

Electronic Supplementary Information (ESI) for:

A rutile-type porous zinc(II)-phosphonocarboxylate framework: local proton transfer and size-selected catalysis

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1. General	2
2. Experiment details	3
3. Single-crystal X-ray crystallography	6
Table S1. Crystal and Structure Refinement Data for 1a and 1b	7
Table S2. Selected bond lengths and angles for 1a	8
Table S3. Selected bond lengths and angles for 1b	9
Figure S1. A perspective view of CBB substrate in the channel of 1a	10
Figure S2. The trinuclear Zn ₃ -SBU in 1a	11
Figure S3. The trinuclear Zn ₃ -SUB in 1b	12
Figure S4. The molecule structure of 1a-100	13
Figure S5. A view of the crystal structure transformation from 1a to 1a-100 to 1b	14
Figure S6. A view of hydrogen bonds of hydrated protons.	15
Figure S7. The shrinking of the small channels and the movement of water molecules from 1a to 1a-100	16
Figure S8. The coordination motif of in {Zn ₃ (pbdc) ₂ ·(Htea)·H ₃ O·XH ₂ O}	17
Figure S9. PXRD patterns of 1a , 1a' comparing to the simulated data from CIF data of 1a	18
Figure S10. TGA curve for 1a	19

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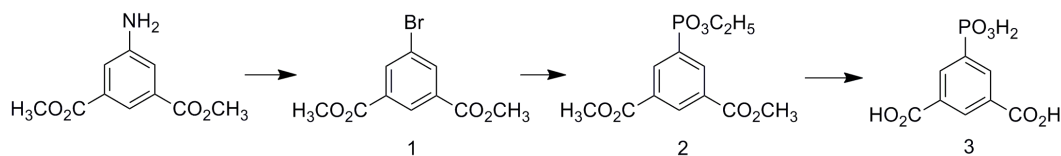
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1. General

All reagents were purchased from commercial sources and used as received except the H₄pdbc synthesized by the method described in the experiment details. ¹HNMR spectra in solution were recorded on a JEOL ECA400 nuclear magnetic resonance spectrometer. Chemical shifts are given in ppm. Powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 powder diffractometer at 40 kV, 40 mA with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 0.2 s/step and a step size of 0.02° (2 θ). Thermogravimetric analyses (TGA) were carried out with a METTLER TOLEPO TGA/SDTA851 analyzer in N₂ with a heating rate of 10 K·min⁻¹. Elemental analyses were done on the Elementar Vario EL III microanalyzer. IR spectra were measured from a KBr pellets on a Nicolet Nexus 470 FT-IR spectrometer in the range 4000 – 400 cm⁻¹. GC-MS spectrometry was recorded on the Agilent (Hewlett Packard) HP 6890/5973 GC/MS system.

2. Experiment details

H₄pbdc was synthesized according to the route shown in scheme S1.



Scheme S1. Synthesis process of the ligand H₄pbdc.

Synthesis of compound 1: Dimethyl 5-amino-1,3-benzenedicarboxylate (10 g, 47.6 mmol) was dissolved in 225 ml of 15% hydrobromic acid, cooled to 5 °C. 23 ml of 2.5 M sodium nitrite solution was introduced slowly accompanied by rapid stirring, giving a solution of diazonium bromide. The solution of diazonium bromide was added to a solution containing 9.8 g CuBr and 90 ml 15% hydrobromic acid under stirring, and the temperature was kept under 5 °C. After the addition was completed, it is kept on stirring under room temperature for 2h. Compound 1 (11.4 g, 42 mmol) was obtained in 88% yield. ¹H NMR (CHCl₃): 8.61(s, 1H), 8.36(s, 2H), 3.96(s, 6H). Elemental analysis calcd. for 1: C₁₀H₉BrO₄ (273.08): C, 43.94; H, 4.39%. Found: C, 43.51; H, 4.43%.

