Supporting information for

# An unprecedented dynamic porous metal-organic framework assembled from fivefold interlocked closed nanotubes with selective gas adsorption behaviors

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## Experimental section

**General remarks:** All of the chemicals were commercially available and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4000~400 cm$^{-1}$ region using KBr pellets and a Bruker EQUINOX 55 spectrometer. TG analysis were performed on a Netzsch TG 209 instrument under nitrogen atmosphere with a heating rate of 10 °C/min. Variable-temperature powder X-ray diffraction measurements were performed on D8 ADVANCE X-Ray Diffractometer. The single crystal data were collected on an Oxford Diffraction Xcalibur Nova X-ray single-crystal diffractometer for **1**, and a Bruker Smart 1000 CCD diffractometer for [NiL]($ClO_4$)$_2$.

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled with care, and prepared only in small quantities.*

**[NiL]($ClO_4$)$_2$:** To a stirred solution of $NiCl_2\cdot 6H_2O$ (2.36 g, 10.0 mmol) and N,N-bis(2-aminoethyl)-1,3-propanediamine (1.6 g, 10.0 mmol) in 60 mL of methanol was slowly added paraformaldehyde (0.6 g, 20.0 mmol), and 2-amino-1-butanol (0.88 g, 10.0 mmol). The resulting solution was refluxed for 72 h, the solution gradually became brown. The solution was filtered while hot and the filtrate was concentrated to about half of the original volume. The solution was allowed to stand in a refrigerator until purple precipitate of [NiL]$Cl_2$ formed, which was filtered off, washed with methanol, and dried under vacuum. Yield: 32%. Elemental analysis: calcd(%) for [(NiL)$Cl_2$]·$H_2O$ ($C_{13}H_{33}N_5Ni_1O_2Cl_2$): C 37.08, H 7.90, N 16.63; found: C 37.40, H 7.44, N 16.78. IR (KBr): $v$ = 3453 (m), 3421 (m), 3267 (w), 3245 (s), 3213 (vs), 2925 (s), 2860 (s), 1480 (m), 1449 (m), 1392 (m), 1359 (w), 1286 (m), 1270 (m), 1247 (w),1193 (w), 1175 (w), 1105 (s), 1074 (vs),1058 (vs),1020 (m), 992 (s), 960 (m), 927 (s), 882 (m), 820 (w), 763 (w), 567 (w), 471 (w), 419 (m) $cm^{-1}$.

The orange crystals of [NiL]$(ClO_4)_2$ were obtained by slow evaporating an acetone solution of [NiL]$Cl_2$ and $NaClO_4$. The products were filtered off, washed with acetone, and dried under vacuum. Yield: 95%. Elemental analysis: calcd(%) for [NiL]$(ClO_4)_2$ ($C_{13}H_{31}N_5Ni_1O_9Cl_2$): C 29.40, H 5.88, N 13.19; found: C 29.35, H 5.85, N 13.20. IR (KBr): $v$ = 3427 (m), 3298 (m), 3171 (m), 3082(m), 2930 (m), 2864(m), 1637 (w), 1462 (w), 1438 (w), 1411 (w), 1305 (w), 1287(w), 1143 (vs), 1114 (vs), 1087 (vs), 1026 (m), 992 (m), 941 (w), 901 (w), 825 (w), 627 (s), 498 (w) $cm^{-1}$.

