A bi-polyoxometallate-based host-guest metal-organic framework

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Materials and Characterization. All Chemicals were purchased from commercial sources and used as received without further treatment. The single crystal X-ray diffraction data were collected on Bruker D8 Venture diffractometer (**1**) or Oxford Diffraction / Agilent SuperNova (dual source) diffractometer (**2**-**4**) using MoKα radiation. Calculations were performed with SHELXL-2018 / 1 program package, and the structures were solved by direct method and refined on F^2 by full-matrix least-squares method.[S1] Thermogravimetric analyses were performed with a TGA / DSC 1 STAR^e system under N_2 atmosphere. FT-IR spectra was collected by a VERTEX70 infrared analyzer. *In situ* variable temperature FT-IR spectra from 30 ^oC to 160 ^oC were collected by a EQUINOX55 infrared analyzer at air atmosphere with a heating rate of 5 ℃ min^{-1}. UV-Vis spectra were collected by a Lambda 950 analyzer. Powder X-ray diffraction (PXRD) were carried out on Rigaku desktop MiniFlex 600 diffractometer with CuKα radiation (λ =1.54184 Å). *In situ* variable-temperature PXRD were carried out at air atmosphere on Rigaku desktop Ultima-IV diffractometer with CuKα radiation (λ =1.54184 Å). Water adsorption isotherm was performed using IGA100B intelligent gravimetric sorption analyser at 298 K with P_0 = 30 mbar. The relative humidity and temperature were controlled by a Labonce-60CH incubator. Element analysis was measured with a vario MICRO analyzer.

Synthesis of 1. PW$_9$ was prepared by the literature method.[S2] 0.3 g (0.12 mmol) **PW$_9$**, 0.8 g (3.4 mmol) $NiCl_2 \cdot 6H_2O$ and 0.5 g (1.9 mmol) NaH_2SIP were completely dissolved in 10 mL water, and then 0.6 mL enMe was added to the transparent solution. After ultrasonic treatment for 10 min, the resulting mixture was sealed in a 25 mL stainless steel reactor with a Teflon liner, which was then heated in an oven at 150 ^oC for five days. When the temperature cooled down to room temperature, 0.23 g green crystals of **1** were collected by convenient filtration. According to element analysis and TG analysis, there were five enMe molecules and thirty-three water molecules in the structure, which couldn't be clearly located by X-ray single diffraction.

FT-IR (KBr, cm^{-1}) for $Na[Ni(enMe)_2]_4[Ni(enMe)_2(H_2O)_2]_2\{[Ni_6(\mu_3\text{-}OH)_3(enMe)_3(SIP)_{1.5}(B\text{-}\alpha\text{-}PW_9O_{34})]_2[H_3PNiW_{11}O_{40}]\}\cdot 5enMe\cdot 33H_2O$ **(1)**: 3258 ~ 3490 (s), 2958 (w), 2874 (w), 1597 (m), 1553 (m), 1356 (m), 1203 (m), 1046 (s), 942 (s), 820 (s), 705 (s). Anal. Calcd (%) for **1**: C 9.71, H 2.77, N 5.60. Found: C 9.09, H 2.40, N 5.07. Crystal data of **1**: M_r = 21056.44, monoclinic, space group *C*2/*m*, a = 23.311(3), b = 39.040(4), c = 27.663(5) Å, β = 106.026(4)^o, V = 24197(6) Å^3, Z = 4, ρ = 2.890 g cm^{-3}, μ = 15.302 mm^{-1}, *F(000)* = 19250.0, GOF = 1.142. A total of 177017 reflections were collected in the range 2.223 ≤ θ ≤ 25.500, 22879 of which were unique (R_{int} = 0.087). $R_1(wR_2)$ = 0.0422(0.1197) for 1494 parameters and 16904 reflections (I > 2σ(I)). CCDC -1948678.

Syntheses of 2-4. Compound **2**-**4** were obtained by the same procedure as that for **1** but using equivalent isophthalic acid (**L_2**), 5-hydroxy isophthalic acid (**L_3**) and 5-amino isophthalic acid (**L_4**) in place of NaH_2SIP, respectively.

