**Electronic Supplementary Information (ESI) for**

# Single-side and double-side swing behaviours of a flexible porous coordination polymer with the rhombic-lattice structure

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**Experimental details.**

**Materials and Methods**. All reagents and solvents were commercially purchased and used without further purification unless otherwise noted. The ligand Hpypz was synthesized according to the literature method [*Dalton Trans.* **2005**, 1598.]. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer, and all the samples were heated to remove the guest molecules before measurement. Thermogravimetry analyses were carried out on a TA-Q50 system under $N_2$ flow with a heating rate of 10 $^{o}$C $min^{-1}$. Power X-ray diffraction (PXRD) data were collected using a Bruker D8 advance X-ray powder diffractometer (Cu K$\alpha$, $\lambda$ = 1.5418 Å) at room temperature with a scanning speed of 0.02 $^{o}$/step and 0.2 sec/step. $CO_2$ sorption isotherms were measured with a Micromeritics ASAP 2020M instrument, in which the measurement temperature (195 K) was obtained by a dry-ice acetone bath. Before the sorption experiment, the as-synthesized samples were activated under high vacuum at 200 °C for 6 h.

**Syntheses.** $[Zn_2(pypz)_2(bdc)]\cdot$guest (**1**). A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.298 g, 1 mmol), $H_2bdc$ (0.088 g, 0.5 mmol), Hpypz (0.144 g, 1 mmol), and *N*,*N*-dimethylformide (DMF, 60 mL) was stirred for 30 min in air, then transferred and sealed in a 100-mL Teflon reactor, heated at 140 °C for 72 hours, and finally cooled to room temperature at a rate of 5 °C $h^{-1}$. The obtained colorless crystals were filtered, washed by DMF, and dried under vacuum (yield *ca*. 90%). Anal. Calcd (%) for $[Zn_2(C_8H_4O_4)(C_8H_6N_3)_2]\cdot 2.7H_2O$ ($C_{24}H_{21.4}Zn_2N_6O_{6.7}$): C, 45.62; H, 3.41; N, 13.30. Found: C, 45.79; H, 3.13; N, 13.13. $[Zn_2(pypz)_2(bdc)]\cdot$guest (**2**). The procedure was the same as for **1**, except that $Zn(NO_3)_2\cdot 6H_2O$ was replaced by $Zn(CH_3COO)_2\cdot 2H_2O$ (0.219 g, 1 mmol). Anal. Calcd (%) for $[Zn_2(C_8H_4O_4)(C_8H_6N_3)_2]\cdot 3.1H_2O$ ($C_{24}H_{22.2}Zn_2N_6O_{7.1}$): C, 45.11; H, 3.50; N, 13.15. Found: C, 45.32; H, 3.69; N, 12.81.

**Crystallography**. Single-crystal X-ray diffraction data were collected on an Oxford Gemini-S Ultra CCD-detector diffractometer with mirror-monochromated Cu Kα radiation or a Rigaku XtaLAB P300DS single-crystal diffractometer by using graphite-monochromated Cu Kα radiation. The structures were solved by the direct method and refined with the full-matrix least-squares method on $F^2$ by the SHELXTL package. Anisotropic thermal parameters were used to refine all host-framework non-hydrogen atoms. The SQUEEZE routine implemented in PLATON program was used to remove the residual electron densities of disordered guests in **1** and **2**. Single crystals of **3** were obtained by heating the as-synthesized **1** or **2** to 200$^{o}$C at the rate of 0.1 $^{o}$C/min under $N_2$ atmosphere. Hydrogen atoms were generated geometrically. The crystal data and structure refinement results are listed in Table S1. CCDC 1869230, 1869231 and 1883610 contain the supplementary crystallographic data.

