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Electronic Supplementary Information

Solvent-induced single-crystal to single-crystal transformation of a Zn_4O-containing doubly interpenetrated metal-organic framework with a *pcu* net

Jae Hwa Lee,[a] Tae Kyung Kim,[a] Myunghyun Paik Suh,*[b] and Hoi Ri Moon*[a]

[a] Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea. E-mail: hoirimoon@unist.ac.kr

[b] Department of Chemistry, Hanyang University, Seoul 133-791, Republic of Korea. E-mail: mpsuh@snu.ac.kr

Experimental section

All chemicals and solvents used in the syntheses were of reagent grade and they were used without further purification. H_2CPMA (bis(4-carboxyphenyl)-*N*-methylamine) was prepared by the methods reported in the previous study.[S1] Elemental analyses were performed at the UNIST Central Research Facilities Center (UCRF) in Ulsan National Institute of Science and Technology (UNIST). IR spectra were recorded with a ThermoFisher Scientific Nicolet 6700 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) were performed under N_2(g) atmosphere at a scan rate of 5 °C min^{-1} using Q50 from TA instruments. X-ray powder diffraction data were recorded on a Bruker D2 phaser diffractometer at 30 kV and 10 mA for Cu Kα (λ = 1.541 Å), with a step size of 0.02° in 2θ.

Synthesis of [$Zn_4O(CPMA)_3$]·6DMF (1)

H_2CPMA (0.040 g, 1.5 × 10^{-4} mol) was dissolved in DMF (2 mL) and added to the DMF solution (3 mL) of $Zn(NO_3)_2$•$6H_2O$ (0.051 g, 1.7 × 10^{-4} mol). The mixture was placed in a Teflon vessel within the autoclave and heated at 110 ºC for 24 h. The solution was cooled to room temperature, which resulted in deep orange block-like crystals. The crystals were filtered and washed briefly with DMF. Yield: 0.039 g (51%). FT-IR for **1** (KBr pellet): ν_{OH}, 3406; $\nu_{CH(aromatic)}$, 3066; $\nu_{CH3(aliphatic)}$, 2930; $\nu_{C=O(DMF)}$, 1664; $\nu_{O\text{-}C=O(carboxylate)}$, 1594; $\nu_{C=C(aromatic)}$, 1553 cm^{-1}. UV/Vis (diffuse reflectance, λ_{max}) = 237, 321, 375(sh), 428(sh) nm. Anal. Calcd for $Zn_4C_{63}H_{75}O_{19}N_9$: C, 49.66; H, 4.96; N, 8.27. Found: C, 47.71; H, 4.75; N, 7.84. Data indicates that some DMF guest molecules are readily released as soon as exposure to air.

Guest-exchange Studies

Three different organic solvents, benzene, *n*-hexane, and methanol, were selected for the guest exchange of DMF molecules in **1**. Crystals of **1** (ca. 120 mg) were immersed in a neat solvent (10 mL) at room temperature for 12 h. The solvent was discarded and the crystals were reimmersed in fresh solvent (10 mL) for another 60 h to exchange all guest DMF molecules. Guest-exchanged single crystalline compounds, namely, [$Zn_4O(CPMA)_3$]·3.5benzene (**1**$_{\textbf{benzene}}$), [$Zn_4O(CPMA)_3$]·3(*n*-hexane) (**1**$_{\textbf{hexane}}$), and [$Zn_4O(CPMA)_3$]·9MeOH·$4H_2O$ (**1**$_{\textbf{MeOH}}$), were obtained. Anal. Calcd for $Zn_4C_{66}H_{54}N_3O_{13}$ (**1**$_{\textbf{benzene}}$): C, 58.35; H, 4.01; N, 3.09. Found: C, 59.79; H, 4.31; N, 3.24. FT-IR (KBr pellet): $\nu_{C=C(aromatic)}$, 3090(m); $\nu_{O\text{-}C=O}$, 1594(s), 1541(s) cm^{-1}. Anal. Calcd for $Zn_4C_{63}H_{75}N_3O_{13}$ (**1**$_{\textbf{hexane}}$): C, 56.31; H, 5.63; N, 3.13. Found: C, 57.59; H, 6.10; N, 3.51. FT-IR (KBr pellet): $\nu_{CH3(aliphatic)}$, 2924(m); $\nu_{O\text{-}C=O}$, 1594(s), 1553(s) cm^{-1}. Anal. Calcd for $Zn_4C_{54}H_{77}N_3O_{26}$ (**1**$_{\textbf{MeOH}}$): C, 44.86; H, 5.37; N, 2.91. Found: C, 44.18; H, 5.37; N, 2.89. FT-IR (KBr pellet): ν_{OH}, 3351(m, br); $\nu_{O\text{-}C=O}$, 1595(s), 1538(s); cm^{-1}. In order to exclude the possibility of dissociation and renucleation in the new solvent system, following experiments were also performed. Crystal **1** was sealed in a glass capillary together with DMF. After the cell parameters of **1** were determined, the crystal was removed from the capillary. Capillaries with a size of 0.5 mm were each filled with different organic solvent, creating an empty space of 1 cm length from the bottom. Crystal **1** was dropped in the solvent layer and a photograph of the crystal was taken immediately. During the immersion of the crystal, photographs were taken to see if the size, morphology, transparency, and position of the crystal were altered. Since no change was observed, the possibility of the dissolution of **1** in the solvent followed by crystallization or renucleation at the surface as well as the growth of a new phase was excluded. The crystal was pushed from the solvent layer to the empty space by using a very thin glass fiber, and most of the solvent was removed, remaining small amount of the solvent in the capillary. The capillary was cut into an appropriate size, sealed, and mounted on Enraf Nonius Kappa CCD X-ray diffractometer to check the cell parameters for the guest exchanged crystal.

