Supporting information for

A rigid calcium 2-ethylhexylphosphate one-dimensional polymer: Synthesis, structure, thermal behaviour and decomposition chemistry

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Fig. S21 FT-IR spectrum of decomposition product of **1** calcined product α-$Ca(PO_3)_2$ produced at 600 °C. (Weil, M. et al. Chem. Mater. **2007**, *19*, 5067-5073.)
Fig. S22 SEM images of α-$Ca(PO_3)_2$ material obtained after thermal decomposition of **1** at 600 °C.
Fig. S23 EDS mapping of α-$Ca(PO_3)_2$ material obtained after thermal decomposition of **1** at 600 °C.
Table S1. Continuous Shape measures of the coordination polyhedra of six coordinated Ca(II) in **1**.
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Table S5. Heat flow vs temperature data for compound **1** in the temperature range from -150 °C to 200 °C.

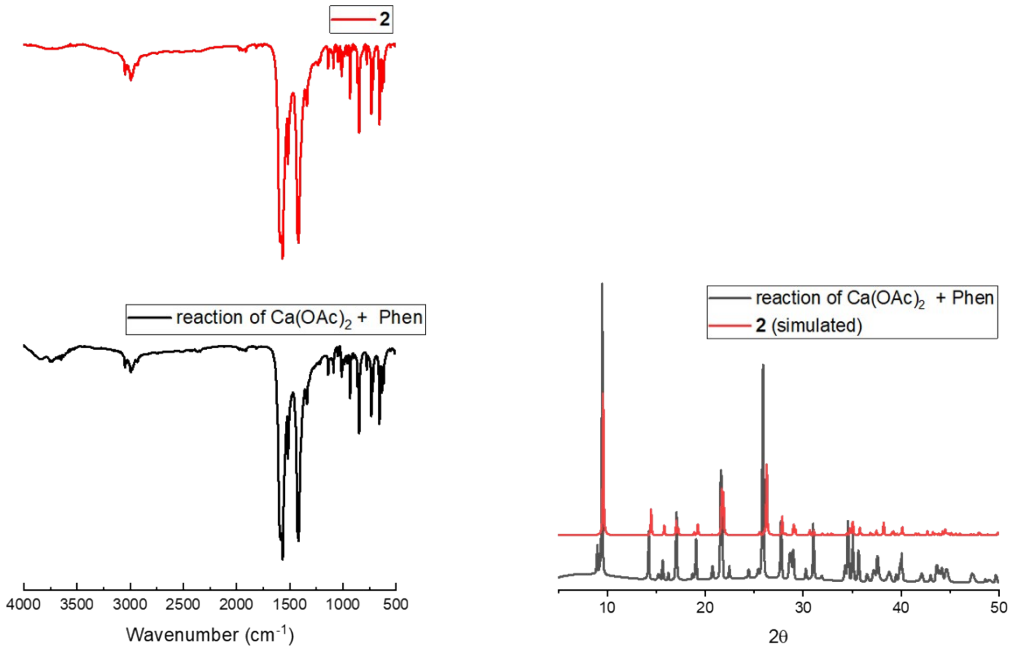
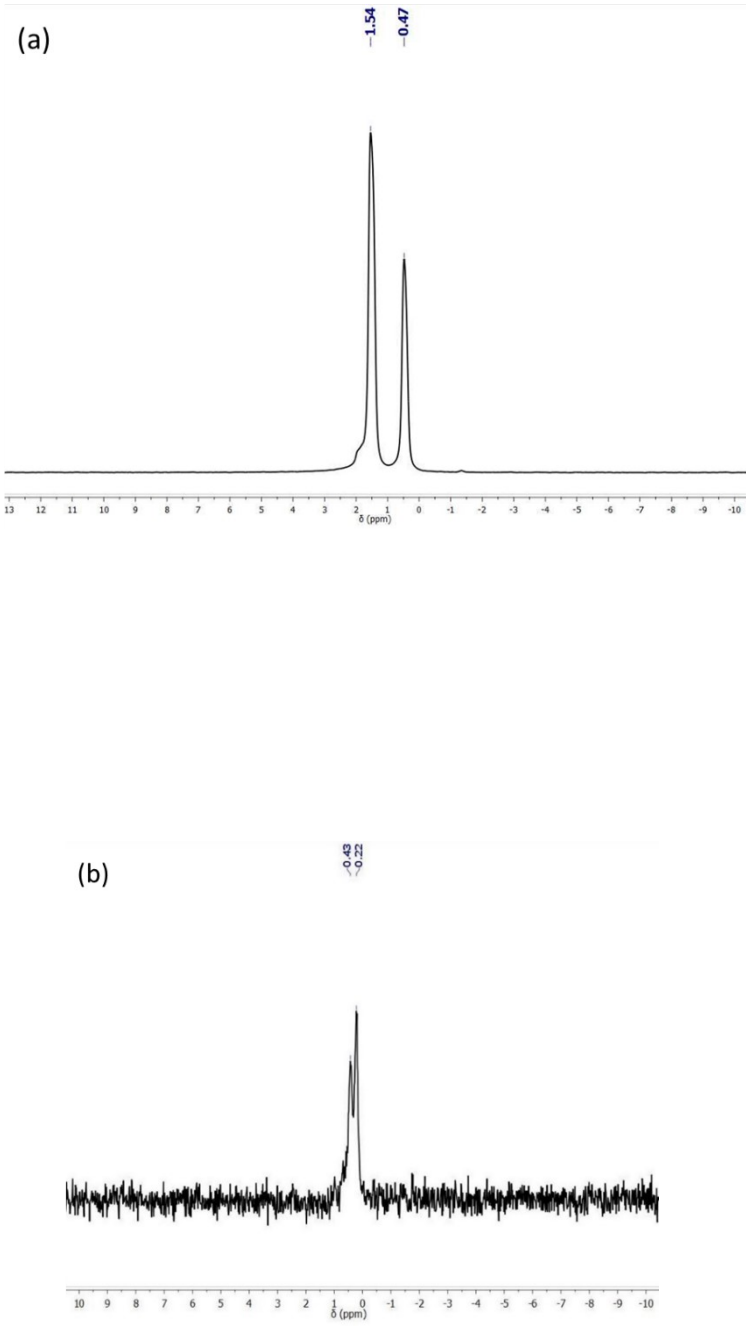


Fig. S1 IR (left) and PXRD (right) for the compound synthesised from the reaction of $Ca(OAc)_2$ and 1,10-phenanthroline.



