An unprecedented twofold interpenetrating (3,4)-connected 3-D metal–organic framework

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General Procedures. All other reagents were purchased from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed at the Elemental Analysis Laboratory of the Korean Institute of Basic Science. FT-IR spectra were recorded as KBr pellets with a Varian 1000 FT-IR spectrophotometer, using the reflectance technique (4000-400 cm^{-1}).

Preparation of *N,N′,N″*-tris(4-pyridinyl)-1,3,5-benzenetricarboxamide (L)[1]

0.9086 g (3.422 mmol) of 1,3,5-benzene tricarbonyl trichloride was dissolved in 40 mL THF, and 1.80 mL (12.9 mmol) of triethylamine was added slowly in an ice bath. Three equivalent amounts of 4-aminopyridine (1.0531 g, 11.190 mmol) were added to the solution and refluxed for two days. The white precipitate formed was filtered and washed with THF and water before being dried under vacuum. Yield 1.38 g, 92.0%. ^{1}H-NMR (300 MHz, d_6-DMSO, ppm) δ 10.95 (s, 1H), 8.76(s, 1H), 8.53 (d, 1H), 7.82 (d, 1H); ^{13}C NMR (75 MHz, d_6-DMSO, ppm) δ 165.90, 151.16, 146.33, 135.64, 131.23, 114.81. IR (KBr): ν(C=O), 1689 cm^{-1}; ν(N–H), 3170 cm^{-1}.

Preparation of complex $[Cu_3L_4(NO_3)_2(H_2O)_3](NO_3)_4$, **1**:

A total of 0.1403 g (0.3200 mmol) of ligand, 0.0465 g (0.248 mmol)of $Cu(NO_3)_2{\cdot}3H_2O$, and 15 mL of dimethylsulfoxide (DMSO) were mixed and stirred for ca. 10 min, then filtered. Blue needle-like crystals were obtained after standing undisturbed at room temperature for three days. The crystals were filtered and freeze dried for a day. Yield 0.0673 g, 31.6%. Elemental analysis: Calcd. for $[Cu_3L_4(NO_3)_2(H_2O)_3](NO_3)_4{\cdot}3(DMSO){\cdot}3(H_2O)$ ($C_{102}H_{102}N_{30}O_{39}S_3Cu_3$, fw = 2658.93): C, 46.08; H, 3.87; N, 15.80%. Found: C, 46.18; H, 3.39; N, 15.47%.

X-ray crystallographic analysis of **1**:

The crystal was coated with paratone oil. The diffraction data were measured at 100 K with synchrotron radiation (λ = 0.7000 Å) on a 4AMXW ADSC Quantum-210 detector with a silicon double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (*Ver*. 0.98.689)[2] was used for data collection, cell refinement, reduction, and absorption correction. The structure was solved by direct methods and refined by full-matrix least squares calculations with the SHELXTL-PLUS software package.[3] $[Cu_3(C_{24}H_{18}N_6O_3)_4(NO_3)_2(H_2O)_3](NO_3)_4{\cdot}8(DMSO){\cdot}8(H_2O)$, fw = 3139.65, orthorhombic, space group *Pnna*, T = 100 K, a = 56.792(11) Å, b = 14.331(3) Å, c = 32.170 (6) Å, V = 26183(9) $Å^3$, Z = 4. All non-hydrogen atoms in the framework of the structure were found from the difference Fourier map, but additional nitrate ions and some solvent molecules (DMSOs and waters) could not be confirmed easily by the difference Fourier map. We found one nitrate anion (O1N, O2N, O3N, N1N) and water molecule (O4A) ligated to the Cu(1) atom. Atoms O4N and O5N are near Cu(2), which could be part of a nitrate ion or part of a DMSO or water molecule. One uncoordinated nitrate site was partially identified (O7N, O8N, O9N). There were at least eight additional uncoordinated solvent sites, four of them were assigened as DMSO molecules and the other four were assigened as water molecules (O1W, O2W, O3W, O4W). Among the four DMSO molecules one was fully identified (S3D, O3D, C5D, C6D), the other three were partially identified, (S4D, O4D, C7D), (S21D, O21D, C31D), (S22D, O22D, C32D) among which atoms S21D and S22D of DMSO were disordered into two positions. Therefore, DMSO molecules were restrained using DFIX and DANG. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. Hydrogen atoms on the water and DMSO molecules in the compounds were not located. All non-hydrogen atoms were refined anisotropically. The final R1 was 0.2193 for observed data with $I > 2\sigma(I)$.

