

Supplementary Information for

Co-templating and modelling in the rational synthesis of zeolitic solids

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- S1. XRD patterns showing co-templating effects of tetraethylammonium ions in the synthesis of SAPO STA-7
- S2. Indexing the XRD pattern of SAPO STA-7
- S3. Solid state NMR of SAPO STA-7
- S4. Analysis and single crystal structure solution of as-prepared SAPO STA-7
- S5. Rietveld refinement of calcined SAPO STA-7
- S6. Structure of K222
- S7. Indexed XRD of as-prepared MgAPO STA-14 (**KFI**)
- S8. Indexed XRD of as-prepared MgAPO-42
- S9. ¹³C MASNMR of as-prepared MgAPO STA-14 (**KFI**)
- S10. Analysis and single crystal structure solution of as-prepared MgAPO STA-14 (**KFI**)
- S11. Rietveld refinement of calcined SAPO STA-14 (**KFI**)
- S12. Molecular Modelling
- S13. N₂ Adsorption isotherms (77 K) on SAPO STA-7 and SAPO STA-14

S1 XRD patterns showing co-templating effects of tetraethylammonium in the synthesis of SAPO STA-7

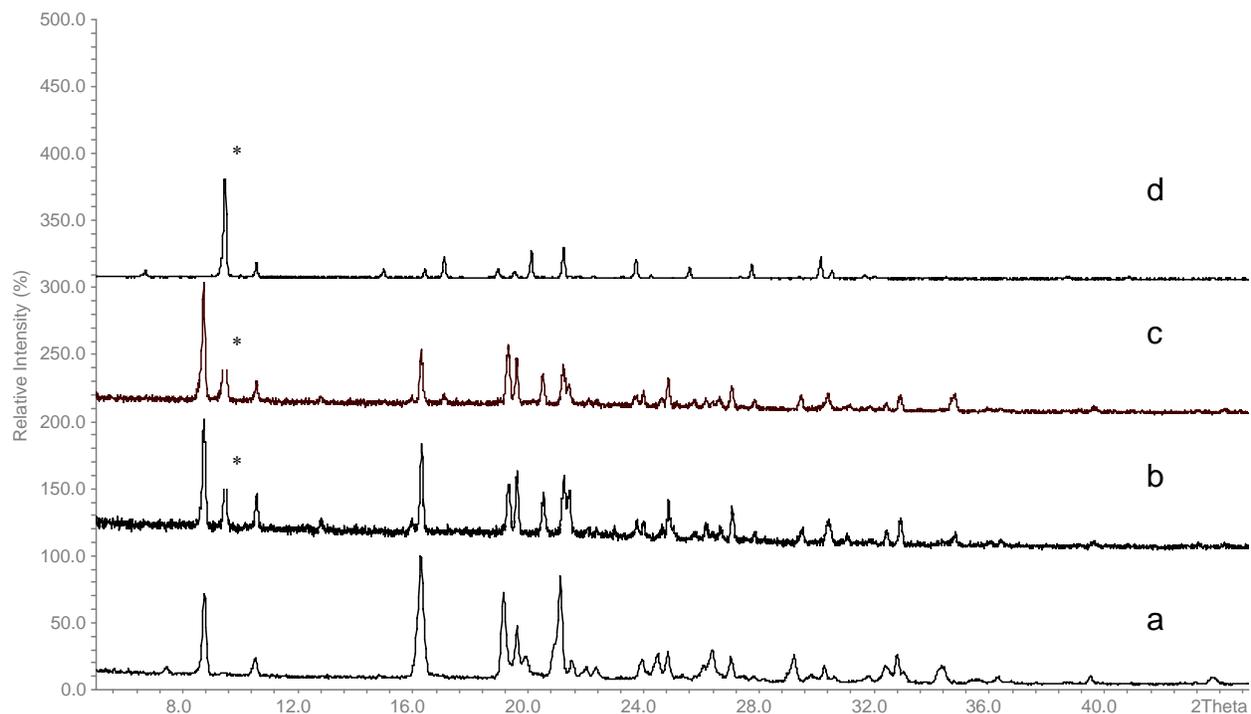
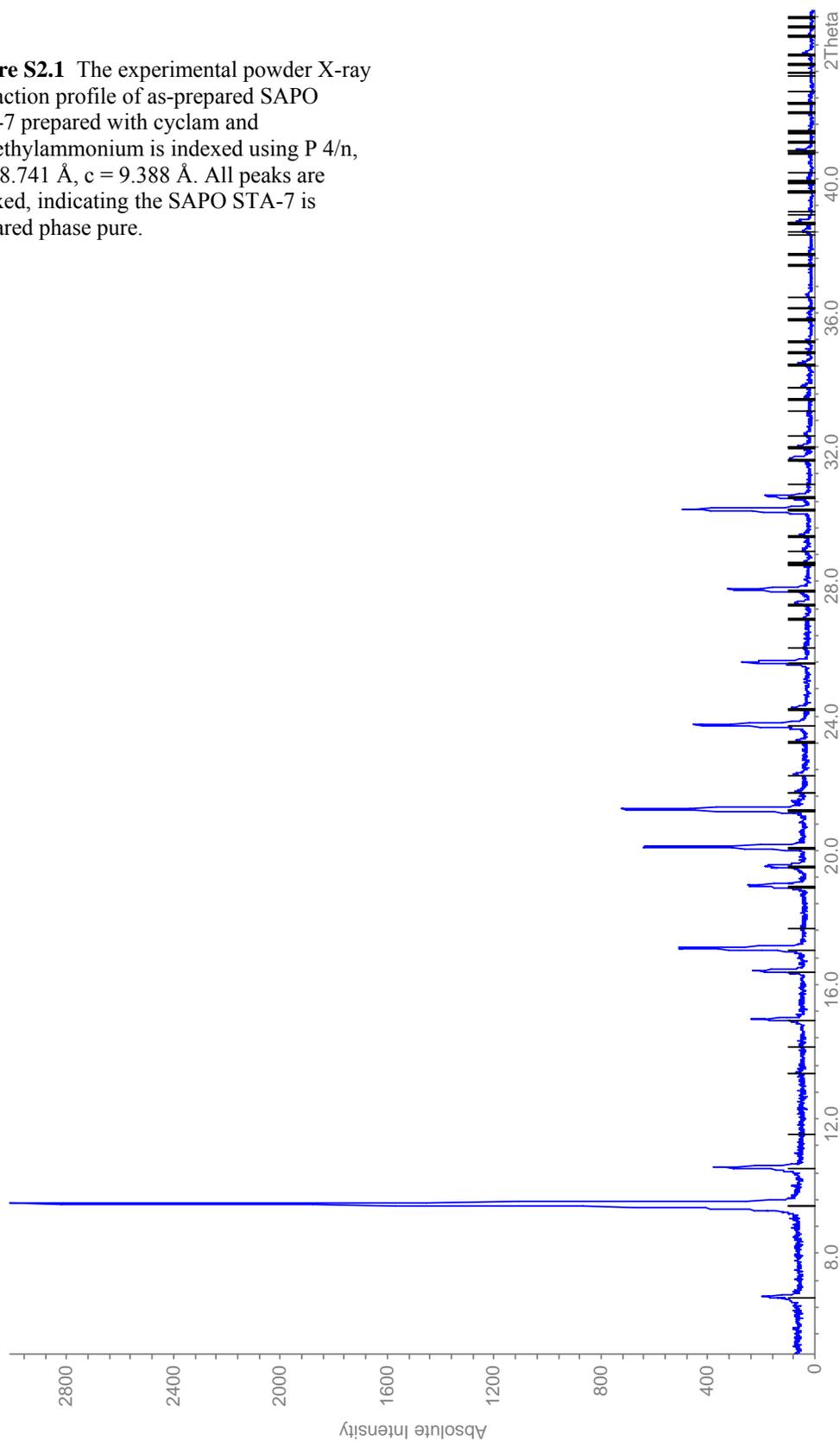