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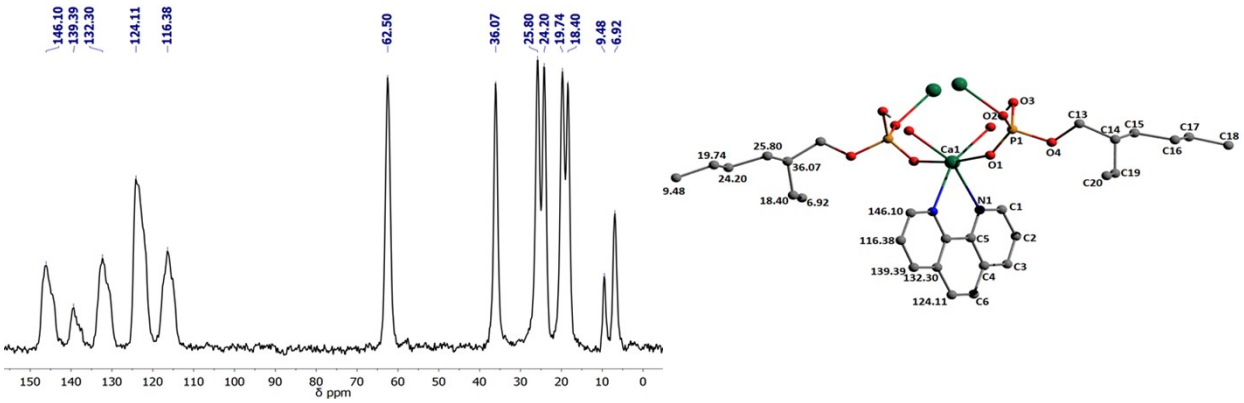


Fig. S3 CP-MAS ^{13}C NMR spectrum of **1** (125 MHz).

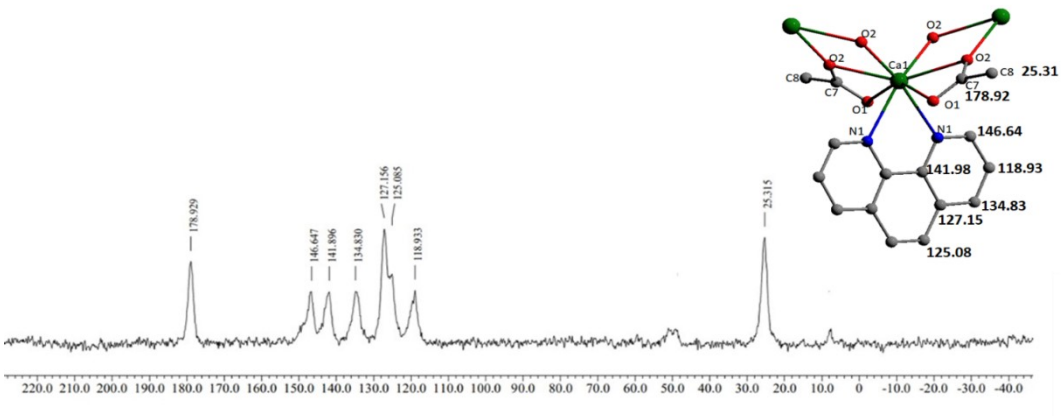


Fig. S4 CP-MAS ^{13}C NMR spectrum of **2** (150 MHz).

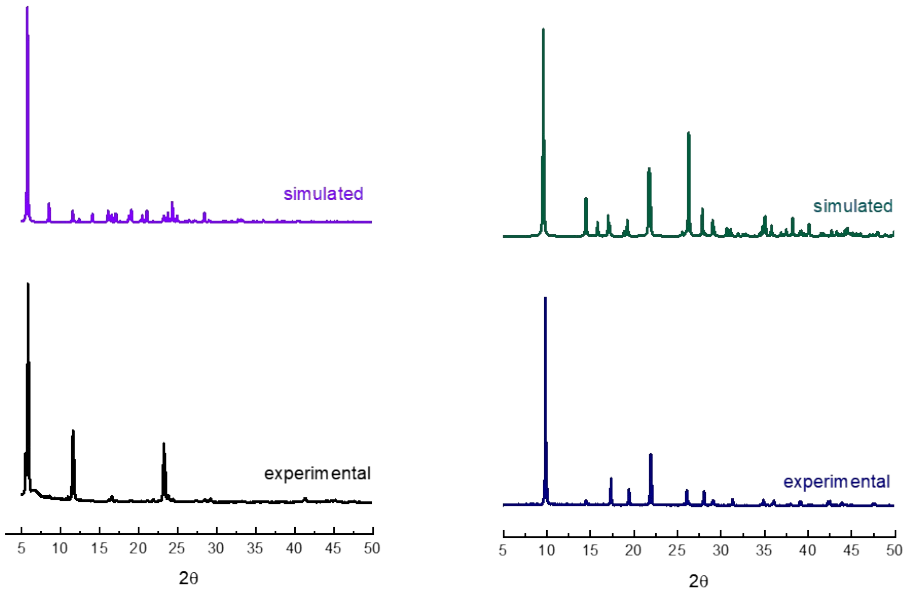


Fig. S5 Experimental and simulated PXRD patterns for **1** (left) at -123 ºC and **2** (right) at RT.

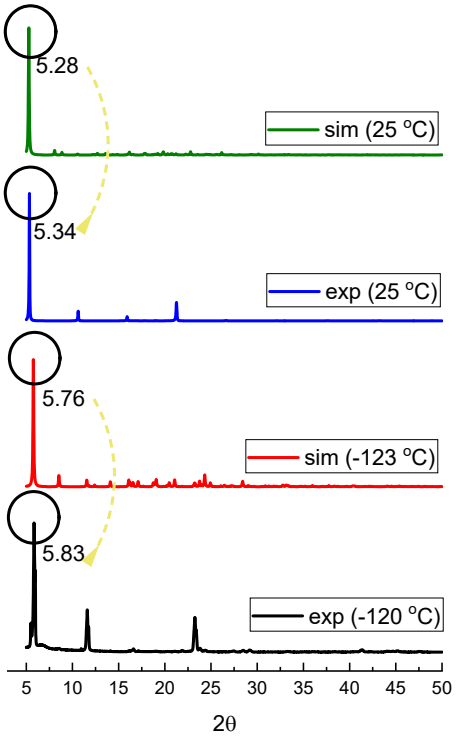


Fig. S6 Experimental and simulated PXRD patterns for **1** at different temperatures.