Monitoring of the guest exchange process

To trace the degree of exchange of DMF guest molecules with benzene, the sample **1** immersed in benzene was occasionally taken and digested in the D_2O with DCl for FT-NMR measurement. The integral ratios of NMR peaks corresponded to the methyl groups of DMF guest molecules and CPMA ligands in the MOF at each time were calculated to show the exchange percentage (Fig. S7).

Single-crystal X-ray crystallography

Single-crystals of **1**, $\mathbf{1_{benzene}}$, $\mathbf{1_{hexane}}$, and $\mathbf{1_{MeOH}}$ were coated with paratone-*N* oil, and the diffraction data were measured at 100 K with synchrotron radiation (λ = 0.64999 Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Republic of Korea. The ADSC Q210 ADX program[S2] was used for data collection, and HKL3000sm (Ver. 703r)[S3] was used for cell refinement, reduction, and absorption correction. The crystal structures were solved by direct methods and refined by full-matrix least-squares calculations with the SHELX-97 computer program.[S4] The positions of all non−hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically using a riding model. In **1**, $\mathbf{1_{benzene}}$, and $\mathbf{1_{MeOH}}$, the final refinement was performed with modification of the structure factors for contribution of the disordered solvent electron densities using the SQUEEZE option of the PLATON program.[S5] For **1**, no solvent molecules were refined in Zn_8 formula unit, and the electron densities of eight disordered DMF molecules were removed by SQUEEZE process. For $\mathbf{1_{benzene}}$, three benzene molecules were refined in Zn_{16} formula unit, and the electron densities of twenty eight disordered benzene molecules were removed by SQUEEZE process. For $\mathbf{1_{hexane}}$, three hexane molecules were refined in Zn_4 formula unit. For $\mathbf{1_{MeOH}}$, six methanol molecules and one water molecule was refined in Zn_4 formula unit, and the electron densities of three methanol and three water molecules were removed by SQUEEZE process. The crystallographic data of **1**, $\mathbf{1_{benzene}}$, $\mathbf{1_{hexane}}$ and $\mathbf{1_{MeOH}}$ are summarized in Table S1-S4. Further crystallographic details for the structure reported in this paper can be obtained from the Cambridge Crystallographic Data Center, on quoting the depository numbers CCDC 1403842-1403845.

References

S1. T. K. Kim, J. H. Lee, D. Moon, H. R. Moon, *Inorg. Chem.* 2013, **52**, 589.

S2. A. J. Arvai, C. Nielsen, *ADSC Quantum-210 ADX Program*, Area Detector System Corporation; Poway, CA, USA, **1983**.

S3. Z. Otwinowski, W. Minor, Methods in Enzymology, Part A. In *Macromolecular Crystallography*; Carter Jr., C. W., Sweet, R. M., Eds.;, Academic Press: New York, **1997**; Vol. 276, pp 307-326.

S4. G. M. Sheldrick, SHELXTL-PLUS, Crystal Structure Analysis Package; Bruker Analytical X-Ray; Madison, WI, USA, 1997.

S5. *PLATON* program: A. L. Spek, *Acta Crystallogr.*, 2015, **C71**, 9.

Table S1. Crystallographic data for **1**. [squeezed data]

Empirical formula	$Zn_8C_{114}H_{122}N_{14}O_{34}$
Formula weight	2755.22
Temperature	100(2) K
Wavelength	0.70000 Å
Crystal system	Trigonal
Space group	*R*32
Unit cell dimensions	*a* = 18.985(3) Å
	b = 18.985(3) Å
	c = 68.340(14) Å
	α = 90°
	β = 90°
	γ = 120°
Volume	21331(6) $Å^3$
Z	6
Density (calculated)	1.287 g cm^{-3}
Absorption coefficient (μ)	1.339 mm^{-1}
F(000)	8496
θ range for data collection	1.91 to 29.00°.
Index ranges	$-26 \le h \le 25$, $-25 \le k \le 25$, $-94 \le l \le 94$
Reflections collected	65641
Independent reflections	12870 [*R*(int) = 0.0417]
Completeness to θ = 28.00°	98.4%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12870 / 12 / 346
Goodness-of-fit on F^2	1.003
$R_1{}^a$, $wR_2{}^b$ [I>2$\sigma(I)$]	0.0551, 0.1717
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0757, 0.1835
Largest diff. peak and hole	0.548 and -0.596 e.$Å^{-3}$
Flack parameter	0.061(15)

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o{}^2) + (0.1219P)^2 + (0.00)P]$, $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table S2. Crystallographic data for $\mathbf{1}_{\mathbf{benzene}}$. [squeezed data]

Empirical formula	$Zn_{16}C_{336}H_{318}N_{12}O_{52}$
Formula weight	6762.24
Temperature	100(2) K
Wavelength	0.70001 Å
Crystal system	Trigonal
Space group	$R32$
Unit cell dimensions	a = 19.168(3) Å
	b = 19.168(3) Å
	c = 67.695(13) Å
	α = 90°
	β = 90°
	γ = 120°
Volume	21540(6) $Å^3$
Z	3
Density (calculated)	1.564 g cm^{-3}
Absorption coefficient (μ)	1.337 mm^{-1}
F(000)	10482
θ range for data collection	1.24 to 25.00°.
Index ranges	$-23 \leq h \leq 23$, $-23 \leq k \leq 23$, $-81 \leq l \leq 81$
Reflections collected	48637
Independent reflections	8835 [R(int) = 0.0374]
Completeness to θ = 25.00°	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8835 / 30 / 385
Goodness-of-fit on F^2	1.056
$R_1{}^a$, $wR_2{}^b$ [I>2σ(I)]	0.0563, 0.1711
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0685, 0.1783
Largest diff. peak and hole	0.429 and -0.498 e.$Å^{-3}$
Flack parameter	0.23(2)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o{}^2) + (0.1194P)^2 + (0.00)P]$, $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table S3. Crystallographic data for $\mathbf{1}_{\mathbf{hexane}}$.