**[(NiL)$_3$(TCBA)$_2$]·12$H_2O$ (1):** An aqueous solution (2 mL) of $H_3$TCBA (0.017 g, 0.04 mmol) and triethylamine (0.012 g, 0.12 mmol) was layered with an acetonitrile solution (3 mL) of [NiL]$(ClO_4)_2$ (0.034 g, 0.06 mmol ) at room temperature. After about six days, pink block-shaped crystals suitable for X-ray analysis formed (0.015 g, 30% yield based on [NiL]$(ClO_4)_2$). Elemental analysis: calcd(%) for $C_{87}H_{153}N_{17}Ni_3O_{27}$: C 51.09, H 7.54, N 11.64; found: C 51.03, H 7.41, N 11.60. IR (KBr): $v$ = 3393 (vs), 3274 (vs), 2928 (vs), 2870 (vs), 1594 (vs), 1552 (vs), 1462 (m), 1383 (vs), 1297 (w), 1254 (w), 1170 (w), 1090 (m), 1063 (m), 1016 (m), 994 (m), 887(w), 849 (w), 812 (w), 775 (m), 709 (w), 664 (w) $cm^{-1}$.

**Single crystal X-ray diffraction:** Orange needle-shaped crystal of $[NiL](ClO_4)_2$ (0.48×0.45×0.42 mm) was used for data collection. Diffraction data were collected at 150 K on a Bruker Smart 1000 CCD diffractometer with Mo-*K*α radiation (λ = 0.71073 Å). The empirical absorption corrections were applied using the SADABS program.[1] Single-crystal X-Ray diffraction data for **1** was collected on an Oxford Diffraction Xcalibur Nova X-ray single-crystal diffractometer with Cu-*Kα* radiation (λ = 1.54178 Å) at 150 K. The empirical absorption corrections were applied using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm.[2] The structures of $[NiL](ClO_4)_2$ and **1** were solved by direct method. The H-atoms were added in ideal positions and refined as riding models. These were refined first isotropically and then anisotropically.

The data quality of the crystal structure of **1** is very poor due to severely disorder of almost all organic building units. The whole framework of **1** exhibits orientational disorder over two sets of positions and can be modeled by splitting method except for the highly disordered 2-aminobutan-1-ol group of azamacrocyclic ligand. $TCBA^{3-}$ as well as $[NiL]^{2+}$(Ni1) group with the positional disorder were treated with FVAR, and the disordered components have been refined with 0.523(6):0.477(6) occupancies. $[NiL]^{2+}$(Ni2) group located in 2-fold axis was refined with half occupancy as a whole, and the positions of the N atom in position 3 and the carbon atom in position 10 were distinguished by the void around them, the position with a larger void around it is the N atom in position 3, and the position with a smaller void around it is the C atom in position

10. Referring to related data from crystal structure of $[NiL](ClO_4)_2$, various restraints (DFIX and SADI) were used to impose equal bond lengths for disordered corresponding parts. The thermal displacement parameters were refined anisotropically and set equal with various constrains (ISOR, DELU and EADP). Hydrogen atoms were relocated in geometrically sensible positions after each refinement cycle and given thermal parameters defined by those applying to the atom to which they are attached. All the calculations were performed using the SHELXTL-97 system of computer programs.[3] The diffraction of **1** was weak due to the presence of highly disordered 2-amino-1-butanol group of L and lattice water molecules, and the attempt to locate the highly disordered 2-amino-1-butanol group and water molecules was unsuccessful. Therefore, the *SQUEEZE* routine of *PLATON* was applied to remove the diffraction contributed from the disordered 2-amino-1-butanol group of L and lattice water molecules.[4] The final composition of **1** were determined by combining the results of single-crystal structures, EA, IR, and TGA data. The crystallographic data for $[NiL](ClO_4)_2$ and **1** are summarized in Table S1, and the selected bond lengths and angles are listed in Table S2.

**Gas sorption measurements:** The low pressure gas sorption experiments were measured with a Micromeritics ASAP2020 gas adsorption instrument. The $N_2$, $H_2$ and $CO_2$ adsorption isotherms were collected in a relative pressure range from $10^{-4}$ to 1 atm. The cryogenic temperature of 77 K required for $N_2$ and $H_2$ sorption tests was controlled using liquid nitrogen bath. The cryogenic temperature of 195 K required for $CO_2$ sorption measurements was controlled by dry ice-acetone bath. The high-pressure gas sorption experiments were measured with BELSORP-HP gas adsorption instrument. The temperatures of 273, 298 and 323 K for $CO_2$ sorption measurements were controlled by ice and water bath, respectively. The initial outgassing process for the sample was carried out under a high vacuum (less than$10^{-6}$ mbar) at 80 ºC for 10 h. The desolvated sample and sample tube were weighed precisely and transferred to the analyzer.

