Electronic Supplementary Information for Dalton Transactions

Yttrium Bisphosphonate STA-13: A Racemic Phosphonate Metal Organic Framework with Permanent Microporosity

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Supporting Information

	Structure **1**	Structure **2**	Structure **2** (dehydrated)
Formula	$Y_2(LH_2)_3 \bullet 5H_2O$	$Y_2(L'H_2)_3 \bullet 7H_2O$	$Y_2(L'H_2)_3$
Unit Cell Composition	$Y_4P_{12}O_{44}N_{12}C_{36}H_{88}$	$Y_4P_{12}O_{51.5}N_{12}C_{42}H_{115}$	$Y_4P_{12}O_{36}N_{12}C_{42}H_{84}$
Formula Weight of Unit Cell	2120.45	2459.08	2060.48
Calculated density / g cm^{-3} (measured density)	1.821	1.798 (1.806)	1.513
Space Group	$P2_12_12$	$P\bar{3}$	$P\bar{3}$
a / Å	8.67363(29)	16.18945(13)	16.1352(2)
b / Å	9.78127(29)	16.18945(13)	16.1352(2)
c / Å	22.7964(9)	10.00355(16)	10.0296(2)
α / °	90	90	90
β / °	90	90	90
γ / °	90	120	120
V / $Å^3$	1934.02(13)	2270.64(4)	2261.32(6)
Diffractometer	Lab/STOE STADI P	ESRF/ID31	ESRF/ID31
Temperature / K	298	100	100
Wavelength / Å	1.54056	0.800178(6)	0.800178(6)
No. reflections	942	861	857
No. atoms (non-H)	27	60.75	53
No. Restraints	77	67	73
R_p	0.0303	0.0409	0.0540
R_{wp}	0.0388	0.0523	0.0677
LS shift/ su max	0.04	0.03	0.05

Table S1 Crystallographic data for STA-13, as-prepared and dehydrated under vacuum at different temperatures. **L** represents the N,N′-piperazinebis(methylenephosphonate) ligand

S1.1 Rietveld Refinement of Structure 1 – $Y_2(\mathbf{L}H_2)_3 \bullet 5H_2O$

The structure of **1** was confirmed by Rietveld refinement of laboratory powder X-ray data collected on a STOE STADI P diffractometer. Data were collected at 298 K in a Debye-Scherrer geometry with the sample mounted in a 0.7 mm borosilicate glass capillary. Data collection was over the range 5-90° 2θ using monochromated Cu $K_{\alpha 1}$ radiation. The GSAS suite of programs was used for the refinement,[1] with the previously reported single crystal structure of $Gd_2(\mathbf{LH_2})_3 \bullet 3H_2O$[2] as a starting model. Distance restraints were used for octahedral Y-O, tetrahedral P-O and P-C, and C-C and C-N bond distances (2.33 Å, 1.49 Å, 1.88 Å, 1.51-1.52 Å and 1.50 Å respectively) and also applied to non-bonding tetrahedral O-O and O-C, and cross piperazine ring C-C, C-N and N-N distances (2.43 Å, 2.76 Å, 2.472-2.892 Å, 2.466 Å and 2.866 Å respectively). One of the piperazine linkers was disordered over two equally occupied chair configurations. Water molecule O atom positions were determined from difference Fourier maps and their occupancies allowed to refine.

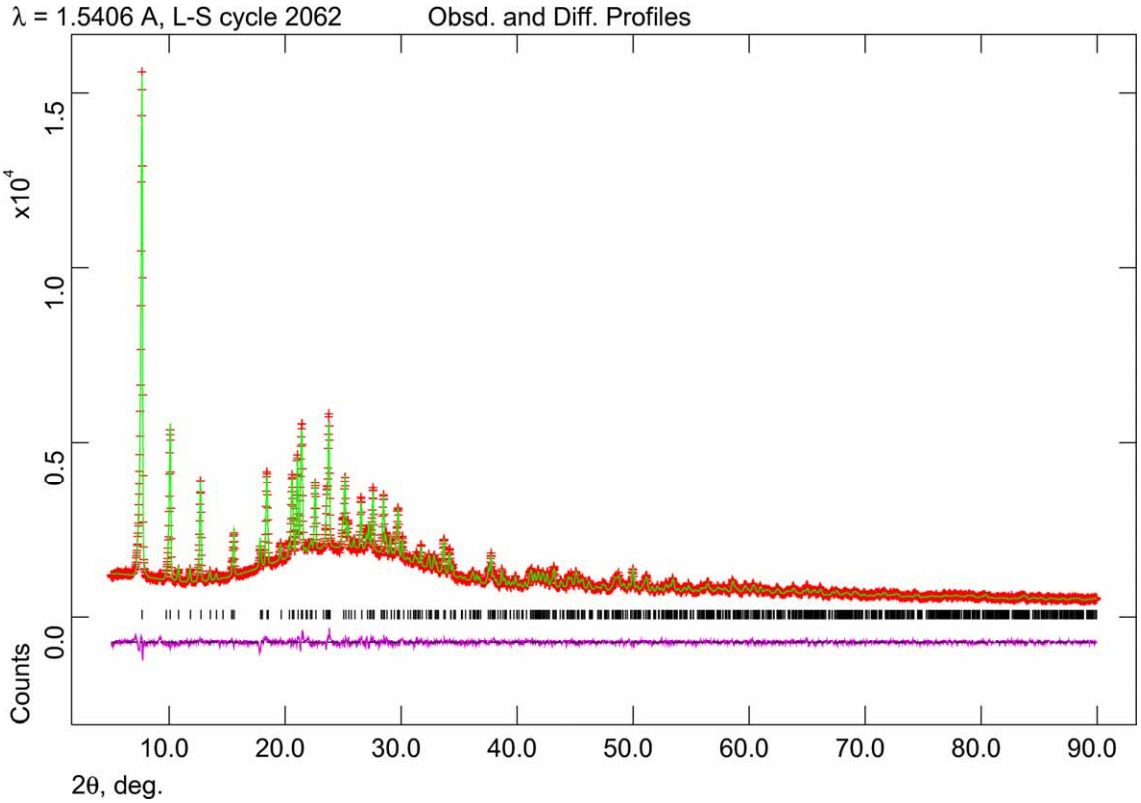

Fig S1.1 Rietveld plot for refinement of structure **1**, showing full range 5 90° 2θ. Continued overleaf

