Supplementary Material (ESI) for Dalton Transactions

Supporting Information

DABCO-Functionalized Metal-Organic Framework Bearing a C_{2h}-Symmetric Terphenyl Dicarboxylate Linker

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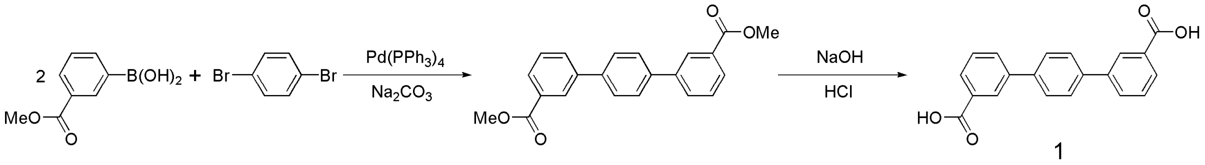
Synthesis of 3,3''-dicarboxy-1,1':4',1''-terphenyl (1)



The 4,4'-dibromobiphenyl (0.936 g, 3.0 mmol, Aldrich), 3-(methoxycarbonyl)phenylboronic acid (1.152 g, 6.4 mmol, TCI), tetrakis(triphenylphosphine)palladium(0) (0.102 g, 0.088 mmol, Strem) were dissolved in deoxygenated ethylene glycol dimethyl ether (100 mL) and 2.0 M sodium carbonate aqueous solution (60 mL) under nitrogen atmosphere. The mixture was heated at 85 °C for 48 h with stirring. After the reaction, the reaction mixture was poured into the mixture of water and chloroform. Organic phase was separated and the solvent was removed under vacuum. The crude solids were purified by silica gel column chromatography (gradient elution starting from hexane : chloroform = 4 : 1 v/v). Yield was 40%. ^{1}H NMR

(200 MHz, $CDCl_3$, *δ*): 8.34 (2 H, *t*, 1.6 Hz), 8.04 (2 H, *dt*, 7.8 Hz, 1.6 Hz), 7.85 (2 H, *dt*, 7.8 Hz, 1.6 Hz), 7.73 (4 H, *s*), 7.54 (2 H, *t*, 7.8 Hz), 3.97 (6 H, *s*). ^{13}C NMR (50 MHz, $CDCl_3$, *δ*): 167.0, 140.7, 139.4, 131.4, 130.7, 128.9, 128.5, 128.1, 127.6, 52.3 ppm. The free acid was obtained by acid hydrolysis. The purified methyl ester compound (1.00 g, 2.89 mmol) was dissolved in ethanol (40 mL) and 6.0 M sodium hydroxide solution (20 mL). The mixture stirred for 24 h at room temperature. The mixture was neutralized with 12.0 M hydrochloric acid until pH 7.0 and then the solids were filtered and washed with distilled water. The white solids were dried for 24 h at 80 °C. Hydrolysis yield was 90%. ^1H NMR (200 MHz, DMSO-*d*$_6$, *δ*): 8.25 (2 H, *t*, 1.6 Hz), 7.98 (4 H, *m*), 7.84 (4 H, *s*), 7.63 (2 H, *t*, 7.8 Hz) ppm. ^{13}C NMR (50 MHz, DMSO-*d*$_6$, *δ*): 167.3, 139.8, 138.7, 131.6, 131.1, 129.5, 128.5, 127.5, 127.2 ppm.

Synthesis of $[Zn(C_{26}H_{24}N_2O_4)]\cdot DMF\cdot H_2O$ (2)

The mixture of $Zn(NO_3)_2\cdot 6H_2O$ (30 mg, 0.1 mmol, Aldrich), the terphenyl ligand **1** (32 mg, 0.1 mmol), and 1,4-diazabicyclo[2,2,2]octane (DABCO) (6 mg, 0.05 mmol, Aldrich) were dissolved in DMF and heated at 120 °C for 4 d. Transparent colorless crystals were retrieved by filtration and washed with DMF. The crystals were dried in air (~ 31 mg). High quality plates were chosen for the X-ray crystallography from the as-prepared sample. The $CHCl_3$-exchanged sample was obtained by shaking the $CHCl_3$ suspension of the fresh as-prepared **2** for 2 d. Elemental analysis of the as-prepared sample: analytically calculated for $C_{29}H_{35}N_3O_7Zn$, C 57.76, H 5.85, N 6.97; found C 58.06, H 4.88, N 5.49 %.