Empirical formula	$Zn_4C_{63}H_{75}N_3O_{13}$
Formula weight	1343.74
Temperature	100(2) K
Wavelength	0.67999 Å
Crystal system	Trigonal
Space group	*R-3c*
Unit cell dimensions	a = 18.653(3) Å
	b = 18.653(3) Å
	c = 65.066(13) Å
	α = 90°
	β = 90°
	γ = 120°
Volume	19605(6) $Å^3$
Z	12
Density (calculated)	1.366 g cm^{-3}
Absorption coefficient (μ)	1.340 mm^{-1}
F(000)	8376
θ range for data collection	2.27 to 31.50°.
Index ranges	$-28 \leq h \leq 28$, $-28 \leq k \leq 28$, $-94 \leq l \leq 94$
Reflections collected	77769
Independent reflections	8067 [R(int) = 0.0367]
Completeness to θ = 26.00°	97.3%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8067 / 34 / 321
Goodness-of-fit on F^2	0.998
$R_1{}^a$, $wR_2{}^b$ [I>2σ(I)]	0.0575, 0.1516
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0819, 0.1753
Largest diff. peak and hole	1.345 and -0.897 e.$Å^{-3}$

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$ where $w = 1/[\sigma^2(F_o^2) + (0.1335P)^2 + (0.00)P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S4. Crystallographic data for $\mathbf{1}_{\mathbf{MeOH}}$. [squeezed data]

Empirical formula	$Zn_4C_{54}H_{77}N_3O_{26}$
Formula weight	1445.67
Temperature	100(2) K
Wavelength	0.64999 Å
Crystal system	Trigonal
Space group	*R-3c*
Unit cell dimensions	a = 18.118(3) Å
	b = 18.118(3) Å
	c = 67.542(14) Å
	α = 90°
	β = 90°
	γ = 120°
Volume	19202(5) $Å^3$
Z	12
Density (calculated)	1.500 g cm^{-3}
Absorption coefficient (μ)	1.226 mm^{-1}
F(000)	9000
θ range for data collection	2.22 to 25.50°.
Index ranges	$-24 \le h \le 23$, $-23 \le k \le 23$, $-88 \le l \le 88$
Reflections collected	53363
Independent reflections	5205 [R(int) = 0.1015]
Completeness to θ = 22.00°	99.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5205 / 13 / 237
Goodness-of-fit on F^2	1.173
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.1078, 0.3161
$R_1{}^a$, $wR_2{}^b$ (all data)	0.1447, 0.3361
Largest diff. peak and hole	1.091 and -0.865 e.$Å^{-3}$

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o{}^2) + (0.2000P)^2 + (0.00)P]$, $P = (F_o{}^2 + 2F_c{}^2)/3$.

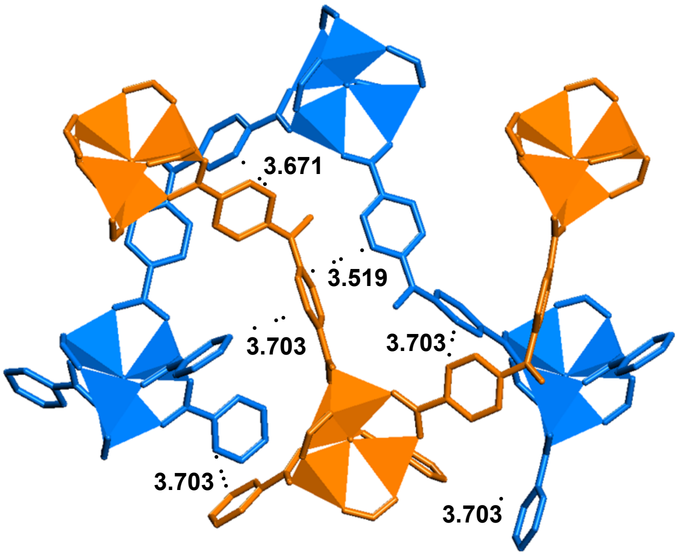

Fig. S1 The interpenetrated structure of two **pcu** nets in **1** which interact each other via π- π interactions.