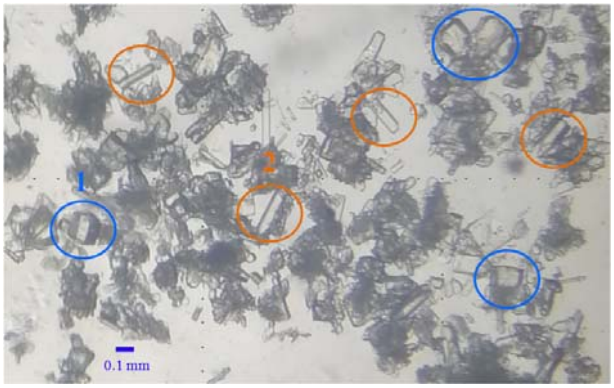


**Fig. S1**. An optical image of $[Zn_2(pypz)_2(bdc)]$ crystals synthesized by using $Zn(NO_3)_2 \cdot 6H_2O$ as metal salt and 5:1 DMF/$H_2O$ as solvent (**1** and **2** are highlighted by blue and orange circles, respectively).

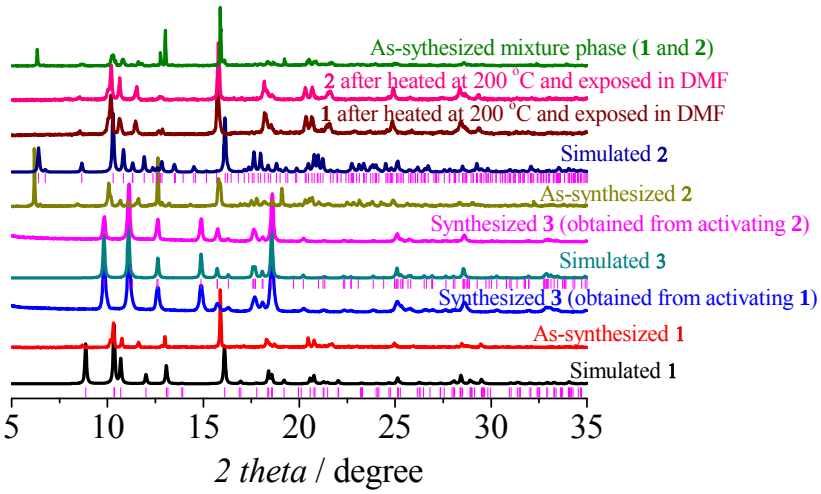


**Fig. S2**. PXRD patterns of **1**, **2**, and **3**.

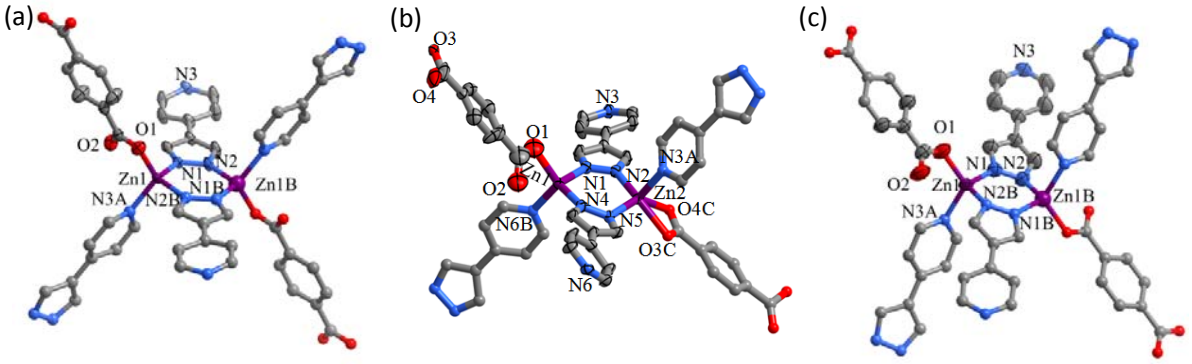


**Fig. S3**. Perspective views of the coordination environments of (a) **1** (symmetry codes: A = x, 1-y, -1/2+z; B = 3/2-x, 1/2-y, 1-z; Zn1-O1 1.970(2) Å, Zn1···O2 2.688 (2) Å, Zn1-N1 1.978(2) Å, Zn1-N2B 2.003(2) Å, Zn1-N3A: 2.026(2) Å), (b) **2** (A = 3/2-x, y, 1/2+z; B = 1/2-x, y, -1/2+z; C = 1-x, -1/2+y, 1/2-z; Zn1-O1 2.027(8) Å, Zn1···O2 2.603(9) Å, Zn1-N1 1.985(6) Å, Zn1-N4 1.997(5) Å, Zn1-N6B 2.035(5) Å, Zn2-O3C 2.176(6) Å, Zn2-O4C 2.238(6) Å, Zn2-N3A 2.059(5) Å, Zn2-N2 2.013(5) Å, Zn2-N5 2.017(4) Å) and (c) **3** (A = -1/2-x, 1/2-y, 1/2+z; B = 1-x, 1-y, 2-z; Zn1-O1 1.910(3) Å; Zn1···O2 2.856(3) Å, Zn1-N1 1.981(4) Å; Zn1-N2B 1.989(3) Å, Zn1-N3A 2.045(4) Å). Hydrogen atoms are omitted for clarity, and thermal ellipsoids of independent atoms are drawn at 50% probability.

