)	O(4)-Zn(1)-O(2)#5	113.18(17)	P(1)#3-O(4)-Zn(1)	131.3(2)
O(3)-Zn(1)#2	1.907(3)	O(4)-Zn(1)-O(3)#6	114.2(2)	C(13)-O(5)-Zn(1)	124.2(3)
O(4)-Zn(1)	1.891(3)	O(2)#5-Zn(1)-O(3)#6	112.15(17)	O(2)-P(1)-O(3)	113.3(2)
O(5)-Zn(1)	1.979(3)	O(4)-Zn(1)-O(5)	106.44(13)	O(2)-P(1)-O(4)#4	115.0(2)
O(1)-P(1)	1.609(3)	O(2)#5-Zn(1)-O(5)	108.45(13)	O(3)-P(1)-O(4)#4	111.5(3)
O(2)-P(1)	1.466(3)	O(3)#6-Zn(1)-O(5)	101.38(13)	O(2)-P(1)-O(1)	107.76(16)
O(3)-P(1)	1.486(4)	P(1)-O(2)-Zn(1)#1	153.6(2)	O(3)-P(1)-O(1)	105.89(17)
P(1)-O(4)#4	1.489(3)	P(1)-O(3)-Zn(1)#2	133.8(2)	O(4)#4-P(1)-O(1)	102.28(18)

Table S5. Selected bond distances [Å] and angles [°] for **3'**.

Zn(1)-O(2)	1.898(4)	O(2)-Zn(1)-O(3)#1	113.9(2)	O(3)-P(1)-O(4)	111.8(3)
Zn(1)-O(3)#1	1.916(4)	O(2)-Zn(1)-O(4)#2	112.64(19)	O(2)-P(1)-O(1)	107.5(2)
Zn(1)-O(4)#2	1.917(4)	O(3)#1-Zn(1)-O(4)#2	115.0(2)	O(3)-P(1)-O(1)	106.7(2)
Zn(1)-O(5)#3	1.970(4)	O(2)-Zn(1)-O(5)#3	110.52(18)	O(4)-P(1)-O(1)	102.1(2)
P(1)-O(2)	1.487(4)	O(3)#1-Zn(1)-O(5)#3	100.46(18)	P(1)-O(4)-Zn(1)#2	125.7(3)
P(1)-O(3)	1.495(5)	O(4)#2-Zn(1)-O(5)#3	102.88(17)	P(1)-O(3)-Zn(1)#5	133.8(3)
P(1)-O(4)	1.516(4)	O(2)-P(1)-O(3)	113.6(3)	P(1)-O(2)-Zn(1)	154.9(3)
P(1)-O(1)	1.603(4)	O(2)-P(1)-O(4)	114.2(3)	C(13)-O(5)-Zn(1)#4	125.1(4)

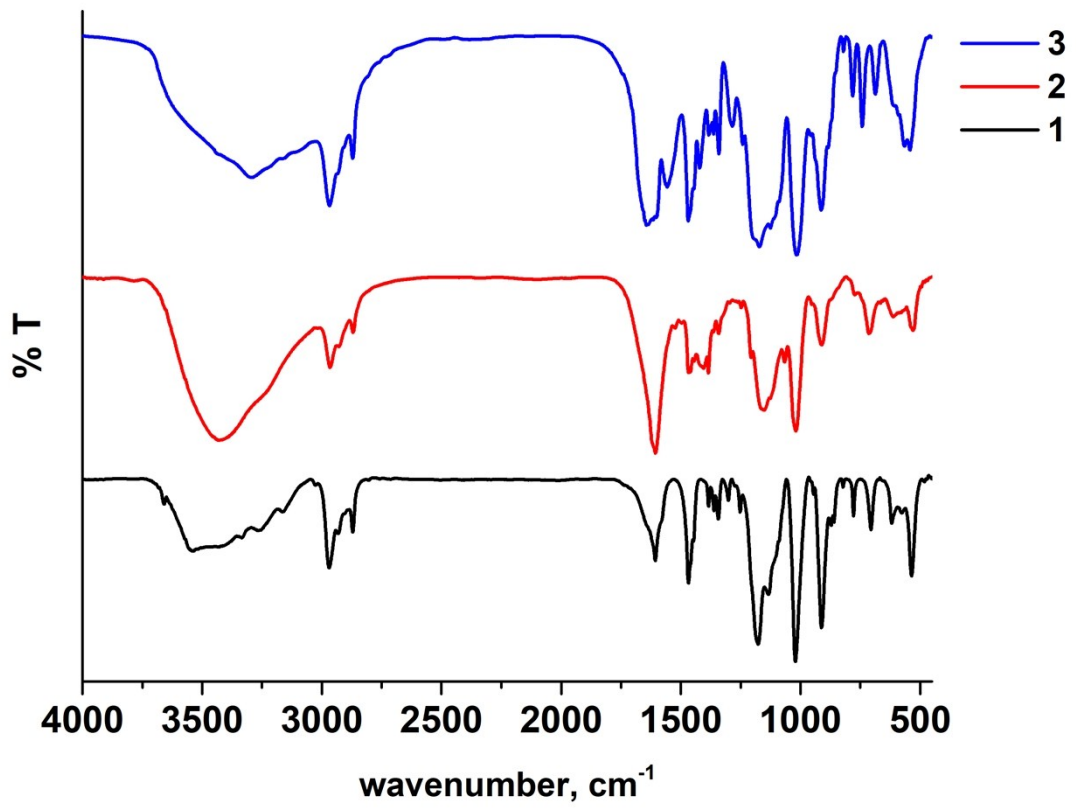


Figure S1. FT-IR spectra of **1-3** as KBr diluted disc.

