Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

A Highly Flexible Inorganic Framework with Amphiphilic Amine Assemblies as Templates

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Table of Contents

Table S1 Crystal data and structure refinement results

Compound name	**1-iba**	**1-cha**
Empirical formula	C8 H28 N2 O13 P4 Zn3	C12 H32 N2 O12.5 P4 Zn3
Formula weight	680.38	724.45
Temperature	296(2) K	100(2) K
Wavelength	0.71073 Å	1.54178 Å
Crystal system	Trigonal	Trigonal
Space group	R -3	R-3
Unit cell dimensions	a = 32.8755(9) Å	a = 32.4965(8) Å
	c = 13.2082(5) Å	c = 13.1823(4) Å
Volume	12362.9(7) $Å^3$	12055.8(6) $Å^3$
Z	18	18
Density (calculated)	1.606 Mg/m^3	1.776 Mg/m^3
Absorption coefficient	2.877 mm^{-1}	5.895 mm^{-1}
F(000)	6048	6552
Crystal size / mm^3	0.14 x 0.02 x 0.02	0.43 x 0.1 x 0.1 mm^3
Theta range for data collection	1.70 to 28.36°.	3.70 to 67.04°
Index ranges	-43≤h≤43, -43≤k≤43, -17≤l≤17	-37≤h≤38, -38≤k≤37, -15≤l≤11
Reflections collected	54091	30753
Independent reflections	6863 [R(int) = 0.0523]	4699 [R(int) = 0.0397]
Completeness	99.8 % (theta = 28.36)	98.5 % (theta = 67.04°)
Max. and min. transmission	0.9281 and 0.7587	0.9287 and 0.6979
Data / restraints / parameters	6863 / 2 / 192	4699 / 1 / 318
Goodness-of-fit on F^2	1.017	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.1005	R1 = 0.0262, wR2 = 0.0683
R indices (all data)	R1 = 0.0467, wR2 = 0.1071	R1 = 0.0279, wR2 = 0.0695
Largest diff. peak and hole	0.548 and -0.432 $e.Å^{-3}$	0.908 and -0.347 $e.Å^{-3}$

(Continued)

1-coa	**1-pa**	**1-ha**
C16 H40 N2 O12.3 P4 Zn3	C10 H18 N2 O12.5 P4 Zn3	C12 H36 N2 O12.3 P4 Zn3
777.36	686.32	725.29
296(2) K	296(2) K	296(2) K
0.71073 Å	0.71073 Å	0.71073 Å
Trigonal	Trigonal	Trigonal
R-3	R-3	R-3
a = 33.9287(3) Å	a = 33.1915(4) Å	a = 33.2781(9) Å
c = 13.6579(1) Å	c = 13.3206(1) Å	c = 13.5625(5) Å
13616.0(2) $Å^3$	12708.9(3) $Å^3$	13007.3(7) $Å^3$
18	18	18
1.696 Mg/m^3	1.595 Mg/m^3	1.655 Mg/m^3
2.625 mm^{-1}	2.801 mm^{-1}	2.741 mm^{-1}
7128	6084	6624
0.22 x 0.03 x 0.03 mm^3	0.2 x 0.03 x 0.03 mm	0.14 x 0.02 x 0.02 mm
2.04 to 28.31°	1.68 to 28.29°	2.06 to 28.32°
-45≤h≤44, -45≤k≤45, -18≤l≤18	-44≤h≤42, -43≤k≤44, -17≤l≤17	-44≤h≤44, -44≤k≤43, -18≤l≤9
60317	56018	56676
7524 [R(int) = 0.0701]	7023 [R(int) = 0.04]	7189 [R(int) = 0.0324]
99.8 % (theta = 28.31°)	99.9 % (theta = 28.29°)	99.9 % (theta = 28.32°)
0.9281 and 0.8370	0.9281 and 0.7888	0.9281 and 0.8507
7524 / 1 / 348	7023 / 1 / 192	7189 / 1 / 192
1.057	0.986	1.027
R1 = 0.0536, wR2 = 0.1464	R1 = 0.0317, wR2 = 0.1011	R1 = 0.0268, wR2 = 0.0850
R1 = 0.0974, wR2 = 0.1836	R1 = 0.0425, wR2 = 0.1045	R1 = 0.0358, wR2 = 0.0872
1.066 and -1.210 e.$Å^{-3}$	0.449 and -0.374 e.$Å^{-3}$	0.598 and -0.514 e.$Å^{-3}$