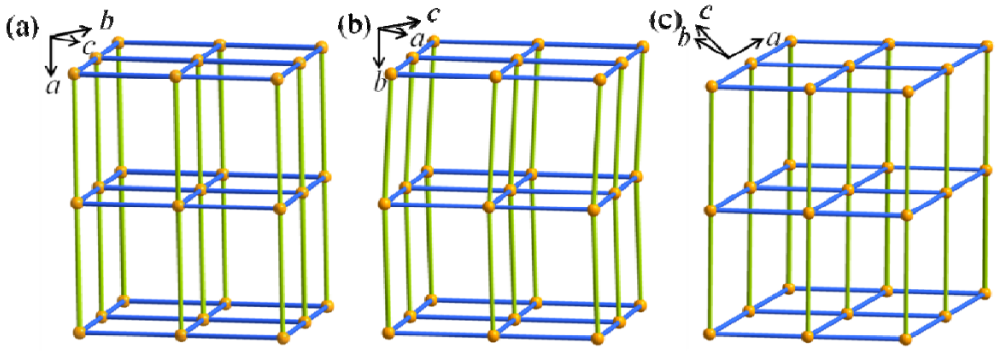


**Fig. S4**. Simplified framework topology of (a) **1**, (b) **2**, and (c) **3** (blue/green stick and yellow spheres represent $pypz^{-}$/$bdc^{2-}$ ligands and $[Zn_2(Rpz)_2]$ units, respectively).