Synthesis of compound 2: To the solution of compound 1 (10.84 g, 40 mmol) in toluene (50 ml), the mixture of palladium acetate (0.90 g, 4 mmol), triphenylphosphine (4.2 g, 16 mmol), diethyl phosphate (6.0 g, 44 mmol), triethylamine (4.5 g, 44 mmol) were added under argon. After stirring at 90 °C under Ar gas for 20 h, the mixture was cooled to room temperature. Pure Dimethyl 5-(diethoxyphosphoryl)isophthalate (8.18 g, 27.2 mmol) was obtained by passing through a SiO₂ column in 68% yield. ¹H NMR (CHCl₃): 8.85(s, 1H), 8.66(s, 1H),

8.63(s, 1H), 4.16(m, 4H), 3.98(m, 6H), 1.35(t, 6H). Elemental analysis calcd. for 2: $C_{14}H_{19}O_7P$ (330.27): C, 50.87; H, 5.75%. Found: C, 51.13; H, 5.73%.

Synthesis of compound 3: 6.4g ligand H_4pbdc were obtained by heating Dimethyl 5-(diethoxyphosphoryl)isophthalate (8g, 26.6mmol) in HCl solution (18%, 50ml) for 20 h, with yield of 98%. 1H NMR(DMSO- d_6): 8.54(s, 1H), 8.44(s, 1H), 8.41(s, 1H). Elemental analysis calcd. for 3: $C_8H_7O_7P$ (246.11): C, 39.01; H, 2.84%. Found: C, 39.13; H, 2.73%.

Synthesis of $\{[Zn_3(pbdc)_2] \cdot (H_3O)_2\}_n$ (1a). A solution of H_4pbdc (0.025 g, 0.1 mmol) and triethylamine (0.043 g, 0.4 mmol) in i-PrOH (5 ml) was carefully layered onto a solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.324 g, 0.15 mmol) in deionized water (5 mL) in a Teflonlined stainless steel autoclave (15 mL). The mixture was heated at 140°C for 3 days, followed by cooling to room temperature. Colorless rod-shape crystals of **1a** were collected by filtration (Yield: 17% based on H_4pbdc). Elemental analysis calculated for **1a** $C_{16}H_{12}P_2O_{16}Zn_3$ (718.3): C, 26.75; H, 1.68%. Found: C, 26.71; H, 1.73%. IR(cm^{-1}): 3436m, 3068w, 2984w, 1614s, 1567m, 1436m, 1368m, 1310w, 1211m, 1110m, 1012m, 990m, 777m, 729m, 574m, 457m.

Synthesis of $\{[Zn_3(pbdc)_2H_2O] \cdot (Htea) \cdot H_3O \cdot XH_2O\}_n$ (X = 2.5~4) (1'). A mixture of H_4pbdc (0.025 g, 0.1 mmol), $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.322 g, 0.15 mmol), triethylamine (0.042 g, 0.4 mmol), deionized water (5 mL), and i-PrOH (5 ml) was stirred for 10 min and then heated at 140 °C for 3 days in a Teflon-lined stainless steel autoclave (15 mL), followed by cooling to room temperature. Colorless rod-shape crystals of **1'** were collected by filtration (Yield: 15 % based on H_4pbdc ,

The crystals were not stable at room temperature due to lose of the lattice waters to form powder after taken away from the mother liquid, while the framework are stable according to the PXRD data). Elemental analysis calculated for **1'** C₂₂H₃₅P₂O₂₀NZn₃ (891.6): C, 29.64; H, 3.96; N, 1.57 %. Found: C, 30.46; H, 3.69 %, N, 1.61 %. IR(cm⁻¹): 3446m, 3117w, 3066w, 2983w, 2946w, 1614s, 1568m, 1436m, 1369m, 1308w, 1211m, 1139m, 1109m, 1012m, 990m, 779m, 732w, 689w, 574m, 454m.

Catalysis of Friedel-Crafts reaction: Six substrates (4-chlorobenzyl bromide, 3-biphenylmethyl bromide, 1,3-di-tert-butylbenzyl bromide, 4-biphenylmethyl chloride, 3-methyl-benzyl chloride, 3-phenoxybenzyl chloride) were used as received. The reaction was carried out with 2.5 mmol substrate in 5ml of toluene. Typically, a mixture of 4-chlorobenzyl bromide (0.50 g, 2.5 mmol), **1a** (0.05 g, 0.15 mmol) and 5 ml of toluene was heated at 100°C for 12h. After cooled to room temperature, the mixture was then filtered and the filtrate was analyzed with Gas Chromatography-Mass Spectrometry (GC-MS).