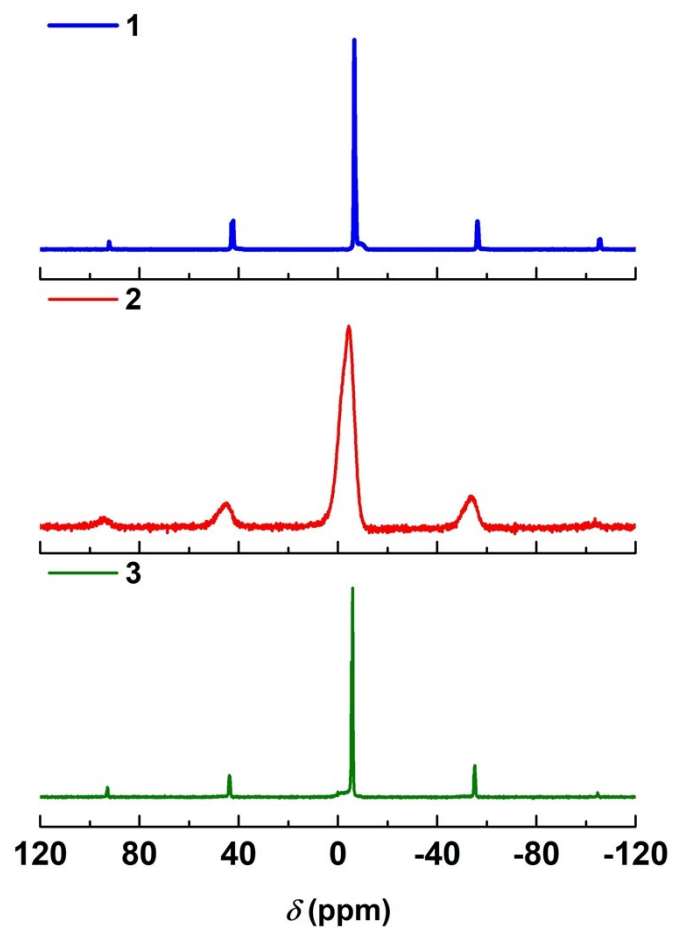


Figure S2. ^{31}P CP-MAS NMR spectra of **1**, **2** and **3**.

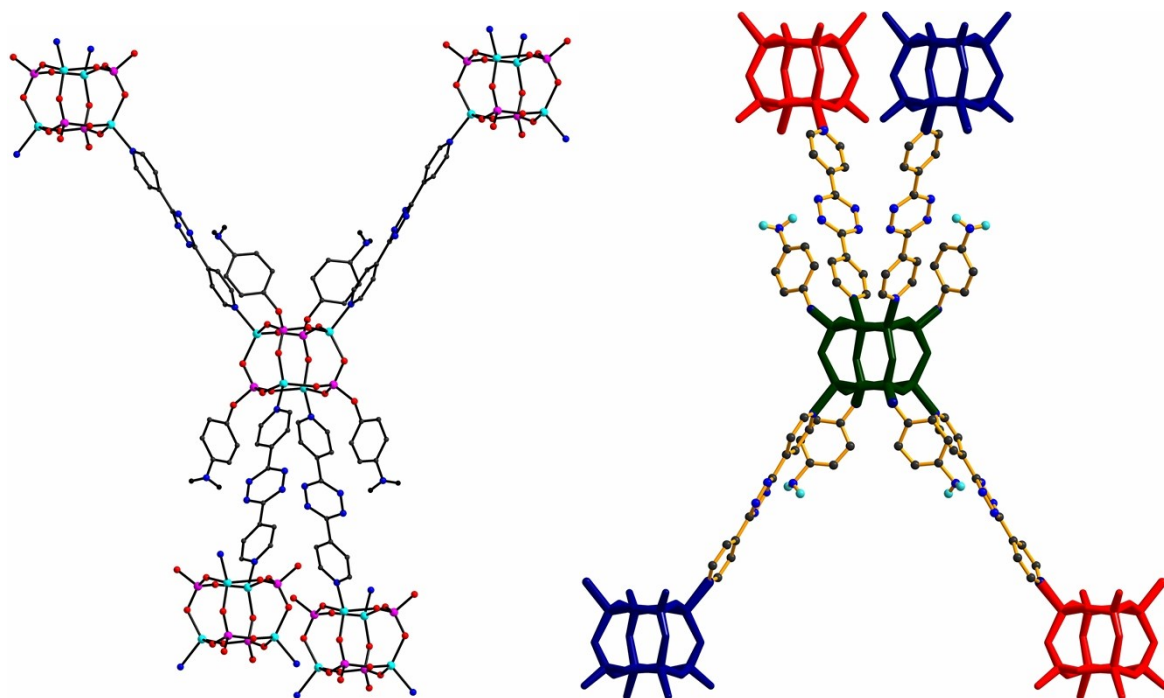


Figure S3. Model representing the linking of D4R SBUs in tetrahedral direction in **2**.