FT-IR (KBr, cm^{-1}) for $[Ni(enMe)_2][Ni_6(\mu_3\text{-}OH)_3(enMe)_3(H_2O)_2(L_2^{2-})(B\text{-}\alpha\text{-}PW_9O_{34})]\cdot 9H_2O$ (2): 3111 ~ 3554 (s), 2958 (w), 2880 (w), 1597 (m), 1533 (m), 1455 (w), 1431 (w), 1361 (m), 1194 (w), 1037 (s), 943 (s), 849 (s), 800 (s), 714 (s). **Anal. Calcd (%) for 2:** C 8.06, H 2.31, N 4.09. Found: C 8.11, H 2.20, N 3.94. **Crystal data for 2:** M_r = 3259.38, orthorhombic, space group $P2_12_12_1$, a = 13.4578(4), b = 14.1507(6), c = 36.0116(11) Å, V = 6858.0(4) Å^3, Z = 4, ρ = 3.157 g cm^{-3}, μ = 17.013 mm^{-1}, $F(000)$ = 5948.0, GOF = 1.014. A total of 62795 reflections were collected in the range $3.302 \leq \vartheta \leq 27.101$, 15049 of which were unique (R_{int} = 0.0611). $R_1(wR_2)$ = 0.0376(0.0793) for 894 parameters and 13681 reflections ($I > 2\sigma(I)$). CCDC -1948679.

FT-IR (KBr, cm^{-1}) for $[Ni(enMe)_2][Ni_6(\mu_3\text{-}OH)_3(enMe)_3(H_2O)_2(L_3^{2-})(B\text{-}\alpha\text{-}PW_9O_{34})]\cdot 10H_2O$ (3): 3121 ~ 3564 (s), 2963 (w), 2885 (w), 1553 (m), 1465 (w), 1351 (m), 1199 (w), 1042 (s), 943 (s), 843 (s), 789 (s), 711 (s). **Anal. Calcd (%) for 3:** C 7.98, H 2.34, N 4.05. Found: C 8.06, H 2.15, N 3.92. **Crystal data for 3:** M_r = 3293.40, orthorhombic, space group $P2_12_12_1$, a = 13.5091(2), b = 14.2789(2), c = 36.1110(6) Å, V = 6965.63(19) Å^3, Z = 4, ρ = 3.140 g cm^{-3}, μ = 16.754 mm^{-1}, $F(000)$ = 6020.0, GOF = 1.042. A total of 40345 reflections were collected in the range $3.384 \leq \vartheta \leq 28.282$, 16970 of which were unique (R_{int} = 0.0396). $R_1(wR_2)$ = 0.0372 (0.0924) for 905 parameters and 16382 reflections ($I > 2\sigma(I)$). CCDC -1948680.

FT-IR (KBr, cm^{-1}) for $[Ni(enMe)_2][Ni_6(\mu_3\text{-}OH)_3(enMe)_3(H_2O)_2(L_4^{2-})(B\text{-}\alpha\text{-}PW_9O_{34})]\cdot 10H_2O$ (4): 3116 ~ 3560 (s), 2963 (w), 1558 (m), 1460 (w), 1341 (m), 1287 (w), 1268 (w), 1194 (w), 1031 (s), 938 (s), 847 (s), 799 (s), 711 (s). **Anal. Calcd (%) for 4:** C 7.98, H 2.37, N 4.67. Found: C 8.09, H 2.17, N 4.45. **Crystal data for 4:** M_r = 3272.38, orthorhombic, space group $P2_12_12_1$, a = 13.4978(5), b = 14.1387(5), c = 35.9568(12) Å, V = 6862.1(4) Å^3, Z = 4, ρ = 3.168 g cm^{-3}, μ = 17.004 mm^{-1}, $F(000)$ = 5972.0, GOF = 1.046. A total of 25626 reflections were collected in the range $2.086 \leq \vartheta \leq 27.103$, 14632 of which were unique (R_{int} = 0.0327). $R_1(wR_2)$ = 0.0371 (0.0826) for 894 parameters and 13643 reflections ($I > 2\sigma(I)$). CCDC -1948681.