Table S2 Elemental analysis for **1-pa**, **1-cha**, and **1-coa**

		N	C	H
1-pa	Calcd.	4.05	17.35	4.66
	Obsd.	4.15	17.55	4.83
1-cha	Calcd.	3.91	20.12	4.5
	Obsd.	3.84	19.15	4.45
1-coa	Calcd.	3.63	24.88	5.22
	Obsd.	3.77	24.97	5.11

Table S3 Molar ratios determined from ICP-AES.

		Zn	Co	P
1-pa	Calcd.	3	0	4
	Obsd.	3.09	0	4
1-cha	Calcd.	3	0	4
	Obsd.	3.31	0	4
1-coa	Calcd.	3	0	4
	Obsd.	3.08	0	4

Table S4 Solvent system and corresponding products in the reaction system of **1-cha**

H_2O : TEG	Major phase	Minor phase
1 : 9	1	L-1
3 : 7	1	L-1
5 : 5	L-1	1
7 : 3	L-1	1
9 : 1	CJ-1	L-1
10 : 0	CJ-1	L-1

Table S6 Empty space in 1 with template in presence

	Void space ($Å^3$)	(%)
1-iba	1952.9	15.8
1-ha	615.8	4.7
1-cha	935.2	7.6
1-coa	738.1	5.4

Table S6 Pressure-dependent cell parameters for 1

a) **1-cha**

P (GPa)	*a*/Å	*c*/Å	volume/Å ^{3}
0.00	32.815	13.200	12310.0
0.09	32.698	13.178	12202.1
0.18	32.564	13.150	12076.0
0.27	32.469	13.129	11986.2
0.48	32.229	13.074	11760.6
0.88	31.897	12.981	11438.2
1.11	31.694	12.917	11237.0
1.52	31.518	12.825	11033.3
1.72	31.500	12.788	10988.5
1.88	31.573	12.758	11014.0
2.07	31.439	12.744	10908.6
2.37	31.159	12.739	10711.4

b) **1-coa**

P (GPa)	*a*/Å	*c*/Å	volume/Å ^{3}
0.14	33.79	13.56	13407
0.72	33.22	13.23	12647
0.94	33.09	13.17	12488
1.12	33.00	13.12	12375
1.32	32.90	13.09	12263
1.53	32.83	13.05	12186