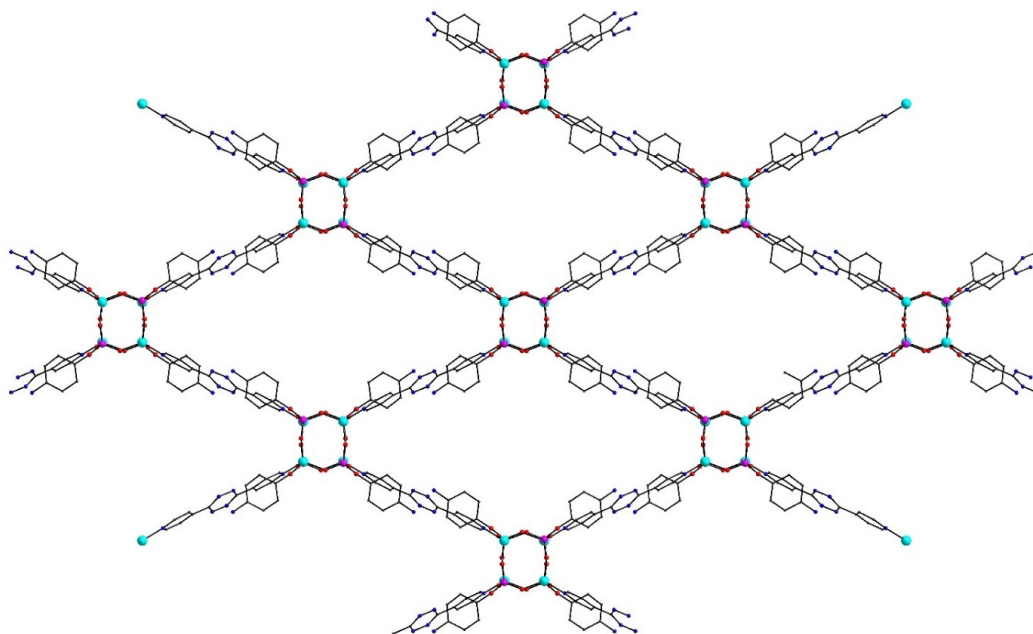


Figure S4. Representation of four connected D4R cubane to form 3D coordination polymer **2** (H-atoms are omitted for clarity).

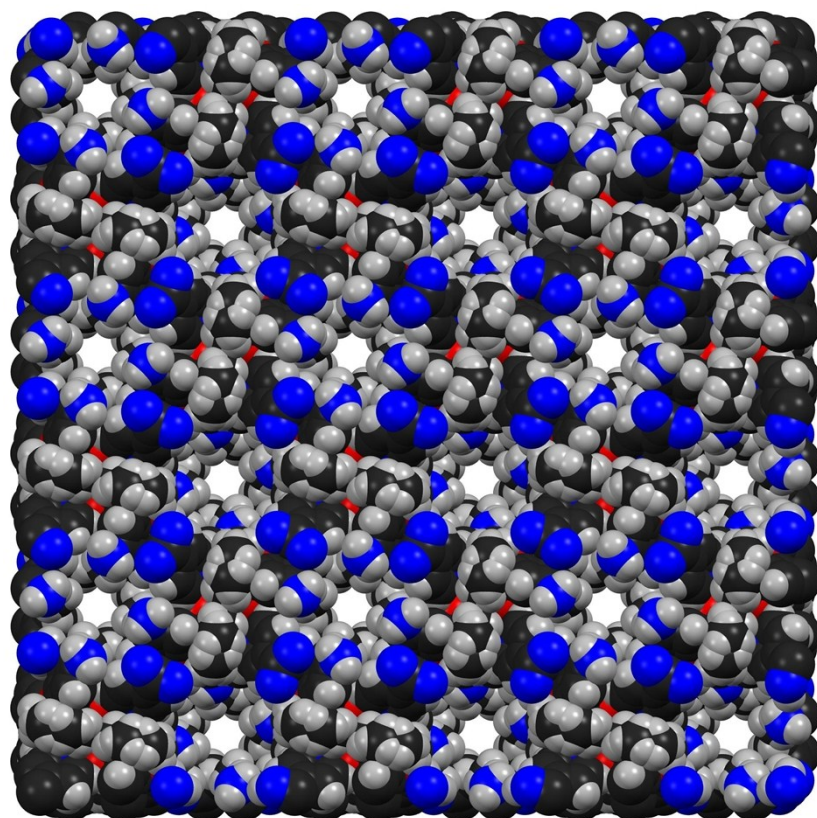


Figure S5. Space-fill model showing the amine functionalities decorating the channels in 3D coordination polymer **2**.

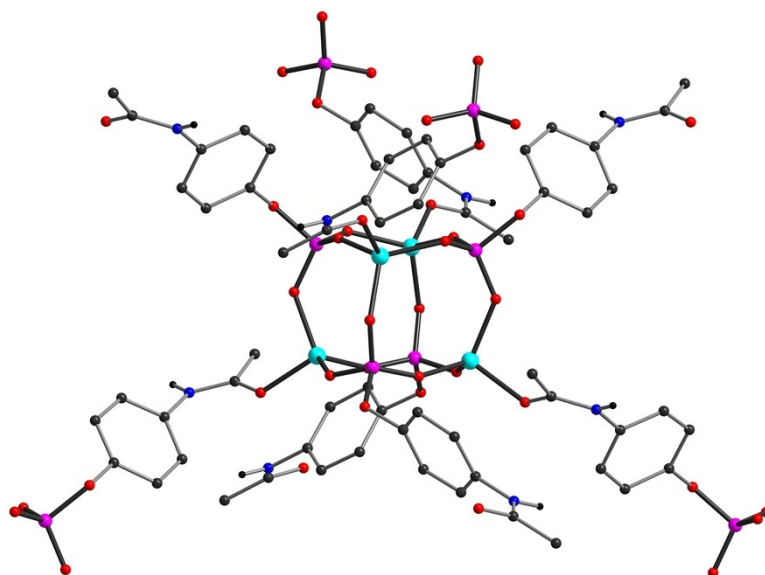


Figure S6. View of eight connected D4R zinc phosphate cubane **3** (H-atoms are omitted for clarity).