General water harvesting process of 1： 0.2354g sample of 1 was heated in an oven at 160°C for 1 h to completely remove free water molecules. Then dehydrated sample was rapidly moved into an incubator with constant temperature of 30 °C and different humidity ranging from 40% to 90% for water adsorption. The sample was kept in the incubator until lost weight caused by heating completely recovered. During water adsorption process, the weight of the sample was recorded every ten minutes. The values in y-axis of Fig. 4(a) were calculated by following expression.

value in y-axis = [(recorded sample weight)/0.2354g]*100%

Recycled dehydration-hydration experiments of 1: Dehydration processes were performed by TGA under N_2 atmosphere from 30 °C to 160 °C with a heating rate of 10 °C / min. Upon the completion of dehydration, the sample was placed in an incubator with constant temperature and humidity of 27 °C and 80% for 2h. After that, next dehydration was carried out. The whole dehydration-hydration procedure was repeated 100 times.

Additional figures:

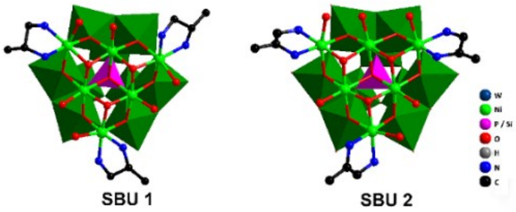

Fig. S1 Two configurations of Ni_6XW_9 (X = P / Si).

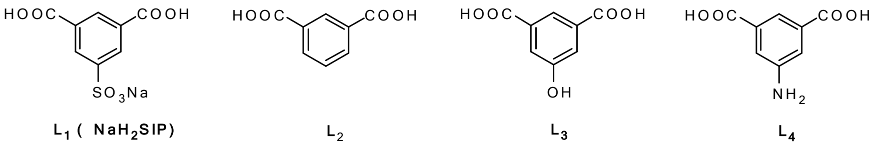

Fig. S2 Related ligands in this work.

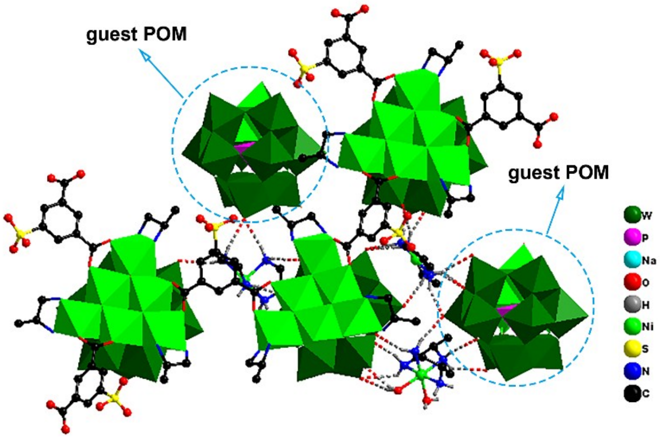

Fig. S3 Partial bridging hydrogen bonds between host and guests.

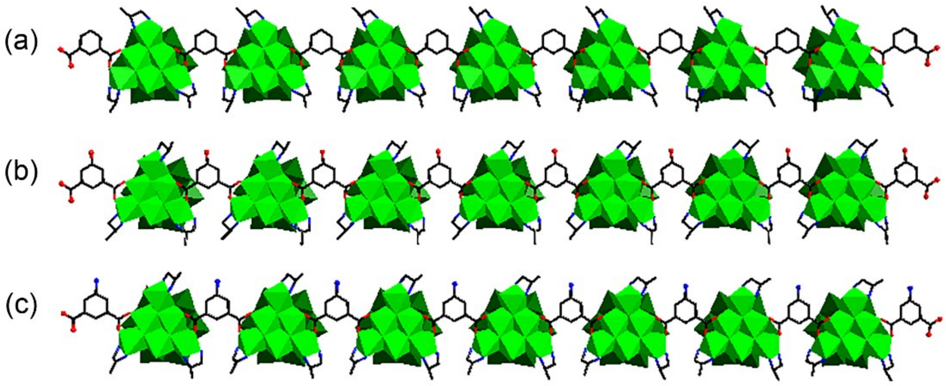

Fig. S4 Structure of (a) **2**; (b) **3**; (c) **4**.