$[Cu_3(C_{24}H_{18}N_6O_3)_4(NO_3)_2(H_2O)_3](NO_3)_4$, fw = 2370.49. Structure refinement following modification of the data

for the non-framework region as disordered with the SQUEEZE routine in PLATON[4] led to better refinement. Only the framework corresponding to the formula, $[Cu_3(C_{24}H_{18}N_6O_3)_4(NO_3)_2(H_2O)_3]^{4+}$, was employed in the final least squares refinement, where the O4N atom coordinated to Cu(2) was tentatively assigned as a water molecule because we could not find further residual electron densities around this atom. Final R1 = 0.0787 ($I > 2\sigma(I)$), wR2 = 0.1739, GOF = 0.687, max./min. residual electron densities 0.212/–0.506 $e \cdot Å^{-3}$.

References

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(4) PLATON program: A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, 194.

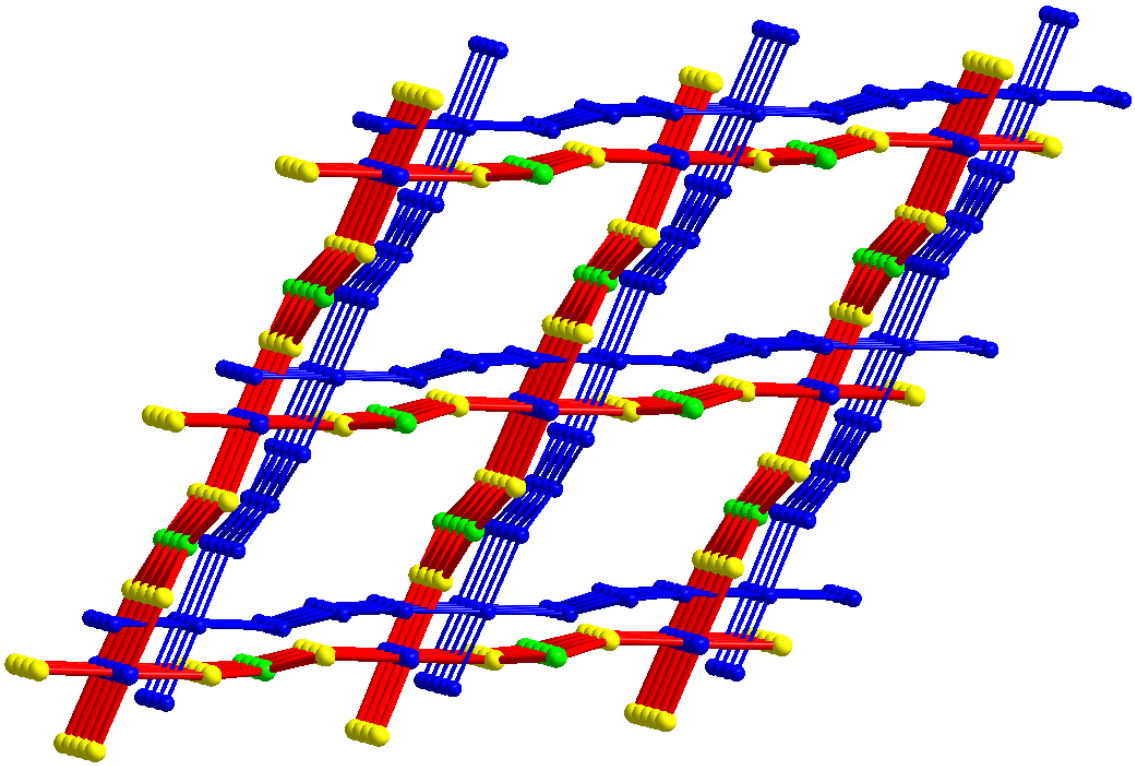

Fig. S1 Simplified view of twofold interpenetrating 3-D structure of **1**. The two nets are shown in different colors (red and blue). Three types of nodes are differentiated by color: yellow refers to three-connected nodes; blue and green refer to two topologically different four-connected nodes.