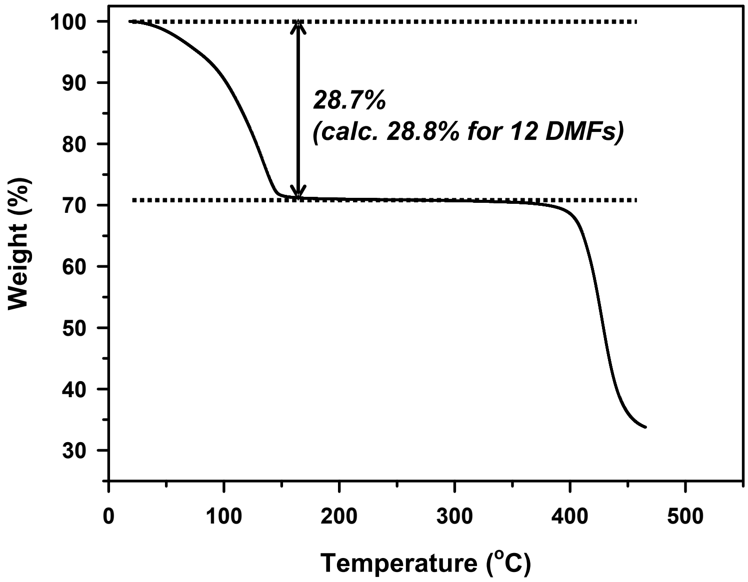

Fig. S2 TGA trace of $[Zn_4O(CPMA)_3]_2$•12DMF (**1**). The result indicates 28.7% weight loss under 150 °C for twelve uncoordinating DMF guest molecules (calc. 28.8%).

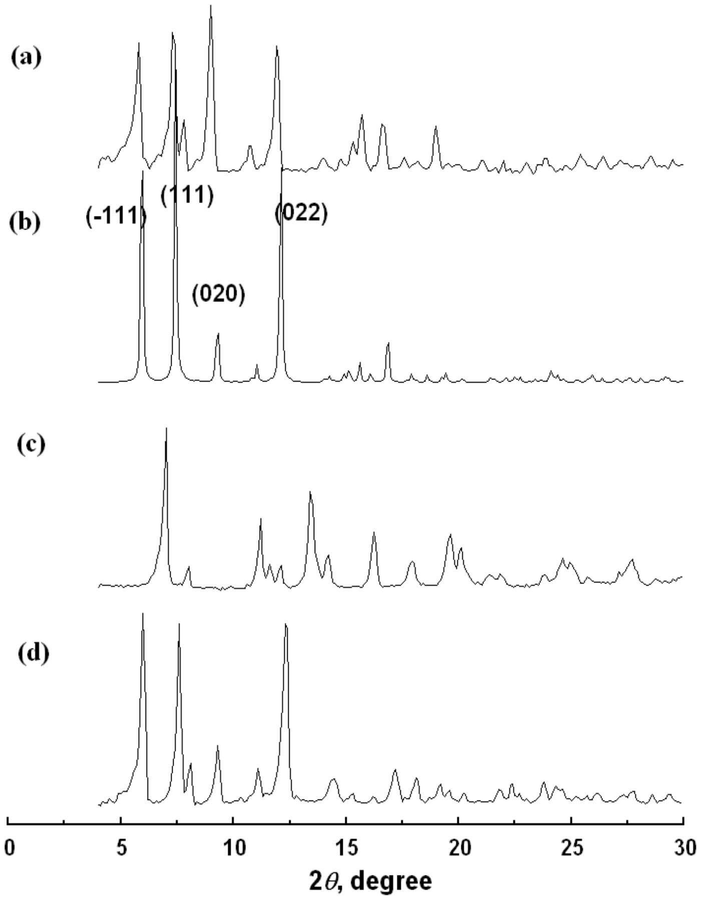

Fig. S3 The XRPD patterns for (a) **1** as-synthesized, (b) simulated pattern from the single-crystal X-ray data of **1**, (c) dried **1** that is prepared by heating **1** at 220 °C under vacuum for 24 h, and (d) solid isolated after exposure of dried **1** to DMF vapor for 3 days.

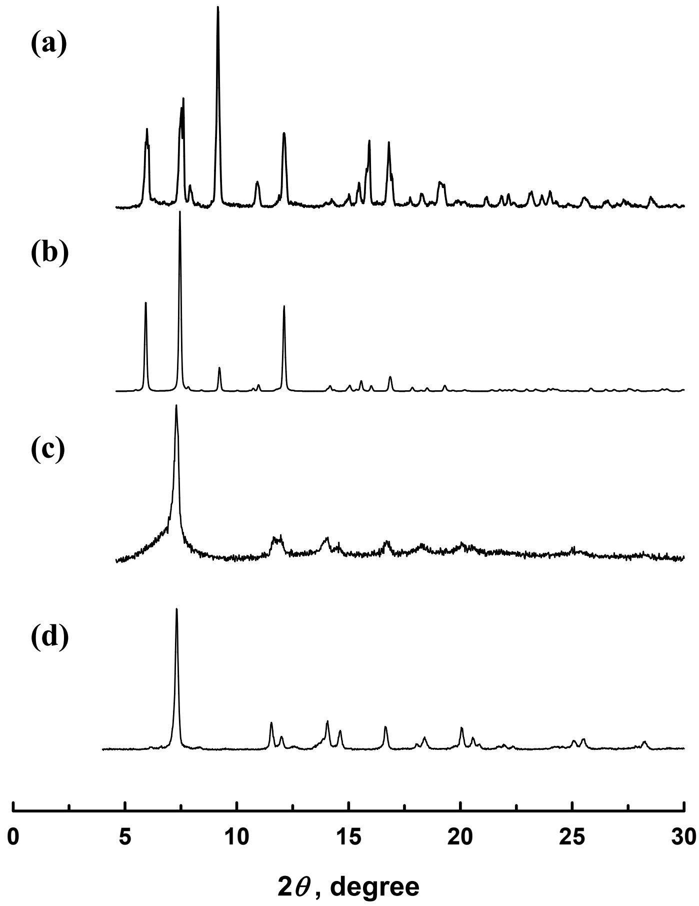

Fig. S4 The XRPD patterns for (a) $\mathbf{1}_{\mathbf{benzene}}$ as-synthesized, (b) simulated pattern from the single-crystal X-ray data of $\mathbf{1}_{\mathbf{benzene}}$, (c) dried $\mathbf{1}_{\mathbf{benzene}}$ that is prepared by heating $\mathbf{1}_{\mathbf{benzene}}$ at 200 ^{o}C under vacuum for 24 h, and (d) solid isolated after immersion of $\mathbf{1}_{\mathbf{benzene}}$ to benzene solvent for 3 d at room temperature.