**Table 1**. Crystal data and structure refinements for $[NiL](ClO_4)_2$ and **1**

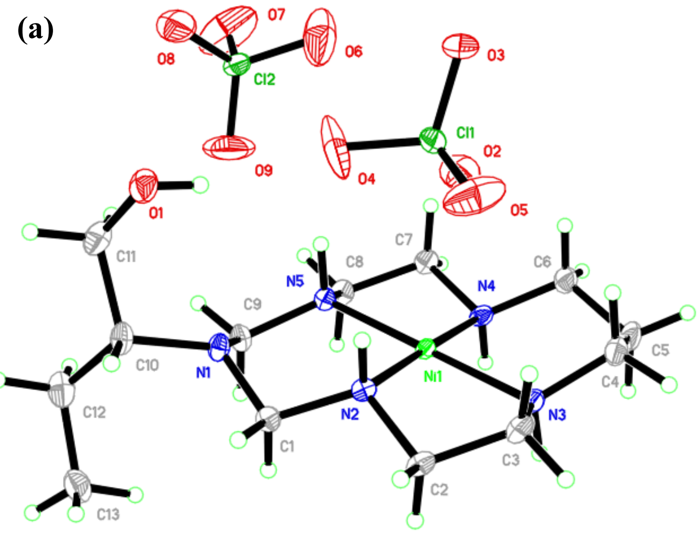
| | $[NiL](ClO_4)_2$ | **1** |
|---|---|---|
| Formula | $C_{13}H_{31}Cl_2N_5NiO_9$ | $C_{87}H_{153}N_{17}Ni_3O_{27}$ |
| Fw. | 531.04 | 2045.39 |
| Crystal system | Monoclinic | Tetragonal |
| Space group | $P2_1/c$ | $I\bar{4}c2$ |
| $a$ (Å) | 8.2272(11) | 30.233(2) |
| $b$ (Å) | 16.486(2) | 30.233(2) |
| $c$ (Å) | 15.625(2) | 22.671(3) |
| $\alpha$ (˚) | 90.00 | 90 |
| $\beta$ (˚) | 93.407(2) | 90 |
| $\gamma$ (˚) | 90.00 | 90 |
| $V$ (Å$^3$) | 2115.6(5) | 20722(4) |
| $Z$ | 4 | 8 |
| $D_c$ (g·cm$^{-3}$) | 1.667 | 1.311 |
| Reflections | 12558 | 15419 |
| / Unique | / 4584 | /7405 |
| $R$(int) | 0.0258 | 0.0559 |
| GOF on $F^2$ | 1.061 | 1.077 |
| $R_1[I \geq 2\sigma(I)]$ | 0.0533 | 0.1244 |
| $wR_2[I \geq 2\sigma(I)]$ | 0.1428 | 0.1931 |

$^a$ $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^b$ $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