X-ray Crystallography

The diffraction data for **2** were collected on a Nonius KappaCCD diffractometer using Mo Kα (λ = 0.71073 Å). The crystal was mounted on a glass fiber under epoxy. The CCD data were integrated and scaled using a Collect, and the structures were solved using SIR-92 and refined using SHELXTL V6.1. Hydrogen atoms were located in the calculated positions. The crystallographic data are listed in Table S1. The selected bond lengths and angles are listed in Table S2. During the refinement of the structure, electron density peaks were located that were believed to be highly disordered solvent molecules (possibly DMF and water). Attempts made to model the solvent molecule were not successful. The SQUEEZE option in PLATON (Spek, 2003) indicated there was a solvent cavity of volume 137 Å^3 containing approximately 57 electrons. In the final cycles of refinement, this contribution to the electron density was removed from the observed data. The density, the $F(000)$ value, the molecular weight and the formula are given without taking into account the results obtained with the SQUEEZE option PLATON (A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7). Similar treatments of disordered solvent molecules were carried out by Stähler *et al.* (*Acta Cryst.*, 2001, **C57**, 26), Cox *et al.* (*Acta Cryst.*, 2003, **E59**, o975), Mohamed *et al.* (*Acta Cryst.*, 2003, **C59**, m84) and Athimoolam *et al.* (*Acta Cryst.*, 2005, **E61**, m2014).

Physical Measurements

Ultrapure grade (99.999%) N_2, CO_2, and H_2 gases were used for the gas sorption experiments. The N_2 sorption analysis was performed on a Belsorp-miniII at 77 K (BEL Japan). The low-pressure CO_2 sorption analyses were performed on a Belsorp-miniII at 196 K, 273 K, and 298 K (BEL Japan). 2-propanol/dry ice bath was used to maintain 196 K. A moisture trap was equipped at the outlet of the CO_2 gas cylinder to avoid moisture contamination. The samples soaked in $CHCl_3$ in a screw-capped vial were shaken for two days. The $CHCl_3$-exchanged samples were dried at 393 K under high vacuum for 2 h before measurements. Low-pressure H_2 adsorption measurements were performed at 77 K on a Belsorp-miniII. The equipment was calibrated by using Cu-BTC (HKUST-1) as a reference material (S. S. -Y. Chui et al., *Science* 1999, **283**, 1148). The as-made HKUST-1 activated at 393 K under high vacuum for 2 h showed hydrogen uptake value of 2.23 wt% at 77 K and 1 bar. This value agrees well with the reported value (2.27 wt%) under the same condition (B. Xiao et al., *J. Am. Chem. Soc.*, 2007, **129**, 1203). The isosteric heats of CO_2 adsorption were obtained by using the subroutine implemented in the BEL Master software of the Belsorp-miniII equipment. The subroutine uses the Clausius-Clapeyron equation to estimate the adsorption enthalpies from the adsorption data measured at 273 K and 298 K. PXRD patterns were obtained by using a Rigaku MiniFlex (30 kV, 15 mA). Thermogravimetric analysis was carried out on a TGA Q5000 (TA Instruments) under nitrogen atmosphere. Elemental analysis was performed by using an EA1112 (CE Instruments, Italy) at the Organic Chemistry Research Center, Sogang University, Seoul, Korea.

Table S1. Crystal and structure refinement data for **2**.

Identification code	k0976twin	
Empirical formula	C26 H24 N2 O4 Zn	
Formula weight	493.84	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/m	
Unit cell dimensions	a = 9.8933(12) Å	α= 90°.
	b = 18.1647(15) Å	β= 94.792(4)°.
	c = 13.4537(16) Å	γ = 90°.
Volume	2409.3(5) Å^3	
Z	4	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	1.053 mm^{-1}	
F(000)	1024	
Crystal size	0.30 x 0.10 x 0.02 mm^3	
Theta range for data collection	2.70 to 25.00°.	
Index ranges	-11<=h<=11, -20<=k<=21, -1<=l<=15	
Reflections collected	7688	
Independent reflections	2191 [R(int) = 0.086]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.012 and 0.807	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2191 / 0 / 157	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0974, wR2 = 0.2646	
R indices (all data)	R1 = 0.1203, wR2 = 0.2799	
Largest diff. peak and hole	1.365 and -0.888 e.Å^{-3}	

Table S2. Bond distances [Å] and angles [°] for **2**.