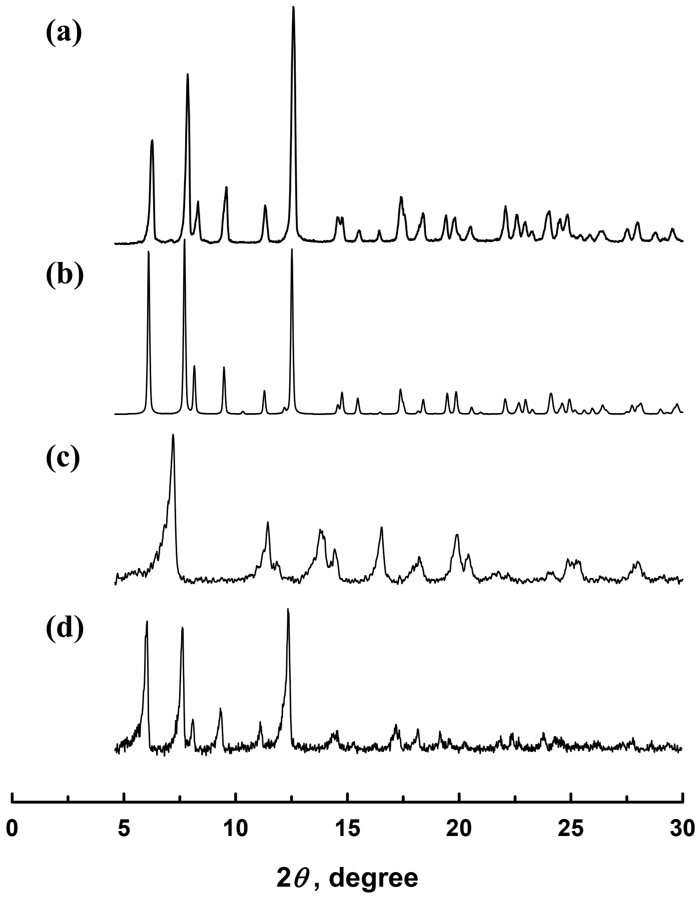

Fig. S5 The XRPD patterns for (a) $\mathbf{1}_{\mathbf{hexane}}$ as-synthesized, (b) simulated pattern from the single-crystal X-ray data of $\mathbf{1}_{\mathbf{hexane}}$, (c) dried $\mathbf{1}_{\mathbf{hexane}}$ that is prepared by heating $\mathbf{1}_{\mathbf{hexane}}$ at 200 °C under vacuum for 12 h, and (d) solid isolated after exposure of dried $\mathbf{1}_{\mathbf{hexane}}$ to hexane vapor for 3 d at room temperature.

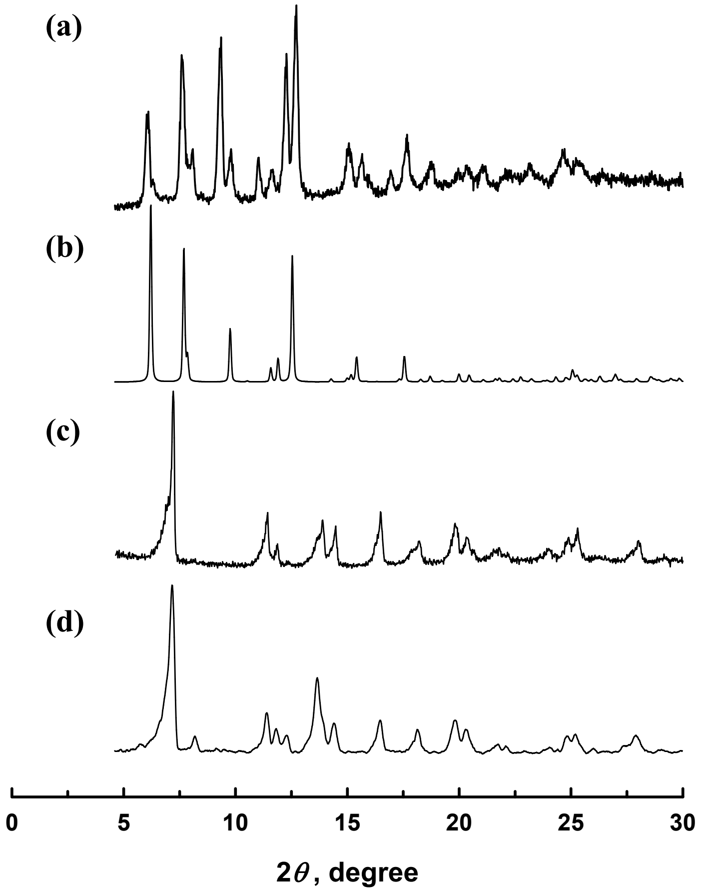

Fig. S6 The XRPD patterns for (a) $\mathbf{1}_{\mathbf{MeOH}}$ as-synthesized, (b) simulated pattern from the single-crystal X-ray data of $\mathbf{1}_{\mathbf{MeOH}}$, (c) dried $\mathbf{1}_{\mathbf{MeOH}}$ that is prepared by heating $\mathbf{1}_{\mathbf{MeOH}}$ at 100 °C under vacuum for 12 h, and (d) solid isolated after exposure of dried $\mathbf{1}_{\mathbf{MeOH}}$ to methanol vapor for 3 d at room temperature.