**Table 2.** Selected bond lengths (Å) and angles (º) for $[NiL](ClO_4)_2$ and **1**$^{a)}$.

| | | | | | |
|---|---|---|---|---|---|
| $[NiL](ClO_4)_2$ | | | | | |
| N(2)-Ni(1) | 1.936(3) | N(3)-Ni(1) | 1.938(3) | N(4)-Ni(1) | 1.946(3) |
| N(5)-Ni(1) | 1.935(3) | | | | |
| N(1)-C(10)-C(12) | 115.8(3) | N(1)-C(10)-C(11) | 109.1(3) | C(12)-C(10)-C(11) | 112.5(3) |
| O(1)-C(11)-C(10) | 114.2(3) | C(13)-C(12)-C(10) | 114.6(4) | C(1)-N(1)-C(9) | 111.9(3) |
| C(1)-N(1)-C(10) | 117.3(3) | C(9)-N(1)-C(10) | 116.4(3) | N(5)-Ni(1)-N(2) | 93.68(12) |
| N(5)-Ni(1)-N(3) | 179.54(13) | N(2)-Ni(1)-N(3) | 86.75(12) | N(5)-Ni(1)-N(4) | 86.65(12) |
| N(2)-Ni(1)-N(4) | 178.03(12) | N(3)-Ni(1)-N(4) | 92.92(13) | | |
| **1** | | | | | |
| O(1)-Ni(1) | 2.125(16) | O(3)-Ni(2) | 2.168(8) | O(5)-Ni(1)#1 | 2.097(12) |
| Ni(1)-O(5)#2 | 2.097(12) | Ni(2)-O(3)#3 | 2.168(8) | Ni(1)-N(5) | 2.030(10) |
| Ni(1)-N(6) | 2.035(10) | Ni(2)-N(8) | 2.059(9) | Ni(2)-N(9) | 1.993(9) |
| Ni(2)-N(10) | 2.026(9) | | | | |
| C(19)-C(18)-C(17) | 133.3(12) | C(20)-C(21)-C(24) | 120.0(7) | C(22)-C(21)-C(24) | 117.6(7) |
| C(23)-C(18)-C(17) | 105.8(11) | N(1)-C(24)-C(21) | 112.3(14) | N(3)-Ni(1)-N(5) | 176.8(7) |
| N(3)-Ni(1)-N(6) | 92.7(7) | N(4)-Ni(1)-N(3) | 89.3(6) | N(4)-Ni(1)-N(5) | 93.9(7) |
| N(4)-Ni(1)-N(6) | 177.9(8) | N(5)-Ni(1)-N(6) | 84.0(6) | N(3)-C(25)-N(2) | 118.0(16) |
| N(3)-C(26)-C(27) | 108.9(16) | N(4)-C(27)-C(26) | 108.9(16) | N(4)-C(28)-C(29) | 111.4(15) |
| N(5)-C(30)-C(29) | 109.9(15) | N(5)-C(31)-C(32) | 112.1(17) | N(6)-C(32)-C(31) | 110.8(16) |
| N(6)-C(33)-N(2) | 120.2(18) | C(33)-N(2)-C(25) | 122.9(17) | C(25)-N(3)-C(26) | 120.0(2) |
| C(28)-N(4)-C(27) | 121(2) | C(30)-N(5)-C(31) | 108(2) | C(33)-N(6)-C(32) | 127.3(18) |

a) Symmetry codes: #1 –y-1/2,-x+3/2,-z+3/2, #2 –y+3/2,x+1/2,-z+3/2, #3 -y+3/2,-x+3/2,-z+1, for **1**.