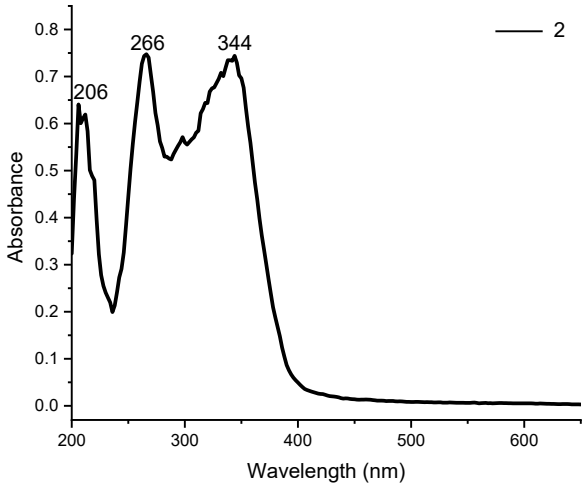


Fig. S7 DR UV-Vis spectrum of **2**.

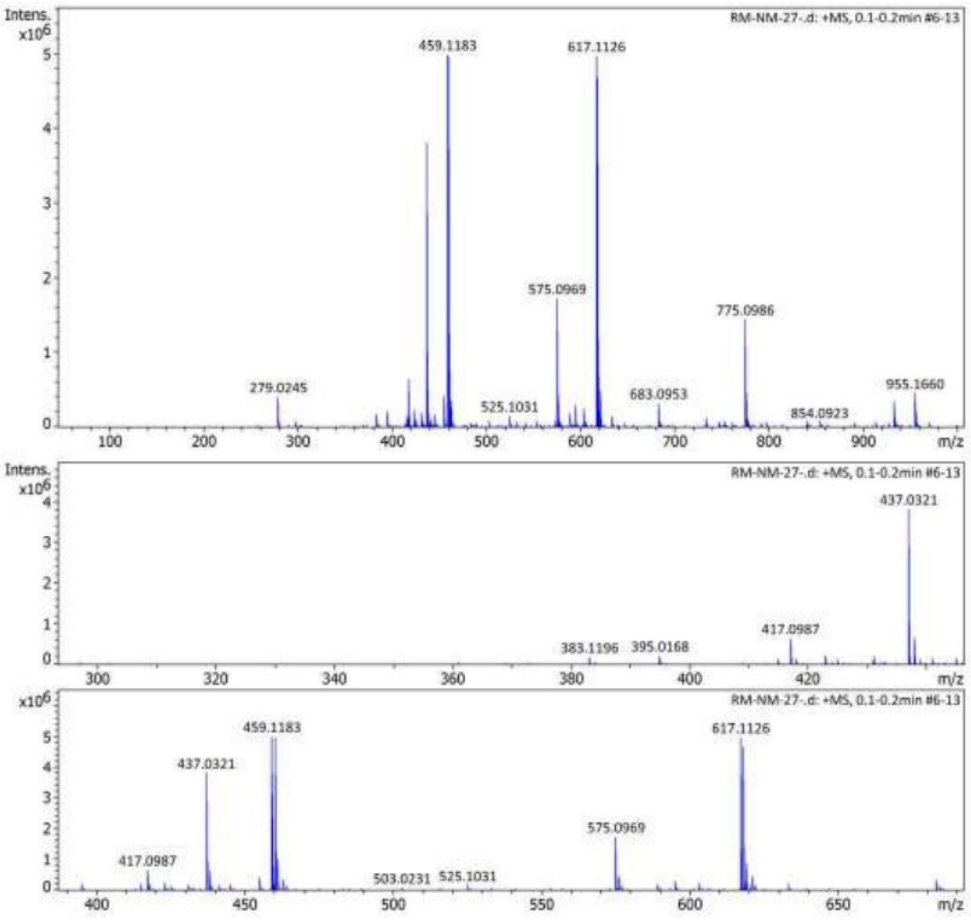


Fig. S8 ESI Mass spectrum of **2** in MeOH showing $[(phen)_2Ca_2(OAc)_3]^+$ peak at 617.11.

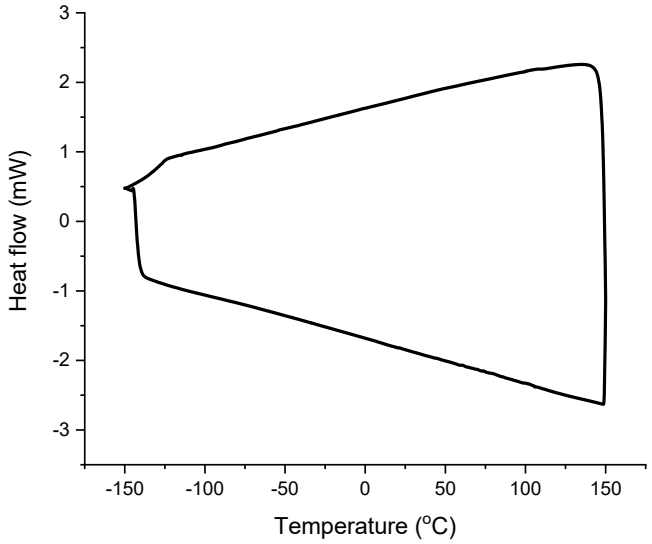


Fig. S9 DSC plot for **2** in the temperature range -150 °C to 150 °C.

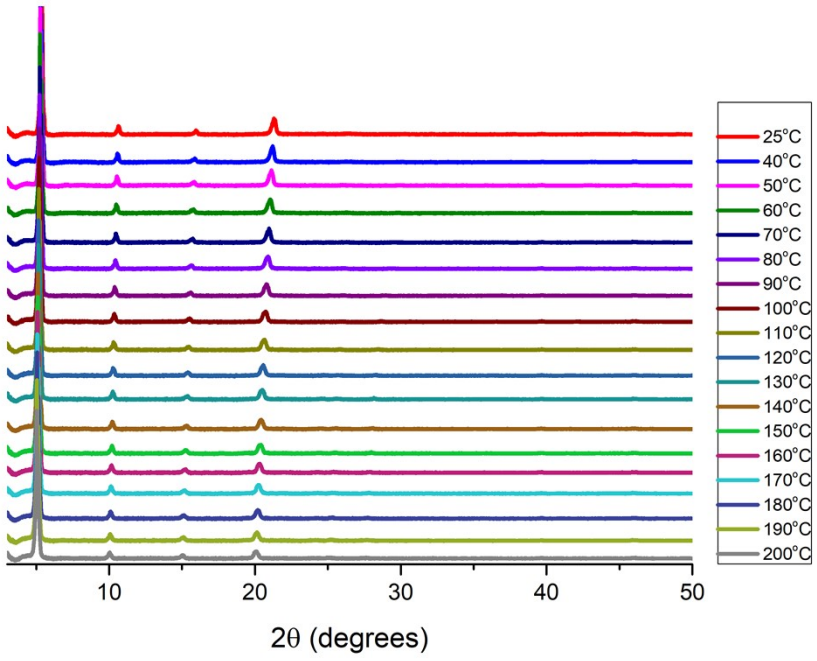


Fig. S10 Variable temperature PXRD of **1** at temperature ranging from 25 °C to 200 °C.