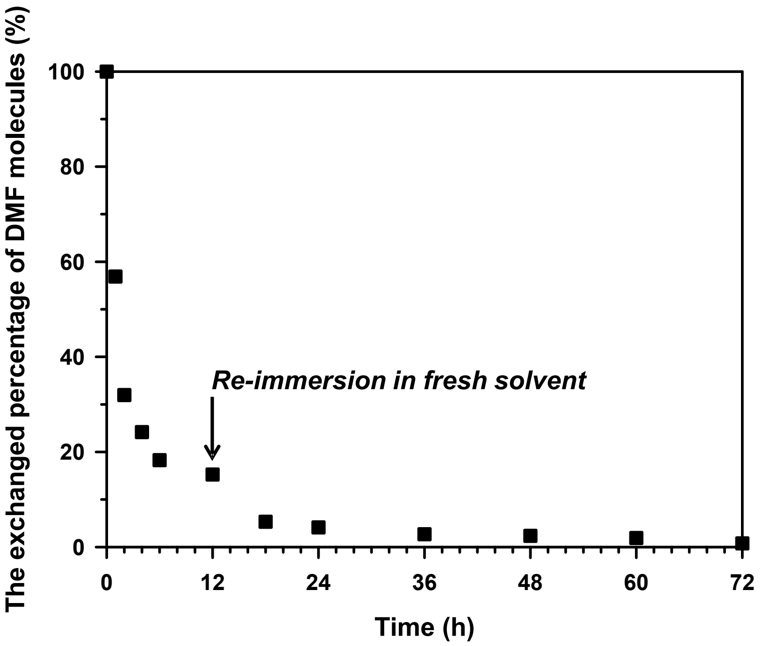

Fig. S7 The exchange degree of **1** with benzene as a function of time.

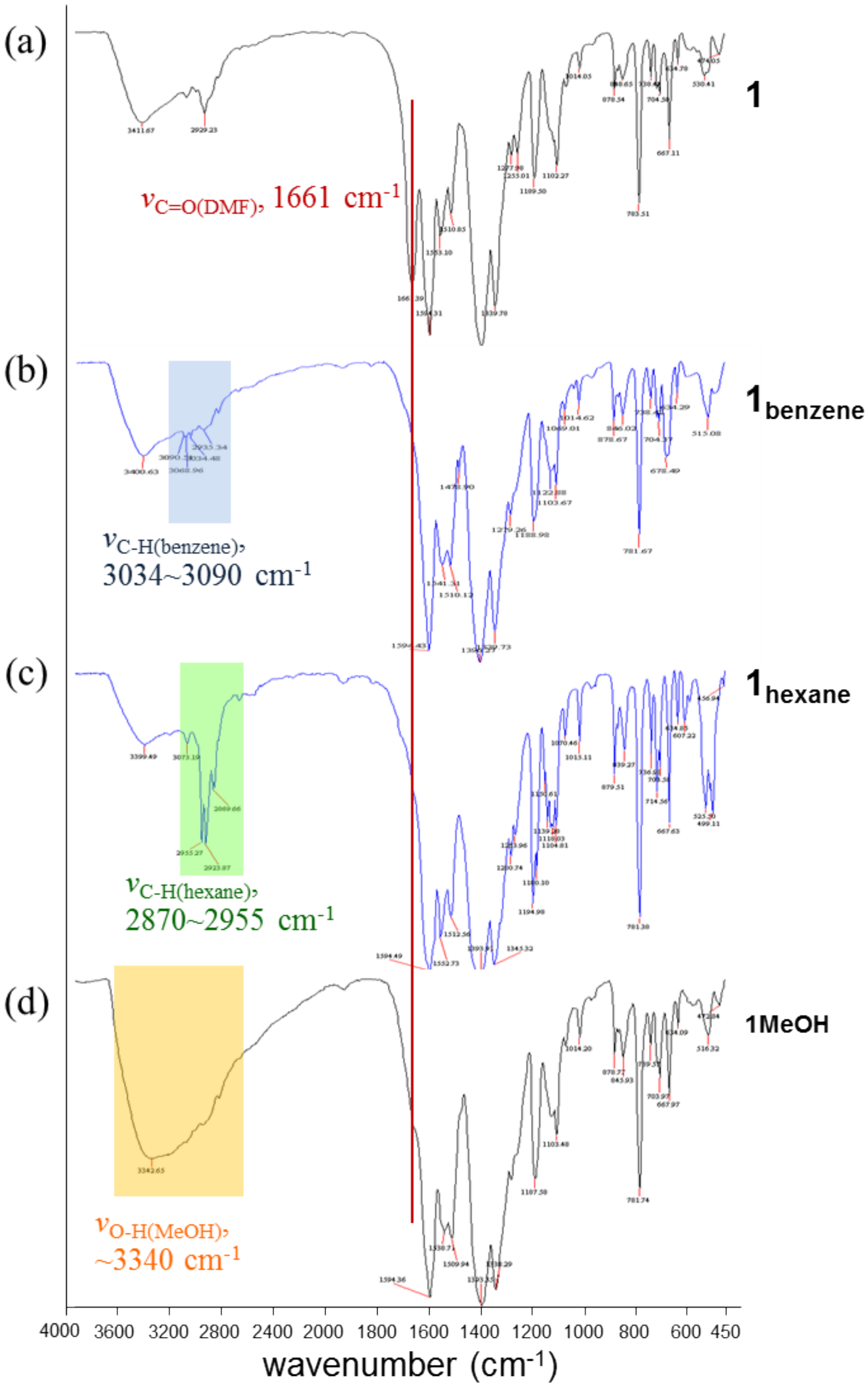

Fig. S8 FT-IR spectra of **1**, **1**$_{\mathbf{benzene}}$, **1**$_{\mathbf{hexane}}$, and **1**$_{\mathbf{MeOH}}$.