Zn(1)-O(2)#1	2.043(6)
Zn(1)-O(2)#2	2.043(6)
Zn(1)-N(1)	2.047(13)
Zn(1)-O(1)	2.048(6)
Zn(1)-O(1)#3	2.048(6)
Zn(1)-Zn(1)#2	3.002(3)
O(1)-C(1)	1.266(10)
O(2)-C(1)	1.290(10)
O(2)-Zn(1)#2	2.043(6)
N(1)-C(12)#3	1.457(13)
N(1)-C(12)	1.457(13)
N(1)-C(13)	1.52(2)
N(2)-C(11)#3	1.426(16)
N(2)-C(11)	1.426(16)
N(2)-C(14)	1.53(3)
C(1)-C(2)	1.476(11)
C(2)-C(7)	1.395(12)
C(2)-C(3)	1.401(13)
C(3)-C(4)	1.386(13)
C(4)-C(5)	1.386(13)
C(5)-C(6)	1.403(12)
C(6)-C(7)	1.409(11)
C(6)-C(8)	1.490(11)
C(8)-C(9)	1.388(18)
C(8)-C(9A)	1.39(2)
C(8)-C(10)	1.396(18)
C(8)-C(10A)	1.40(2)
C(12)-C(11)	1.586(17)
C(13)-C(14)	1.60(3)
C(10)-C(9)#4	1.37(2)
C(9)-C(10)#4	1.37(2)
C(10A)-C(9A)#4	1.35(3)
C(9A)-C(10A)#4	1.35(3)

O(2)#1-Zn(1)-O(2)#2	85.6(3)
O(2)#1-Zn(1)-N(1)	106.5(3)

O(2)#2-Zn(1)-N(1)	106.5(3)
O(2)#1-Zn(1)-O(1)	88.5(2)
O(2)#2-Zn(1)-O(1)	158.2(3)
N(1)-Zn(1)-O(1)	95.3(3)
O(2)#1-Zn(1)-O(1)#3	158.2(3)
O(2)#2-Zn(1)-O(1)#3	88.5(2)
N(1)-Zn(1)-O(1)#3	95.3(3)
O(1)-Zn(1)-O(1)#3	89.3(4)
O(2)#1-Zn(1)-Zn(1)#2	86.46(18)
O(2)#2-Zn(1)-Zn(1)#2	86.46(18)
N(1)-Zn(1)-Zn(1)#2	162.1(4)
O(1)-Zn(1)-Zn(1)#2	72.3(2)
O(1)#3-Zn(1)-Zn(1)#2	72.3(2)
C(1)-O(1)-Zn(1)	137.3(6)
C(1)-O(2)-Zn(1)#2	118.7(5)
C(12)#3-N(1)-C(12)	111.0(14)
C(12)#3-N(1)-C(13)	103.8(10)
C(12)-N(1)-C(13)	103.8(10)
C(12)#3-N(1)-Zn(1)	113.3(8)
C(12)-N(1)-Zn(1)	113.3(8)
C(13)-N(1)-Zn(1)	110.9(10)
C(11)#3-N(2)-C(11)	115.3(19)
C(11)#3-N(2)-C(14)	108.0(12)
C(11)-N(2)-C(14)	108.0(12)
O(1)-C(1)-O(2)	124.2(7)
O(1)-C(1)-C(2)	118.3(8)
O(2)-C(1)-C(2)	117.4(7)
C(7)-C(2)-C(3)	120.0(8)
C(7)-C(2)-C(1)	120.9(8)
C(3)-C(2)-C(1)	119.1(8)
C(4)-C(3)-C(2)	119.6(8)
C(3)-C(4)-C(5)	121.0(9)
C(4)-C(5)-C(6)	120.2(8)
C(5)-C(6)-C(7)	119.0(8)
C(5)-C(6)-C(8)	120.0(7)
C(7)-C(6)-C(8)	121.0(7)
C(2)-C(7)-C(6)	120.2(8)
C(9)-C(8)-C(9A)	82.5(11)