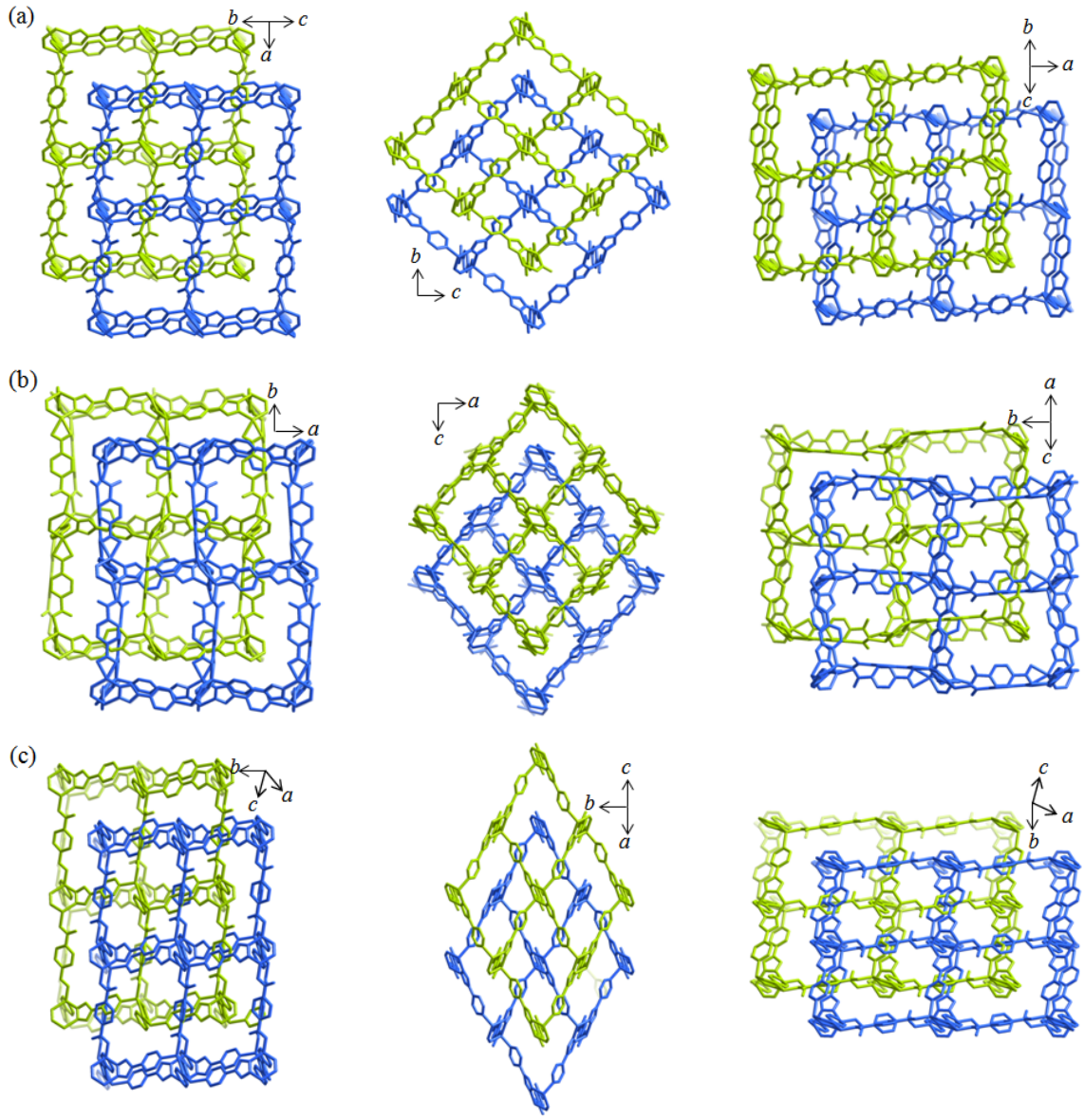


**Fig. S5**. 2-fold interpenetrated structures of (a) **1**, (b) **2**, and (c) **3** (two different colors are used to distinguish two independent networks) viewing along the three representing directions.