3. Single-crystal X-ray crystallography

Single crystal data of **1a** and **1b** were collected at room temperature using a Bruker APEX diffractometer equipped with a normal focus, 3.0 kW sealed tube X-ray source (Mo K α radiation, λ = 0.71073 Å). Data reduction and cell refinement were performed with the SAINT program,^{S1} and the absorption correction program SADABS was employed to correct the data for absorption effects. The structures were solved by direct methods and refined using full-matrix least-squares treatment (SHELXTL-97)^{S2} with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the phenyl were theoretically added, while the hydrogen atoms of the hydrated protons were first located in difference Fourier maps and then fixed in the calculated sites. The disordered oxygen atom (O(8), O(8')) in **1a** were both restrained with displaying models, while only O(8) in **1b** was restrained, so, least-squares restraints are different for **1a** with 12 restraints and **1b** with 6 restraints.

(S1). Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Goettingen: Goettingen, 1996.

(S2) Sheldrick, G. M. SHELXS 97, Program for Crystal Structure Refinement; University of Goettingen: Goettingen, 1997.

Table S1. Crystal and Structure Refinement Data for **1a** and **1b**

	1a	1b
Formula	C ₁₆ H ₁₂ O ₁₆ P ₂ Zn ₃	C ₁₆ H ₁₂ O ₁₆ P ₂ Zn ₃
F.W.	718.31	718.31
Space group	I-42d	I-42d
<i>a</i> (Å)	18.310(6)	18.218(4)
<i>b</i> (Å)	18.310(6)	18.218(4)
<i>c</i> (Å)	23.222(11)	23.552(7)
<i>V</i> (Å ³)	7785(5)	7817(3)
<i>Z</i>	8	8
<i>D_c</i> (g cm ⁻³)	1.226	1.221
<i>μ</i> (mm ⁻¹)	1.964	1.956
<i>F</i> (000)	2848	2848
<i>T</i> (K)	293(2)	293(2)
Total collected	18703	15733
Unique data, <i>R</i> (int)	3484, 0.0527	3433, 0.1222
Observed [<i>I</i> > 2σ(<i>I</i>)]	3079	2140
GOF on <i>F</i> ²	1.18	1.08
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0402, 0.1471	0.0649, 0.1935
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0458, 0.1489	0.1059, 0.2031
Δρ _{max} /Δρ _{min} (e Å ⁻³)	0.70 and -0.50	0.918 and -0.685

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

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

Zn1—O3 ⁱ	1.915(5)	Zn1—O4 ⁱⁱ	1.936(5)
Zn1—O1	1.949(6)	Zn1—O6 ⁱⁱⁱ	1.991(6)
Zn2—O2	1.946(6)	Zn2—O7 ^{iv}	1.971(4)
C7—O5	1.227(9)	C7—O4	1.242(9)
C8—O6	1.237(9)	C8—O7	1.271(8)
O1—P1	1.512(5)	O2—P1	1.513(6)
O3—P1	1.519(5)		
O3 ⁱ —Zn1—O4 ⁱⁱ	122.3(2)	O3 ⁱ —Zn1—O1	107.7(2)
O4 ⁱⁱ —Zn1—O1	110.6(2)	O3 ⁱ —Zn1—O6 ⁱⁱⁱ	109.5(2)
O4 ⁱⁱ —Zn1—O6 ⁱⁱⁱ	98.4(2)	O1—Zn1—O6 ⁱⁱⁱ	107.2(2)
O2 ⁱ —Zn2—O2	124.1(2)	O2 ⁱ —Zn2—O7 ^{iv}	106.8(2)
O2—Zn2—O7 ^{iv}	106.8(2)	O2—Zn2—O7 ⁱⁱⁱ	103.8(2)
O7 ^{iv} —Zn2—O7 ⁱⁱⁱ	111.53(16)	O5—C7—O4	124.0(7)
O6—C8—O7	125.4(6)	O1—P1—O3	112.1(3)
O1—P1—O2	112.7(3)	O3—P1—O2	111.6(3)

Symmetry codes: (i) x, 0.5-y, 1.25-z; (ii) -0.5+y, 1+x, -0.25+z; (iii) 1-y, x, 1-z; (iv)