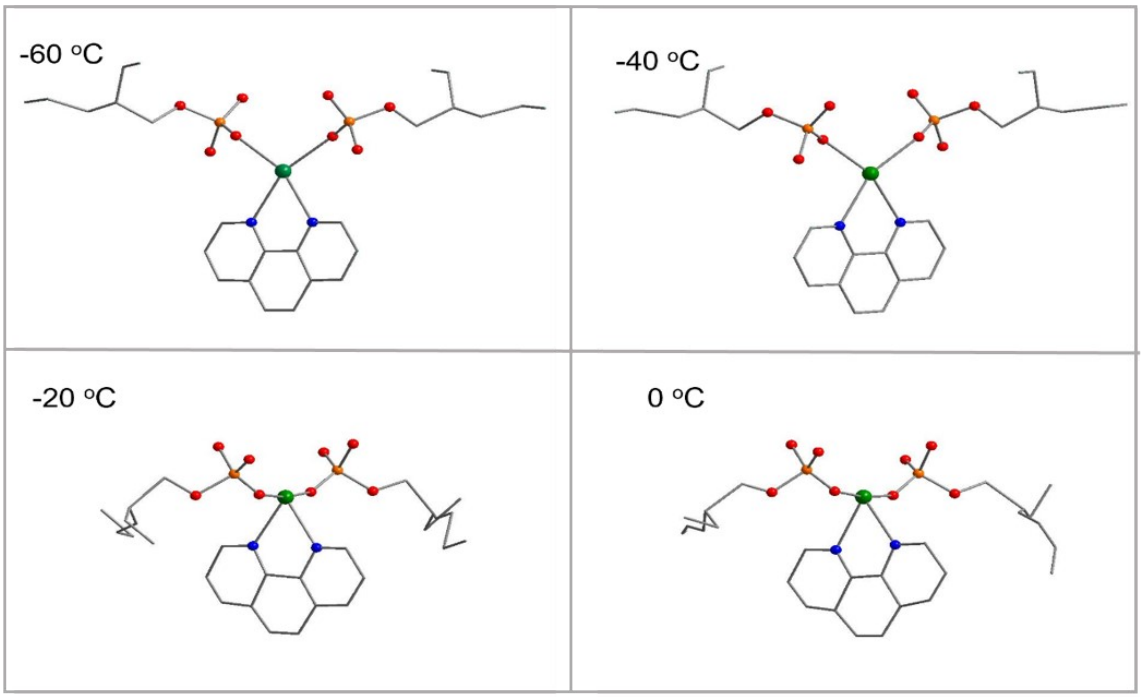


Fig. S11 SC-XRD derived molecular structure of **1** along a-axis at different temperatures.

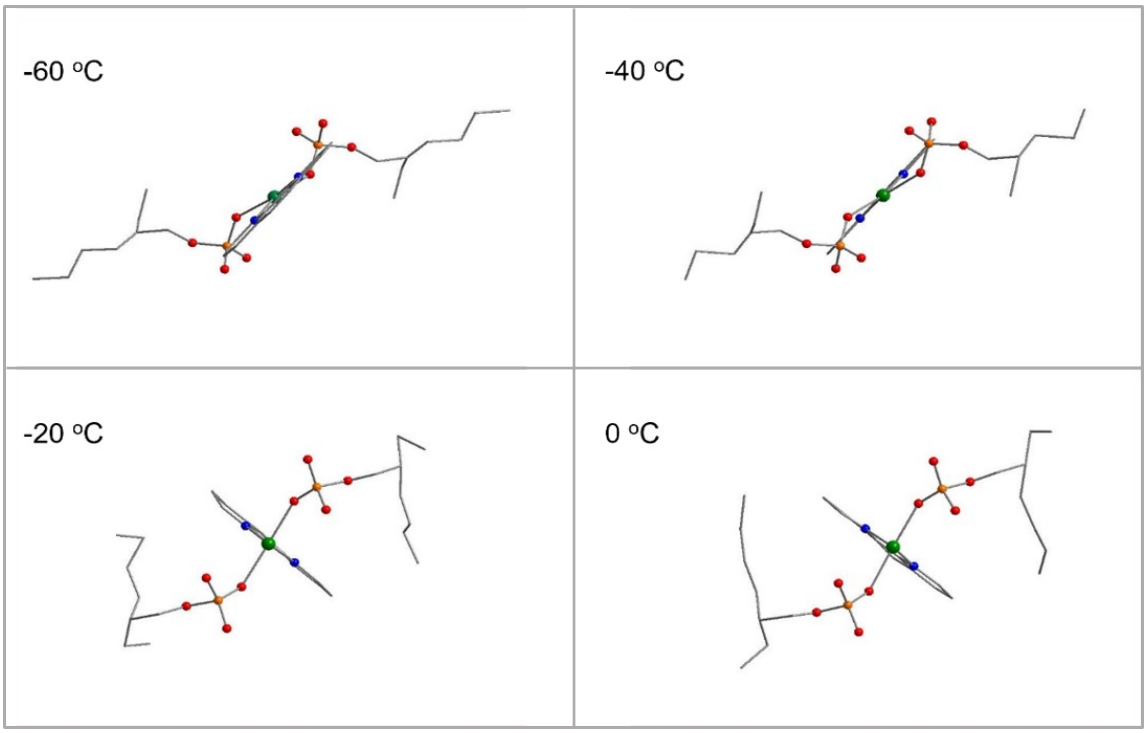


Fig. S12 SC-XRD derived molecular structure of **1** along b-axis at different temperatures.