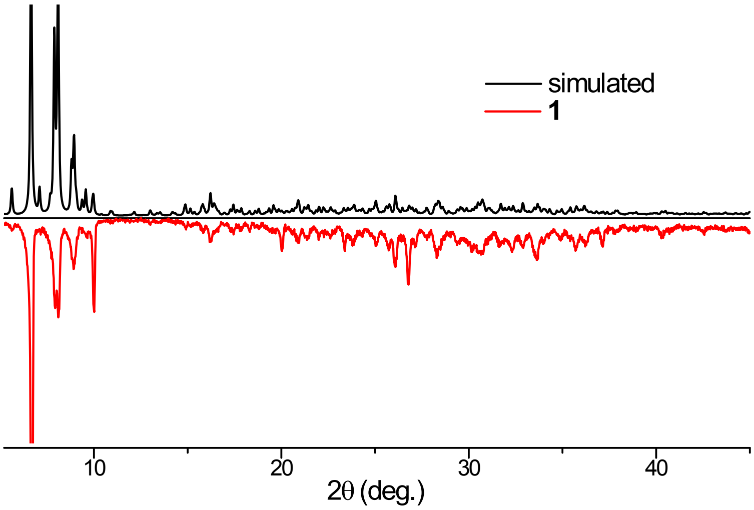

Fig. S5 Simulated and experimental PXRD patterns of **1**.

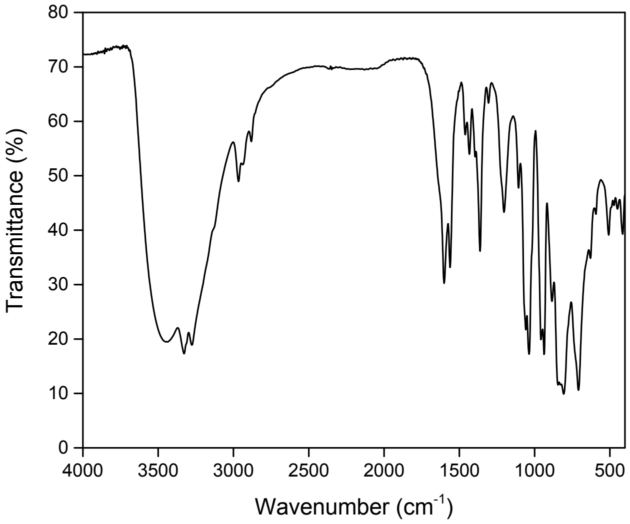

Fig. S6 FT-IR spectra of compound **1**.

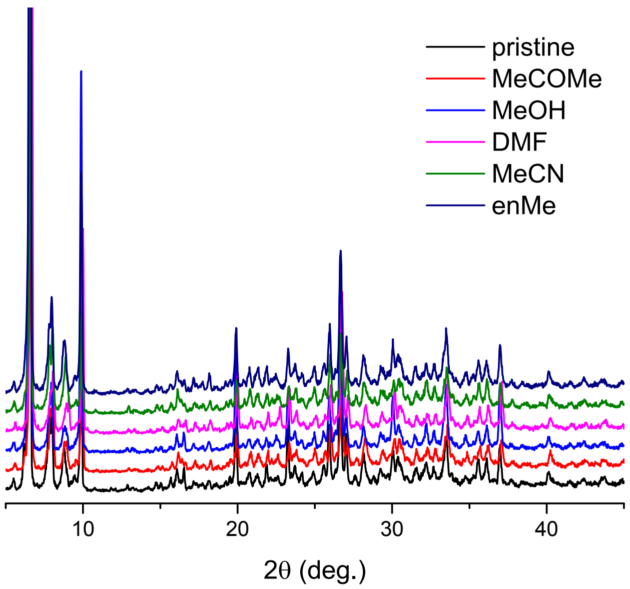

Fig. S7 Stability of compound **1** towards organic solvents.