1-y, 0.5-x, 0.25+z

Table S3. Selected bond lengths [Å] and angles [°] for **1b**

Zn1—O3 ⁱ	1.910(9)	Zn1—O1	1.937(9)
Zn1—O4 ⁱⁱ	1.991(10)	Zn1—O6 ⁱⁱⁱ	2.009(9)
Zn1—O5 ⁱⁱ	2.456(11)	Zn2—O2	1.938(9)
Zn2—O7 ^{iv}	1.985(8)	O4—C7	1.208(2)
O5—C7	1.248(18)	O6—C8	1.232(16)
O7—C8	1.281(15)	P1—O1	1.514(10)
P1—O2	1.518(10)	P1—O3	1.515(10)
O3 ⁱ —Zn1—O1	110.6(4)	O3 ⁱ —Zn1—O4 ⁱⁱ	127.5(5)
O1—Zn1—O4 ⁱⁱ	110.5(5)	O3 ⁱ —Zn1—O6 ⁱⁱⁱ	104.3(4)
O1—Zn1—O6 ⁱⁱⁱ	106.5(4)	O4 ⁱⁱ —Zn1—O6 ⁱⁱⁱ	93.9(4)
O2 ⁱ —Zn2—O2	123.9(4)	O2 ⁱ —Zn2—O7 ^{iv}	102.5(4)
O2—Zn2—O7 ^{iv}	108.9(4)	O7 ^{iv} —Zn2—O7 ⁱⁱⁱ	110.0(4)
O2—P1—O1	113.0(5)	O2—P1—O3	111.8(5)
O1—P1—O3	113.2(5)	O4—C7—O5	122.1(14)
O6—C8—O7	125.3(11)		

Symmetry codes: (i) x, 0.5-y, 0.25-z; (ii) 0.5+y, 1+x, -0.25+z; (iii) -y, x, -z; (iv) -y, 0.5-x, 0.25+z

Figure S1. A perspective view of CBB substrate in the channel of **1a** (The blue surface showing as the Connolly surface)

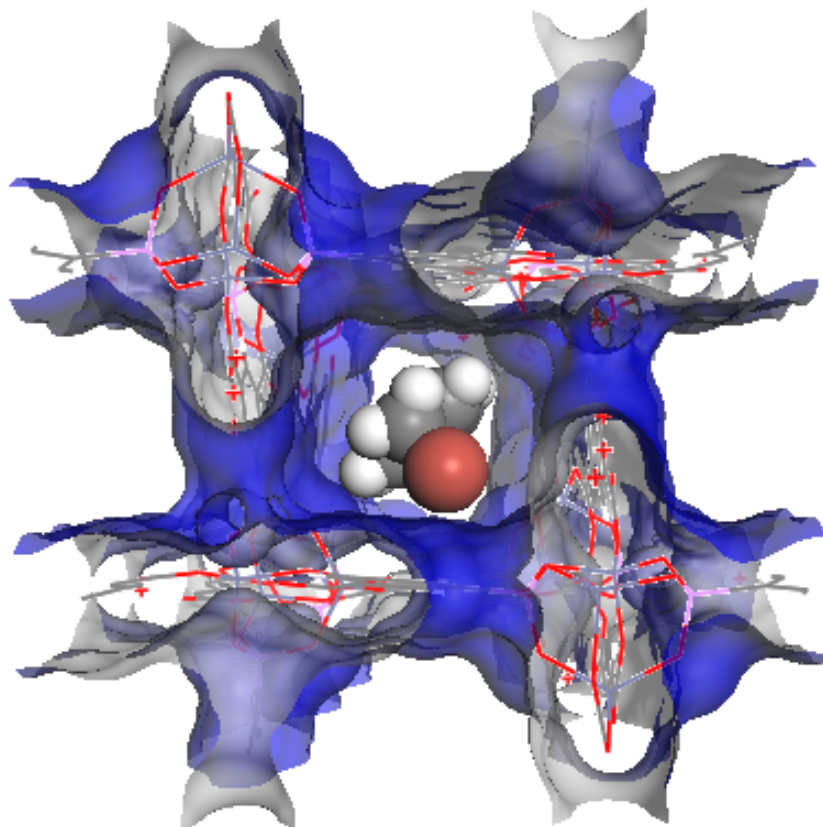


Figure S2. The trinuclear Zn₃-SBU in **1a** (Symmetry codes: (i) $x, 0.5-y, 1.25-z$; (ii) $-0.5+y, 1+x, -0.25+z$; (iii) $1-y, x, 1-z$; (iv) $1-y, 0.5-x, 0.25+z$; (vii)- $0.5+y, 0.5-x, 1.5-z$)