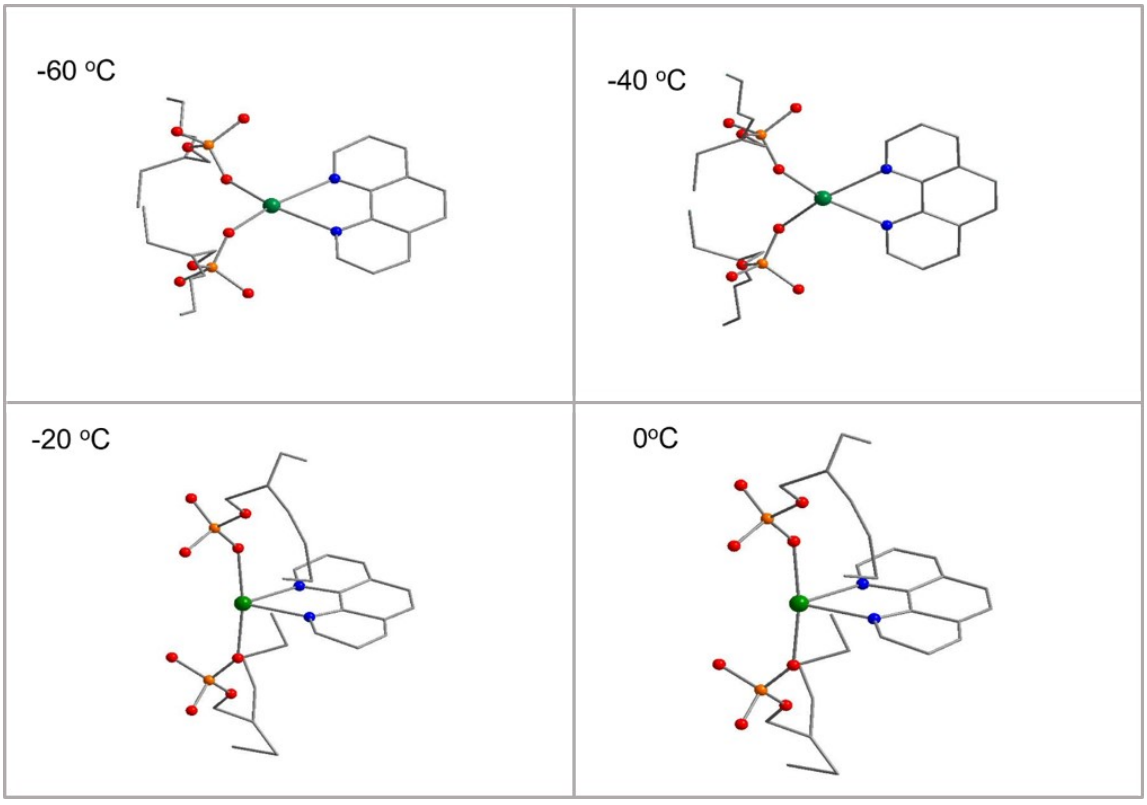


Fig. S13 SC-XRD derived molecular structure of **1** along c-axis at different temperatures.

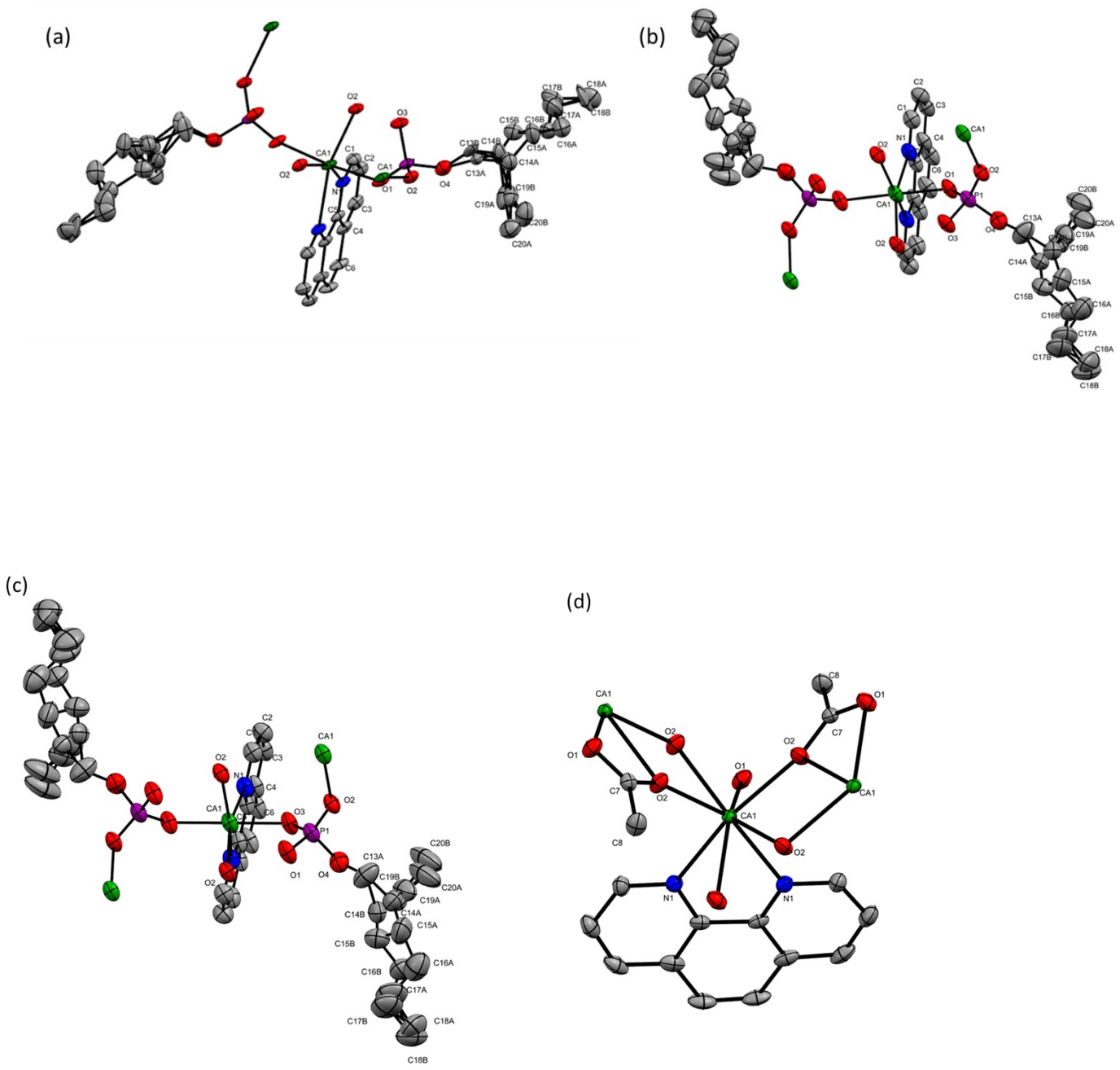


Fig.S14 (a) ORTEP diagram for **1** at -123 ^{o}C (100 K), (b) ORTEP diagram for **1** at -70 ^{o}C (203 K), (c) ORTEP diagram for **1** at -40 ^{o}C (233 K) and (d) ORTEP diagram for **2** at 50 % probability.