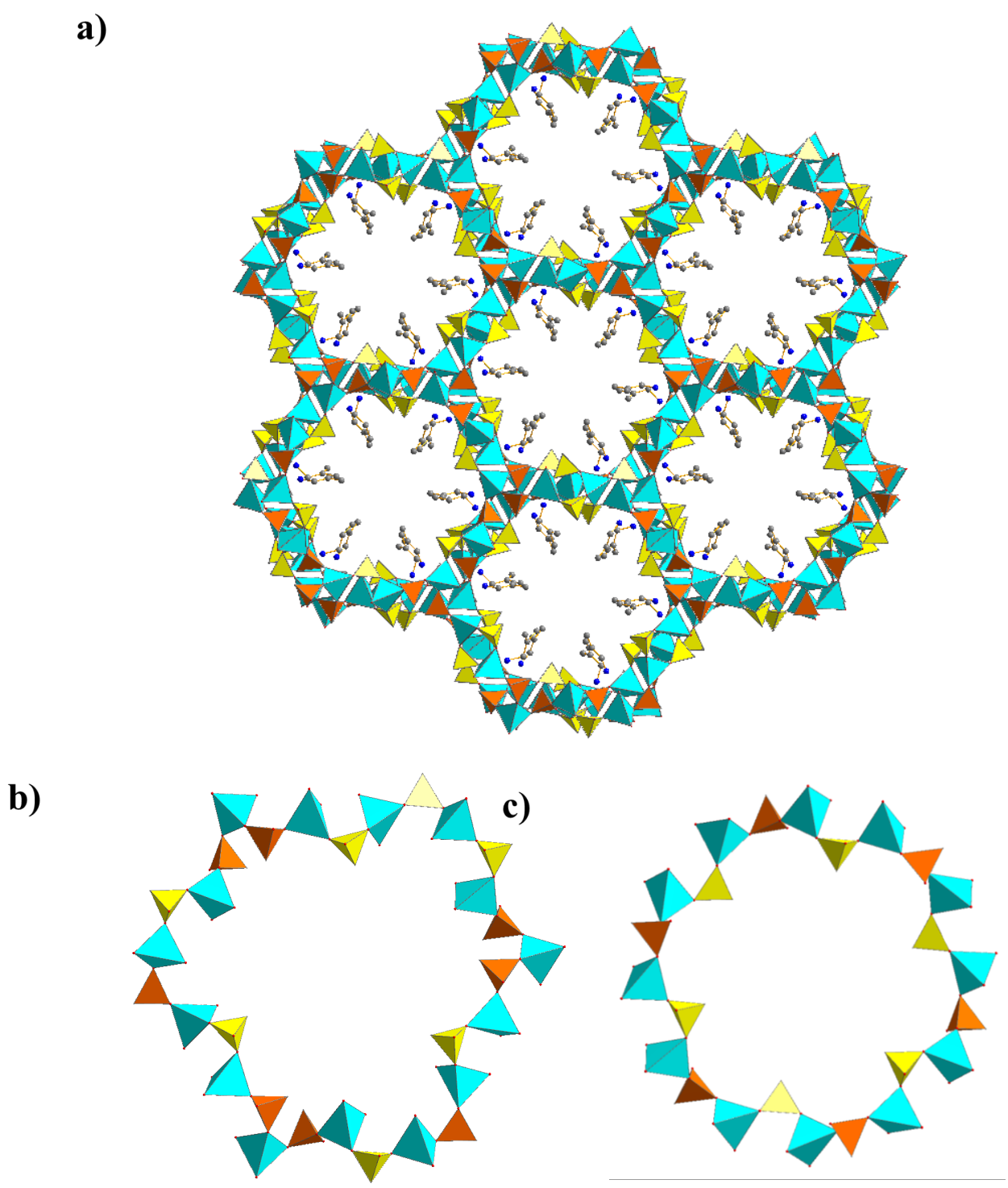

Fig. S1 Polyhedral representation of 1: (a) view along c-axis direction; (b) puckered 30R and (c) 24R channel openings. Tetrahedra in cyan for ZnO_4, yellow for HPO_3 and orange for mixed HPO_3 and HPO_4.