Figure S1.1 XRD patterns of SAPO syntheses. (a) STA-6 prepared with tetramethylcyclam, (b) STA-6 plus minority STA-7 (the main peak of which is denoted by an asterisk in all relevant plots) prepared in the presence of cyclam plus di-n-propylamine, (c) STA-6 prepared using cyclam plus di-isopropylamine as a co-base, (d) SAPO STA-7 prepared using cyclam plus tetraethylammonium hydroxide as a co-base. These show that the tetraethylammonium ions act as a selective co-template for SAPO STA-7.

S2 Indexing the XRD pattern of SAPO STA-7

Figure S2.1 The experimental powder X-ray diffraction profile of as-prepared SAPO STA-7 prepared with cyclam and tetraethylammonium is indexed using P 4/n, $a = 18.741 \text{ \AA}$, $c = 9.388 \text{ \AA}$. All peaks are indexed, indicating the SAPO STA-7 is prepared phase pure.



S3 Solid state NMR of as-prepared SAPO STA-7

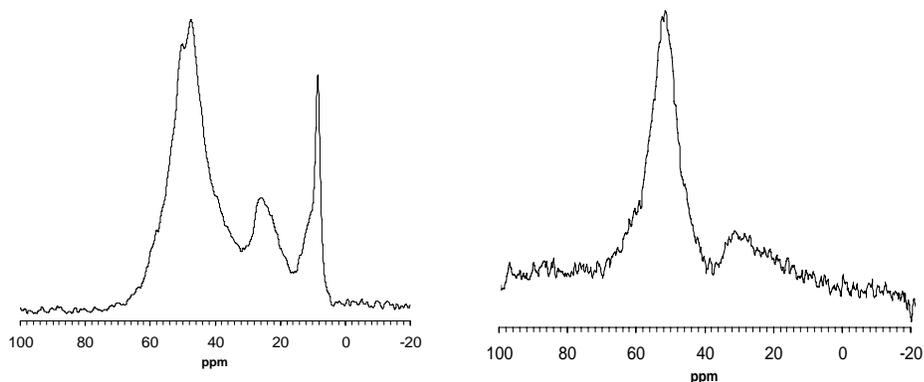


Figure S3.1 (Left) ^{13}C MASNMR of SAPO STA-7 (cyclam/tea⁺)
(Right) ^{13}C MASNMR of cyclam, for comparison