C(9)-C(8)-C(10)	116.9(11)
C(9A)-C(8)-C(10)	64.4(11)
C(9)-C(8)-C(10A)	64.6(11)
C(9A)-C(8)-C(10A)	116.3(12)
C(10)-C(8)-C(10A)	83.5(11)
C(9)-C(8)-C(6)	121.9(10)
C(9A)-C(8)-C(6)	122.7(11)
C(10)-C(8)-C(6)	121.2(9)
C(10A)-C(8)-C(6)	120.9(10)
N(1)-C(12)-C(11)	113.2(11)
N(2)-C(11)-C(12)	108.7(12)
N(1)-C(13)-C(14)	113.6(16)
N(2)-C(14)-C(13)	105.5(15)
C(9)#4-C(10)-C(8)	120.2(15)
C(10)#4-C(9)-C(8)	122.9(15)
C(9A)#4-C(10A)-C(8)	120.2(18)
C(10A)#4-C(9A)-C(8)	123.5(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1 #2 -x,-y+1,-z+1 #3 x,-y+1,z
#4 -x+1/2,-y+3/2,-z

Table S3. The topology analysis results by TOPOS (Topos 4.0 Pro).

```
##################
1:C26 H24 N2 O4 Zn
##################

Topology for Zn1
--------------------
Atom Zn1 links by bridge ligands and has
Common vertex with                                    R(A-A)         f
Zn 1    -0.6021     1.0000     1.4110    (-1 1 2)    16.315A         1
Zn 1    -0.6021     0.0000     1.4110    (-1 0 2)    16.315A         1
Zn 1    -0.3979     1.0000     1.5890    (-1 1 1)    17.294A         1
Zn 1    -0.3979     0.0000     1.5890    (-1 0 1)    17.294A         1
Zn 1     0.6021     0.0000    -0.4110    ( 0 0-1)    17.294A         1
Zn 1     0.6021     1.0000    -0.4110    ( 0 1-1)    17.294A         1