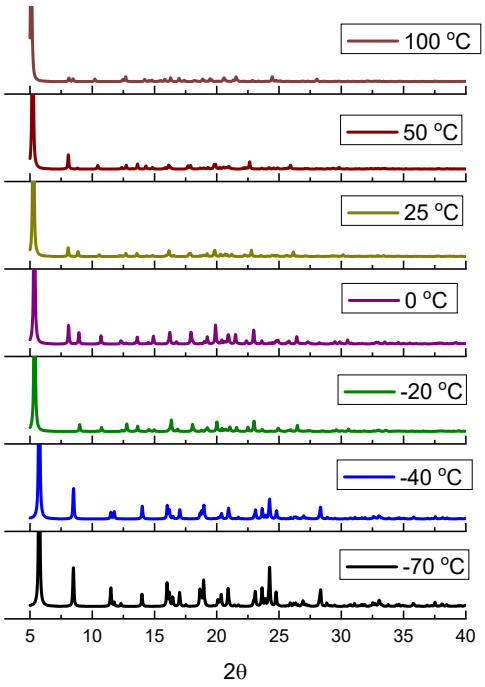


Fig. S15 Calculated PXRD of **1** from the single crystal diffraction data at -70 °C, -40 °C, -20 °C, 0 °C, 25 °C, 50 °C and 100 °C.

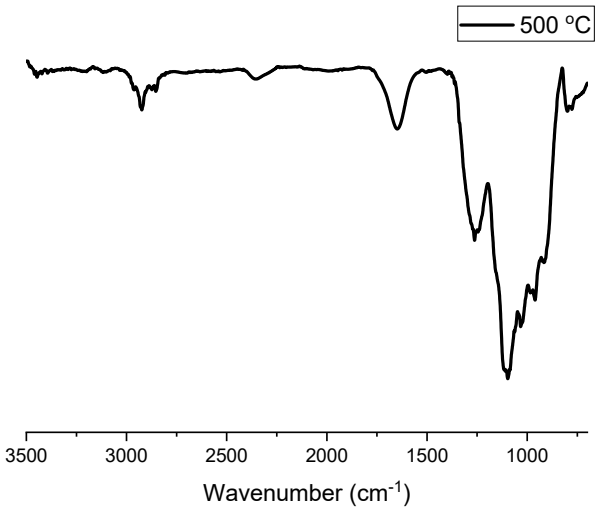


Fig. S16 FT-IR of the decomposition product of **1** heated at 500 °C, corresponding to an amorphous calcium phosphate impregnated in carbon.

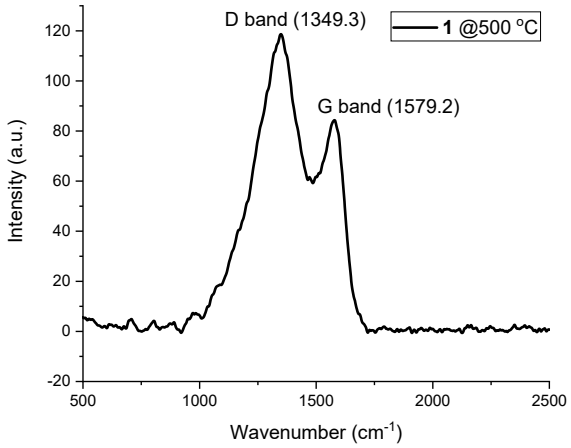


Fig. S17 Raman spectrum of **1** thermolysed at 500 °C showing bands for residual carboneous phase. (Pimenta, M. A. et al. *Phys. Chem. Chem. Phys*., 2007, **9**, 1276–1291.)

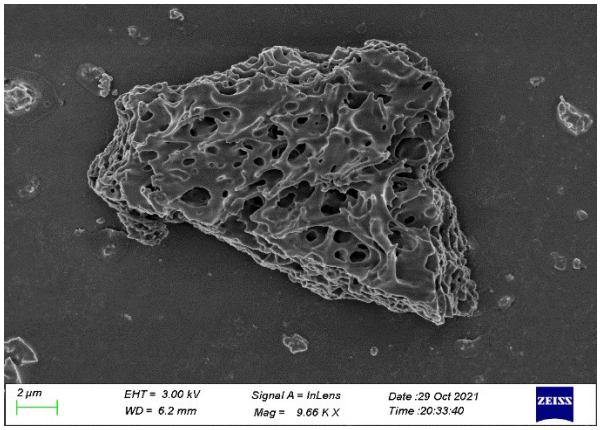
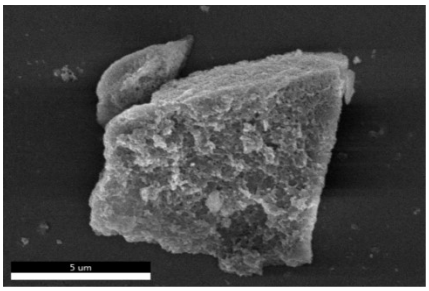
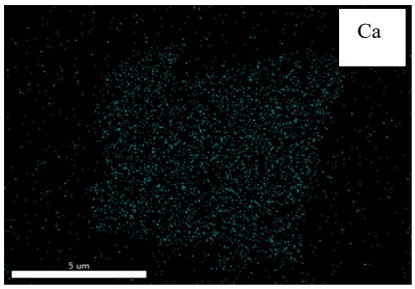
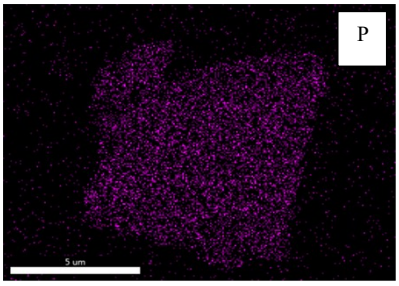
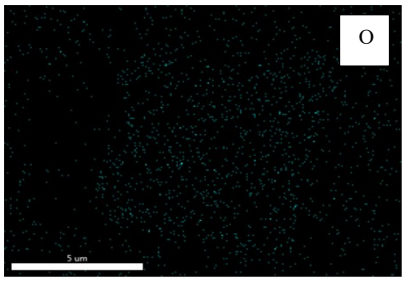


Fig. S18 SEM image of material obtained after thermal decomposition of **1** at 500 °C corresponding to an amorphous calcium phosphate impregnated in carbon.


5 um


Ca
5 um


P
5 um


O
5 um

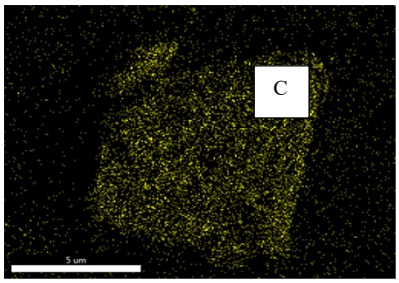

C
5 um

Fig. S19 EDS mapping of material obtained after thermal decomposition of **1** at 500 °C corresponding to an amorphous calcium phosphate impregnated in carbon.