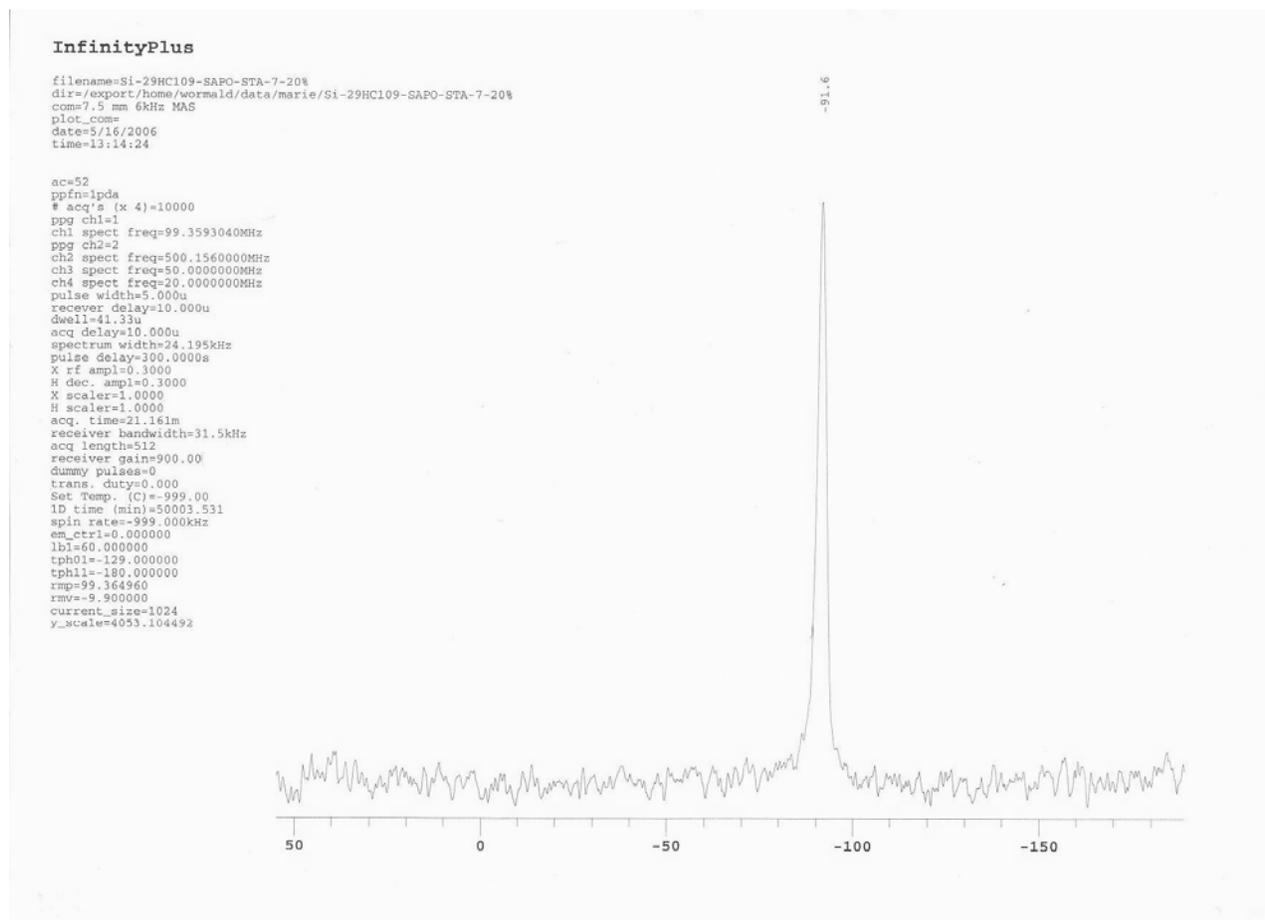


Fig. S3.2 ^{29}Si MASNMR of as prepared SAPO STA-7

S4. Analysis and single crystal structure solution of as-prepared SAPO STA-7

EDX analysis of SAPO STA-7 gave Si/(Al+Si+P) of 0.11. TGA in flowing air indicated a weight loss below 600 °C, attributed to water molecules and organic templates, of 22 %. Elemental analysis gave 10.50wt% C, 2.54 wt% H and 3.33 wt%N. The atomic C/N ratio, 3.7, was between that of the two templates and consistent with a 1 : 1 mix (18/5 = 3.6). By a combination of the overall C and N contents, and weight loss, the unit cell composition was estimated at $[(\text{NC}_8\text{H}_{20})_{1.8}(\text{N}_4\text{C}_{10}\text{H}_{26})_{1.8}(\text{H}_2\text{O})_{11}][\text{Al}_{24}\text{P}_{18.5}\text{Si}_{5.5}\text{O}_{96}]$. (Calculated: C 10.49 wt%, H 2.73 wt% N 3.40wt%), with cages 90% occupied.