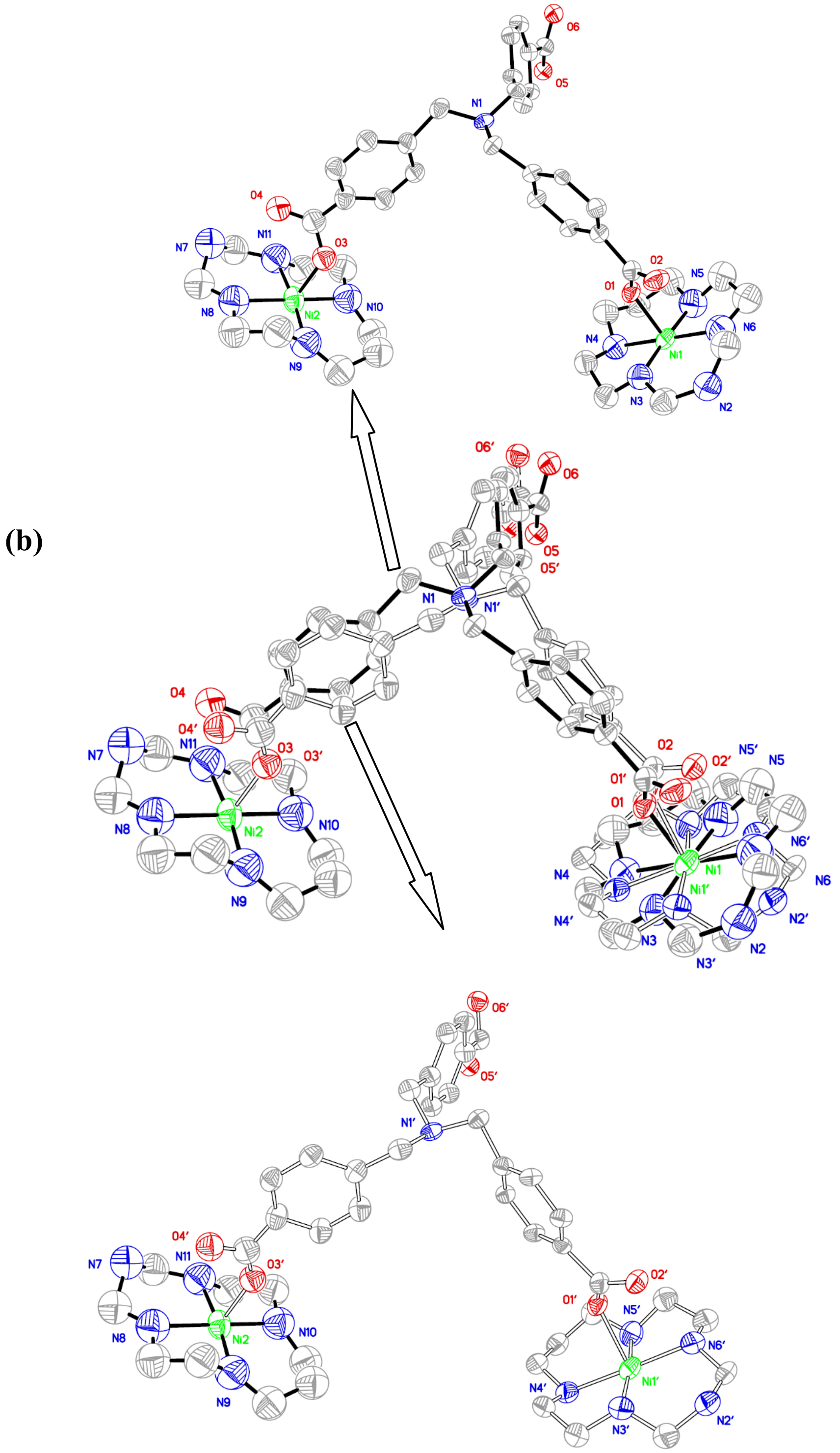


**Fig. S1.** (a) The structure of [NiL]$(ClO_4)_2$. (b) An illustration of the asymmetric unit of **1** with thermal ellipsoids and orientational disorder over two sets of positions.