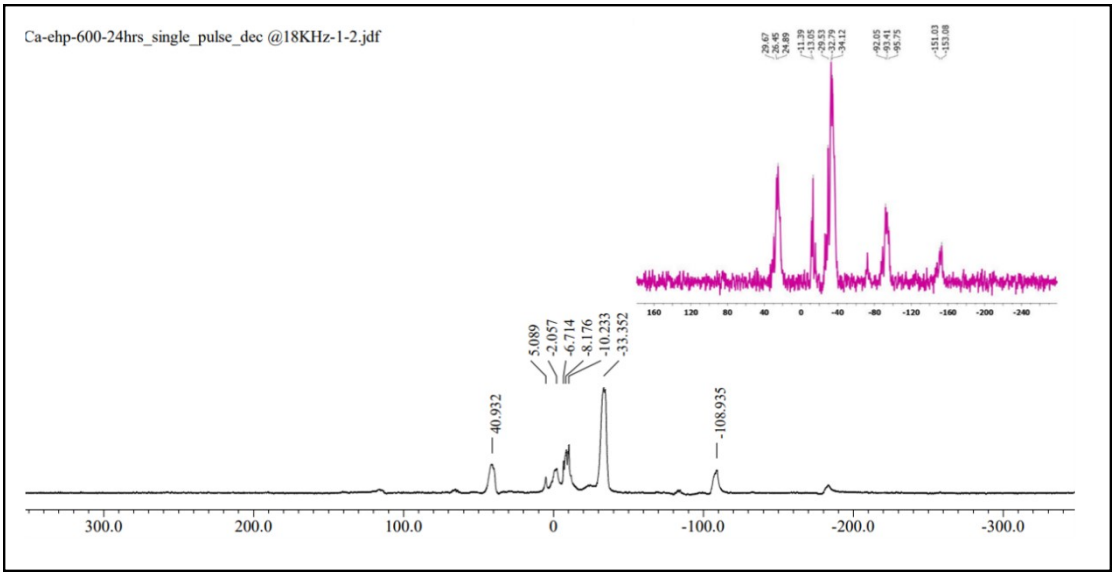


Fig. S20 ^{31}P NMR of decomposition product of **1** at 600 °C corresponding to α-$Ca(PO_3)_2$. Inset: for comparison the ^{31}P MAS NMR spectrum of decomposition product $[Ca(dtbp)_2]_n$ at 600 °C producing same material. (S. Verma and R. Murugavel, *Inorg. Chem.*, 2020, **59**, 13233–13244.)

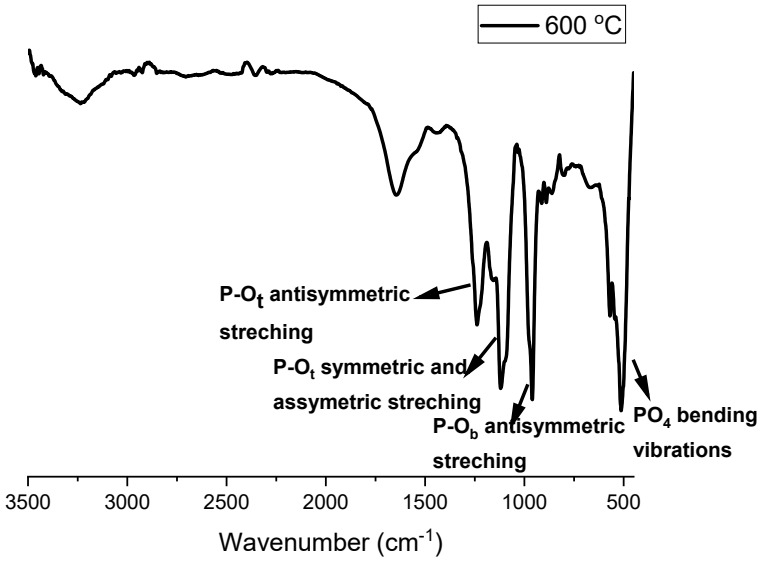


Fig. S21 FT-IR spectrum of decomposition product of **1** calcined product α-Ca$(PO_3)_2$ produced at 600 °C. (Weil, M. et al. *Chem. Mater*. 2007, **19**, 5067-5073.)

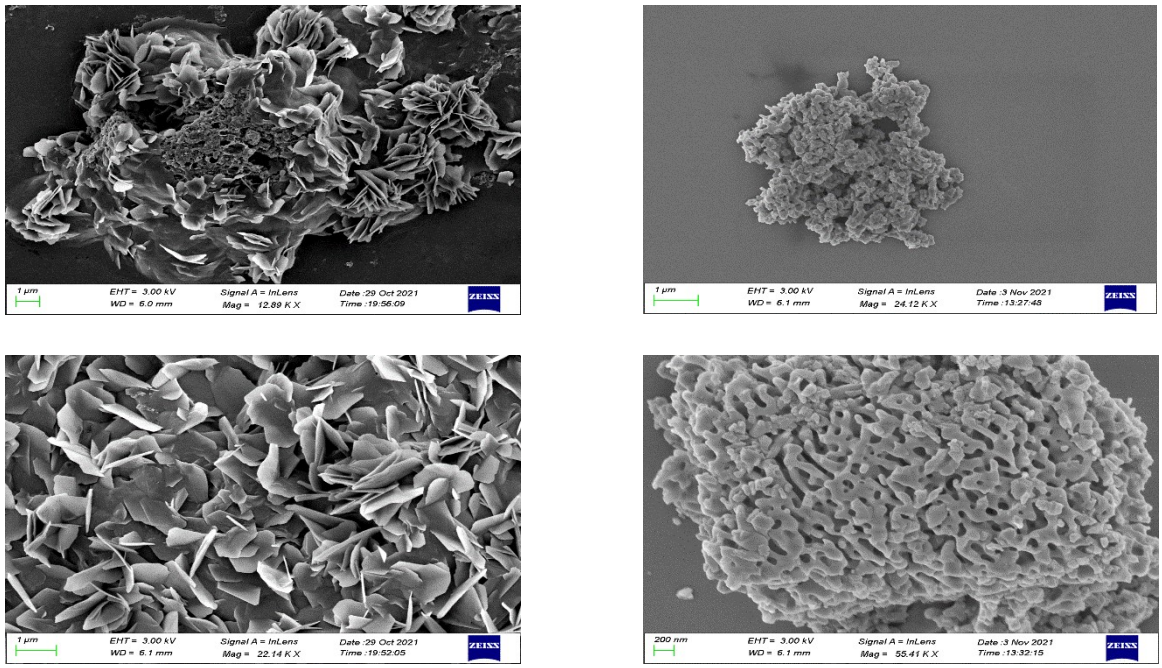


Fig. S22 SEM images of α-Ca$(PO_3)_2$ material obtained after thermal decomposition of **1** at 600 °C.