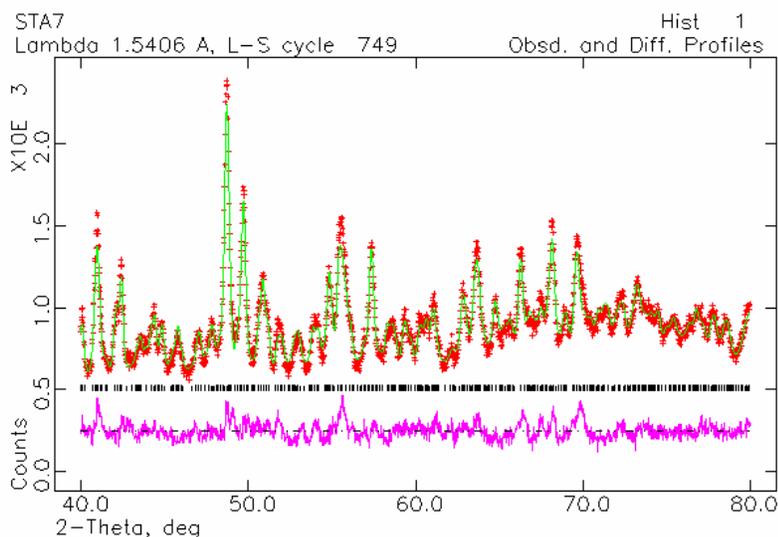
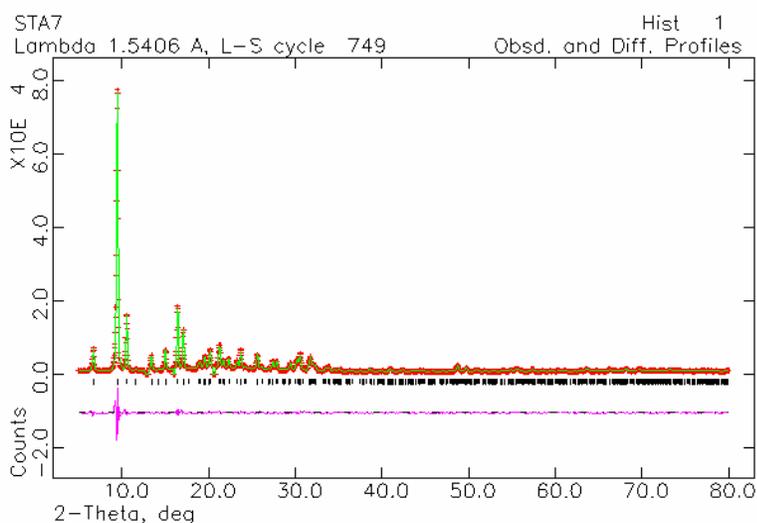
Details of the single crystal structure solution are given in the cif file. It was possible to determine the position of the tetraethylammonium ions in the smaller cages, disordered over two symmetrically related positions, but not to determine the positions of the cyclam molecules. Including cyclam in a modelled position slightly improved the fit, but the thermal parameters refined to an unreasonably large value. The positions of some extra-framework density was refined as extra-framework oxygen atoms.

We also thank one referee for the following comment.

‘After removing the water oxygen atoms from the model, a SQUEEZE calculation (PLATON)¹ shows there to be two voids of 500 containing a total of ca. 390 e per unit cell, which is in reasonable agreement with the proposed 1.8 cyclam molecules plus 11 water molecules per unit cell.’

1. P. van der Sluis and A. L. Spek *Acta Cryst A*, 1990, **46**, 1194

S5. Rietveld refinement of calcined SAPO STA-7 ($\text{AlP}_{0.78}\text{Si}_{0.22}\text{O}_4$) $P 4/n$ $a = 18.6931(7) \text{ \AA}$ $c = 9.4191(5) \text{ \AA}$
X-ray powder diffraction of a calcined sample of SAPO STA-7, dehydrated and sealed in a 0.7 mm quartz glass capillary, was performed on a STOE Stadi/p laboratory diffractometer using monochromated X-rays of wavelength 1.54056 \AA , with data collected from $5 - 80^\circ 2\theta$. The coordinates of the framework atoms derived from the single crystal structure of as-prepared SAPO STA-7 were taken for the starting model. The background was modeled using a cosine Fourier series with 32 terms and the peak profiles modelled using a pseudo-Voigtian profile incorporating an asymmetry parameter. Zero-point and unit cell parameters were also varied, and 2θ regions $12.6-13.0$, $15.9-16.1$ and $20.5-20.8$, which included small impurity peaks, were excluded. Atomic coordinates were refined with restraints, so that P-O distances were $1.53(6) \text{ \AA}$ and Al-O $1.74(7) \text{ \AA}$. The thermal parameters of the atoms were assigned a single value, which refined to $0.020(2) \text{ \AA}^2$. A good fit to the X-ray profile was obtained, $R_{\text{wp}} = 7.8\%$, $R_p = 5.4\%$. (Fig. S.3.1, below)



Fractional Atomic Coordinates for calcined SAPO STA-7

P1	1.0677(11)	-0.1669(8)	0.0964(19)
P2	0.8385(9)	-0.0556(9)	-0.1526(21)
P3	0.9478(10)	0.0650(10)	0.3377(23)
Al1	0.8395(9)	0.0644(12)	0.0826(22)
Al2	0.6678(10)	-0.0424(9)	-0.1566(23)
Al3	1.0677(11)	-0.0526(11)	0.3338(24)
O1	0.8803(14)	0.0525(19)	0.2452(27)
O2	0.9825(12)	0.1398(12)	0.2983(26)
O3	0.7571(10)	-0.0632(11)	-0.1837(22)
O4	0.8428(15)	-0.0209(12)	-0.0106(25)
O5	0.9894(13)	-0.0023(10)	0.3141(23)
O6	1.0624(20)	-0.1326(13)	0.2374(26)
O7	0.8824(10)	-0.1264(10)	-0.1639(23)
O8	0.9300(18)	0.0786(16)	0.4894(24)
O9	1.1369(12)	-0.1394(14)	0.018(4)
O10	1.0730(10)	-0.2517(9)	0.1123(21)
O11	1.0001(12)	-0.1476(15)	0.0030(24)
O12	0.8664(15)	-0.0057(14)	-0.2761(28)

Selected Bond lengths

P1_O6	1.479(19)	Al1_O1	1.725(19)
P1_O9	1.575(19)	Al1_O4	1.821(20)
P1_O10	1.595(20)	Al1_O9	1.749(19)
P1_O11	1.582(20)	Al1_O10	1.673(24)
P2_O3	1.556(18)	Al2_O2	1.819(26)
P2_O4	1.489(19)	Al2_O3	1.733(18)
P2_O7	1.562(20)	Al2_O7	1.605(25)
P2_O12	1.580(20)	Al2_O11	1.742(26)
P3_O1	1.551(18)	Al3_O5	1.749(19)
P3_O2	1.586(19)	Al3_O6	1.752(19)
P3_O5	1.497(18)	Al3_O8	1.735(19)
P3_O8	1.489(18)	Al3_O12	1.732(20)