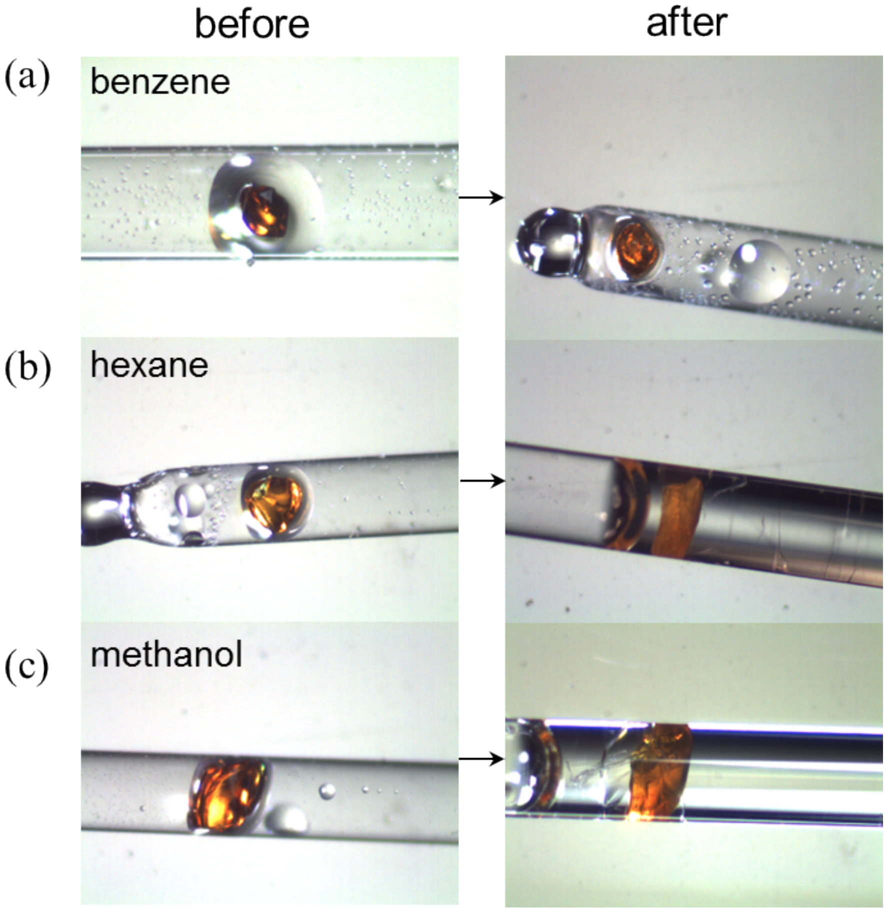

Fig. S9 Photographs of **1** crystals in guest-exchange processes. Left column: **1** as-synthesized sealed in a glass cappillary together with the mother liquor. Right column: After immsion in each organic solvent for 60 h. (a) benzene, (b) *n*-hexane, and (c) MeOH.

$\mathbf{1}_{\mathbf{MeOH}}$

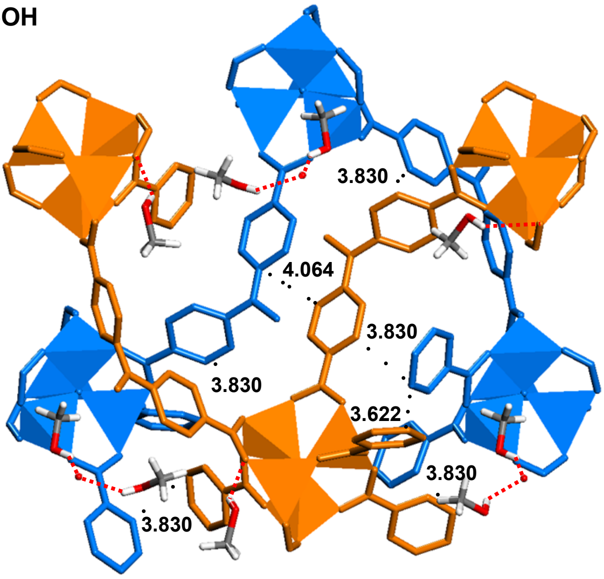

Fig. S10 π-π interactions between doubly interpenetrated **pcu** nets and hydrogen bond interactions of MeOH molecules with water molecules or carboxylate oxygen atoms in $\mathbf{1}_{\mathbf{MeOH}}$.