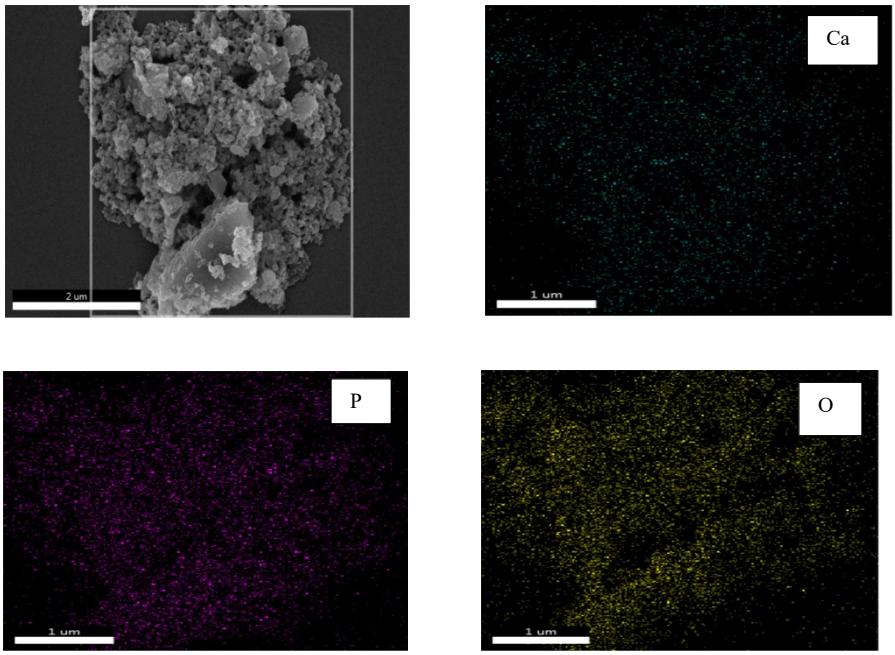


Fig. S23 EDS mapping of α-$Ca(PO_3)_2$ material obtained after thermal decomposition of **1** at 600 °C.

Table S1. Continuous Shape measures of the coordination polyhedra of six coordinated Ca(II) in **1**.

Label	Symmetry	Shape	Deviation
HP-6	D6h	Hexagon	31.544
PPY-6	C5v	Pentagonal pyramid	21.695
OC-6	**Oh**	**Octahedron**	**2.581**
TPR-6	D3h	Trigonal prism	9.049
JPPY-6	C5v	Johnson pentagonal pyramid J2	25.742

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

Ca(1)-O(1)	2.	O(1)#1-Ca(1)-O(2)#3	90.81(7)
Ca(1)-O(2)#2	2.	O(1)-Ca(1)-N(1)#1	87.86(7)
Ca(1)-N(1)	2.	O(1)#1-Ca(1)-N(1)#1	99.61(8)
P(1)-O(1)	1.	O(1)#1-Ca(1)-N(1)	87.86(7)
P(1)-O(2)	1.	O(2)#3-Ca(1)-O(2)#2	103.8(1)
P(1)-O(3)	1.	O(2)#2-Ca(1)-N(1)	158.40(7)
P(1)-O(4)	1.	O(1)-P(1)-O(2)	118.4(1)
O(4)-C(13A)	1. (1)	O(1)-P(1)-O(4)	105.7(1)
O(4)-C(13A)	1.	O(2)-P(1)-O(3)	107.4(1)
N(1)-C(1)	1.	O(2)-P(1)-O(4)	108.1(1)
N(1)-C(5)	1.	O(3)-P(1)-O(4)	105.1(1)
O(1)-Ca(1)-O(1)#1	171.	O(1)-P(1)-O(3)	110.6 (1)
O(1)-Ca(1)-O(2)#2	83.	O(3)-P(1)-O(4)	105.1(1)

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$1/2-X,+Y,1-Z; $^{\#2}$1-X,2-Y,1-Z ; $^{\#3}$-1/2+X,2-Y,+Z

Table S3. Continuous Shape measures of the coordination polyhedra of eight coordinated Ca(II) in **2**.

Label	Symmetry	Shape	Deviation
OP-8	D8h	Octagon	29.810
HPY-8	C7v	Heptagonal pyramid	22.798
HBPY-8	D6h	Hexagonal bipyramid	11.013
CU-8	Oh	Cube	9.091
SAPR-8	D4d	Square antiprism	6.991
TDD-8	D2d	Triangular dodecahedron	6.446
JGBF-8	D2d	Johnson gyrobifastigium J26	9.434
JETBPY-8	D3h	Johnson elongated triangular bpy J14	21.767
JBTPR-8	C2v	Biaugmented trigonal prism J50	6.219
BTPR-8	**C2v**	**Biaugmented trigonal prism**	**5.819**
JSD-8	**D2d**	**Snub diphenoid J84**	**5.414**
TT-8	Td	Triakis tetrahedron	9.931

ETBPY-8	D3h	Elongated trigonal bipyramid	17.670

Table S4. Bond lengths [Å] and angles [°] for **2.**

Ca(1)-O(2)	2.352(2)
Ca(1)-N(1)	2.526(2)
Ca(1)-O(1)#2	2.555(2)
O(1)-C(7)	1.244(3)
O(2)-C(7)	1.278(3)
N(1)-C(1)	1.324(2)
N(1)-C(5)	1.359(3)

[#1] X, 1-Y,-1/2+Z; [#2] 1-X,1-Y,2-Z; [#3] 1-X,+Y,3/2-Z

O(1)#1-Ca(1)-O(1)#2	146.42(8)
O(2)#3-Ca(1)-O(1)#2	119.39(6)
O(2)#1-Ca(1)-O(2)#2	149.68(8)
O(2)-Ca(1)-N(1)	158.45(7)
N(1)-Ca(1)-O(1)#2	79.63(7)
N(1)-Ca(1)-O(2)#1	120.59(6)
N(1)#3-Ca(1)-N(1)	65.6(1)
O(1)-C(7)-O(2)	121.4(2)
O(1)-C(7)-C(8)	119.9(2)
O(2)-C(7)-C(8)	118.7(2)

Symmetry transformations used to generate equivalent atoms:

[#1] 1-X, 1-Y, 2-Z; [#2] +X, 1-Y, -1/2+Z; [#3] 1-X, +Y, 3/2-Z

Table S5. Heat flow vs temperature data for compound **1** in the temperature range from -150 °C to 200 °C.

	T_{mid} (heating) (°C)	T_{mid} (cooling) (°C)	Enthalpy of transition (heating) (J/g)	Enthalpy of transition(cooling) (J/g)
Peak 1	-14.3	-44.2	20.1	18.5
Peak 2	73.0	79.0	0.3	0.3

* T_{mid} represents the mid-point of the corresponding transition in the DSC curve.