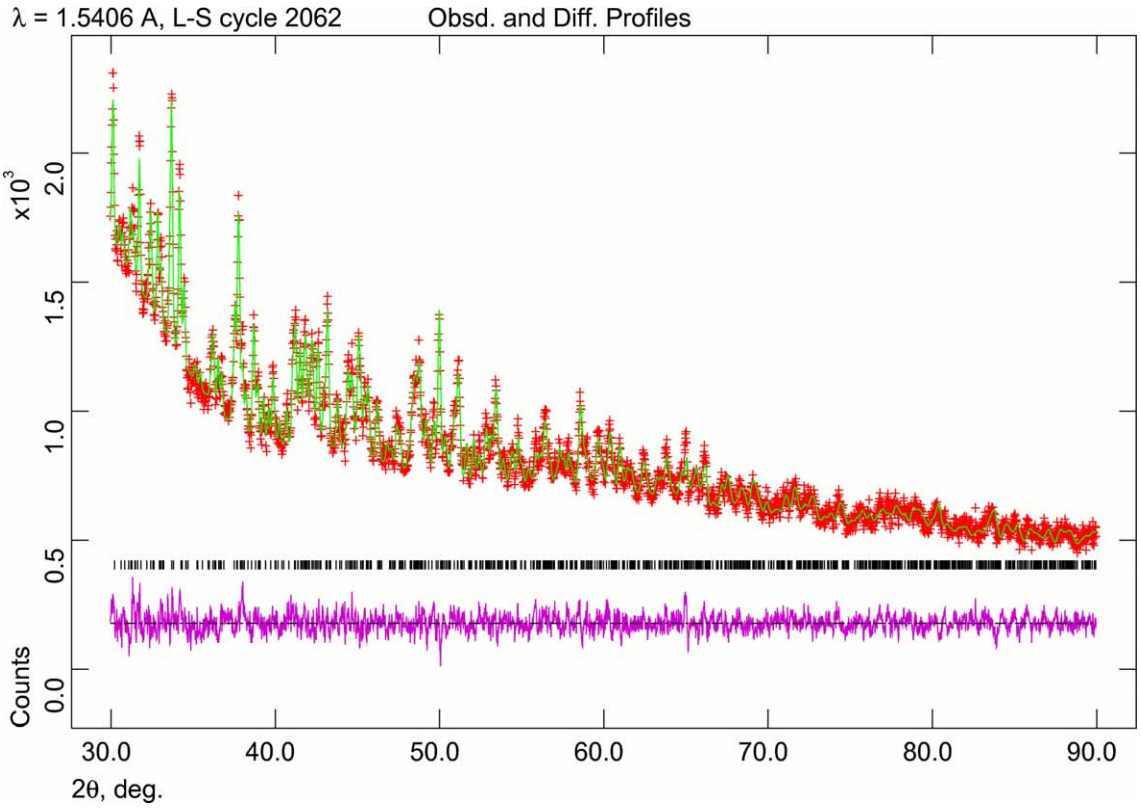

Fig S1.1(Continued) Rietveld plot for refinement of structure **1**, showing region 30-90° 2θ

S1.2 Rietveld Refinement of Structure 2 – $Y_2(\mathbf{L'}H_2)_3 \bullet 7H_2O$

The structure of **2** (STA-13) was determined from synchrotron powder X-ray diffraction data, collected at station ID31 at the ESRF. Measurement was carried out at 100 K in Debye-Scherrer geometry with the sample mounted in a sealed quartz glass 0.7 mm diameter capillary. Data were collected over the range 0-46º 2θ using monochromated radiation of wavelength 0.800178(6) Å. To minimise the effect of sample degradation in the beam, 25 data collections of two minutes were performed on freshly exposed regions of the sample, the final data set being the sum of all of the collections. The data was indexed using DICVOL[3] as a metrically trigonal or hexagonal cell, a = 16.1784 Å, c = 9.9902 Å, V = 2264.55 Å^3 (F.O.M. M(20) = 53.7).[4] Sixteen space groups are consistent with the pattern of systematic absences in the powder data. Using the EXPO2004 program suite,[5] four different space groups were initially tried to obtain a

model (P3, $P\bar{3}$, P6 and $P\bar{6}$) as any additional symmetry present in the other twelve space groups would be obvious from the final model. The trigonal space group $P\bar{3}$ gave the most promising results, locating the Y, P and O atoms of the inorganic chains. In addition, a small single crystal of STA-13 was analysed on a Rigaku Saturn CCD diffractometer, fitted with a graphite monochromator and using Cu K_α radiation. This gave a partial structure solution in $P\bar{3}$, but not in the other space groups, again locating the Y, P and O atoms and additionally the phosphonate C atoms. An initial model for the position of the ligands was obtained by molecular modeling using the Cerius program.[6] P---P distances between chains indicated the mode of linking via bisphosphonate groups, and this was taken as a starting point for a restrained Rietveld refinement, using the GSAS suite of programs.[1] Methyl group C atoms were placed geometrically on C atoms of the piperazine ring, in equatorial positions.

Restraints were applied to the ring, but the methyl group Cs were allowed to move freely. Subsequent refinement indicated that the fit was improved by inclusion of a methyl group, C8, in an equatorial position on C3 but not by a methyl group on the other piperazine ring C atoms. Removal of the disorder from the organic moiety and application of suitable restraints to ensure a chemically sensible geometry for the methyl carbon gave satisfactory values for the displacement parameters. In the final refinement, distance restraints were applied to octahedral Y-O, tetrahedral P-O and P-C, C-C and C-N (2.36 Å, 1.49 Å, 1.88 Å, 1.50-1.52 Å, 1.50-1.51 Å respectively) and also non-bonding tetrahedral O-O and O-C, and cross piperazine ring C-C, C-N and N-N distances (2.44 Å, 2.75 Å, 2.41-2.892 Å, 2.39-2.466 Å, 2.866 Å respectively) to give a satisfactory fit to the data. Solid state ^{13}C MASNMR spectra indicate disorder in the methyl environment, so that a second, lower occupancy methyl carbon (C7, 25 % occupied; C8 75 % occupancy) was placed on C2 with equatorial geometry, with the same restraints as C8, yielding a final Rietveld fit with $R_{wp} = 5.23$ %. Both enantiomers of the linker are incorporated in the final structure, each in two different orientations, related across an inversion centre.