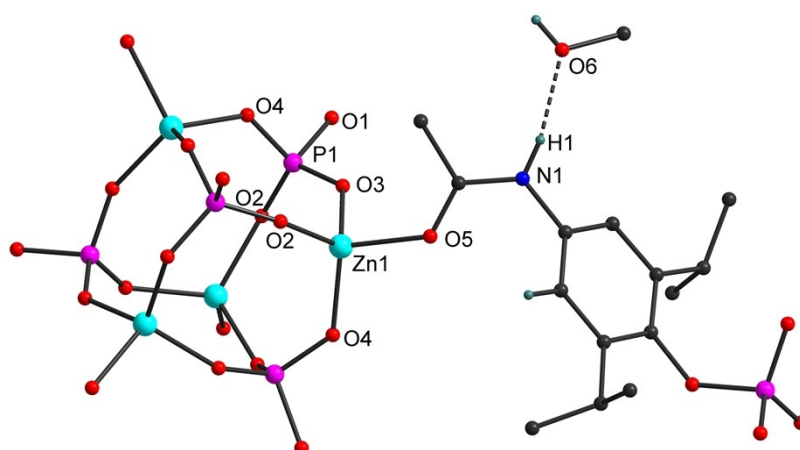


Figure S7. Hydrogen bonding between solvent and phosphate ligand of core of **3** (H-atoms are omitted for clarity).

Table S6. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(6)	0.88	2.23	2.944(7)	138.3

Symmetry transformations used to generate equivalent atoms:

#1 $-y+1, x, -z+1$ #2 $-x+3/2, -y+1/2, z+1/2$ #3 $-y+1, x-1, -z+1$
 #4 $y+1, -x+1, -z+1$ #5 $y, -x+1, -z+1$ #6 $-x+3/2, -y+1/2, z-1/2$

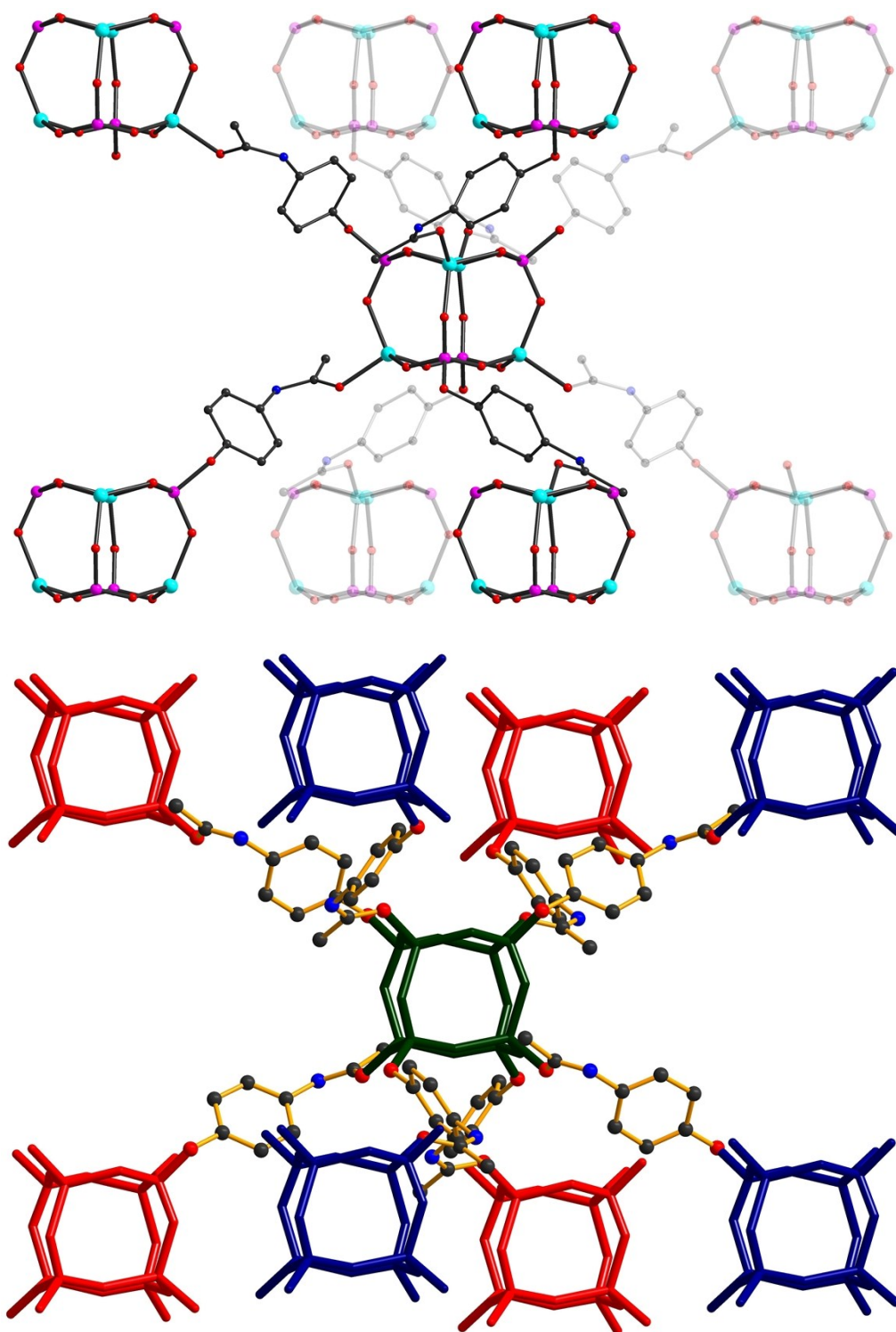


Figure S8. Models representing different views of a rare eight connected D4R cubane **3** (H-atoms and isopropyl groups are omitted for clarity). Blue, red and green cubane signify D4R SBUs above, below and on the plane, respectively giving rise to the 8-connected 3D network **3**.