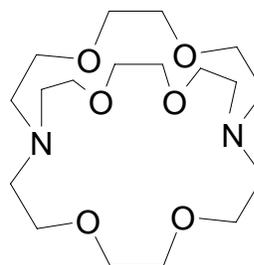
Angles

O6_P1_O9	109.4(20)	O4_P2_O7	113.7(18)
O6_P1_O10	110.5(17)	O4_P2_O12	112.8(19)
O6_P1_O11	110.3(19)	O7_P2_O12	106.0(17)
O9_P1_O10	108.6(16)	O1_P3_O2	109.5(19)
O9_P1_O11	108.8(16)	O1_P3_O5	102.3(17)
O10_P1_O11	109.2(17)	O1_P3_O8	112.6(19)
O3_P2_O4	105.2(16)	O2_P3_O5	119.6(17)
O3_P2_O7	115.0(16)	O2_P3_O8	99.5(19)
O3_P2_O12	103.8(16)	O5_P3_O8	113.7(18)
O1_Al1_O4	107.4(16)	O3_Al2_O7	105.1(14)
O1_Al1_O9	118.4(18)	O3_Al2_O11	116.0(17)
O1_Al1_O10	107.3(16)	O7_Al2_O11	109.4(15)
O4_Al1_O9	115.5(17)	O5_Al3_O6	110.9(17)
O4_Al1_O10	101.4(16)	O5_Al3_O8	105.8(15)
O9_Al1_O10	105.2(15)	O5_Al3_O12	102.9(15)
O2_Al2_O3	107.9(14)	O6_Al3_O8	105.1(16)
O2_Al2_O7	111.7(15)	O6_Al3_O12	114.5(17)
O2_Al2_O11	106.9(16)	O8_Al3_O12	117.4(17)

S6 Structural formula of K222

4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]kexacosane (K222)

$C_{18}N_2O_6H_{36}$



S7 Indexed XRD pattern of MgAPO STA-14 (KFI)

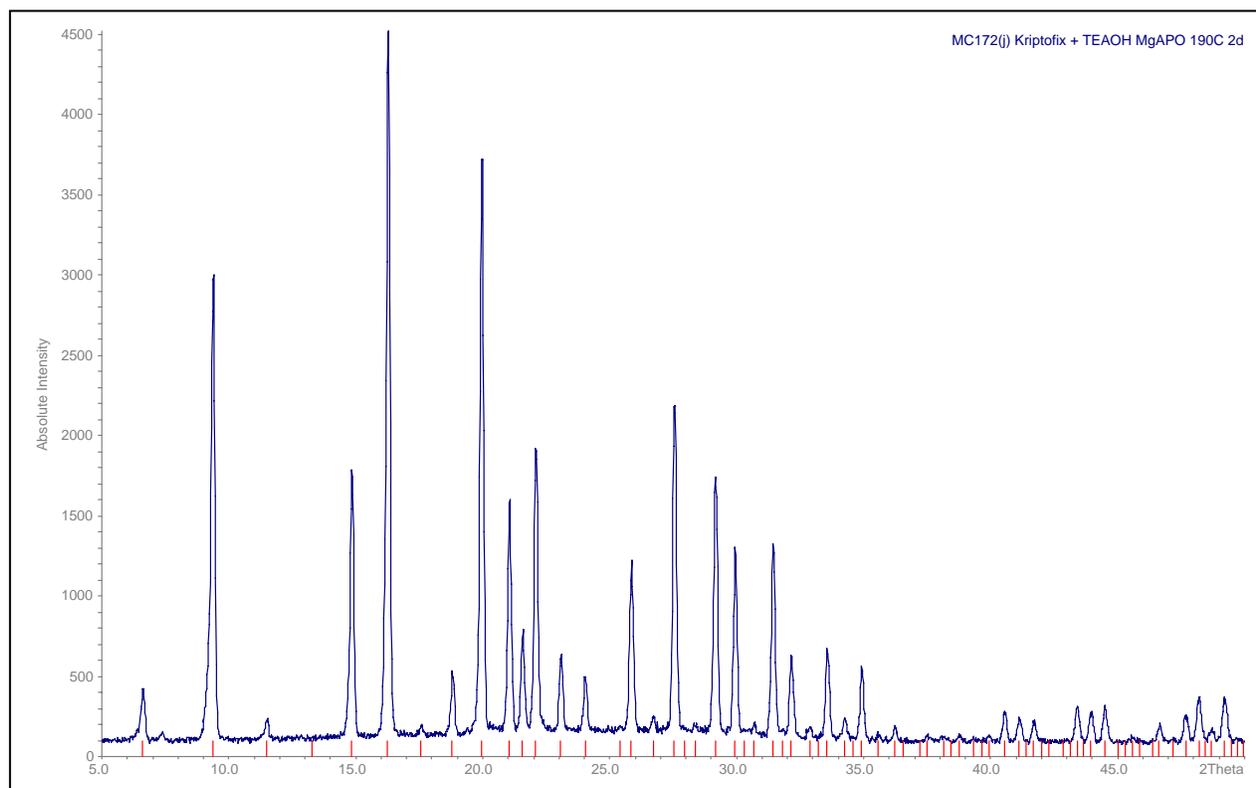


Figure S7.1 XRD pattern of MgAPO STA-14 (KFI) prepared with K222 plus tetraethylammonium hydroxide. The pattern is fully indexed by tick marks generated from P n -3 n, with $a = 18.8673(17) \text{ \AA}$, indicating the material is pure.