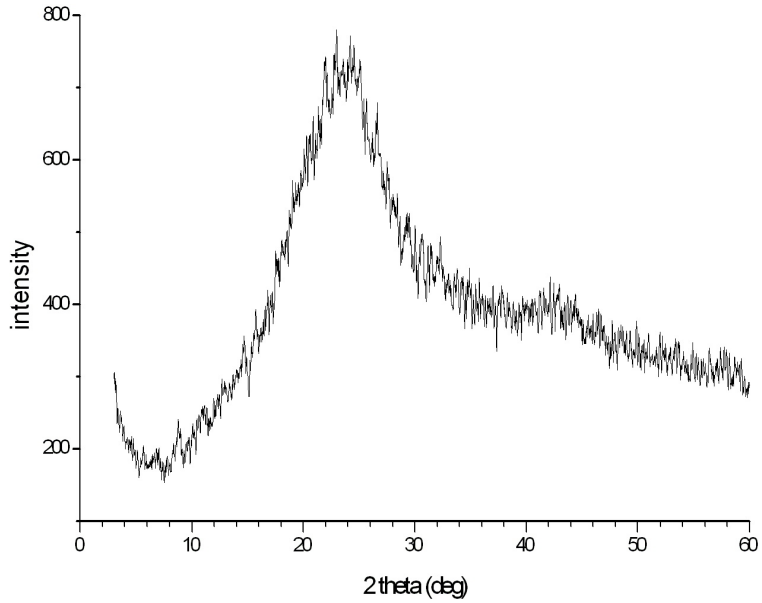

Fig. S2 XRD data of the air-dried network **1**.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$Cu_3C_{96}H_{78}N_{30}O_{33}$	
Formula weight	2370.49	
Temperature	100(2) K	
Wavelength	0.70000 Å	
Crystal system	Orthorhombic	
Space group	*Pnna*	
Unit cell dimensions	a = 56.792(11) Å	α= 90°.
	b = 14.331(3) Å	β= 90°.
	c = 32.170(6) Å	γ = 90°.
Volume	26183(9) $Å^3$	
Z	4	
Density (calculated)	0.588 Mg/m^3	
Absorption coefficient	0.279 mm^{-1}	
F(000)	4740	
Crystal size	0.40 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.23 to 20.61°.	
Index ranges	-56<=h<=56, 0<=k<=14, -32<=l<=32	
Reflections collected	49789	
Independent reflections	13803 [R(int) = 0.2134]	
Completeness to theta = 20.61°	98.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13803 / 0 / 660	
Goodness-of-fit on F^2	0.687	
Final R indices [I>2sigma(I)]	R1 = 0.0787, wR2 = 0.1739	
R indices (all data)	R1 = 0.1664, wR2 = 0.1931	
Extinction coefficient	0.00009(2)	
Largest diff. peak and hole	0.212 and -0.506 $e.Å^{-3}$	

Table S2. Bond lengths and angles for **1** (Å and °).

Cu(1)-N(1A)	2.020(8)
Cu(1)-O(4A)	2.447(8)
Cu(1)-O(1N)	2.711(9)
Cu(1)-N(3A)#1	1.971(6)
Cu(1)-N(2B)#2	2.005(7)
Cu(1)-N(3B)#3	2.028(6)
Cu(2)-N(2A)	1.876(7)
Cu(2)-N(1B)	1.967(6)
Cu(2)-O(4N)	2.545(4)
Cu(2)-N(2A)#4	1.876(7)
Cu(2)-N(1B)#4	1.967(6)
Cu(2)-O(4N) #4	2.545(4)

N(3A)#1-Cu(1)-N(2B)#2	169.5(4)
N(3A)#1-Cu(1)-N(1A)	89.5(3)
N(2B)#2-Cu(1)-N(1A)	89.7(3)
N(3A)#1-Cu(1)-N(3B)#3	89.5(2)
N(2B)#2-Cu(1)-N(3B)#3	90.2(3)
N(1A)-Cu(1)-N(3B)#3	173.3(4)
N(3A)#1-Cu(1)-O(4A)	92.4(3)
N(2B)#2-Cu(1)-O(4A)	98.1(3)
N(1A)-Cu(1)-O(4A)	94.6(3)
N(3B)#3-Cu(1)-O(4A)	92.0(3)
N(3A)#1-Cu(1)-O(1N)	88.4(3)
N(2B)#2-Cu(1)-O(1N)	81.1(3)
N(1A)-Cu(1)-O(1N)	83.4(3)
N(3B)#3-Cu(1)-O(1N)	90.0(3)
O(4A)-Cu(1)-O(1N)	177.90(14)
N(2A)#4-Cu(2)-N(2A)	86.4(4)
N(2A)#4-Cu(2)-N(1B)	172.7(3)
N(2A)-Cu(2)-N(1B)	91.4(2)
N(2A)#4-Cu(2)-N(1B)#4	91.4(2)
N(2A)-Cu(2)-N(1B)#4	172.7(3)
N(1B)-Cu(2)-N(1B)#4	91.6(3)
N(2A)#4-Cu(2)-O(4N)	87.4(2)
N(2A)-Cu(2)-O(4N)	93.8(2)

N(1B)-Cu(2)-O(4N)	85.8(2)
N(1B)#4-Cu(2)-O(4N)	93.1(2)

Symmetry transformations used to generate equivalent atoms:

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

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

Table S3. Hydrogen bonds for **1** (Å and °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4B)-H(4B)...O(2N)#5	0.88	2.22	3.066(8)	162.3

Symmetry transformations used to generate equivalent atoms:
#5 -x+1/2, -y+1, z