Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

A crystalline $AlPO_4$-5 intermediate: designed synthesis, structure and phase transformation

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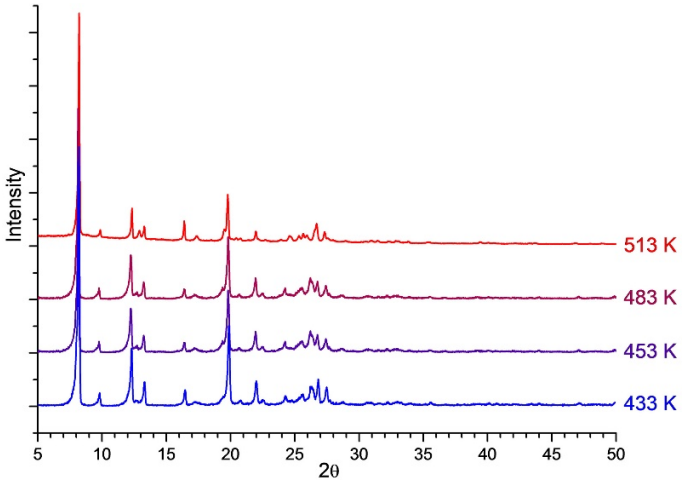

Fig. S1 PXRD patterns of **1** synthesized under different temperatures.

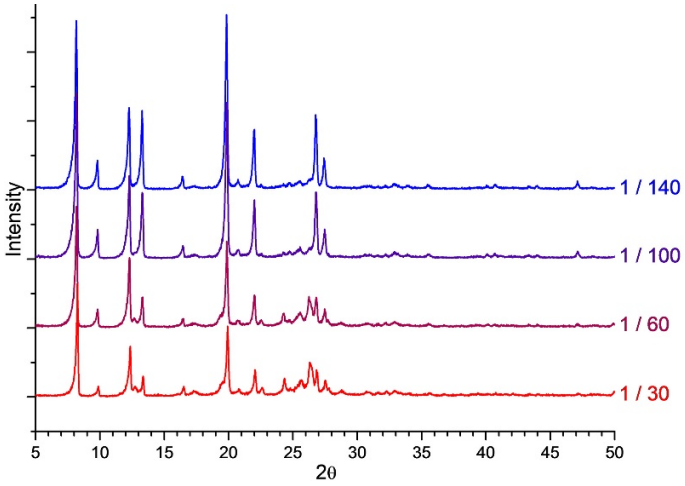

Fig. S2 PXRD patterns of **1** synthesized with a series of water amounts (shown in mole ratios of Al_2O_3 / H_2O).

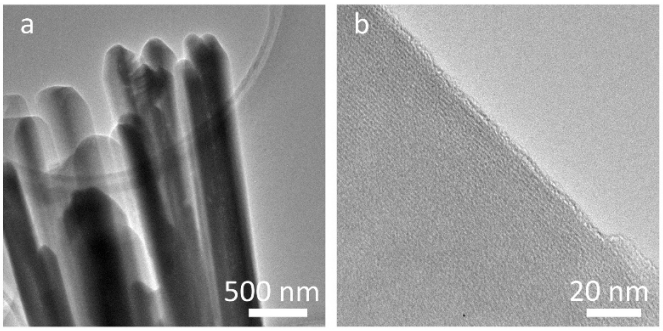

Fig. S3 TEM images of **1**. a) Small plate-aggregated broom-like morphology. b) Direct observation of the layer accumulation.

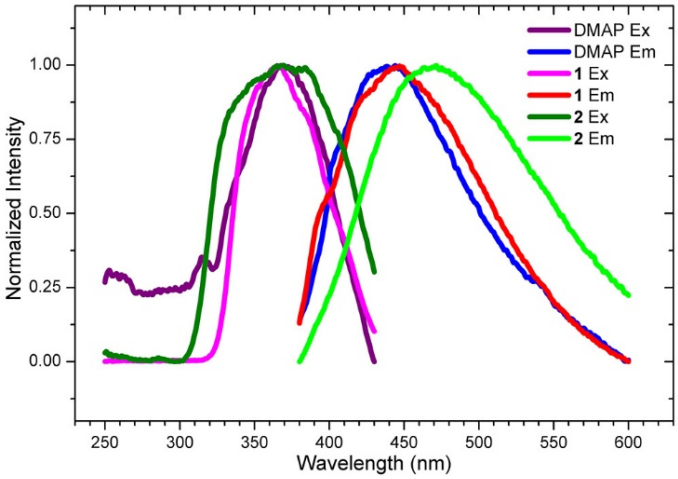

Fig. S4 Fluorescence spectra of the DMAP solid, **1** and **2**.