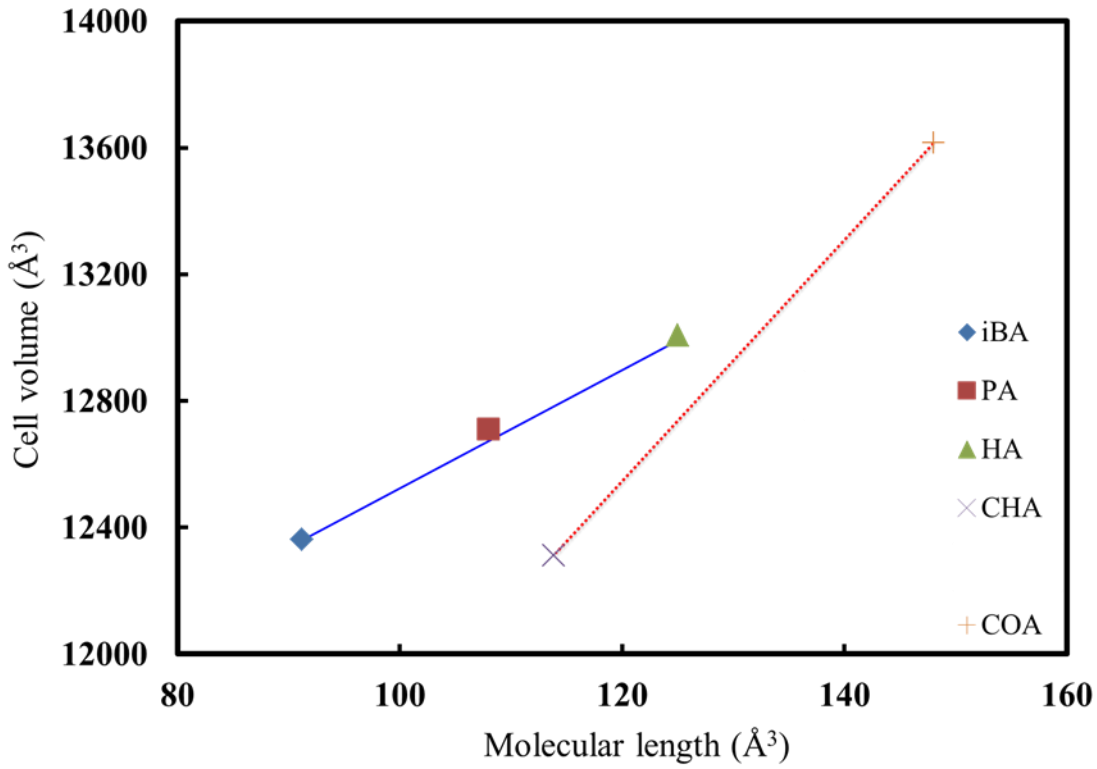

Fig. S2 Template effect on lattice volume of 1.

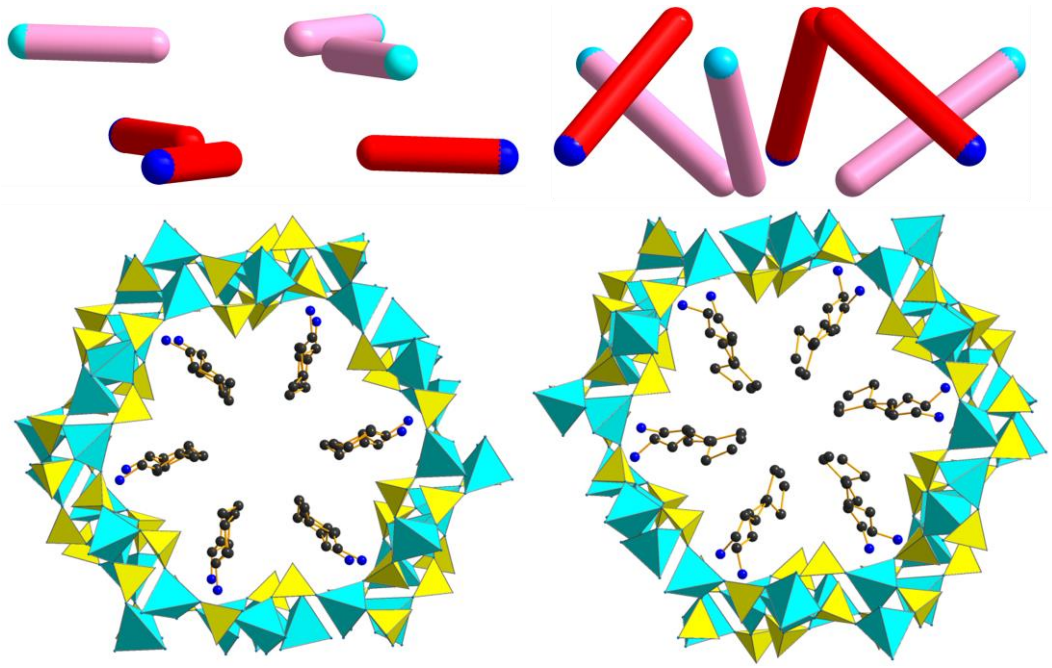

Fig. S3 Template arrangement in 1: (left) parallel mode in **1-cha** and (right) non-parallel mode in **1-ha**.