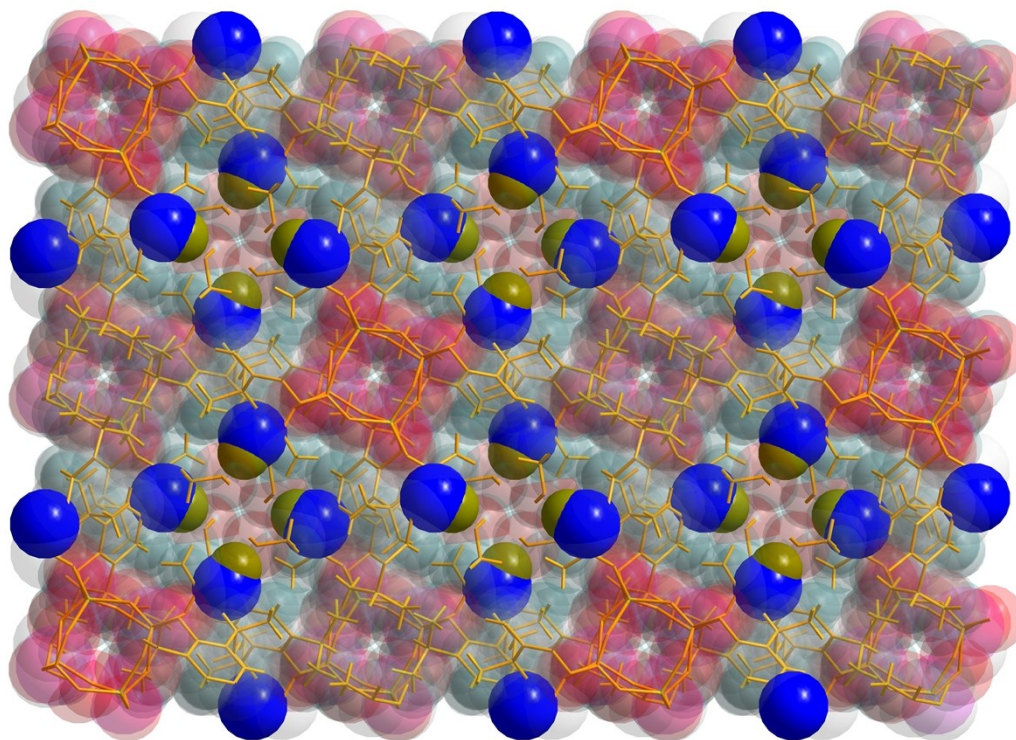


Figure S9. Spacefill model showing the -NH functionalities in **3**. The voids shown are occupied by the H-bonded methanol solvates.

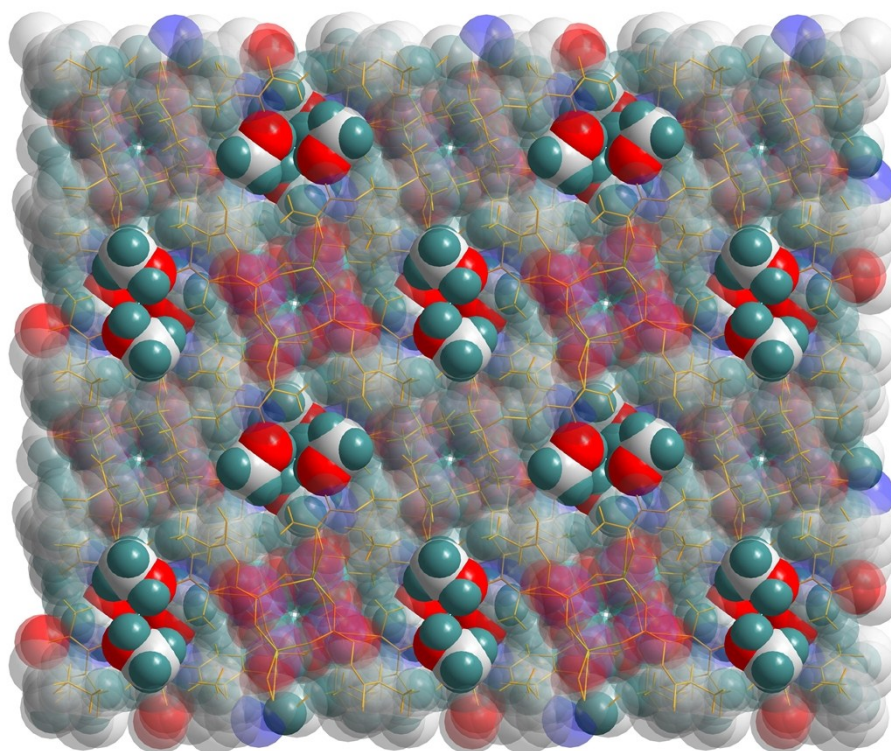


Figure S10. Spacefill model showing the lattice methanol molecules occupying the void spaces in the 3D-framework of **3**.