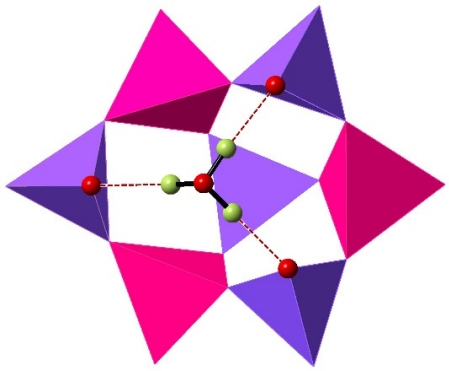

Fig. S5 The hydrogen bonding interaction between the water molecule and the PO_4-capped 6-membered ring. AlO_4 and PO_4 tetrahedra are shown in rose red and violet, respectively. O and H atoms are shown in red and dark green, respectively.

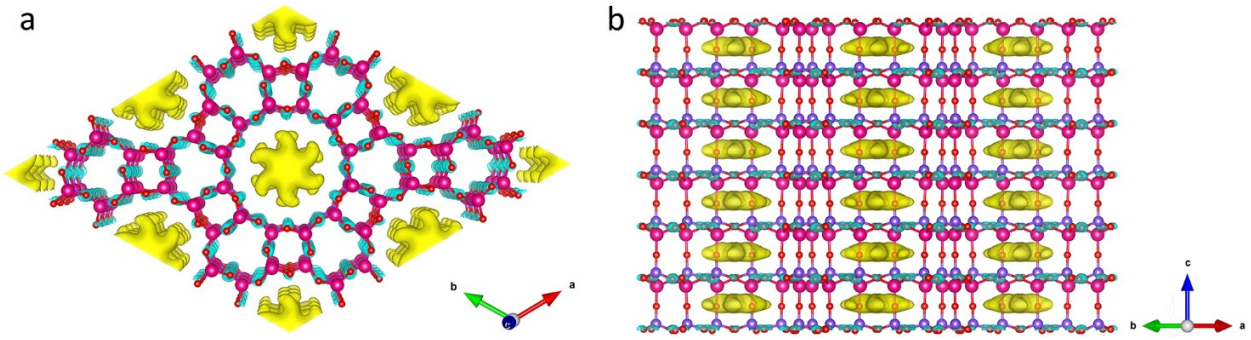

Fig. S6 The difference electron density maps of the as-made $AlPO_4$-5 after initial scaling, showing the positive differences only. a) Viewed from the *c*-axis. b) Viewed from the [110] direction. Al, P and O atoms are shown in rose red, violet and red, respectively.

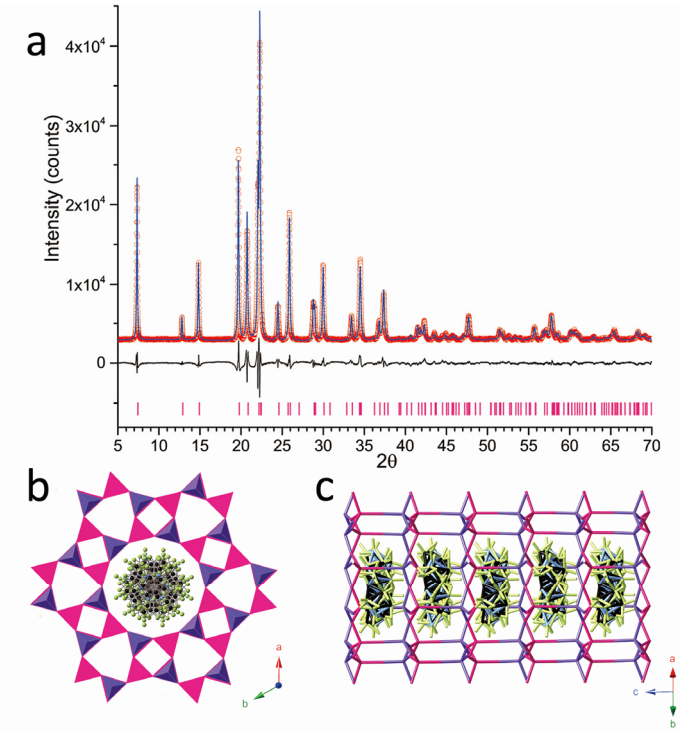

Fig. S7 Structure of the as-made $AlPO_4$-5. a) Rietveld refinement of the PXRD data. Red circle, blue solid line, black curve and rose red line represent the observed data, calculated pattern, difference curve and the expected reflection positions. b) The $AlPO_4$-5 structure containing DMAP molecules viewed from the *c*-axis. c) Position of the π-π stacked DMAP molecules inside the $AlPO_4$-5 channel viewed from [110] direction. Note that the disorder of the DMAP molecules is induced by the 6-fold axis of the structure. AlO_4 and PO_4 tetrahedra are shown in rose red and violet, respectively, while Al, P, C, H, N atoms are shown in rose red, violet, black, dark green and blue, respectively.