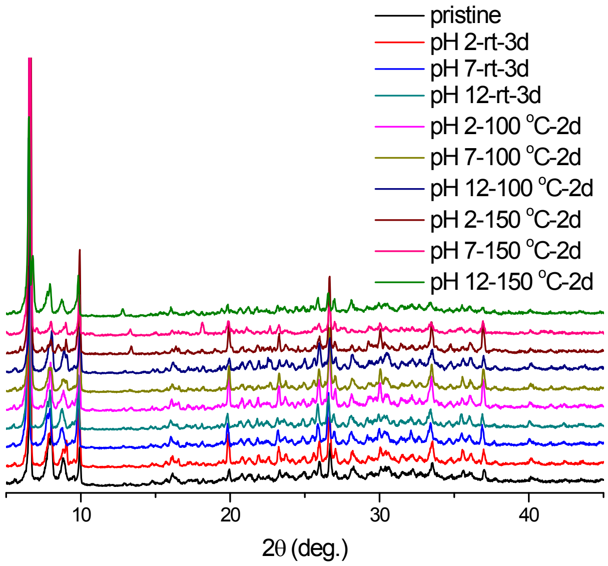

Fig. S8 Stability of compound **1** towards aqueous solution with pH range of 2-12 at different temperatures. (pH = 2 aqueous solution was prepared by H_2SO_4 and pH = 12 aqueous solution was achieved by NaOH. The heating procedure was realized by putting the Teflon-lined stainless steel reactor stocked by sample and aqueous solution in an oven.)

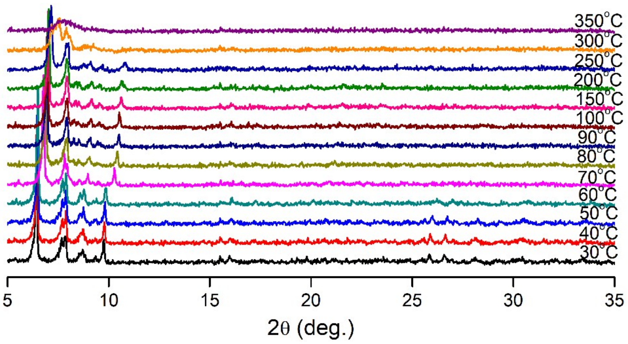

Fig. S9 *In situ* variable temperature PXRD patterns of **1** under room atmosphere.

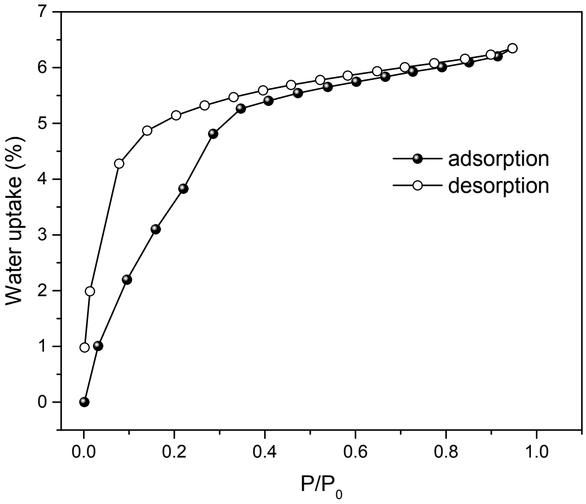

Fig. S10 Water adsorption isotherm of **1**.

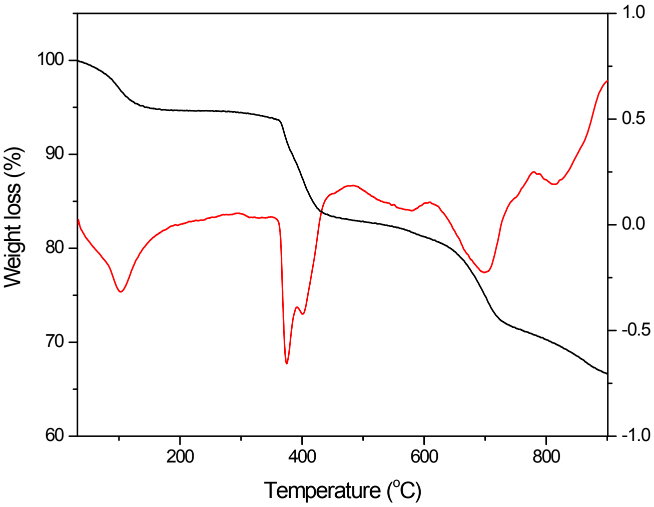

Fig. S11 TG curve of compound **1**.