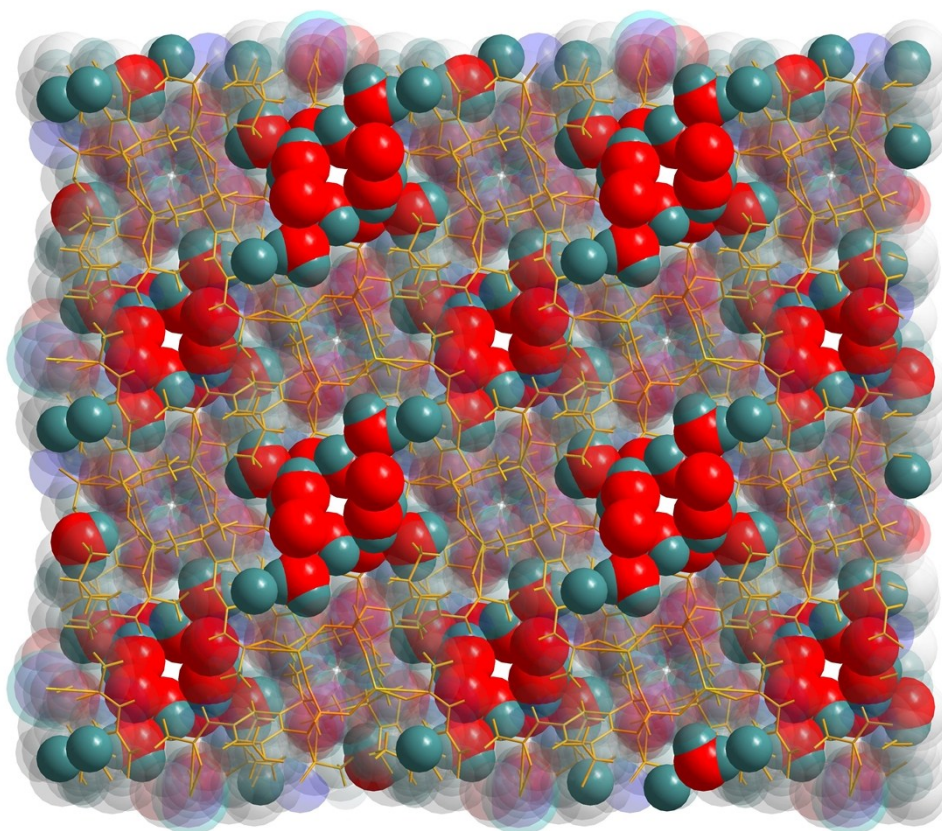


Figure S11. Spacefill model of **3'** framework showing the water molecules along the one-dimensional channels in the voids.

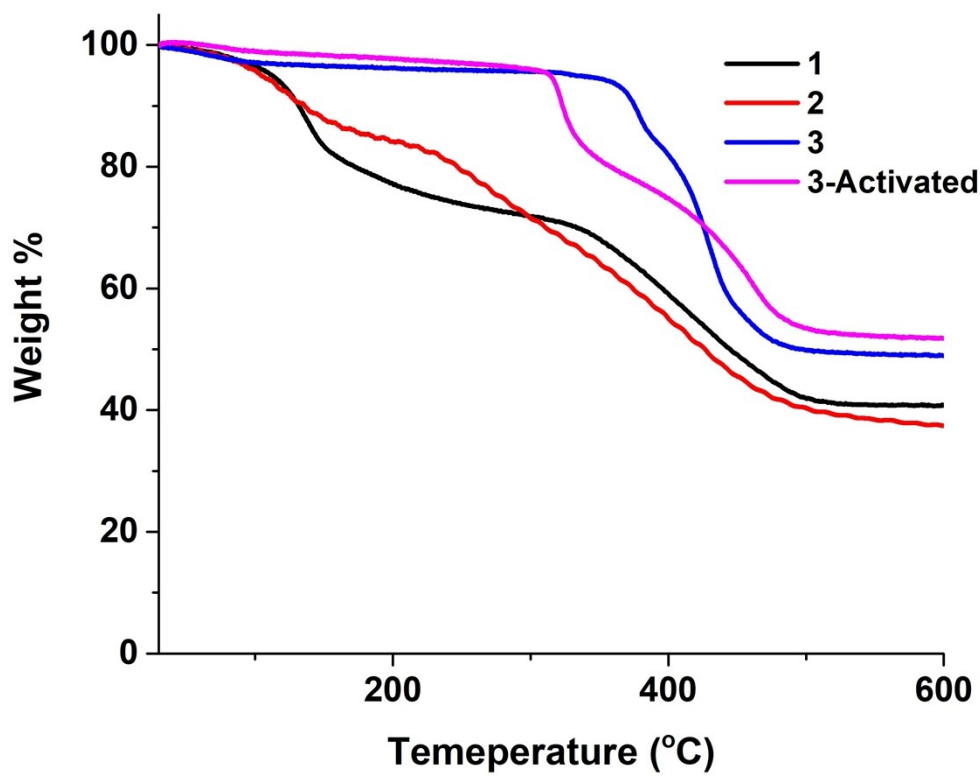


Figure S12. TGA profile of 1-3 at a heating rate of 10 °C/min under N₂ atmosphere.