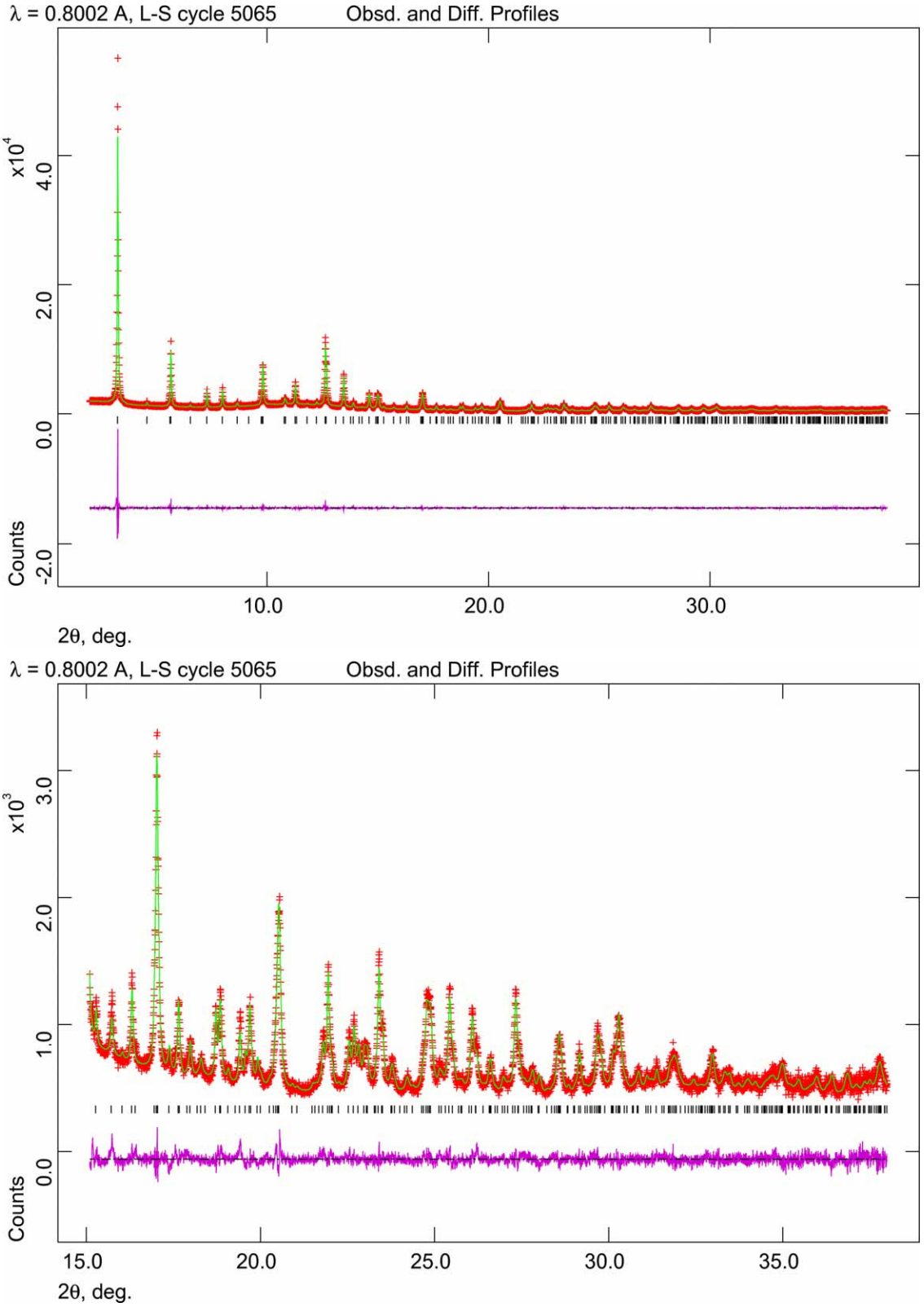

Fig S1.2 Rietveld plots of refinement of **2**, showing the full range 2-38° 2θ (top) and the range 15-38° 2θ (bottom)

S1.3 Rietveld refinement of Structure 2(Dehydrated) – $Y_2(\mathbf{L'}H_2)_3$

Synchrotron powder X-ray diffraction data on a sample of **2** dehydrated under vacuum at 200 °C was collected using identical methods as for the as-prepared sample. Indexing the powder pattern with DICVOL[3] gave a metrically trigonal or hexagonal cell a = 16.1196 Å, c = 10.0278 Å, V = 2256.53 Å^3 (F.O.M. M(20) = 54.0).[4] Additional peaks not indexed by this cell are observed at 3.37° and 5.86° 2θ and are thought to belong to an unidentified, minor impurity phase.

Due to the similarity of the patterns of as-prepared **2** and the dehydrated material, a Rietveld refinement using the GSAS program suite[1] was attempted, taking the as-prepared structure with water molecules (O101-O104) removed and the cell parameters from DICVOL as the starting model. The region from 3.337-3.429° 2θ was excluded to prevent the larger of the two impurity peaks (at 3.37°) from affecting the refinement; the second peak at 5.86° is low intensity, thus excluding a region around this peak was not necessary. Distance restraints were applied to octahedral Y-O, tetrahedral P-O and P-C, C-C and C-N (2.36 Å, 1.49-1.50 Å, 1.88 Å, 1.50-1.52 Å, 1.50-1.51 Å respectively) and also non-bonding octahedral O-O, tetrahedral O-O and O-C, and cross piperazine ring C-C, C-N and N-N distances (3.338 Å, 2.434 Å, 2.761 Å, 2.44-2.865 Å, 2.40-2.45 Å, 2.855 Å respectively). The final refined structure (R_{wp} = 6.77 %) is closely related to the as-prepared solid.

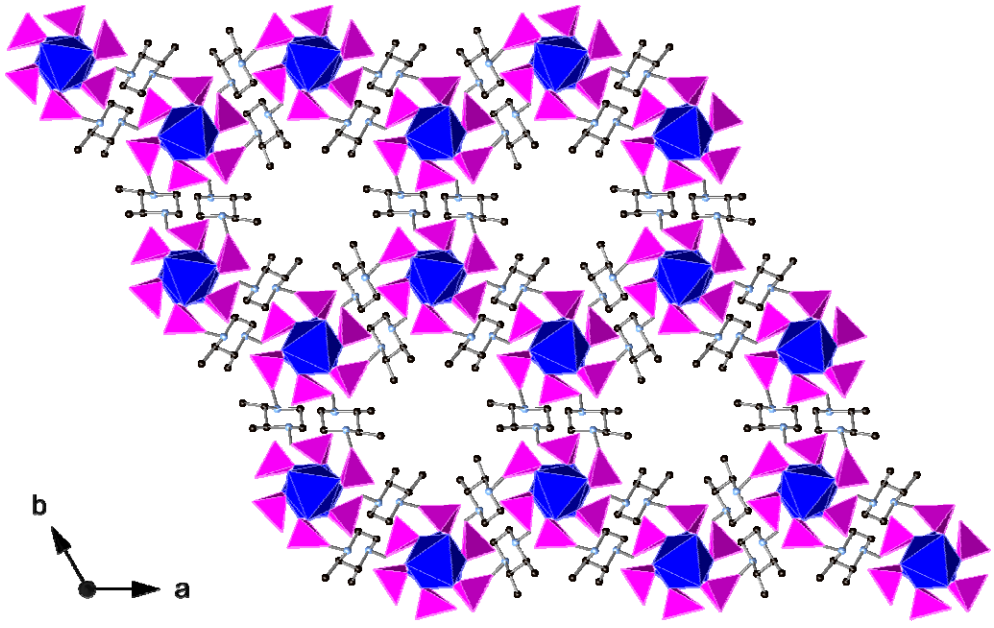

Fig S1.3 Structure **2**(Dehydrated), viewed along the *c*-axis showing vacant 3 Å channels.