S8 Indexed XRD pattern of as-prepared MgAPO-42

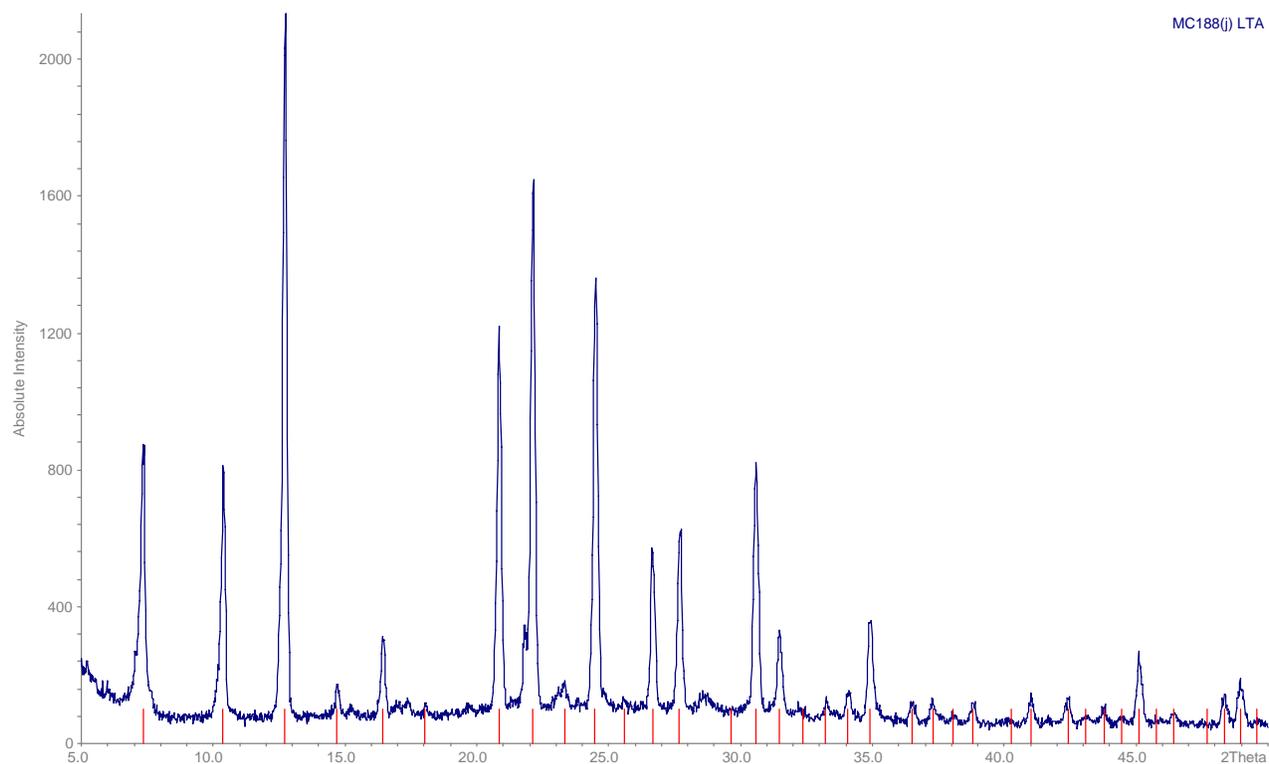


Figure S8.1 XRD pattern of MgAPO-42 (LTA) prepared using K222 plus tetrapropylammonium hydroxide. The pattern is indexed by tick marks generated for Pm-3m, $a = 12.048(4) \text{ \AA}$, indicating the product is MgAPO-42 with only very minor impurities.

S9 ^{13}C MASNMR of as-prepared MgAPO STA-14 (KFI)

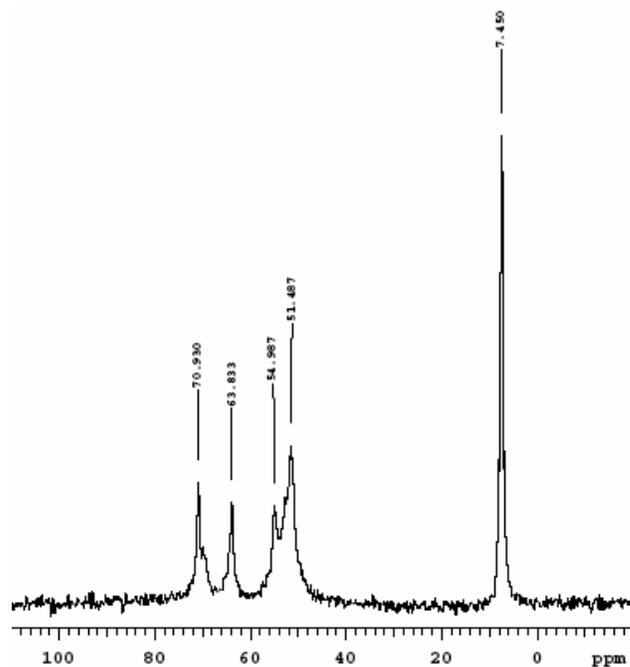


Figure S8.1 ^{13}C CP MASNMR of as-prepared MgAPO STA-14. ($\text{N}(\text{CH}_2\text{CH}_3)_4$ 7.45 and $\text{N}(\text{CH}_2\text{CH}_3)_4$ 51.5; $\text{H}^+\text{N}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_3\text{NH}^+$: 55.0, 63.8, 70.9)

S10. Analysis and single crystal structure solution of as-prepared MgAPO STA-14 (KFI)

EDX analysis of MgAPO STA-14 gave an estimated inorganic unit cell composition of $[\text{Mg}_{10}\text{Al}_{38}\text{P}_{48}\text{O}_{192}]$

TGA in flowing air indicated a weight loss below 700 °C, attributed to water molecules and organic templates, of 25 %.