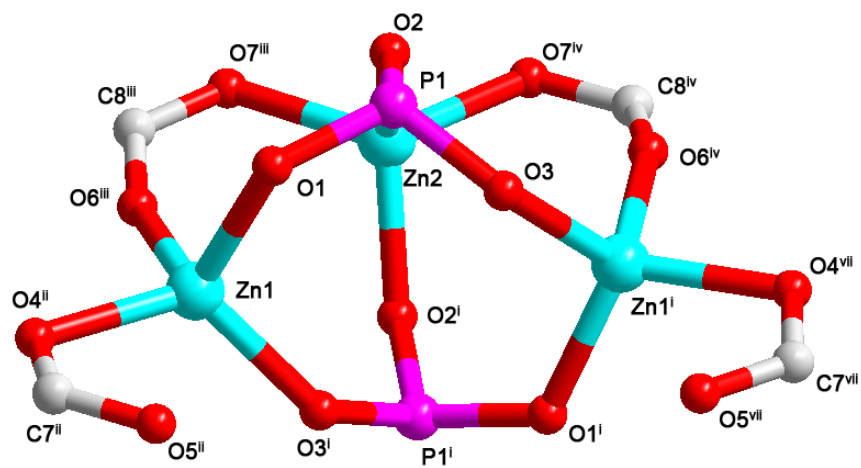


Figure S3. The trinuclear Zn₃-SUB in **1b** (Symmetry codes: (i) $x, 0.5-y, 0.25-z$; (iii) $-y, x, -z$; (iv) $-y, 0.5-x, 0.25+z$; (vii) $0.5+y, x, -0.25+z$; (viii) $0.5+y, 0.5-x, 0.5-z$)

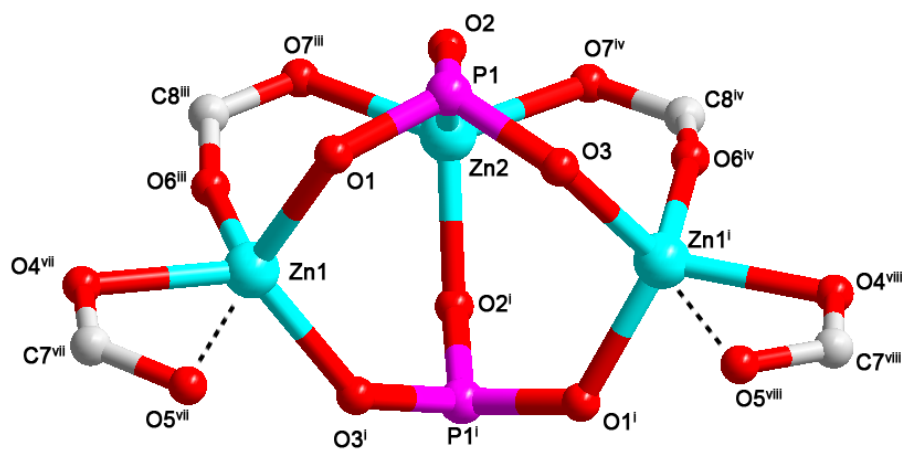
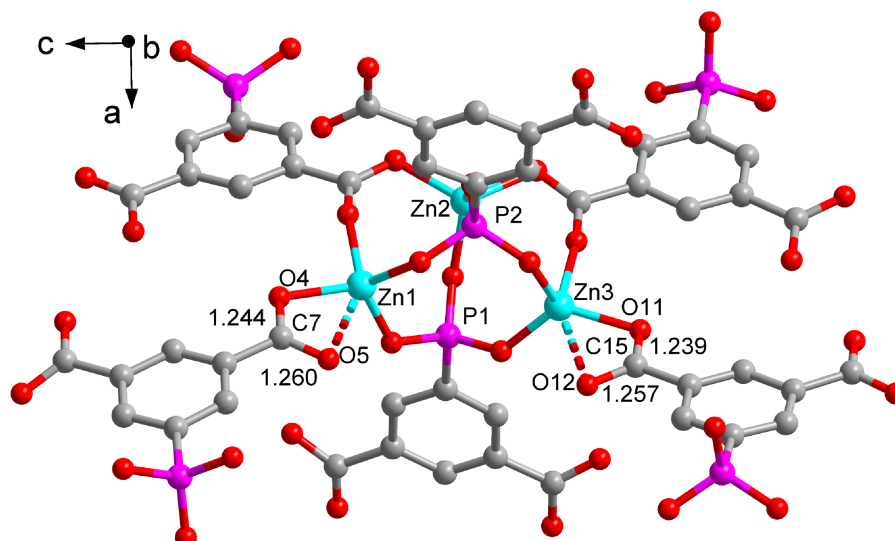