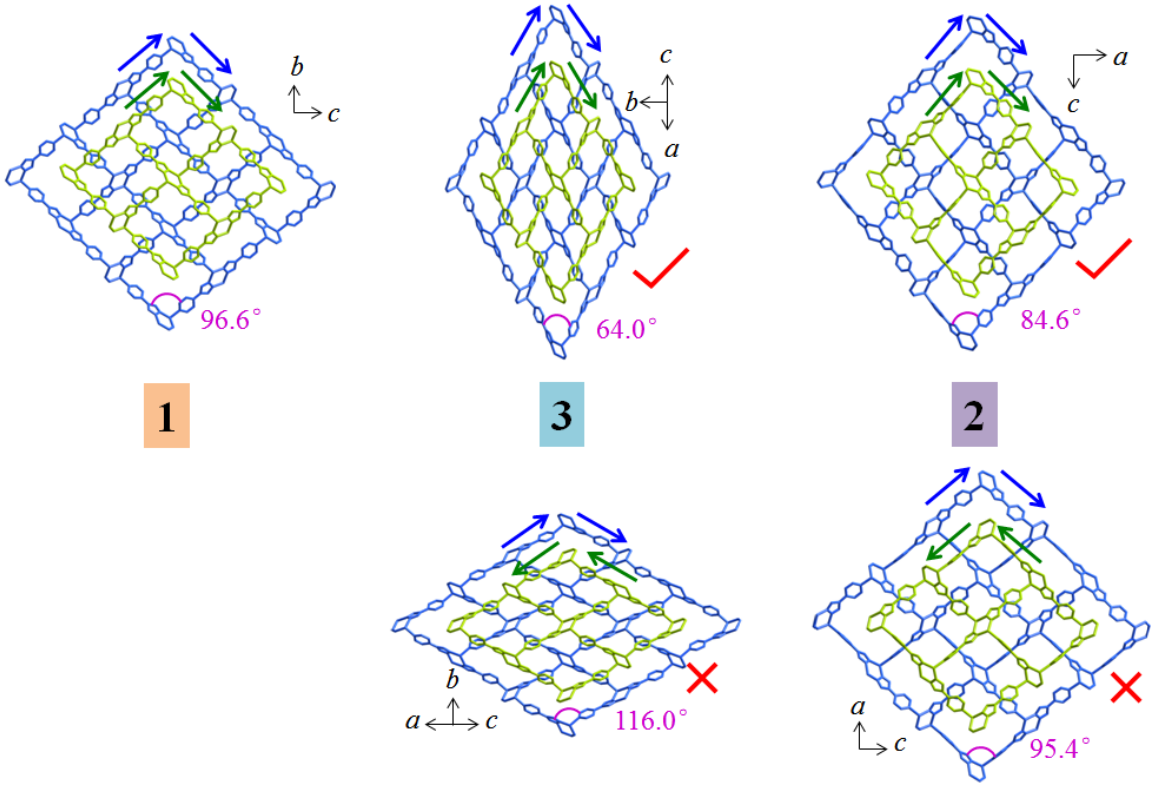


**Fig. S6**. Explanation of the selection/definition of $\varphi$ (acute or obtuse) of the rhombic lattices in **1**, **2**, and **3**. The blue and green arrows highlight the orientations of the $pypz^-$ ligands.