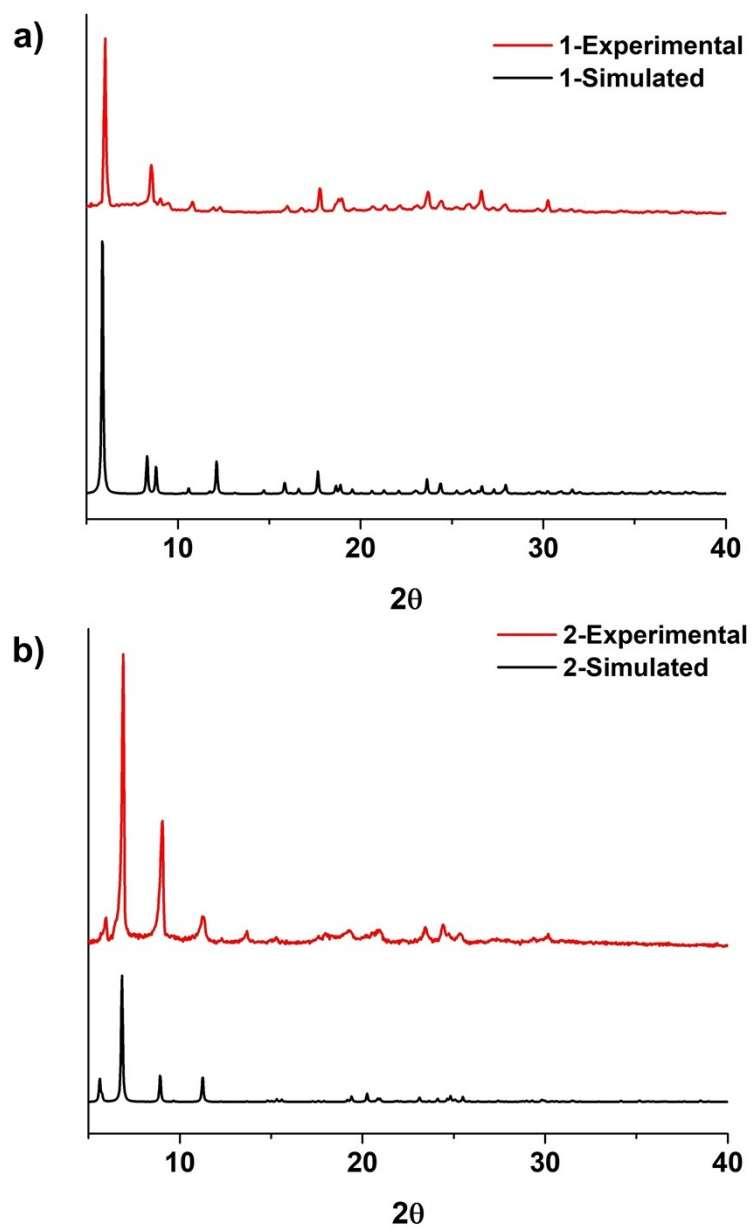


Figure S13. Simulated and experimental powder X-ray diffractogram of bulk samples of **1** (a) and **2** (b).

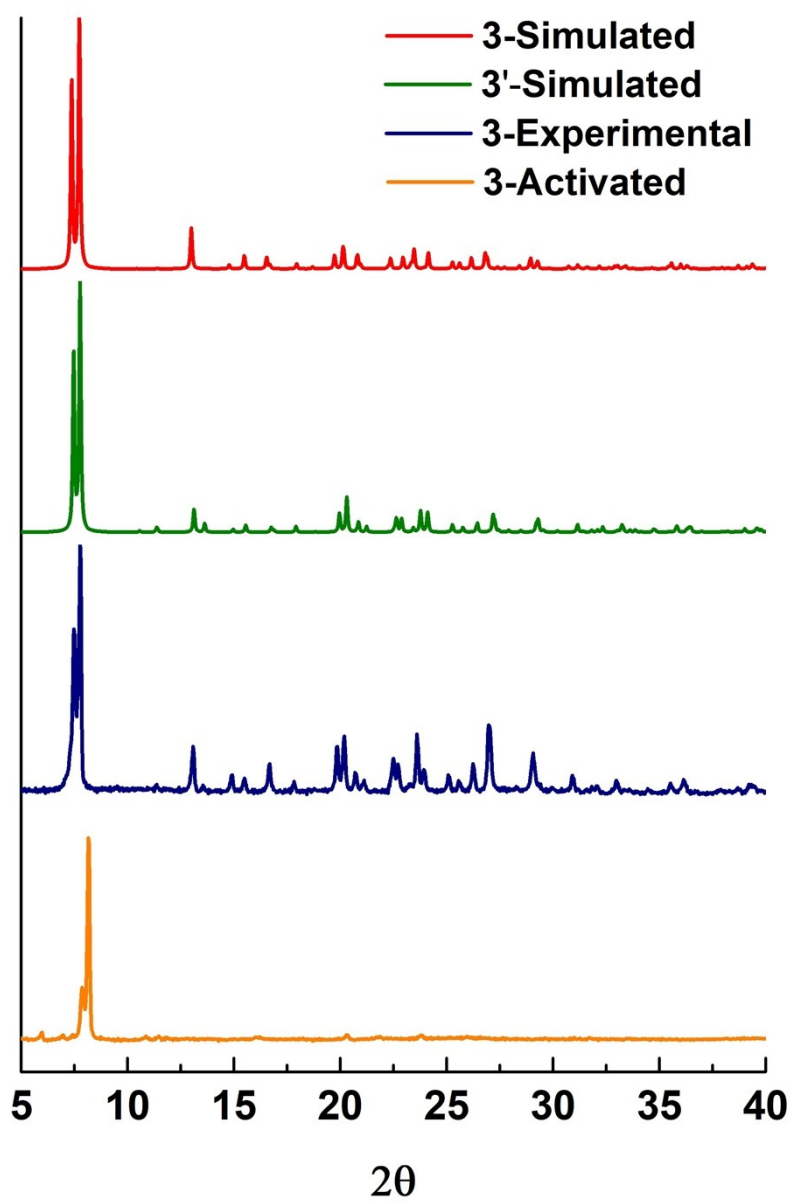
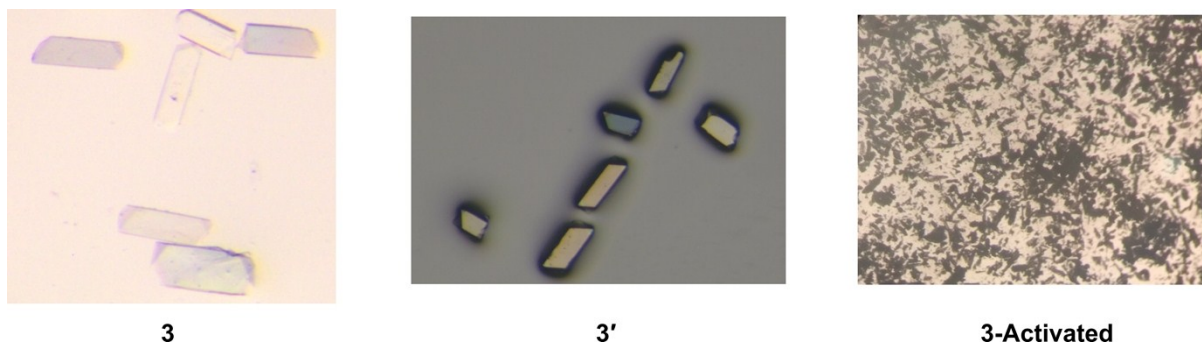


Figure S14. Simulated and experimental powder X-ray diffractogram of bulk samples of **3**.