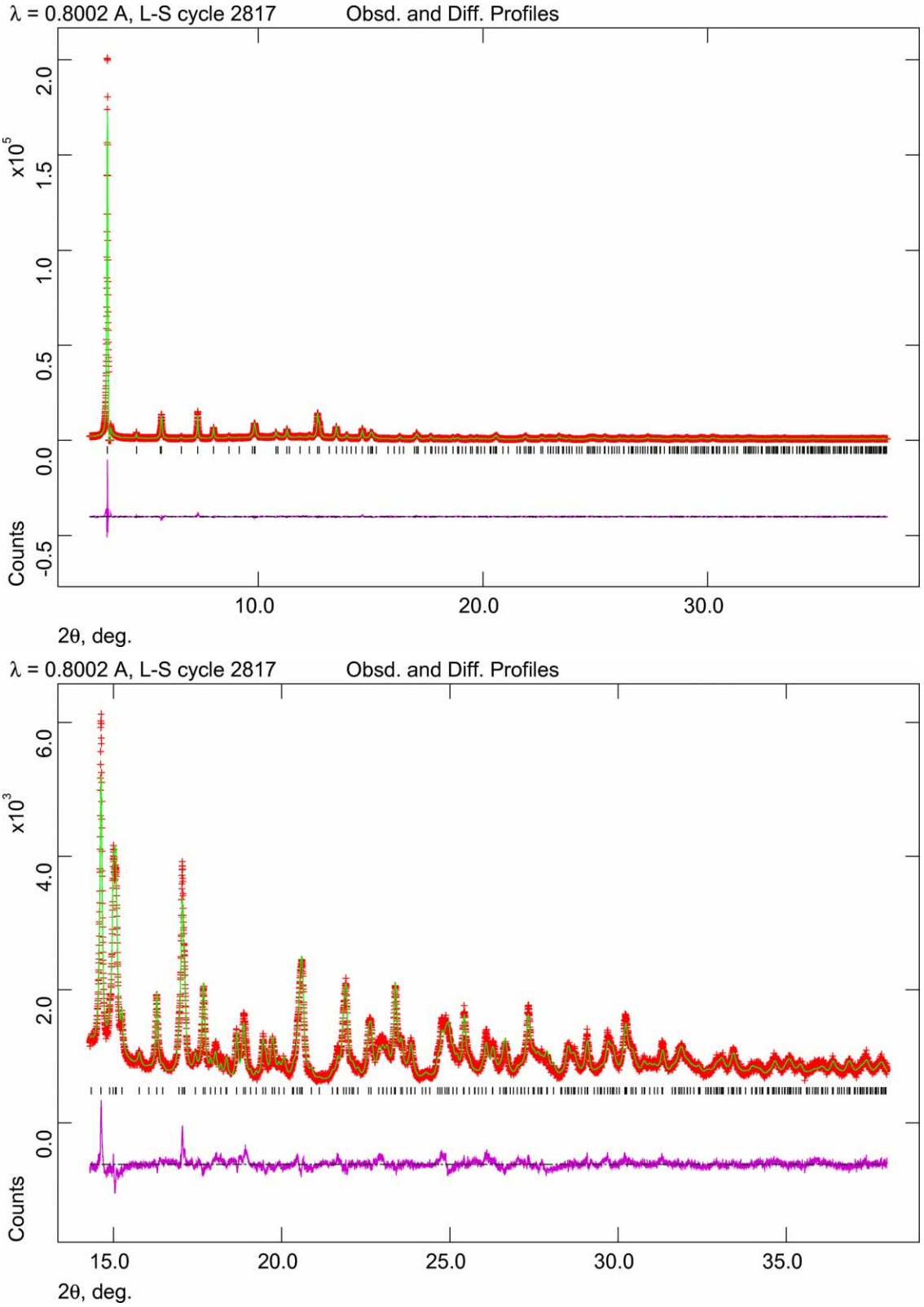

Fig S1.4 Rietveld plots of refinement of Structure **2**(Dehydrated), showing the full range 2-38° 2θ (top) and the range 15-38° 2θ (bottom)

S1.4 Selected Bond Distances and Angles for Structures 1, 2 and 2(Dehydrated)

Structure 1

Bond	Length / Å	Bond	Length / Å
Y1-O1	2.304(16)	N1-C1	1.49(2)
Y1-O2	2.334(14)	N1-C2	1.50(2)
Y1-O4	2.293(15)	N1-C6	1.54(3)
Y1-O5	2.305(14)	C2-C3	1.48(3)
Y1-O11	2.303(15)	C5-C6	1.48(3)
Y1-O12	2.343(8)	N4-C3	1.56(3)
P1-O1	1.442(19)	N4-C4	1.54(3)
P1-O3	1.501(19)	N4-C5	1.46(2)
P1-O2	1.528(19)	N11A-C11	1.51(2)
P1-C1	1.920(16)	N11A-C12	1.50(3)
P4-O4	1.504(18)	N11A-C13	1.47(3)
P4-O5	1.475(11)	C12-C13	1.44(2)
P4-O6	1.543(14)	C12-C14	1.50(3)
P4-C4	1.907(14)	N11B-C11	1.43(2)
P11-O11	1.471(18)	N11B-C12	1.49(3)
P11-O12	1.513(17)	N11B-C14	1.48(3)
P11-O13	1.498(18)		
P11-C11	1.90(2)		

Table S1.2 List of bond distances for all bonds in Structure **1**

Bond Angle	Angle / °	Bond Angle	Angle / °
O1-Y1-O2	176.3(9)	O1-P1-O3	118.2(15)
O1-Y1-O4	93.7(8)	O1-P1-O2	107.9(11)
O1-Y1-O5	93.3(7)	O1-P1-C1	109.2(13)
O1-Y1-O11	83.2(8)	O2-P1-O3	106.4(14)
O1-Y1-O12	84.1(7)	O2-P1-C1	106.7(13)
O2-Y1-O4	83.2(7)	O3-P1-C1	107.8(10)
O2-Y1-O5	89.8(8)	O4-P4-O5	109.9(13)
O2-Y1-O11	94.6(8)	O4-P4-O6	106.9(12)
O2-Y1-O12	98.2(8)	O4-P4-C4	108.2(11)
O4-Y1-O5	172.9(9)	O5-P4-O6	111.2(13)
O4-Y1-O11	89.2(8)	O5-P4-C4	110.4(12)
O4-Y1-O12	94.3(8)	O6-P4-C4	110.1(10)
O5-Y1-O11	91.3(8)	O11-P11-O12	109.6(12)
O5-Y1-O12	86.8(7)	O11-P11-O13	112.4(14)
O11-Y1-O12	167.0(8)	O11-P11-C11	110.2(12)
		O12-P11-O13	112.2(14)
		O12-P11-C11	106.5(11)
		O13-P11-C11	105.7(12)

Table S1.3 List of selected bond angles for YO_6 and PO_3C polyhedra in Structure **1**

Structures 2 and 2(Dehydrated)

Bond	Structure **2** Length / Å	Structure **2** (Dehydrated) Length / Å
Y1-O1	2.261(9)	2.362(7)
Y1-O1	2.260(9)	2.361(7)
Y1-O1	2.260(9)	2.361(7)
Y1-O4	2.376(8)	2.352(6)
Y1-O4	2.377(8)	2.353(6)
Y1-O4	2.375(8)	2.352(6)
Y2-O2	2.316(7)	2.302(4)
Y2-O2	2.315(7)	2.301(4)
Y2-O2	2.315(7)	2.301(4)
Y2-O5	2.354(7)	2.318(6)
Y2-O5	2.354(7)	2.319(6)
Y2-O5	2.353(7)	2.317(6)
P1-O1	1.470(6)	1.513(7)
P1-O2	1.481(5)	1.459(5)
P1-O3	1.508(10)	1.543(5)
P1-C1	1.880(8)	1.833(7)
P4-O4	1.506(8)	1.500(8)
P4-O5	1.463(7)	1.517(8)
P4-O6	1.483(9)	1.528(7)
P4-C4	1.887(8)	1.813(7)
N1-C1	1.487(6)	1.472(6)
N1-C2	1.497(13)	1.522(8)
N1-C6	1.454(10)	1.508(8)
C2-C3	1.462(13)	1.529(6)
C2-C7	1.494(10)	1.497(3)
C3-C8	1.479(9)	1.484(3)
C5-C6	1.453(9)	1.484(6)
N4-C3	1.477(13)	1.543(6)
N4-C4	1.494(8)	1.536(8)
N4-C5	1.462(12)	1.510(9)

Table S1.4 Comparison of bond distances of all bonds in Structure **2** (middle) and Structure **2**(Dehydrated) (right)

Bond Angle	Structure **2** Angle / °	Structure **2** (Dehydrated) Angle / °
O1-Y1-O1	88.4(4)	92.0(3)
O1-Y1-O1	88.4(4)	92.0(3)
O1-Y1-O4	89.8(4)	85.8(2)
O1-Y1-O4	89.6(4)	88.5(2)
O1-Y1-O4	177.4(4)	177.7(3)
O1-Y1-O1	88.4(4)	92.0(3)
O1-Y1-O4	177.3(4)	177.7(3)
O1-Y1-O4	89.8(4)	85.8(2)
O1-Y1-O4	89.6(4)	88.5(2)
O1-Y1-O4	89.6(4)	88.5(2)
O1-Y1-O4	177.3(4)	177.7(3)
O1-Y1-O4	89.8(4)	85.8(2)
O4-Y1-O4	92.1(4)	93.8(3)
O4-Y1-O4	92.2(4)	93.8(3)
O4-Y1-O4	92.2(4)	93.8(3)
O2-Y2-O2	86.0(4)	81.9(2)
O2-Y2-O2	86.0(4)	81.9(2)
O2-Y2-O5	83.4(3)	85.2(2)
O2-Y2-O5	96.0(3)	96.0(2)
O2-Y2-O5	169.1(3)	167.1(3)
O2-Y2-O2	86.0(4)	81.9(2)
O2-Y2-O5	169.00(3)	167.0(3)
O2-Y2-O5	83.4(3)	85.2(2)
O2-Y2-O5	96.1(3)	96.1(2)
O2-Y2-O5	96.0(3)	96.0(2)
O2-Y2-O5	169.1(3)	167.1(3)
O2-Y2-O5	83.4(3)	85.3(2)
O5-Y2-O5	94.9(3)	96.5(3)
O5-Y2-O5	94.9(3)	96.5(3)
O5-Y2-O5	94.9(3)	96.5(3)