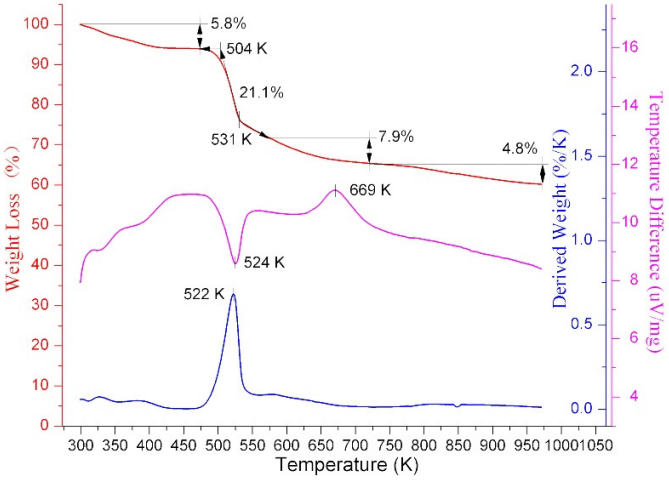

Fig. S8 TG-DSC curve of the as-made **1**.

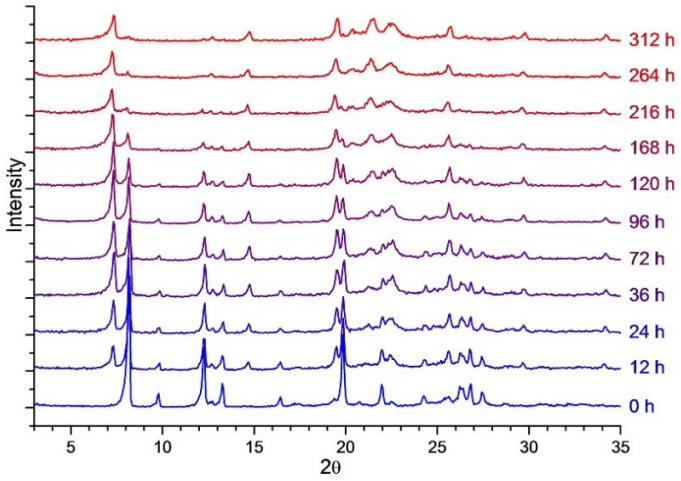

Fig. S9 PXRD patterns of **1** heated under 383 K for different time.

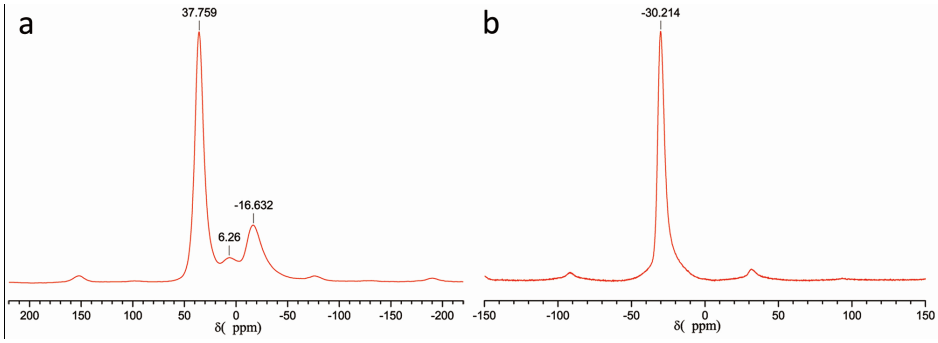

Fig. S10 MAS NMR spectra of **1** calcined at 723 K for 10 h. a) ^{27}Al. b) ^{31}P. Those small peaks without index are spinning sidebands.