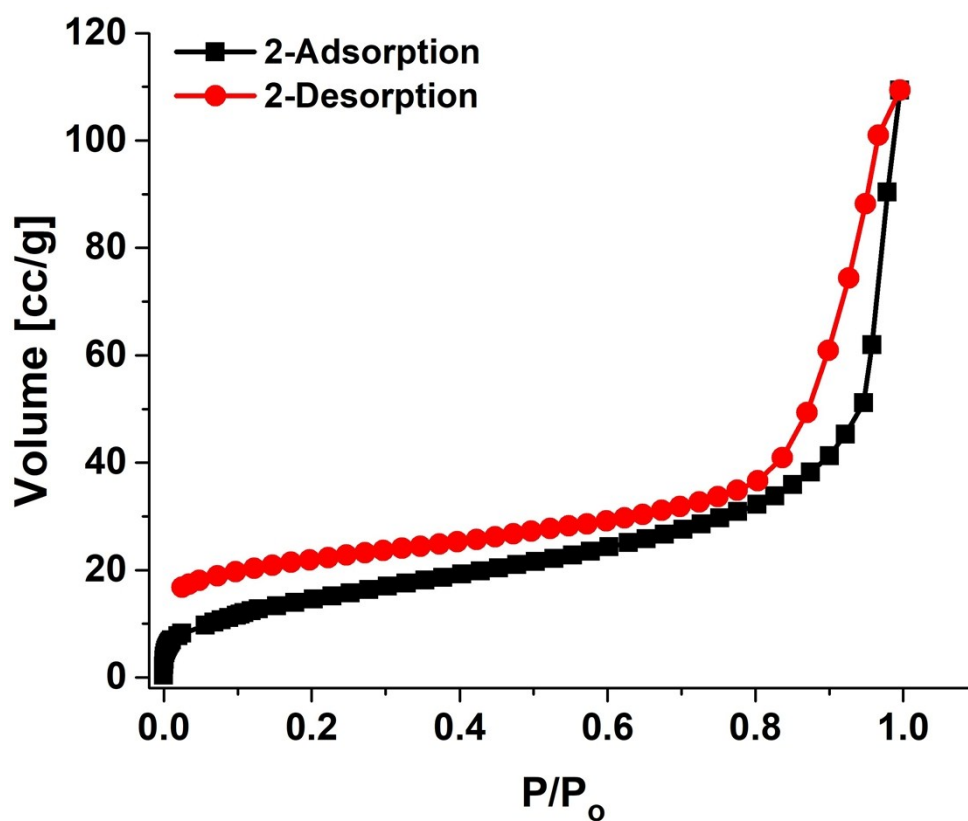


Figure S15. Nitrogen adsorption and desorption isotherms of 2 at 77K.

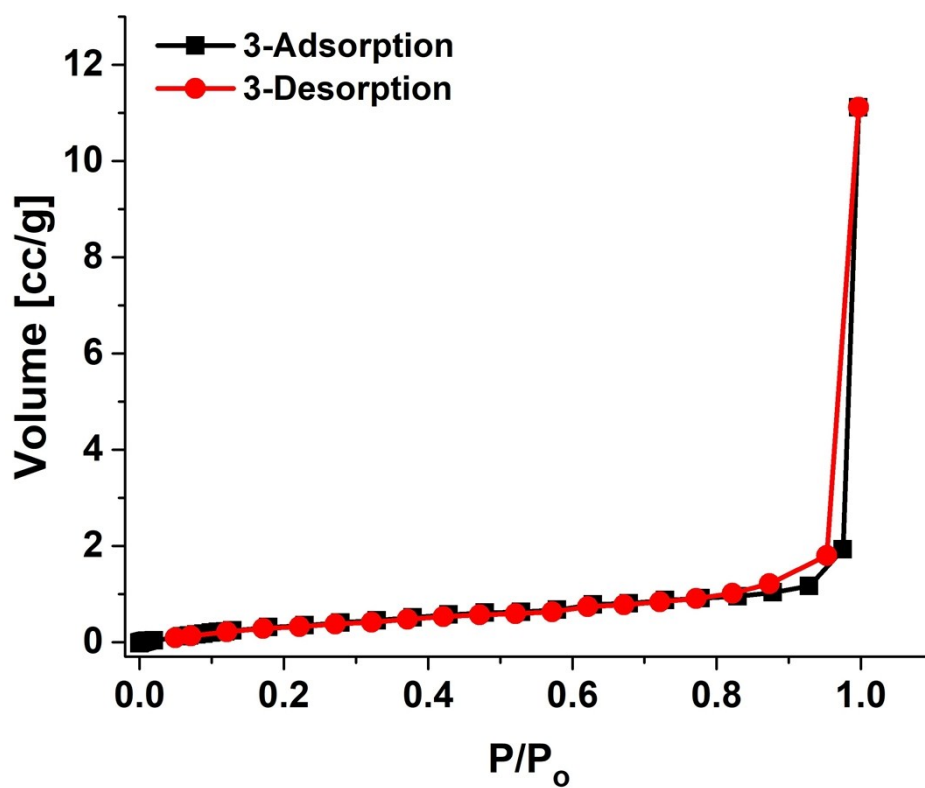


Figure S16. Nitrogen adsorption and desorption isotherms of 3 at 77K.

References

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