Table S1.5 Comparison of selected bond angles for YO_6 and PO_3C polyhedra in Structure **2** (middle) and Structure **2**(Dehydrated) (right). Continued overleaf

Bond Angle	Structure **2** Angle / °	Structure **2** (Dehydrated) Angle / °
O1-P1-O2	108.1(6)	109.3(4)
O1-P1-O3	109.6(7)	105.7(4)
O1-P1-C1	107.6(8)	111.0(4)
O2-P1-O3	110.7(7)	107.2(4)
O2-P1-C1	107.9(5)	112.9(4)
O3-P1-C1	112.8(7)	110.4(4)
O4-P4-O5	109.4(7)	107.6(5)
O4-P4-O6	111.0(6)	106.3(5)
O4-P4-C4	107.5(7)	112.9(5)
O5-P4-O6	112.0(6)	106.7(5)
O5-P4-C4	110.7(6)	111.0(4)
O6-P4-C4	106.1(8)	111.9(5)

Table S1.5(Continued) Comparison of selected bond angles for YO_6 and PO_3C polyhedra in Structure **2** (middle) and Structure **2**(Dehydrated) (right).

S2. TGA Data for Structures 1, 2 and 1-*R*

All TGA data were collected using a Netzsch TG 209, under a flow of dry air over the temperature range 20-900 ºC.

Structure 1

TGA of **1** shows two main weight loss events: the first at 25-100 ºC of 8.92 %, indicating the loss of ~5 molecules of water per formula unit; and a second weight loss starting at 325 ºC and continuing to above 900 ºC, indicating framework decomposition.

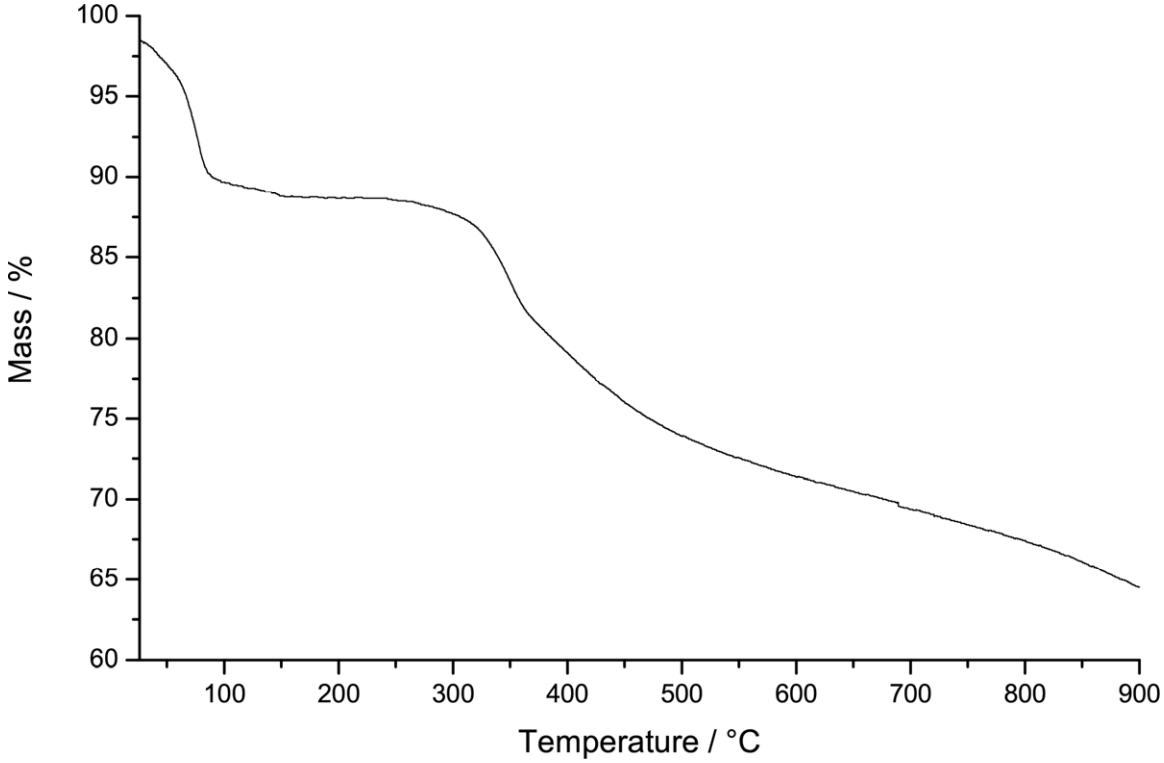

Fig S2.1 TGA of **1** in dry air, from 25-900 °C

Structure 2

TGA of **2** shows again two principal weight loss events: the first at 25-120 °C of 10.90 %, indicating the loss of ~7 molecules of water per formula unit; and a second weight loss starting at 275 °C and continuing to above 900 °C, indicating framework decomposition.