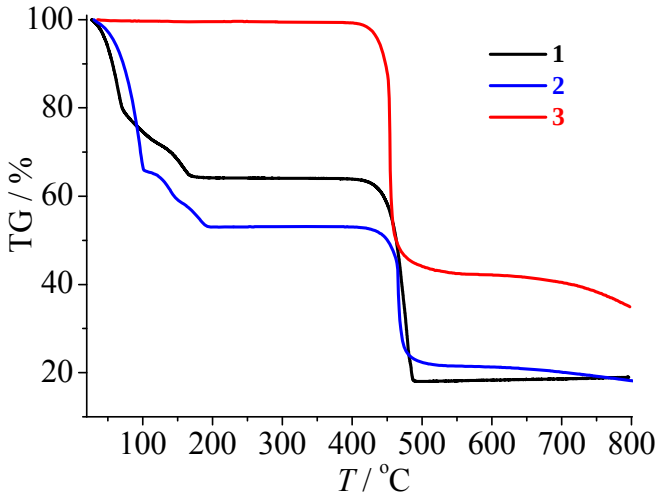


**Fig. S7**. Thermogravimetry curves of **1**, **2**, and **3**.

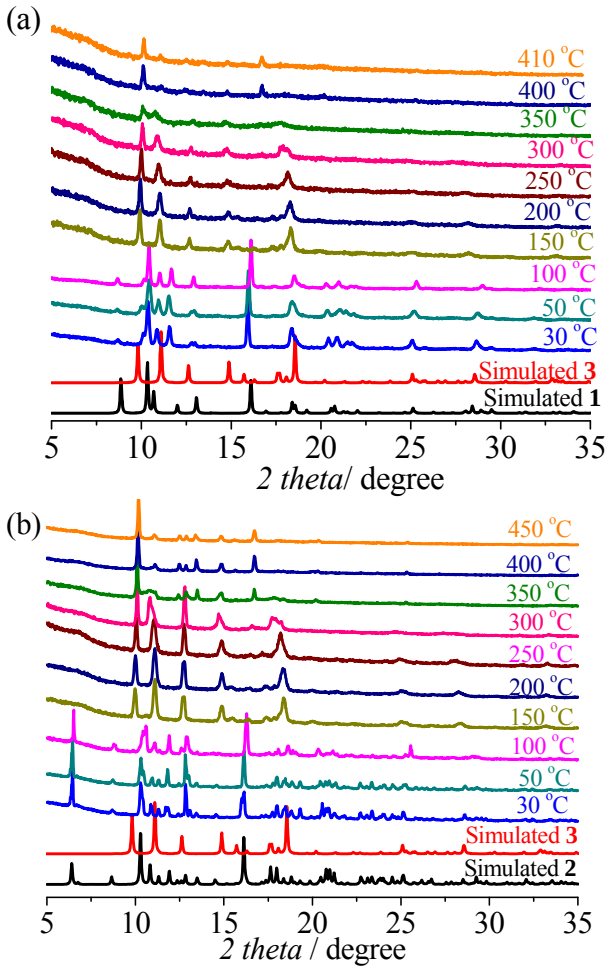


**Fig. S8**. Variable-temperature PXRD pattern of (a) **1** and (b) **2**.

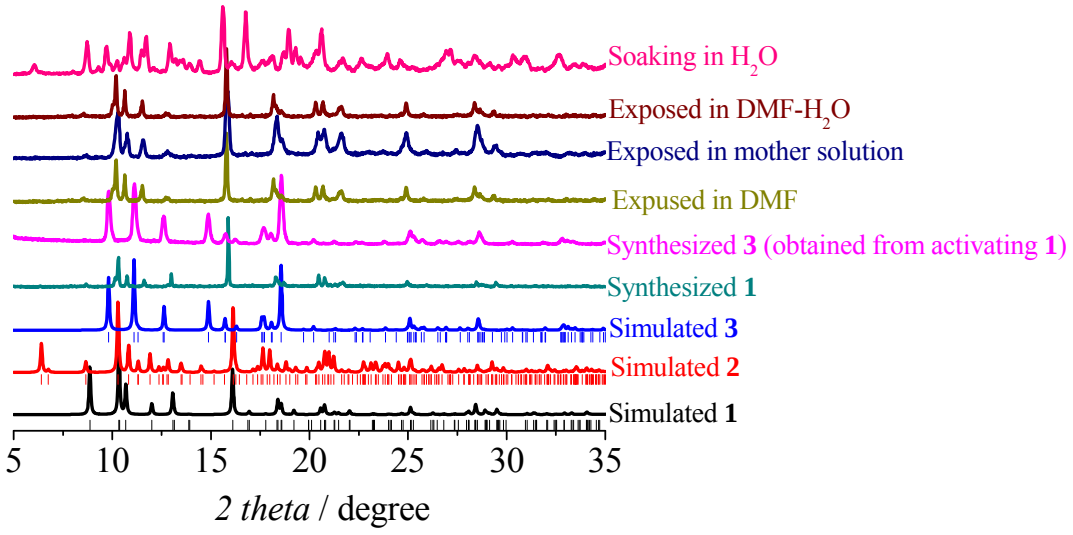


**Fig. S9**. PXRD patterns of **3** (obtained from **1**) after exposed in saturated vapor or immersed directly in the solvent.

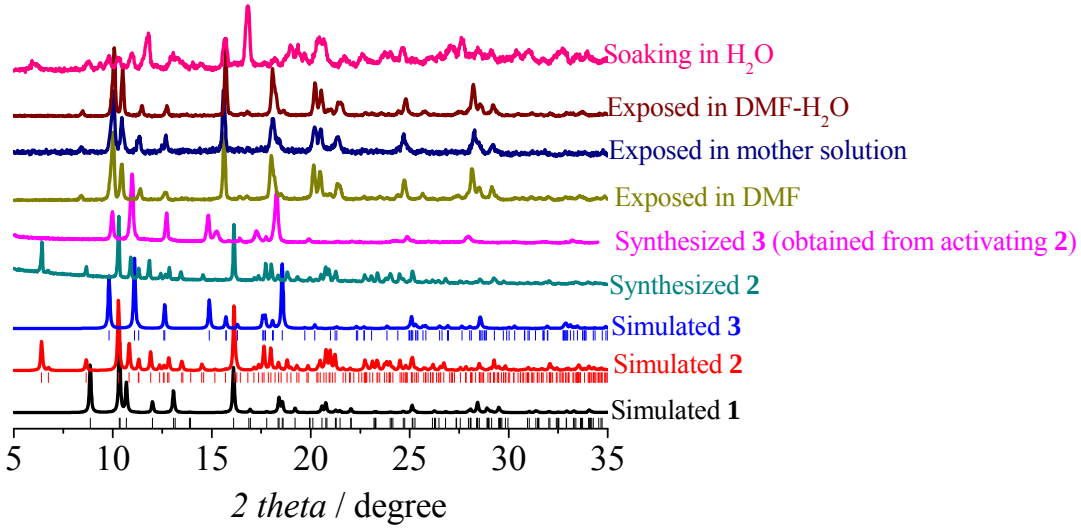


**Fig. S10**. PXRD patterns of **3** (obtained from **2**) after exposed in saturated vapor or immersed directly in the solvent.