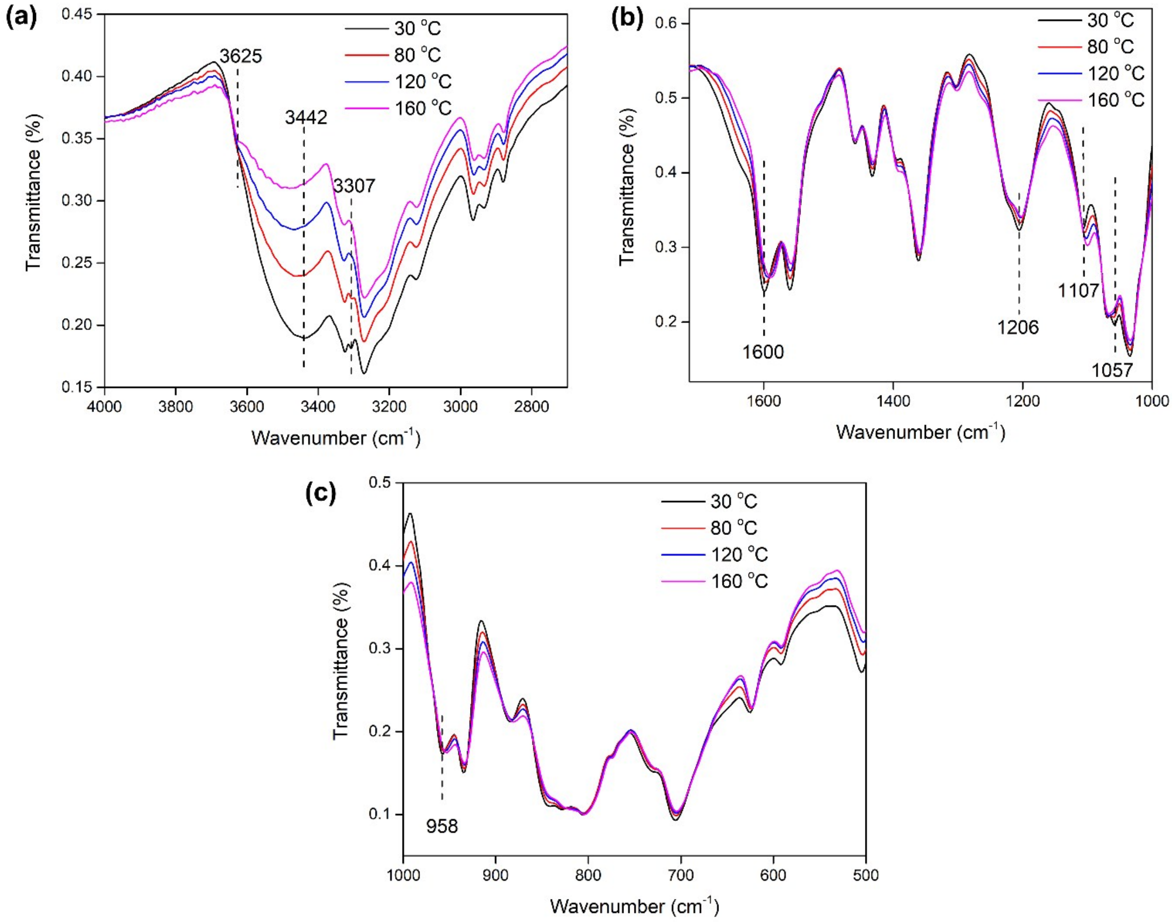

Fig. S12 *In situ* variable temperature FT-IR spectra of **1**. (a) 4000 ~ 2700 cm^{-1}; (b) 1715 ~ 1000 cm^{-1}; (c) 1000 ~ 500 cm^{-1}.

The appearance of small peak at 3625 cm^{-1} was attributed to the μ_3-OH in **1**. It could only be observed in highly dehydrated sample (120 ^{o}C, 160 ^{o}C) because it was overlapped by neighbouring broad peak belonging to water in hydrated sample. The gradual reduction of the broad peak at 3442 cm^{-1} was caused by the loss of water with increasing temperature and the slight blue shift of the peak indicated that the bond strength of O-H in water changed in the heating process. It was rationalized that the change was caused by breakdown of hydrogen bond between water and main moieties of **1**, as well as that between water and water. The disappearance of the peak at 3307 cm^{-1} and the slight red shift and shape change of the peak at 1600 cm^{-1} suggested that the chemical environment of –NH_2 groups in the structure changed. The slight changes of features belonging to sulfo group at 1206, 1107 and 1057 cm^{-1} and that belonging to terminal W=O at 958 cm^{-1} were also observed. These changes could also be explained by breakdown of hydrogen bond between water and these moieties of **1**.