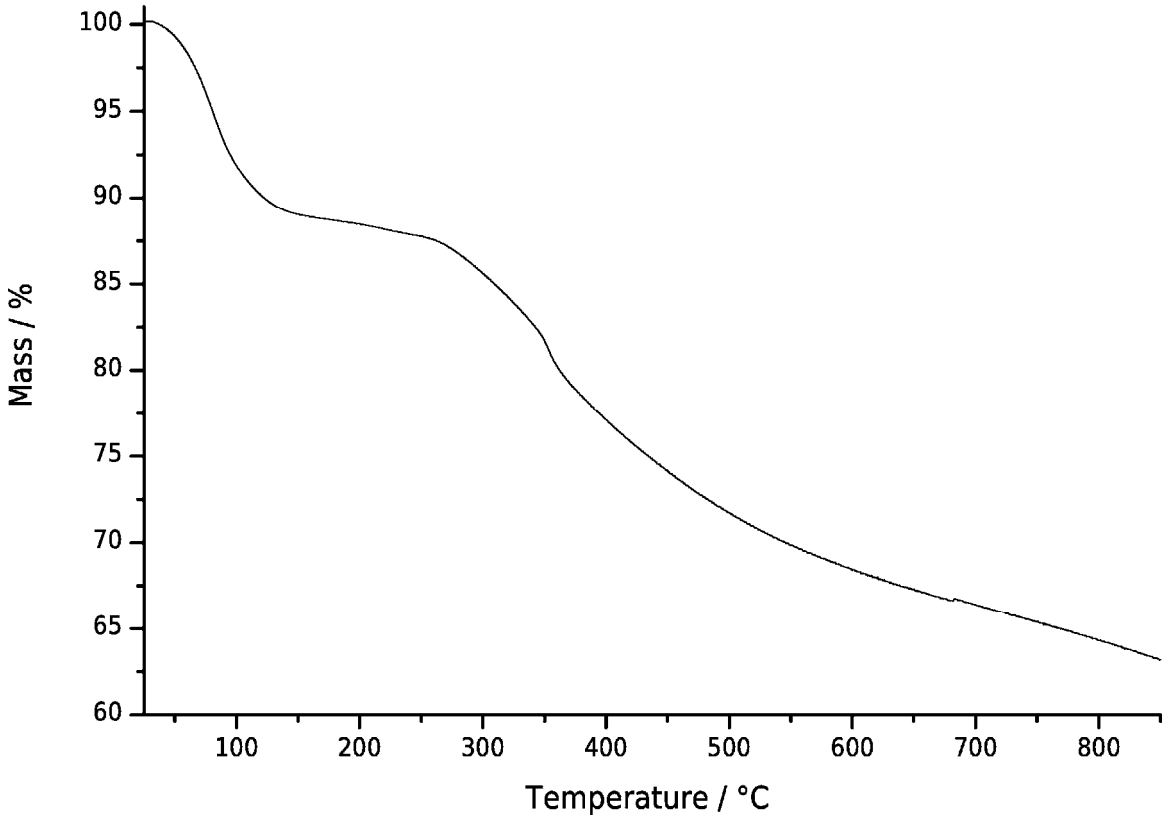

Fig S2.2 TGA of **2** in dry air, from 25-900 °C

Structure 1-*R*

Structure **1-*R*** also shows two major weightloss events: the first at 25-120 °C of 6.78 % indicating the loss of ~4 molecules of water per formula unit; and a second weightloss starting at 260 °C and continuing to above 900 °C indicating framework decomposition,

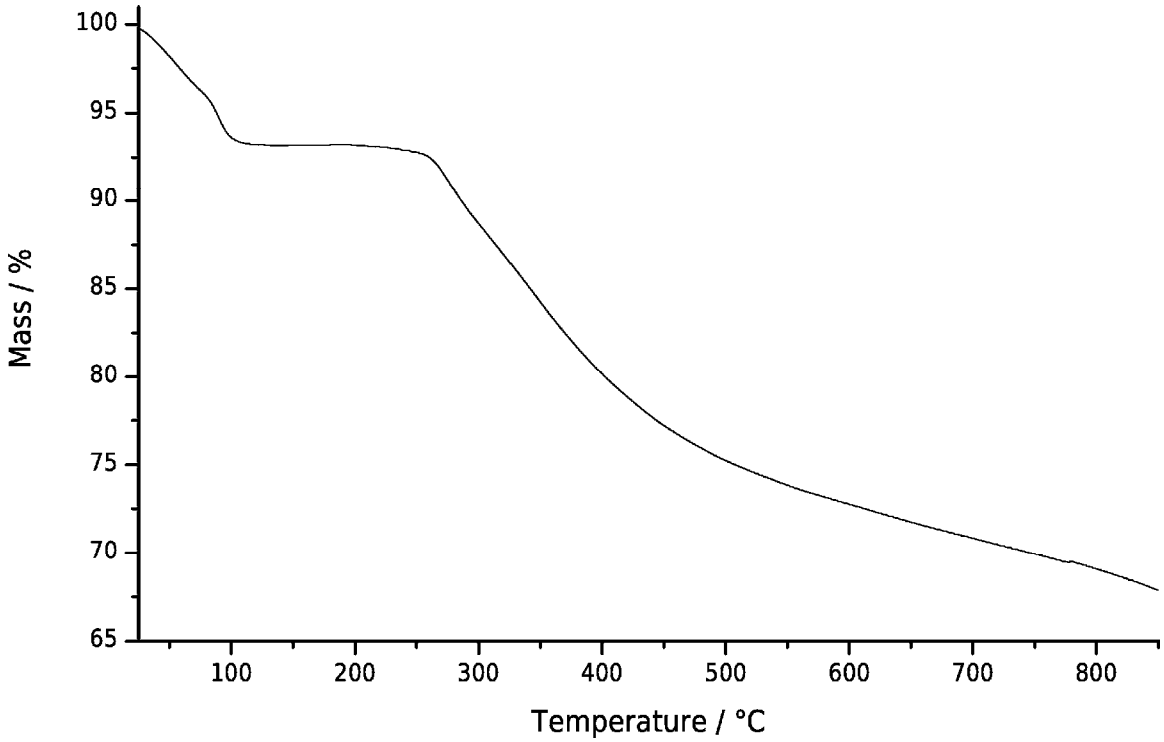

Fig S2.3 TGA of **1-*R*** in dry air, from 25-900 °C

S3. X-ray Powder Diffraction Data for Structures 1, 1-*R*, 2 and 2(Dehydrated)

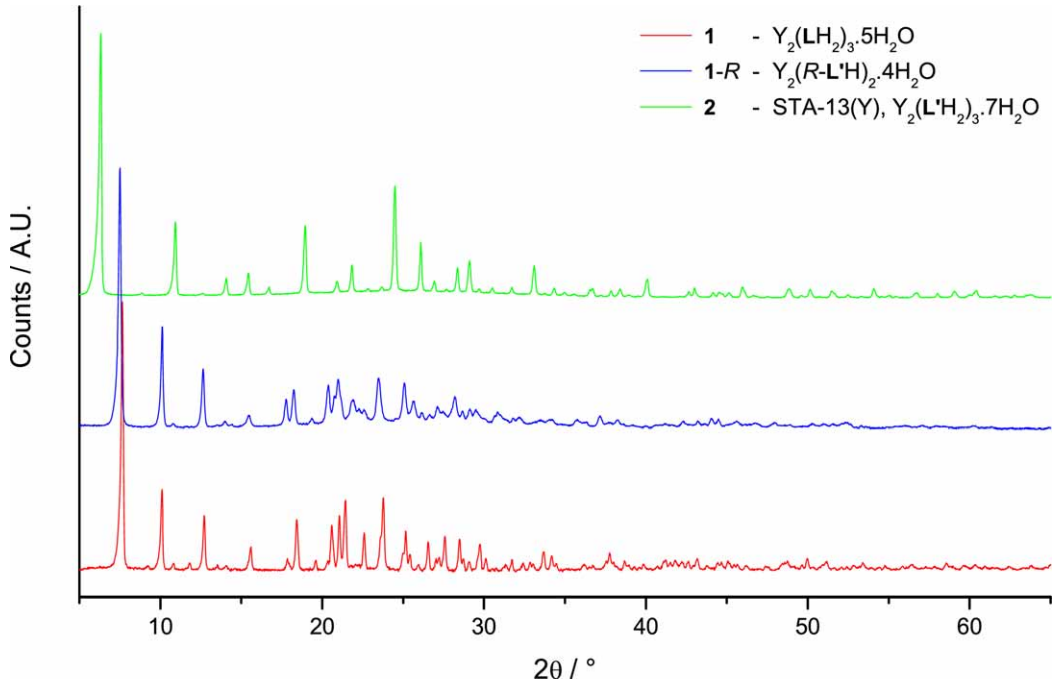

Fig S3.1 Comparison of the diffraction patterns of as-prepared samples of Structure **1** (bottom), Structure **1**-*R* (middle) and Structure **2** (top)