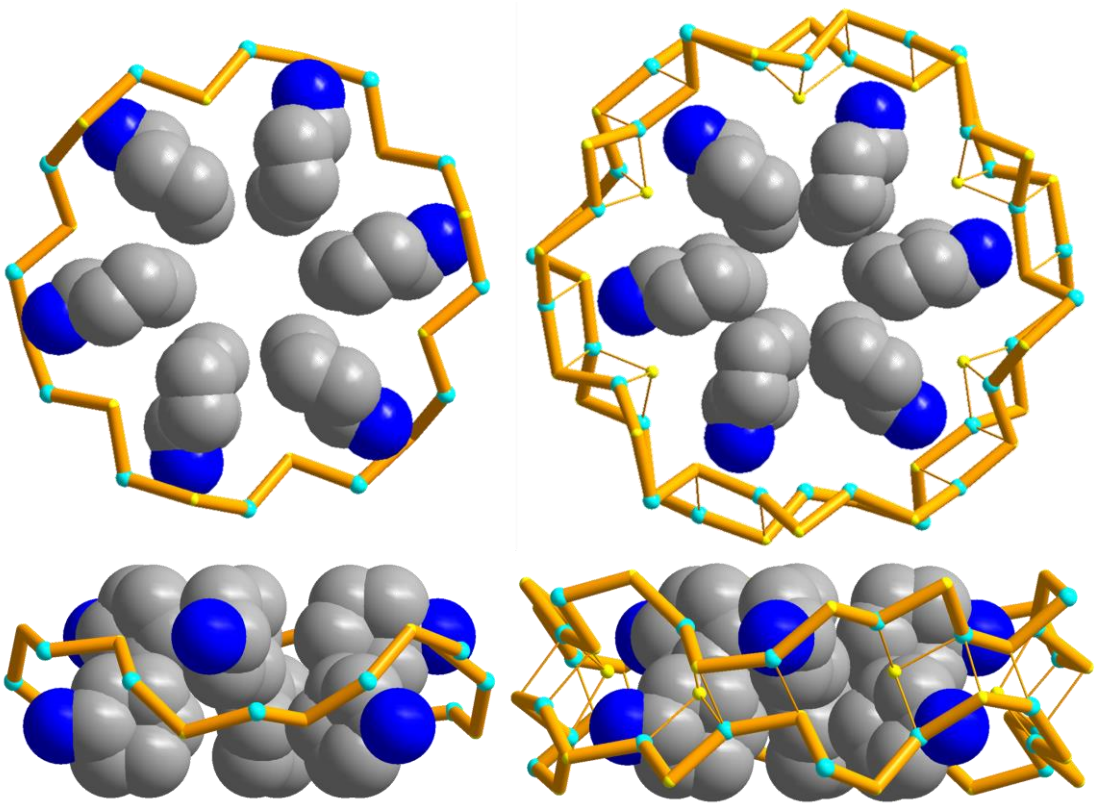

Fig. S4 Top (top) and side (bottom) view of organic template encapsulated in 30R (left) and 24R (right)

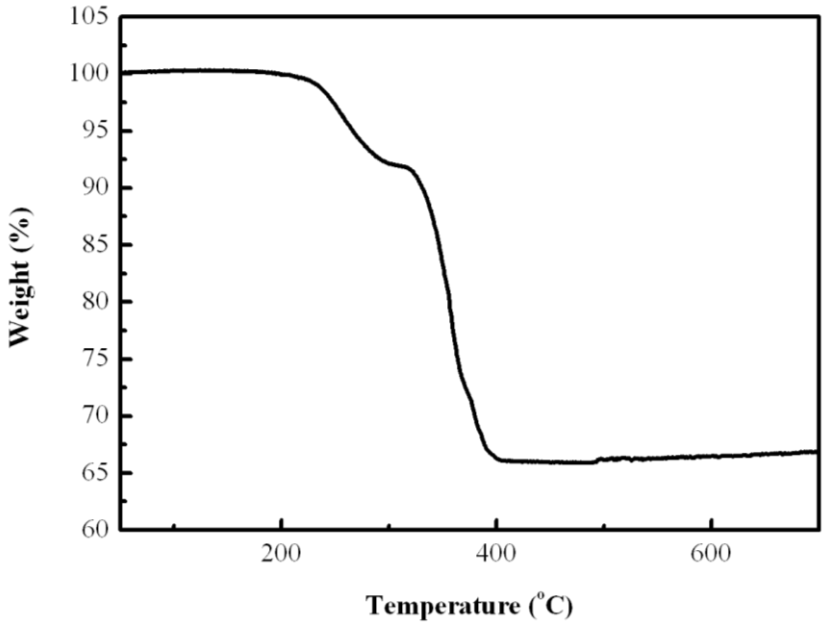

Fig. S5 TGA curve for **1-coa** in flowing N_2 gas.