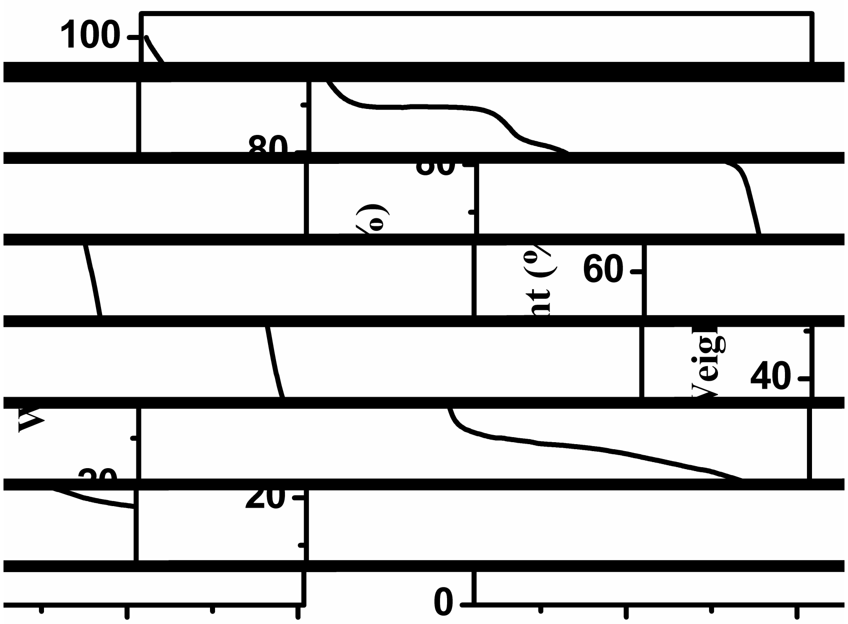
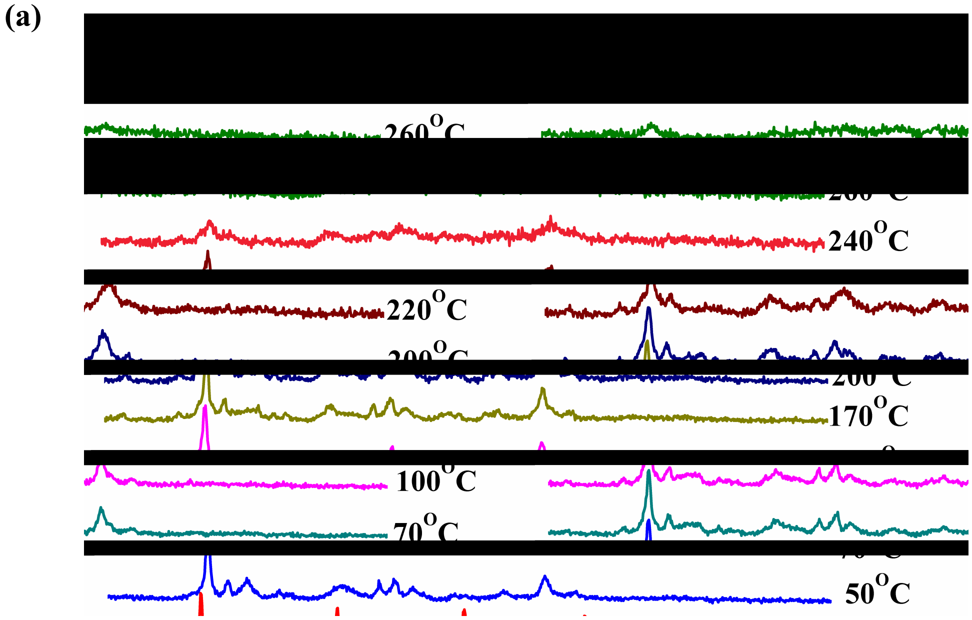