Figure S4. The molecule structure of **1a-100** (crystal sample of 1a heated at 100 for 3 hours, then cool down to room temperature in glovebox under N₂ condition and sealed in glass tube for single-crystal diffraction, further high temperature could not be indexed)



Note: Crystal data for **1a-100**: C₁₆H₆O₁₄P₂Zn₃, 2(O); M = 712.32, Orthorhombic, Fdd2, a = 23.530(7), b = 27.556(9), c = 23.363(7) Å, V = 15148(8) Å³, Z = 16, D_c = 1.249 g cm⁻³, μ = 2.018 mm⁻¹, F(000) = 5600, GOF = 1.03, R₁ and wR₂ are 0.0555 and 0.1697, respectively, for 15738 total data and 4868 observed data [*I* > 2σ(*I*)].

Figure S5. A view of the crystal structure transformation from **1a** (as-made) to **1a-100** to **1b** (cooling down crystal after 200 °C).

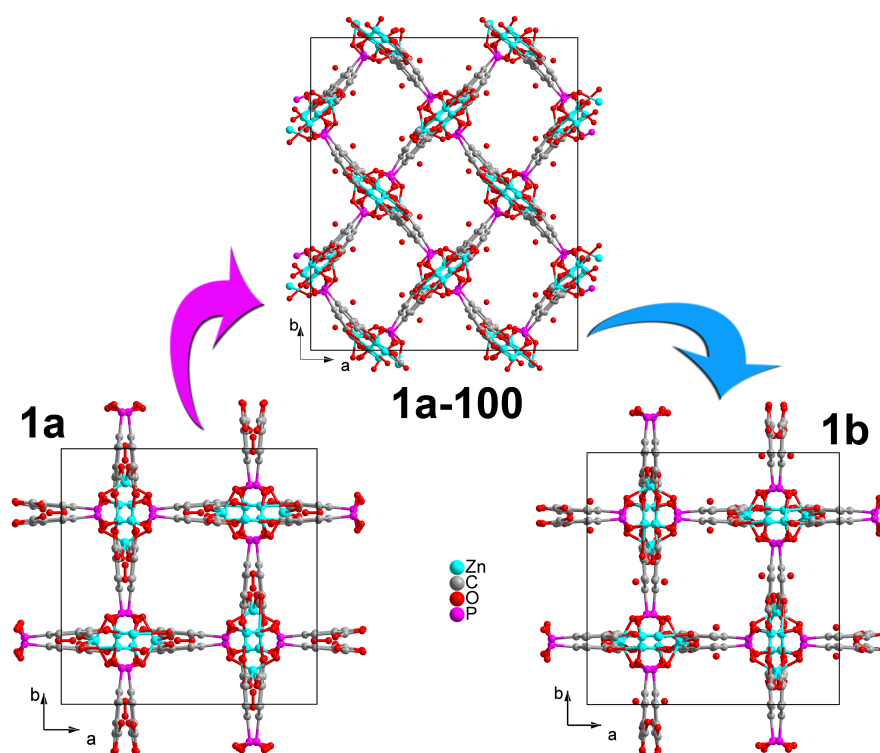


Figure S6. A view of hydrogen bonds of hydrated protons connected to the neighboring carboxylate groups.