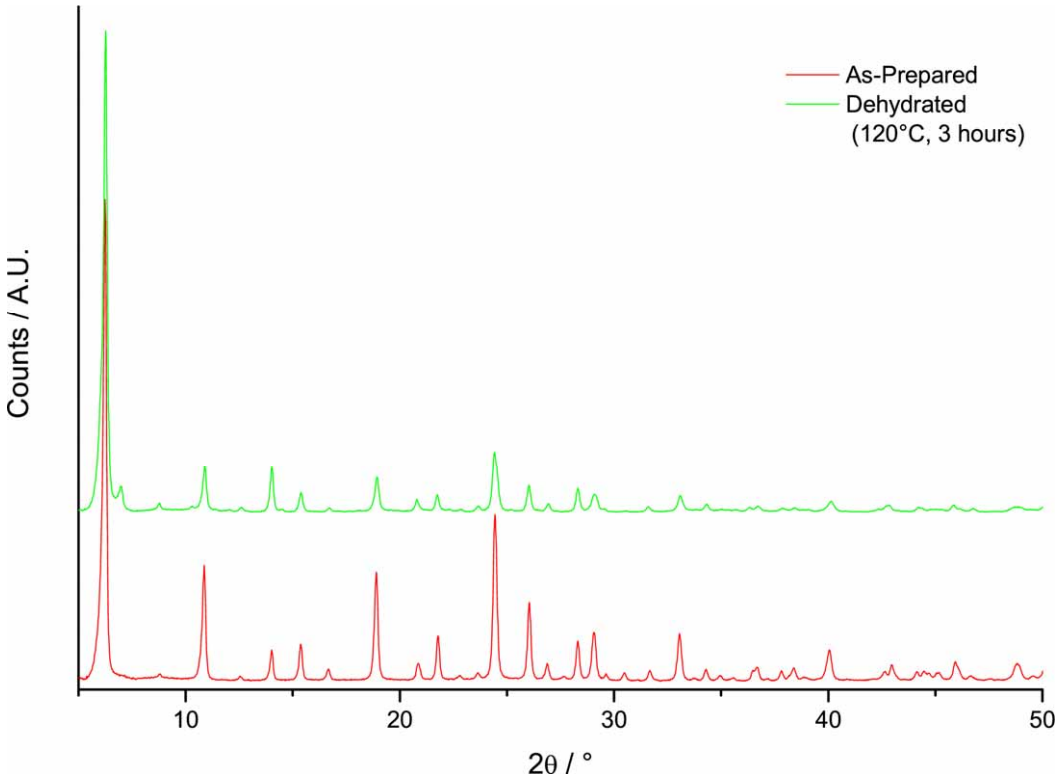

Fig S3.2 Comparison of the X-ray powder diffraction patterns of as-prepared STA-13(Y) Structure **2**) and dehydrated STA-13(Y) (Structure **2**(Dehydrated))

S4. N_2 and CO_2 Adsorption Isotherms on STA-13(Y) – Structure 2(Dehydrated)

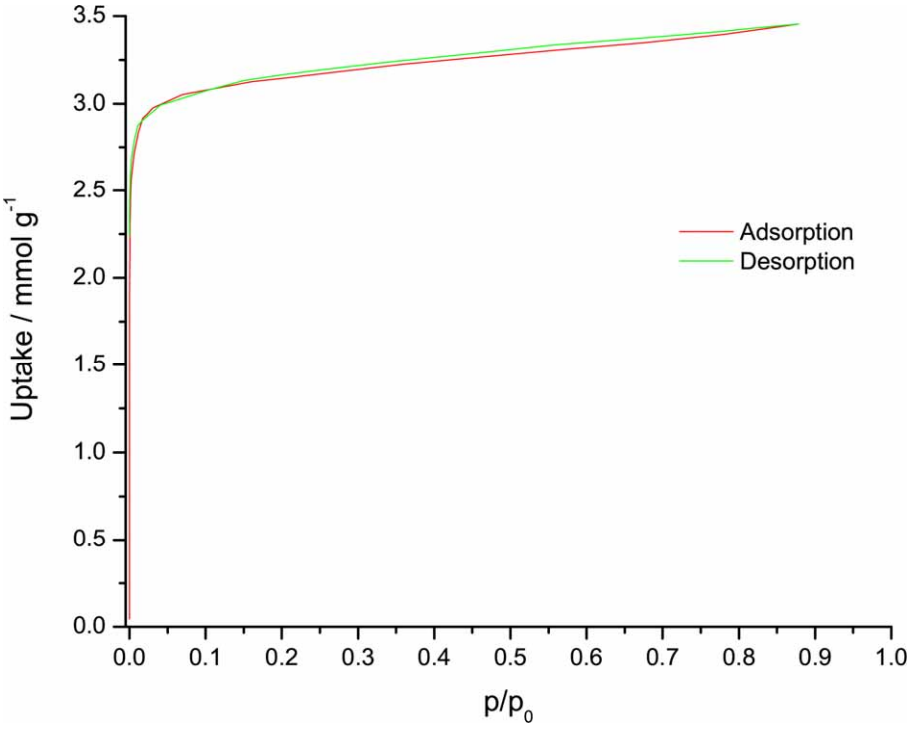

Fig S4.1 N_2 isotherm at 77 K for STA-13(Y) – dehydrated at 120 °C for three hours.

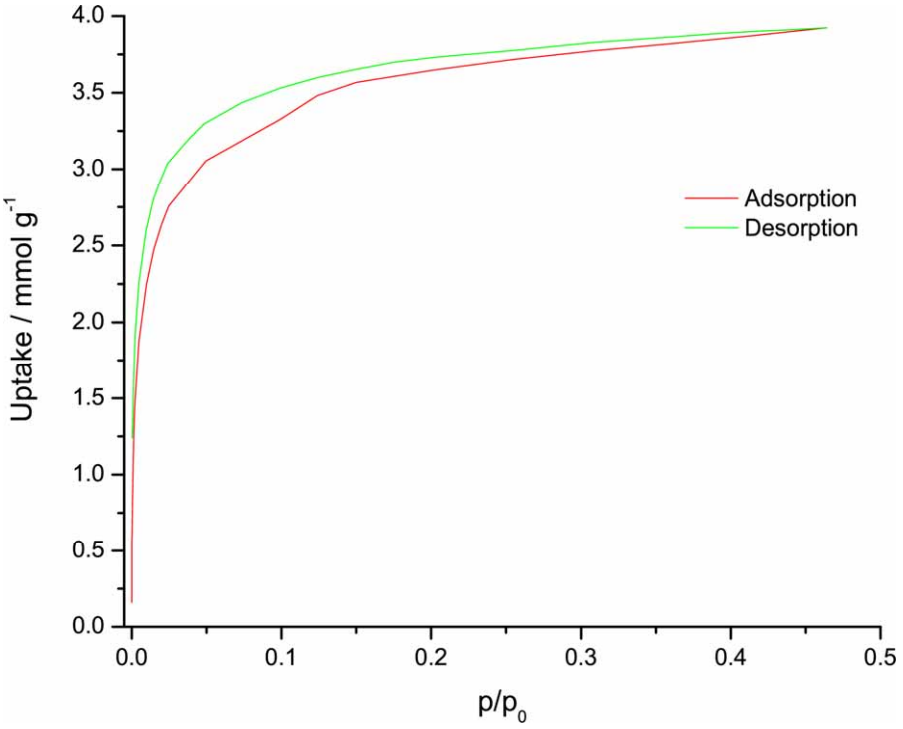

Fig S4.2 CO_2 isotherm at 196 K for STA-13(Y) – dehydrated at 120 °C for three hours.