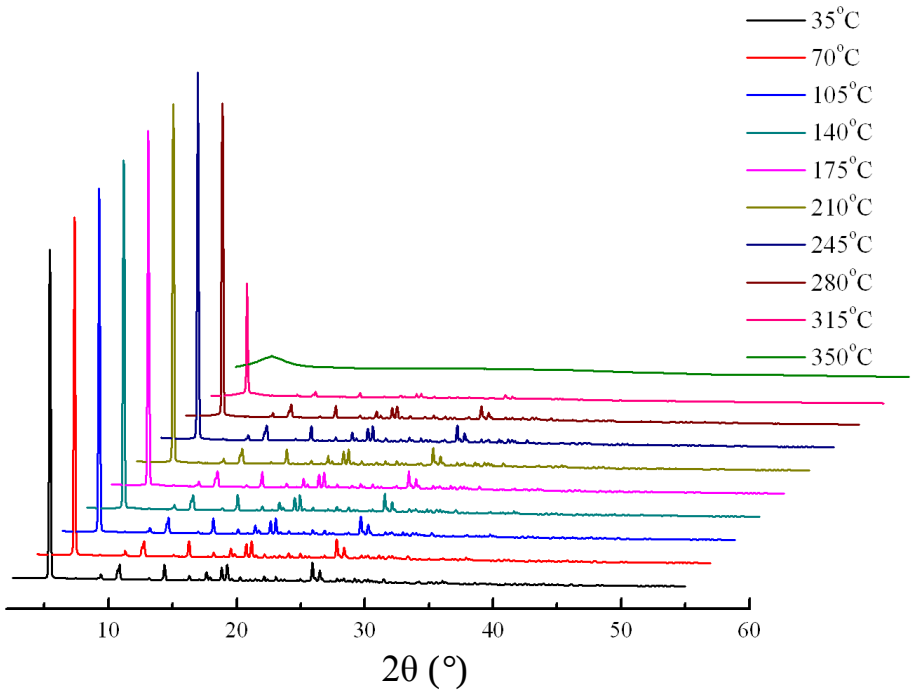

Fig. S6 In-situ temperature-dependent PXRD pattern for **1-coa**.

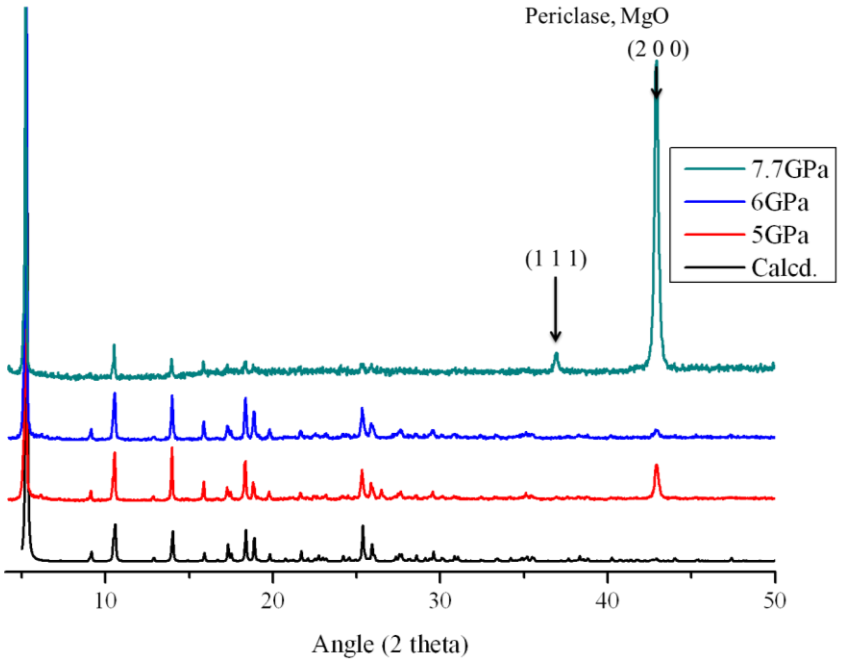

Fig. S7 Pressure-dependent PXRD pattern for **1-cha**.