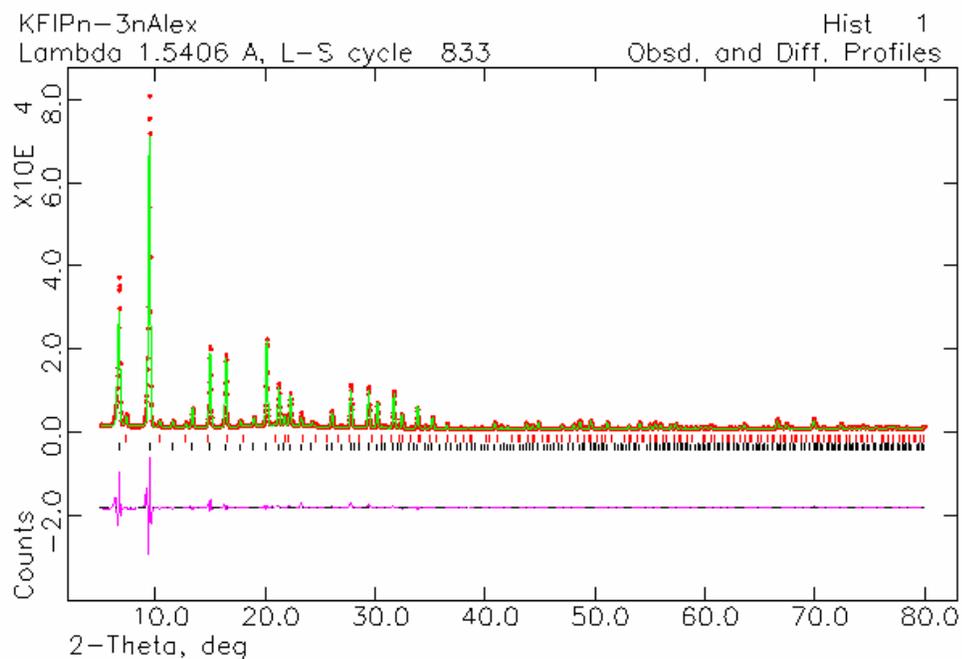
Elemental analysis gave 10.20 wt% C, 2.34 wt% H and 1.73 wt%N. From single crystal diffraction, it appeared that the tetraethylammonium ions occupy the MER cages with an occupancy close to 100% (taken as a fractional occupancy of 1). C and N contents can then be fitted if 1 of the two alpha cages are occupied by K222, and final charge balancing is by ammonium ions, as breakdown products of the organic bases. A combination of the overall C and N contents and the weight loss in the TGA gives a unit cell composition estimated at

$(\text{NC}_8\text{H}_{20})_6(\text{N}_2\text{C}_{18}\text{O}_6\text{H}_{38})_1(\text{H}_2\text{O})_{40}(\text{NH}_4)_2[\text{Mg}_{10}\text{Al}_{38}\text{P}_{48}\text{O}_{192}]$ Calculated: C 10.2 wt%, H 3.04 wt% N1.80 wt%).

Details of the single crystal structure solution are given in the cif file. It was possible to determine the position of the tetraethylammonium ions in the smaller cages, disordered over two different positions, with *ca.* 80% in the tt.tt configuration described in the paper. A small amount of residual electron density in the cages was refined (C3) as disorder in the tea configuration (20%). It was not possible to determine the positions of the K222 molecules, which exhibit disorder. Including K222 in a modelled position slightly improved the fit, but the thermal parameters refined to an unreasonably large value. Some extra-framework electron density in the α -cage was refined as oxygen and nitrogen atoms.

S11 Rietveld refinement of calcined SAPO STA-14 (KFI) $Pn-3n$ $a = 18.7354(4)$

X-ray powder diffraction of a sample of SAPO STA-14, calcined at 550 °C and subsequently dehydrated at 150 °C and sealed in a 0.7 mm od quartz glass capillary, was performed on a STOE Stadi/p laboratory diffractometer using monochromated X-rays of wavelength 1.54056 Å, with data collected from 5 – 90 °2 θ . The coordinates of the framework atoms derived from the single crystal structure of as-prepared SAPO STA-14 were taken for the starting model. The background was modeled using a cosine Fourier series with 25 terms and the peak profiles modelled using a pseudo-Voigtian profile incorporating an asymmetry parameter. A second, minor phase was identified to be SAPO-42, was also and was included and refined within a 2-phase refinement. For the AlPO-42, atomic parameters were taken from a previous single crystal refinement [M. J. Maple, E. F. Philp, A. M. Z. Slawin, P. Lightfoot, P. A. Cox and P.A.Wright, *J. Mater. Chem.*, 2001, **11**, 98] and not refined, because the peaks were so small. Zeropoint and unit cell parameters of both phases were allowed to vary, as well as their relative fractions. The starting model for the calcined SAPO STA-14 was that of the framework of the as-prepared MgAPO STA-14, and the structure was refined in space group $Pn-3n$, which permits ordering of Al and P in alternating tetrahedral sites. Atomic coordinates of SAPO STA-14 were refined with restraints, so that P-O distances were 1.53(6) Å and Al-O (1.74(7) Å. Al and P thermal parameters were constrained to be the same, as were those of all framework oxygen atoms. Some extra-framework scattering was located in the MER cages by difference Fourier analysis, which was attributed to fragments of residual organics and water molecules and refined as oxygen atoms with a thermal parameter of 0.05 Å² (fixed). An acceptable fit to the X-ray profile was obtained, $R_{wp} = 11.5\%$, $R_p = 7.4\%$, although the asymmetry of the largest peaks was imperfectly modelled. According to the refinement, only 2.5% of the mixture was made up by the SAPO-42 impurity.