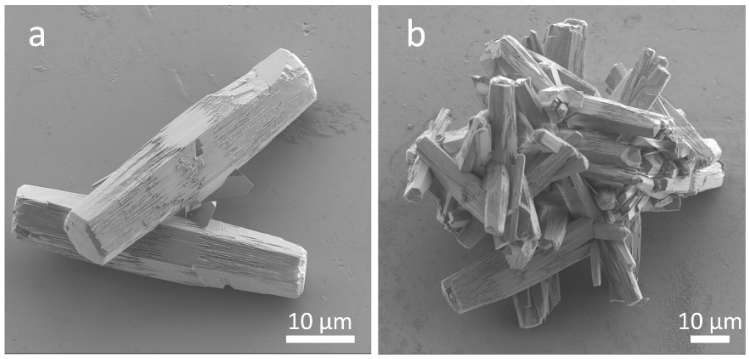

Fig. S11 SEM images of the **1** sample after SAC treatment under 453 K for 24 h, showing the typical hexagonal prism morphology.

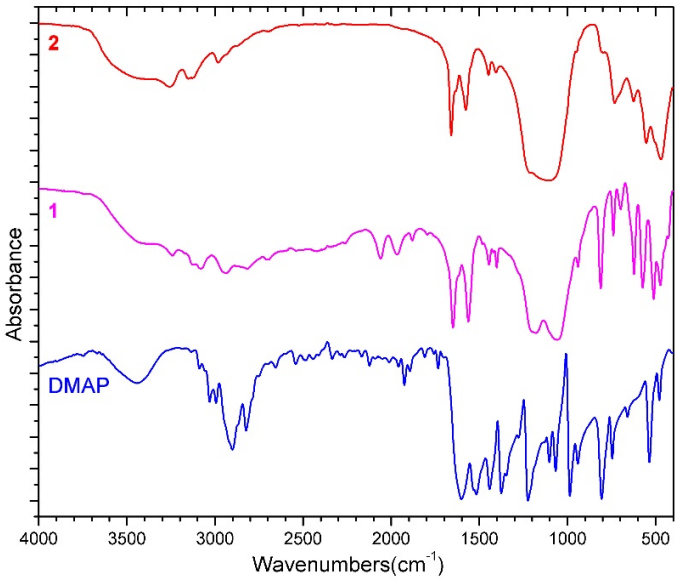

Fig. S12 FT-IR spectra of DMAP solid, **1** and **2**.

Table S1 Crystallographic data and structure refinements for **1**.

Compound	**1**
Empirical formula	$(C_7H_{11}N_2)_2(H_3O)(Al_3P_4O_{16})\cdot(H_2O)_{2.5}$
Formula weight	771.2429
Temperature (K)	180.0(10)
Crystal size (mm^3)	0.08 × 0.01 × 0.01
Crystal system	Monoclinic
Space group	$P\ 2_1/c$
a / Å	8.9973(7)
b / Å	14.6074(11)
c / Å	21.2615(15)
α / °	90
ß / °	94.108(7)
γ / °	90
V / $Å^3$	2787.2(4)
Z	4
F(000)	1488
Reflection collected	4279
Independent reflections	3001
Restraints / parameters	0 / 392
Limiting indices	-9 ≤ h ≤ 9, -14 ≤ k ≤ 17, -25 ≤ l ≤ 23
GoF on F^2	1.049
Final *R* indexes [I≥2σ(I)]	R_1 = 0.0623, wR_2 = 0.1501
Final *R* indexes [all data]	R_1 = 0.0942, wR_2 = 0.1698
Residual density max / min (e $Å^{-3}$)	1.161 / -0.468

Note that $R_1 = \sum(\Delta F/\sum(F_o))$, $wR_2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$, $w = 1/[\sigma^2(F_o^2)]$.

Table S2 Crystallographic data and structure refinements for the as-made $AlPO_4$-5 (**2**).

Compound	**2**
Empirical formula	$(C_7H_{10}N_2)_{0.17}(AlPO_4)\cdot(H_2O)_{0.28}$
Formula weight	147.7657
Temperature (K)	298
Crystal system	Hexagonal
Space group	*P* 6cc
Unit cell dimensions	*a* = 13.6998(6) Å *c* = 8.5145(8) Å
V / Å^3	1383.97(20)
Z	12
X-ray source	Cu Kα1
Wavelength / Å	1.5406
2θ range / °	5.000 – 70.000
Number of reflections	119
Number of data points	9285
Number of independent parameters	74
Refinement method	Rietveld refinement
Rp	0.12527
Rwp	0.09420
Rexp	0.0499
GoF	1.8798

Note that the amount of the water was determined from the first weight loss ~3.43 % before 393 K from the TG-DSC curve (not shown), and the amount of the DMAP was derived from the element analysis. Thus the amount of those species were then directly included in the formula of **2**.