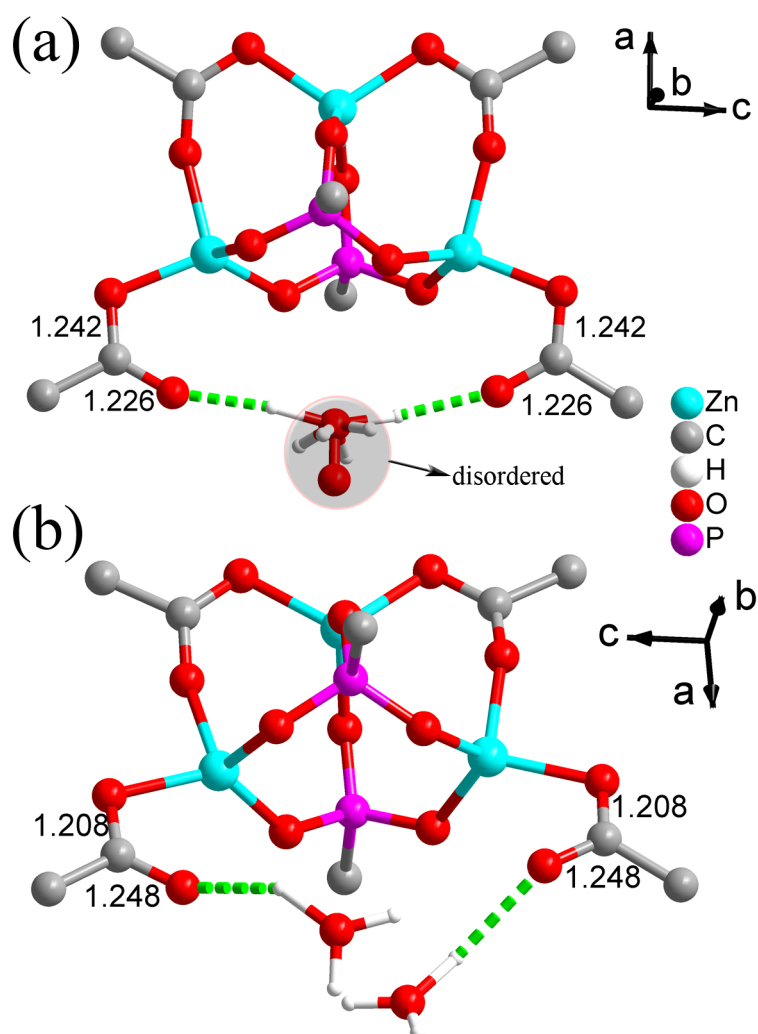


Figure S7. The shrinking of the small channels and the movement of water molecules from **1a** to **1a-100** viewing along *a* axis

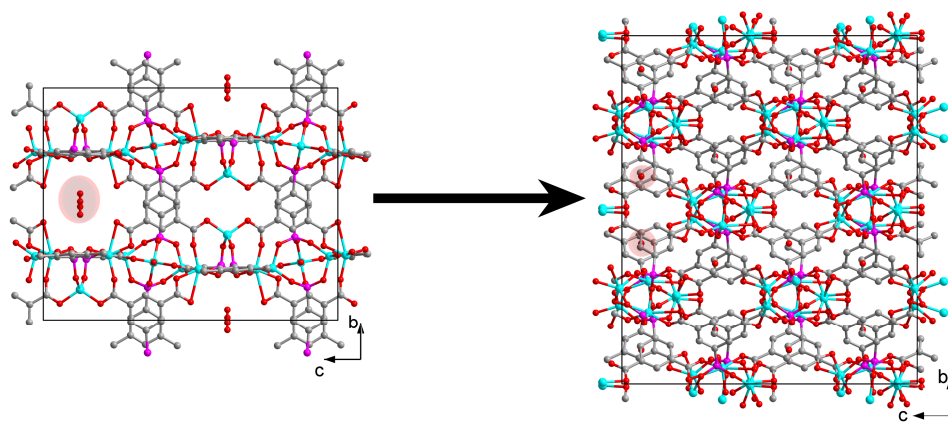


Figure S8. The coordination motif of in $\{Zn_3(pbdc)_2(Htea) \cdot H_3O \cdot XH_2O\}$ (Symmetry codes: (i) $-0.5+x, y, 1.5-z$; (ii) $0.5-x, 0.5+y, z$; (iii) $0.5+x, 1.5-y, 2-z$; (iv) $-0.15-x, -0.5+y, z$; (v) $-0.5-x, -0.5+y, z$)