S5. X-ray Powder Diffraction Data for STA-13 (Sc, Y, Dy, Yb) (Structure 2)

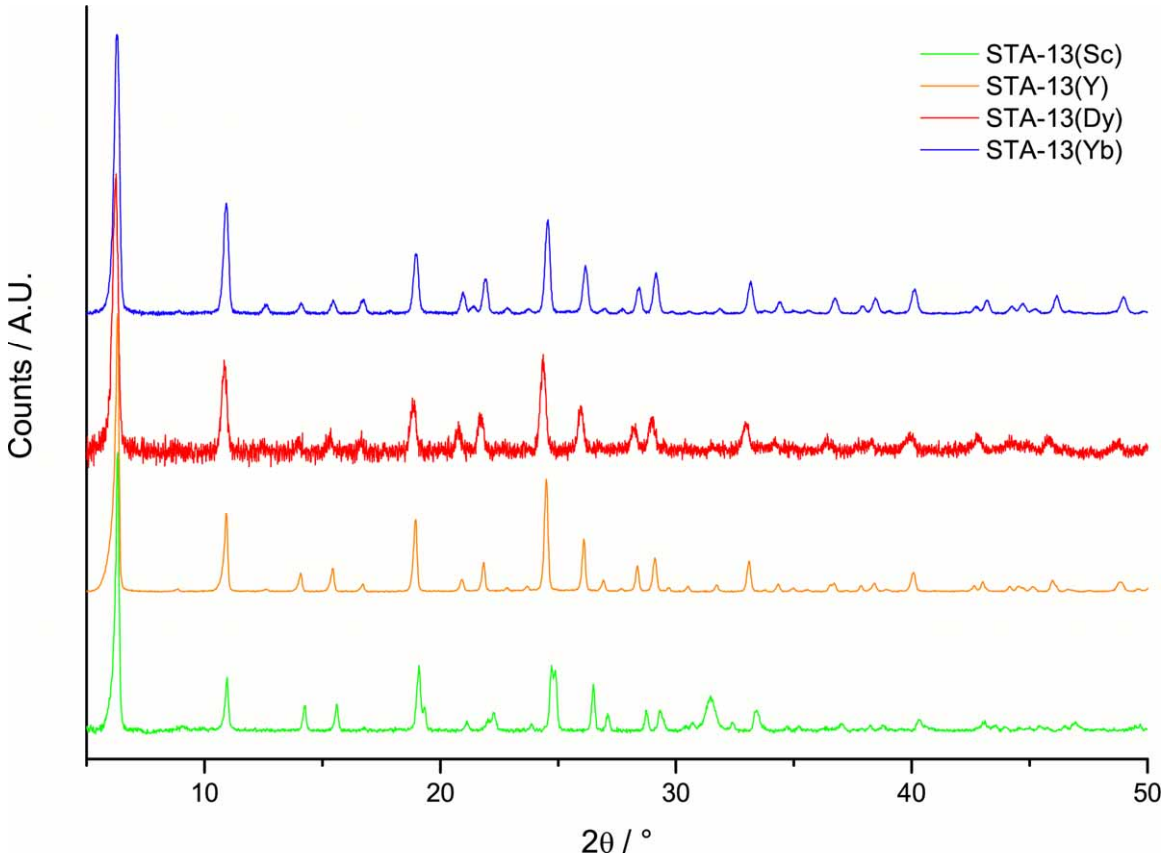

Fig S5 Comparison of the X-ray powder diffraction patterns of STA-13 prepared with Sc (green), Y (orange), Dy (red) and Yb (blue)

	STA-13(Sc)	STA-13(Yb)	STA-13(Y)	STA-13(Dy)
M Radius / pm	74.5	86.8	90.0	91.2
a / Å	16.05147(13)	16.1808(7)	16.1895(3)	16.224(2)
b / Å	16.05147(13)	16.1808(7)	16.1895(3)	16.224(2)
c / Å	9.69167(13)	9.9291(6)	10.00355(16)	10.0215(15)
α / °	90	90	90	90
β / °	90	90	90	90
γ / °	120	120	120	120
V / Å^3	2162.51(3)	2251.35(14)	2270.64(4)	2284.5(5)

Table S5 Comparison of the unit cell dimensions of STA-13 prepared with Sc, Y, Dy and Yb

S6. Impossible Positions for Methyl Groups in Structure 1-*R*

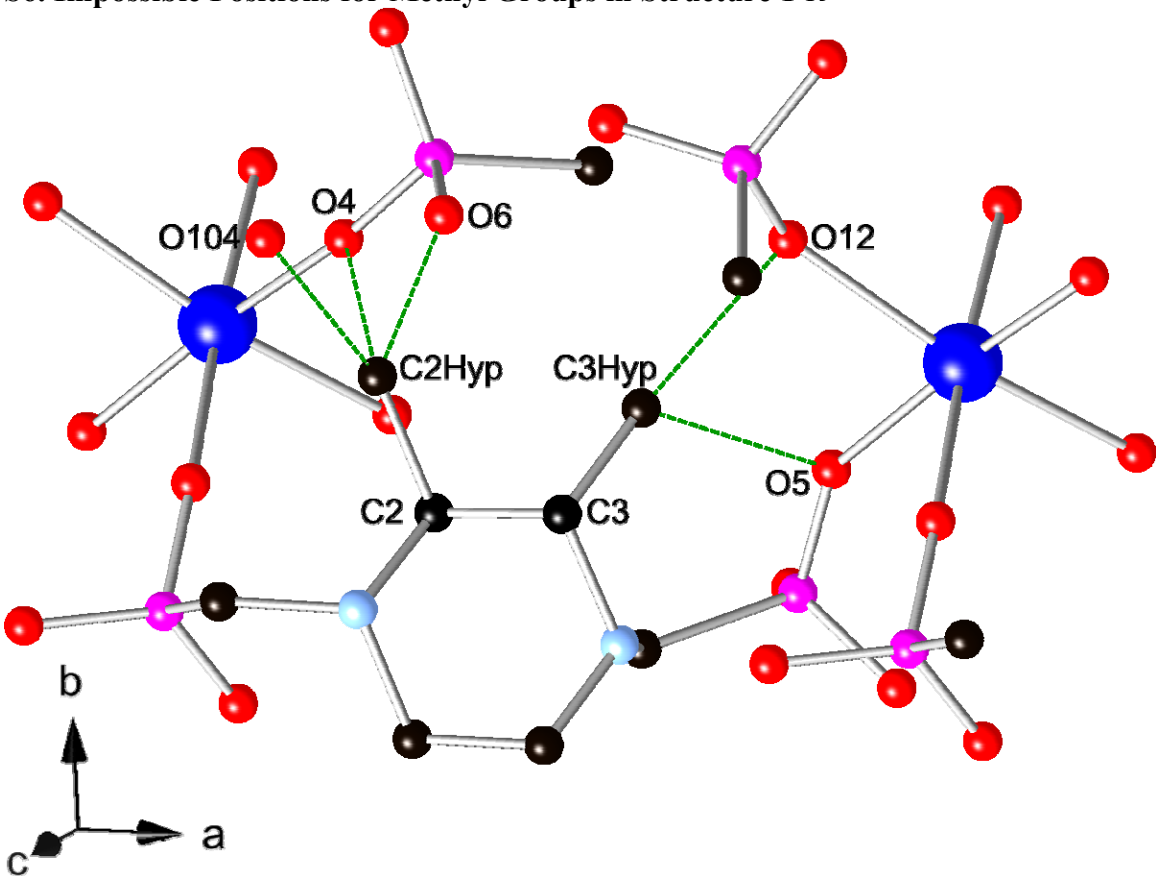

Fig 6 Short contacts for impossible sites of hypothetical methyl carbon atoms, C2Hyp and C3Hyp, in Structure **1**-*R*

Contact	Length / Å	Contact	Length / Å
C2Hyp-O4	2.703	C3Hyp-O5	2.544
C2Hyp-O6	1.866	C3Hyp-O12	2.457
C2Hyp-O104	2.522		

Table 6.1 Contact distances for impossible sites of hypothetical methyl carbon atoms, C2Hyp and C3Hyp, in Structure **1**-*R*

S7. References

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