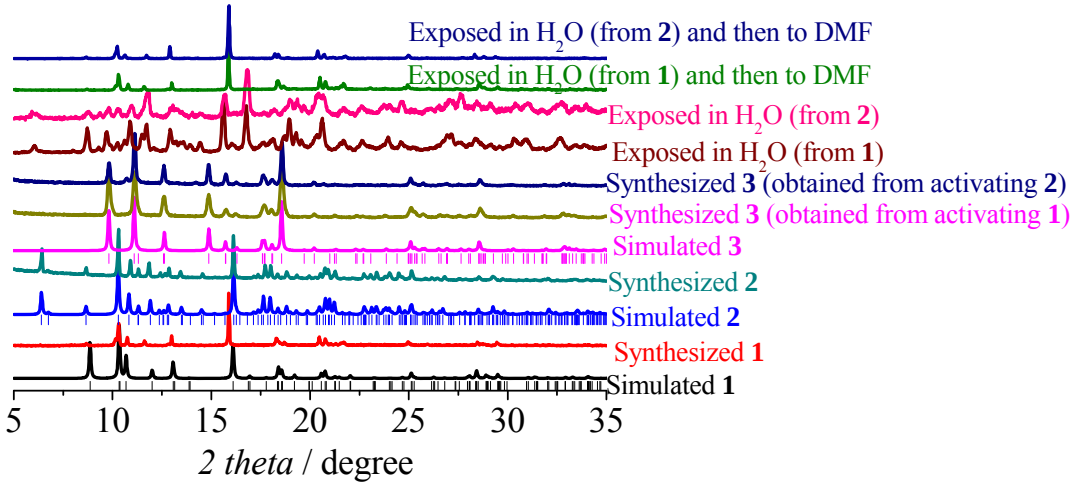


**Fig. S11**. PXRD patterns of **3** after exposed in saturated $H_2O$ vapor and then exposed in DMF.

**Table S1**. Crystallographic data of **1**, **2** and **3**.

| Compound | **1** | **2** | **3** (obtained from activating **1**) | **3** (obtained from activating **2**) |
|---|---|---|---|---|
| Formula | $C_{12}H_8N_3O_2Zn$ | $C_{12}H_8N_3O_2Zn$ | $C_{12}H_8N_3O_2Zn$ | $C_{12}H_8N_3O_2Zn$ |
| Formula weight | 291.58 | 291.58 | 291.58 | 291.58 |
| Temperature (K) | 150 (2) | 150 (2) | 298 (2) | 298 (2) |
| Crystal system | *C*2/*c* | *Pccn* | $P2_1/n$ | $P2_1/n$ |
| Space group | Monoclinic | Orthorhombic | Monoclinic | Monoclinic |
| *a*/Å | 13.5403(3) | 14.8436(5) | 11.2067(5) | 11.370(2) |
| *b*/Å | 14.7298(3) | 27.5747(8) | 11.2671(6) | 11.739(2) |
| *c*/Å | 16.5400(3) | 16.3246(5) | 11.6106(5) | 11.377(2) |
| *β*/º | 90.2418(18) | 90 | 104.136(4) | 104.04(3) |
| *V*/Å$^3$ | 3298.81(12) | 6681.8(4) | 1421.64(12) | 1473.2 (6) |
| *Z* | 8 | 16 | 4 | 4 |
| $D_c$ /g cm$^{-3}$ | 1.1743 | 1.159 | 1.362 | |
| reflns coll. | 12526 | 5231 | 8256 | |
| unique reflns | 3383 | 3792 | 2384 | |
| $R_{int}$ | 0.0256 | 0.0473 | 0.0402 | |
| $R_1$ [I > 2σ(I)][a] | 0.0368 | 0.0661 | 0.0463 | |
| $wR_2$ [I > 2σ(I)][b] | 0.1124 | 0.1797 | 0.1193 | |
| $R_1$ (all data) | 0.0390 | 0.0861 | 0.0655 | |
| $wR_2$ (all data) | 0.1143 | 0.1932 | 0.1319 | |
| GOF | 1.112 | 1.088 | 1.031 | |

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$.

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