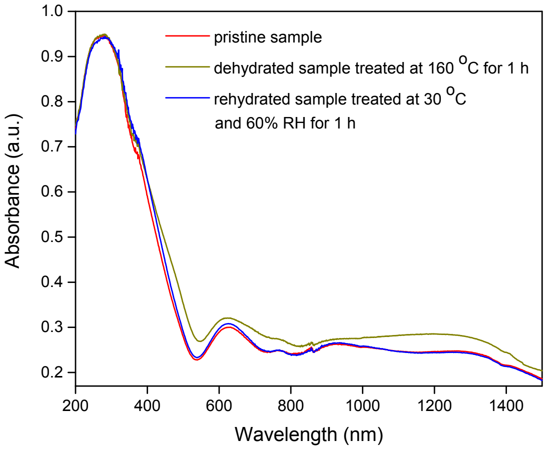

Fig. S13 UV-Vis spectra of pristine sample, dehydrated sample and rehydrated sample of **1**.

Initially, pristine sample was compressed into a tablet to collect its UV-Vis spectrum. Then the tablet was heated in an oven at 160 °C for 1 h. The UV-Vis spectrum of dehydrated sample was collected immediately after the tablet was taken out from the oven. After that, the tablet was placed into an incubator at 30 °C and 60% RH for 1 h. Finally, The UV-Vis spectrum of rehydrated sample was collected.

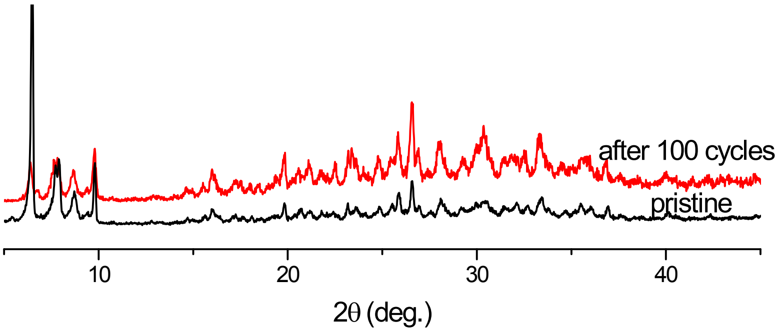

Fig. S14 PXRD comparation of **1** after 100 water desorption-adsorption cycles with pristine sample.

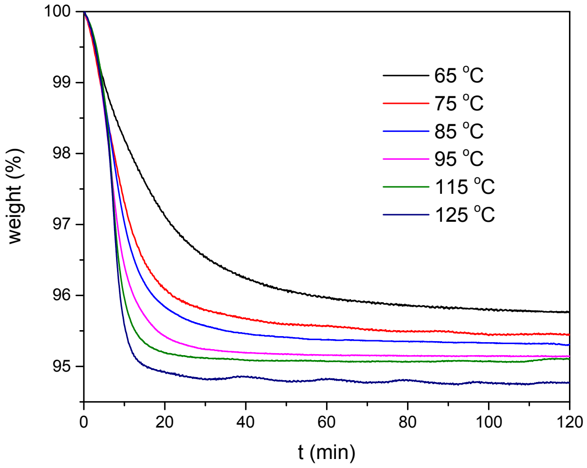

Fig. S15 Dehydration of **1** under different temperature.

Table S1 Comparation of water uptake between **1** and other MOFs.

MOF	Maximum water adsorption capacity (g g^{-1})	P/P_0 for main loading lift (testing temperature)	Regeneration temperature (degree of regeneration)	Ref.
Compound **1**	0.052	0 – 0.35 (25 °C)	65 °C (~81%) 85 °C (~90%) 125 °C (100%)	this work
MIL-160	0.37	0.08 – 0.18 (30°C)	100 °C (partial)	Ref. 13a
CAU-10	0.32	0.18 – 0.22 (25 °C)	100 °C (partial)	Ref. 13a
MIL-101(Cr)	~1.7	0.3 – 0.48 (30°C)	70 °C (partial)	Ref. 13b
MIL-100(Fe)	~ 0.9	0.27 – 0.57 (30°C)	70 °C (partial)	Ref. 13b
MIL-100 (Al)	~ 0.52	0.24 – 0.4 (25 °C)	--	Ref. 13c
KAUST-8	~ 0.234	0 – 0.05 (35 °C)	~105 °C (100%)	Ref. 10
Co_2Cl_2(BTDD)	0.968	0.28 – 0.3 (25 °C)	45 °C (partial)	Ref. 13d
MOF-801	~0.4	0 – 0.2 (25 °C)	~65 °C	Ref. 12a
MOF-841	~0.6	0.22 – 0.3 (25 °C)	--	Ref. 13e