**Fig. S2.** The TG curve of **1.**



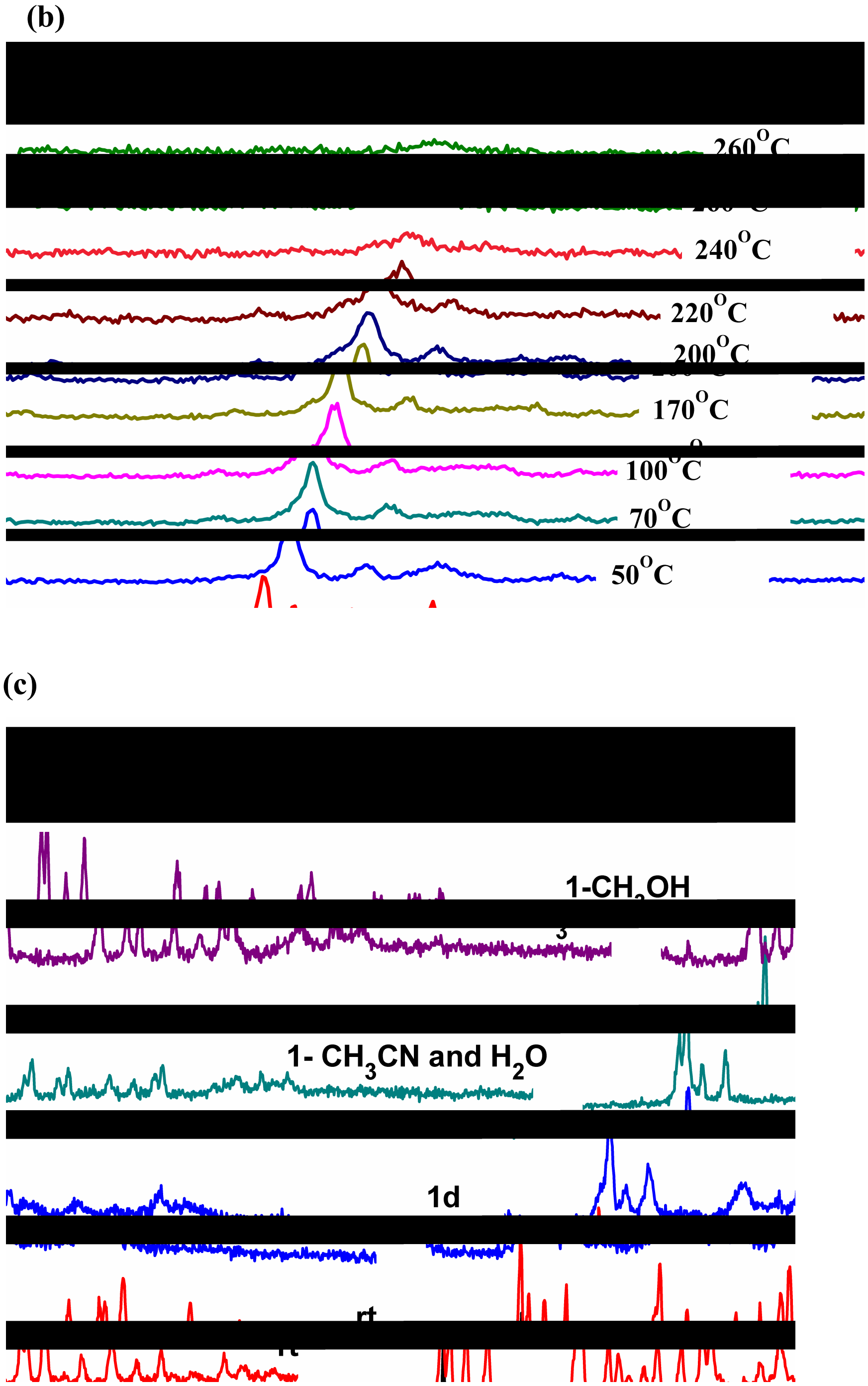


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**Fig. S3.** (a) Variable-temperature PXRD for **1**. (b) The position of the peaks at 7.6 and 7.7° for **1** moved to higher degree with increase of temperature. (c) The PXRD patterns simulated from X-ray crystal diffraction data of **1**, as synthesized **1** (rt), **1d,** resolvated by immersion of **1d** in $CH_3CN/H_2O$ mixture (8:1, v/v) and $CH_3OH$ for 2 min, demonstrating the original framework of **1** was restored.

## References

1. G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, 1996.

2. SCALE3 ABSPACK scaling algorithm. CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.38.

3. G. M. Sheldrick, SHELXS 97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, 1997.

4. P. van der Sluis and A. L. Spek, *Acta Cryst*., 1990, **A46**, 194.