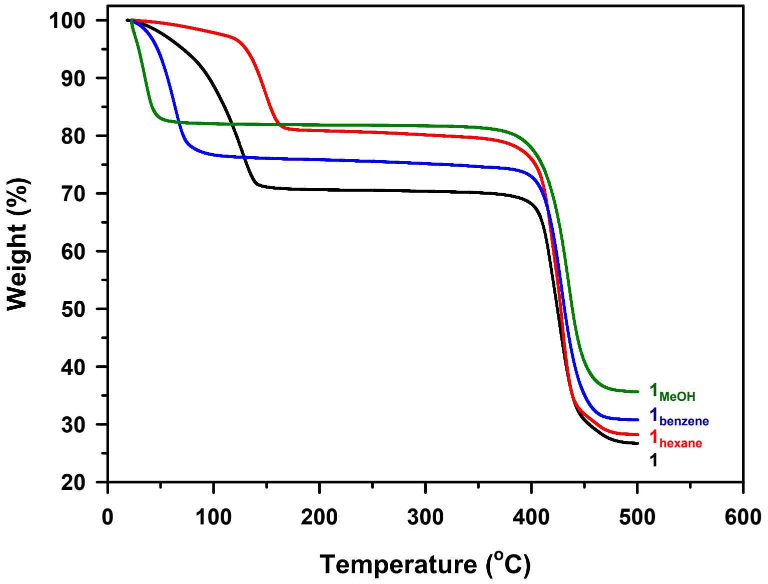

Fig. S11 TGA traces of $[Zn_4O(CPMA)_2]_2 \cdot 12DMF$ (**1**, black), $[Zn_4O(CPMA)_3]_2 \cdot 6(n\text{-hexane})$ ($\mathbf{1_{hexane}}$, red), $[Zn_4O(CPMA)_3]_2 \cdot 7\text{benzene}$($\mathbf{1_{benzene}}$, blue), and $[Zn_4O(CPMA)_3]_2 \cdot 9MeOH \cdot 5H_2O$ ($\mathbf{1_{MeOH}}$, green).

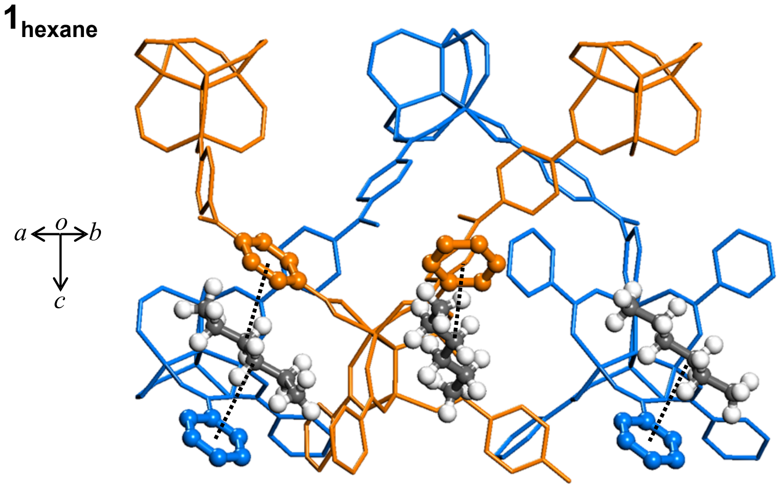

Fig. S12 CH-π interactions between hexane molecules and phenyl rings of CPMA^{2-} ligands in the framework, $\mathbf{1}_{\mathbf{hexane}}$.

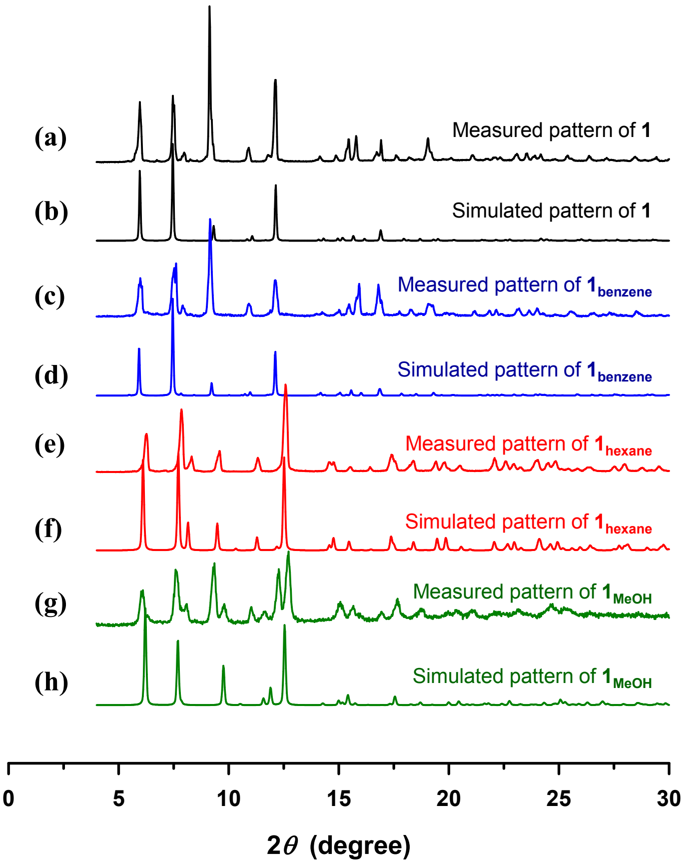

Fig. S13 The XRPD patterns for (a) **1** as-synthesized, (b) that simulated based on X-ray single-crystal data of **1**, (c) a solid isolated $\mathbf{1_{benzene}}$ after immersion of **1** in benzene for 60 h, (d) that simulated based on X-ray single-crystal data of $\mathbf{1_{benzene}}$, (e) a solid isolated $\mathbf{1_{hexane}}$ after immersion of **1** in *n*-hexane for 60 h, (f) that simulated based on X-ray single-crystal data of $\mathbf{1_{hexane}}$, (g) a solid isolated after immersion of $\mathbf{1_{MeOH}}$ in MeOH for 60 h, and (h) that simulated based on X-ray single-crystal data of $\mathbf{1_{MeOH}}$.