BTDD = bis(1*H*-1,2,3-triazolo[4,5-*b*],[4′,5′-*i*])dibenzo[1,4]dioxin

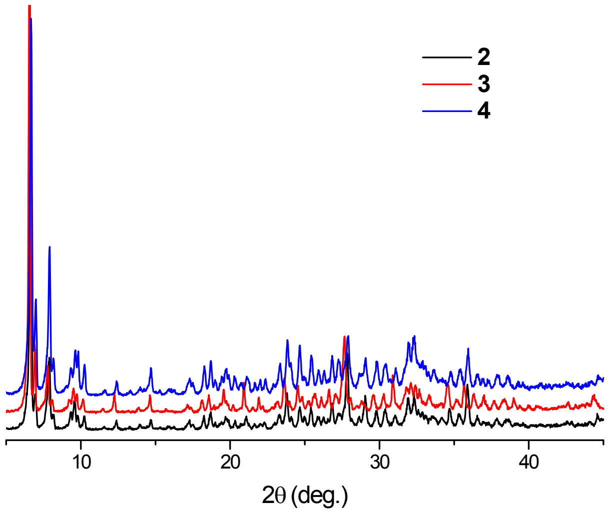

Fig. S16 PXRD patterns of **2**-**4**.

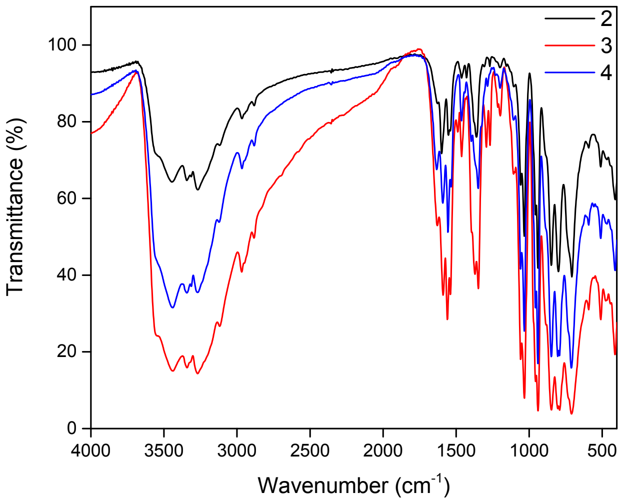

Fig. S17 FT-IR spectra of of **2**-**4**.

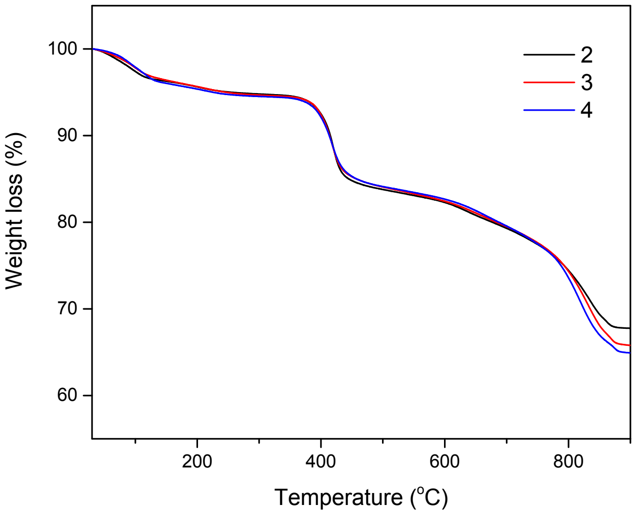

Fig. S18 TG curve of **2**-**4**.

References

[S1] G. M. Sheldrick, *Acta cryst.,C*, **2015**, *71*, 3-8.

[S2] A. P. Ginsberg, in *Inorganic Syntheses*, *Vol. 27*, Wiley, New York, **1990**, pp. 85-100.