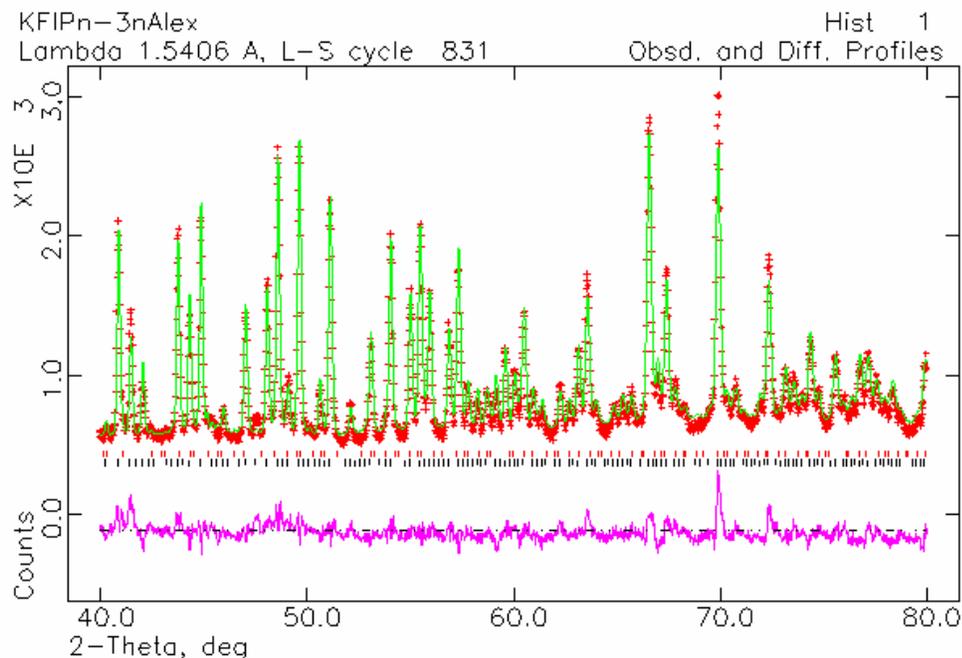


Figure S11.1 Rietveld plots for calcined SAPO STA-14 (KFI), with experimental data (red crosses), fitted profile (green solid line) and difference plot (purple), shown for the whole profile (above) and from 40 to 80° 2θ (below).

Tables S6.1 Atomic Coordinates

Coordinates				Occup	U/ Å ²
P1	0.0716(5)	0.5500(5)	0.6666(5)	1	0.003(1)
Al1	-0.0468(5)	0.4311(6)	0.6656(6)	1	0.003(1)
O1	0.1396(7)	0.5068(10)	0.6419(8)	1	0.012(1)
O2	0.0055(6)	0.5088(6)	0.6542(4)	1	0.012(1)
O3	0.0708(6)	0.6216(6)	0.6251(7)	1	0.012(1)
O4	0.0826(5)	0.5655(5)	0.7473(8)	1	0.012(1)
Ow1	0.25	0.75	0.25	0.61(2)	0.05
Ow2	0.25	0.75	0.00	0.56(2)	0.05

Bond lengths

P1_O1	1.580(14)
P1_O2	1.478(13)
P1_O3	1.550(14)
P1_O4	1.553(13)
Al1_O1	1.766(15)
Al1_O2	1.766(14)
Al1_O3	1.684(15)
Al1_O4	1.689(13)

Angle

O1_P1_O2	111.3(9)
O1_P1_O3	107.7(11)
O1_P1_O4	105.9(8)
O2_P1_O3	111.5(8)
O2_P1_O4	111.2(7)
O3_P1_O4	109.1(8)
O1_Al1_O2	106.9(8)
O1_Al1_O3	110.0(10)
O1_Al1_O4	105.5(8)
O2_Al1_O3	116.2(8)
O2_Al1_O4	110.9(7)
O3_Al1_O4	106.8(7)

S12 Molecular Modelling

The energy minimised locations of bases within theoretical aluminophosphate frameworks SAV and KFI were obtained by molecular modelling.

The experimentally-determined framework coordinates of STA-7 determined for MAPO versions were taken from previous studies [Wright et al., 2000] and the AlPO_4 coordinates for KFI were found by modelling by GULP to possess Pn-3n symmetry.

Energy minimisation was performed using Monte Carlo – Simulated annealing routines in the program Discover [implemented in MS Modelling 4.0 by Accelrys Inc (MS Modelling version 4.0, Accelrys Inc, San Diego, USA, 2005). Van der Waals interactions were calculated using the universal forcefield [K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff [UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations, *J. Am. Chem. Soc.*, 1992, 114, 10024].

S13. N_2 Adsorption on SAPO STA-7 and SAPO STA-14