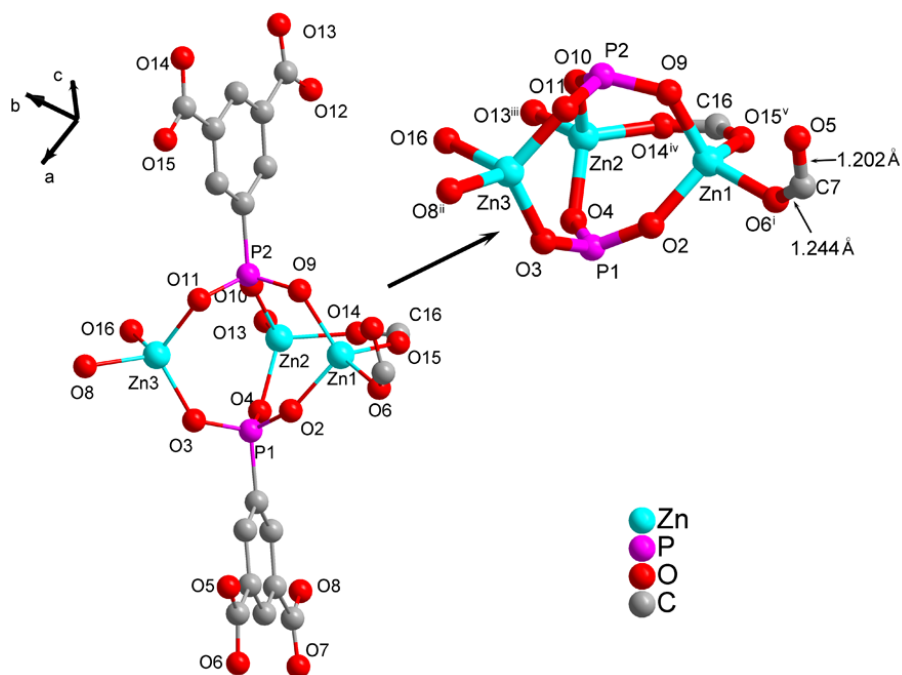


Figure S9. PXRD patterns of **1a** (blue), **1a'** (heated at 200 °C showing as pink) comparing to the simulated data (red) from CIF data of **1a**

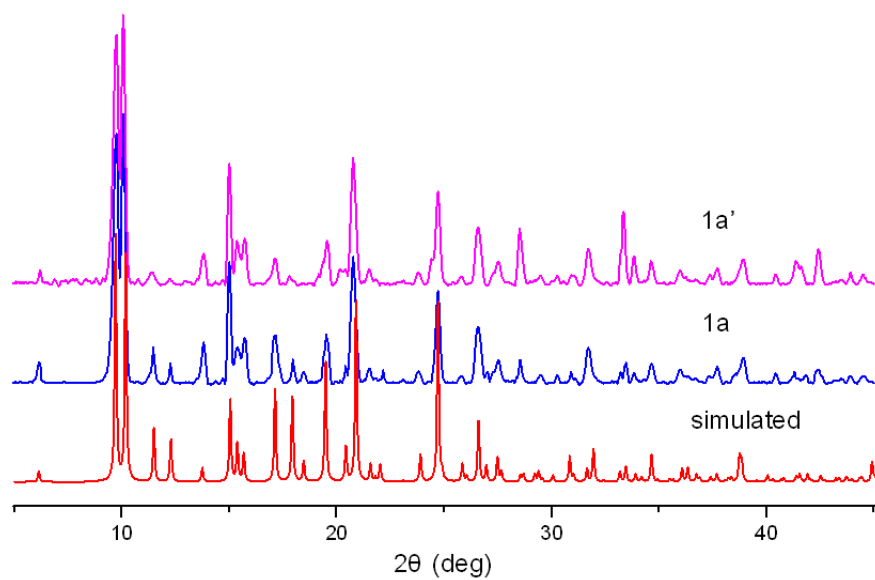


Figure S10. TGA curve for **1a**