Zn 1     0.3979     0.0000    -0.5890    ( 0 0 0)    18.709A         1
Zn 1     0.3979     1.0000    -0.5890    ( 0 1 0)    18.709A         1
Common face with                                      R(A-A)
Zn 1    -0.1021     0.5000     0.4110    ( 0 0 1)     3.002A         4
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Structural group analysis
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Structural group No 1
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Structure consists of layers (2 0 1) with ZnO4N2C26H22

Coordination sequences
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Zn1:   1   2   3   4    5    6    7    8    9   10
Num     9 16 24 32   40   48   56   64   72   80
Cum   10 26 50 82 122 170 226 290 362 442
Rad 15.8(4.9) 29.3(6.9) 42.7(8.9) 56.3(11.2) 70.1(13.6) 83.8(16.0) 97.7(18.5) 111.5(20.9) 125.4(23.4)
139.2(25.9)
Cmp Zn9 Zn16 Zn24 Zn32 Zn40 Zn48 Zn56 Zn64 Zn72 Zn80
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TD10=442

Vertex symbols for selected sublattice
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Zn1 Point (Schlafli) symbol:{3^12;4^24}
Extended point symbol:
[3.3.3.3.3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3)]
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Point (Schlafli) symbol for net: {3^12;4^24}
9-c net; uninodal net

New topology, please, contact the authors (66909 types in 9 databases).
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Figure S1. The detailed structure of the 1D channels where DMF solvates and hydrogen atoms are omitted for clarity: a packing diagram along the *a*-axis (a), *c*-axis (b) and *b*-axis (c) represented in a CPK model. Different color codes indicate different layers.

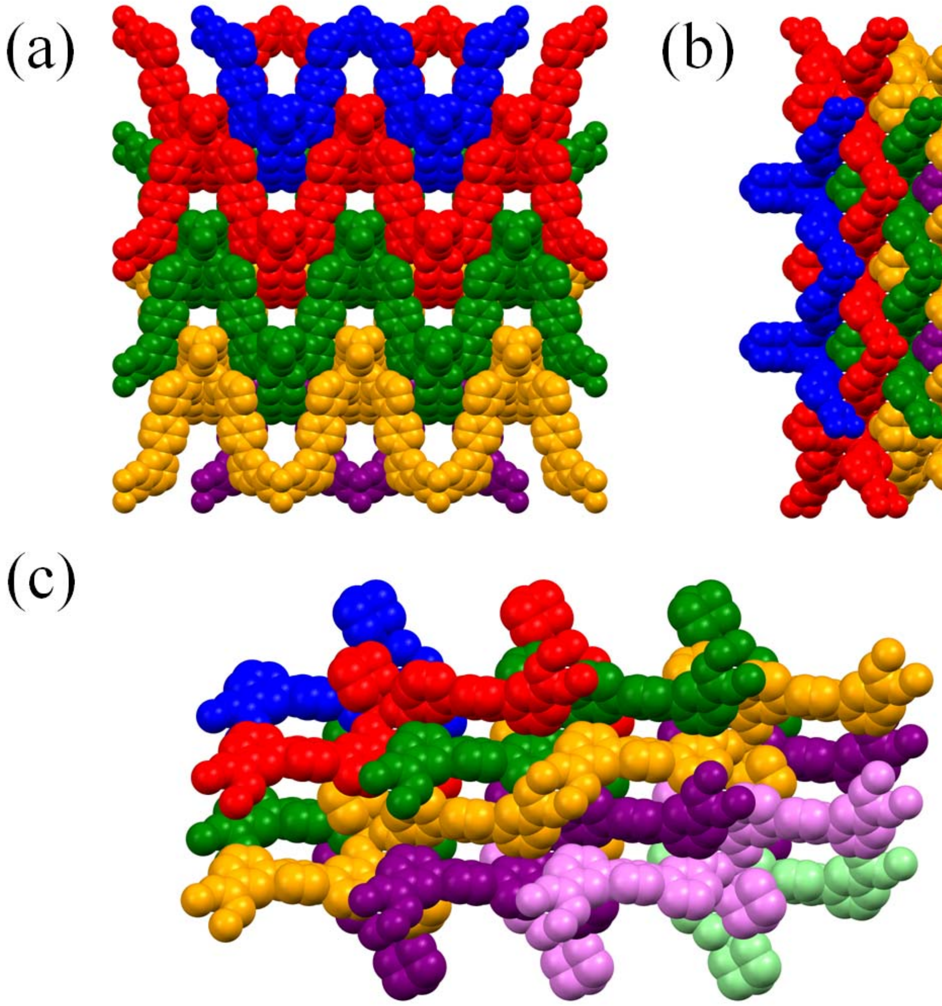

Figure S2. TG profiles of the free ligand **1** (dotted red line) and as-prepared MOF **2** (solid blue line) under nitrogen atmosphere.

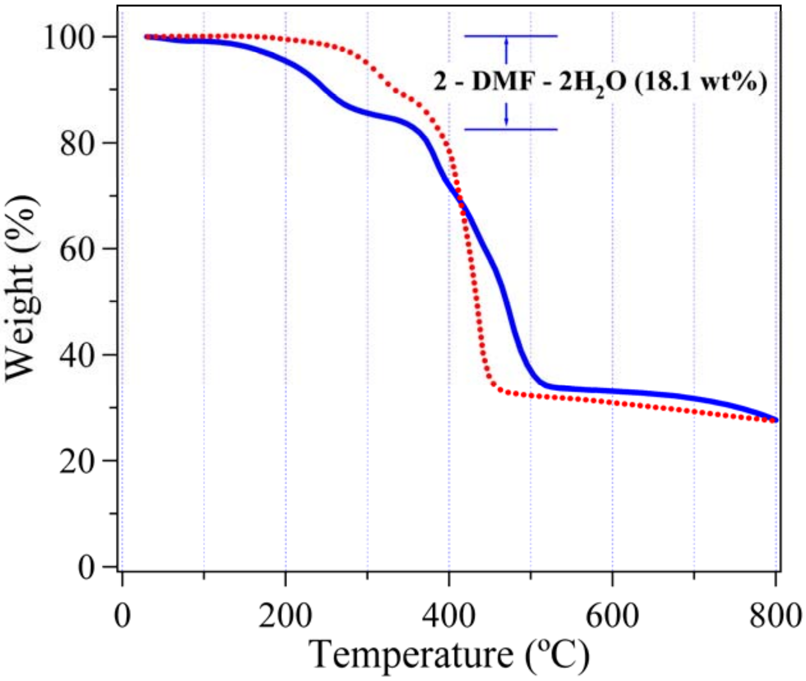

Figure S3. The dimensions of the 1D channel based on the atom-to-atom distances of the closest contacts.

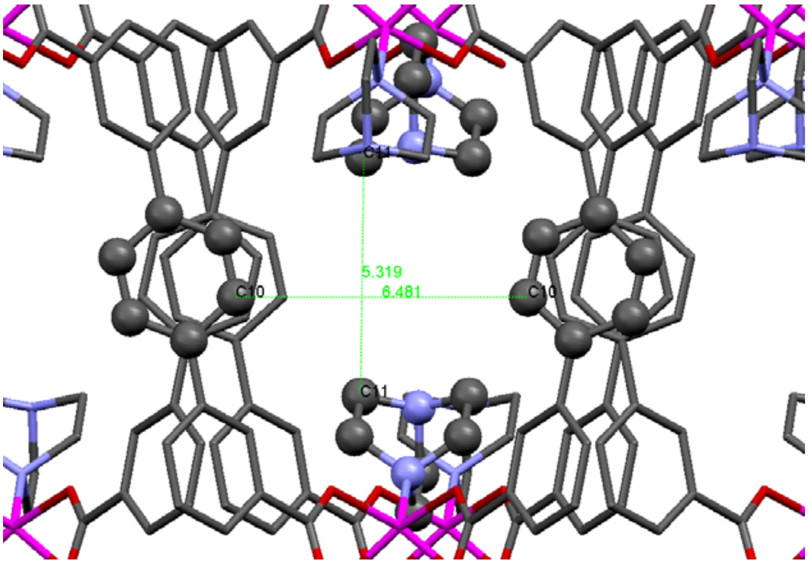

Figure S4. PXRD patterns of MOF **2** under various conditions along with a simulated pattern from the data obtained by X-ray crystallography.

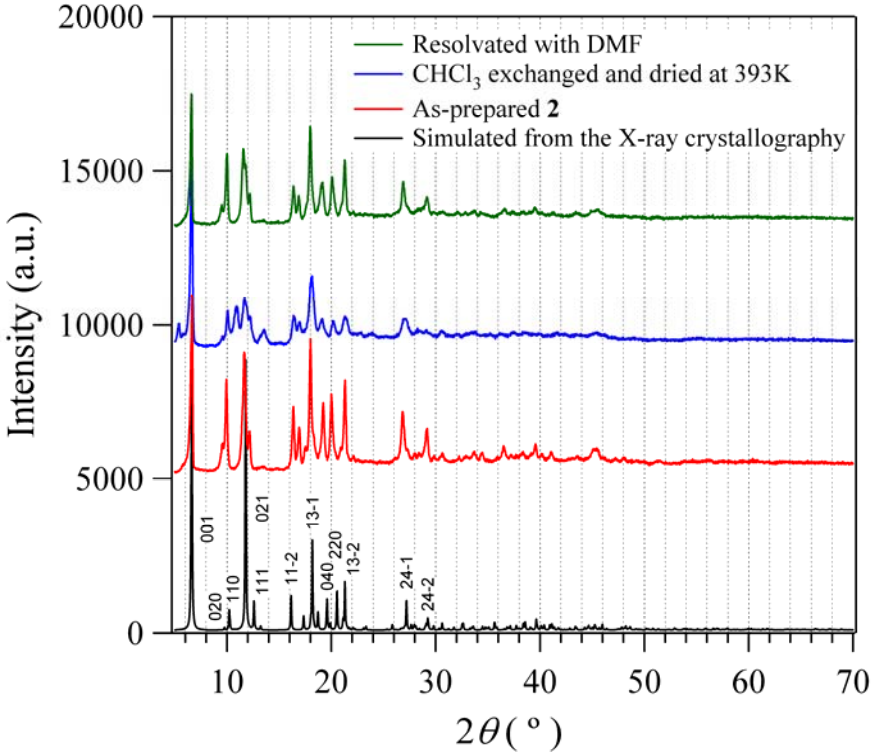

Figure S5. Digital photo images of the crystalline as-made MOF **2** (a) and after the activation at 120 °C for 2 h (b). Apparently, the crystals were found to be intact after the activation.