Supplementary Information

A Double-Walled Triangular Metal–Organic Macrocycle Based on a $[Cu_2(COO)_4]$ Square Paddle-Wheel Secondary Building Unit

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General procedures

All other reagents were purchased from commercial sources and were used without further purification. Elemental analyses were conducted at the Elemental Analysis Laboratory of the Korean Basic Science Institute, Korea. Mass spectral data were obtained on a Jeol JMS 700 high resolution mass spectrometer at the Korean Basic Science Institute (Daegu). FT–IR spectra were recorded as KBr pellets with a Varian 1000 FT–IR spectrophotometer (4000–400 cm^{-1}). Powder X-ray diffraction (PXRD) data were recorded using a Rigaku D/M 2200T automated diffractometer at room temperature with a step size of 0.02° in 2θ angle. Simulated PXRD patterns were calculated with the Material Studio program[S1] using the single-crystal data. 1,4-Bis(3-carboxylphenylethynyl)benzene (H_2L) was prepared using a reported procedure.[S2]

Crystallographic data collection and refinement of the structure

A single crystal of **1** was coated with paratone oil. The diffraction data were measured at 89 K with synchrotron radiation (λ = 0.90000 Å) on a 6B MX-I ADSC Quantum-210 detector with a silicon (111) double-crystal monochromator at the Pohang Accelerator Laboratory, Korea. The ADSC Quantum-210 ADX program (Ver. 1.92)[S3] was used for data collection, and HKL2000 (Ver. 0.98.699)[S4] was used for cell refinement, reduction, and absorption correction. The crystal structure of **1** was solved by a direct method and refined by full-matrix least-squares calculation with the SHELXTL-Plus (Ver. 5.1) software package.[S5] Three copper paddle-wheel centers with six dicarboxylate ligands, two DMF, and four water molecules as ligated solvent molecules at the axial sites of the paddle-wheel centers, and five additional DMF molecules and one water molecule as lattice solvent molecules were identified as an asymmetric unit. Because the refined geometries of the lattice DMF molecules with no restraints were poor, the geometries of the DMF molecules were restrained to that of a ligated DMF molecule using the SAME command of the SHELXTL program. All non-hydrogen atoms were refined anisotropically except for the lattice solvent molecules, which were refined isotropically; the hydrogen atoms of the ligands were assigned isotropic displacement coefficients U(H) = 1.2 U(C), and their coordinates were allowed to ride on their respective atoms. The hydrogen atoms attached to the solvent molecules were not included in the model. Although several additional lattice solvent sites were partially identified, they were not included in the model because of severe disordering and/or poor refinement behavior. The least-squares refinement of the structure with no geometry restraints has led to geometries of some aromatic rings in slight distorted hexagonal geometries. The refinement of the model converged to $R1$= 0.2078 and $wR2$ = 0.4870 for 15379 reflections of $I > 2\sigma(I)$. Structure refinement after modification of the data for the lattice solvent sites with the SQUEEZE routine of PLATON (5988 Å^3, 52.7% of the crystal volume, 597 solvent electrons [~15 DMF molecules] per unit cell)[S6] led to better refinement and data convergence. Refinement converged at a final $R1$ = 0.1160 and $wR2$ = 0.3199 for 13814 reflections with $I > 2\sigma(I)$; $R1$ = 0.1370 and $wR2$ = 0.3366 for all reflections. The largest difference peak and hole were 0.588 and –0.420 $e{\cdot}$Å^{-3}, respectively. Even though the data collection was performed using a synchrotron radiation, because of the large asymmetric unit, the large solvent content of the crystal, and poor crystal quality, the data quality itself was not good enough to show better refinement and data convergence. A summary of the crystal and intensity data is given in Table S1.

References

S1. Materials Studio program, version 4.3, Accelrys, San Diego, CA, 2008.

S2. X. Song, X. Liu, M. Oh and M. S. Lah, *Cryst. Growth & Design*, 2010, DOI: 10.1021/cg100357q.

S3. A. J. Arvai and C. Nielsen, ADSC Quantum-210 ADX Program, Area Detector System Corporation; Poway, CA, USA, 1983.

S4. Z. Otwinowski and W. Minor, *in Methods in Enzymology*, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press: New York, 1997, 276, part A, pp. 307.

S5. G. M. Sheldrick, SHELXTL−PLUS, *Crystal Structure Analysis Package*; Bruker Analytical X-ray, Madison, WI, USA, 1997.

S6. A. L. Spek, Platon program. (Ver 1.08), *Acta Crystallogr., Sect. A*, 1990, **46**, 194.

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

Empirical formula	$C_{165}H_{131}N_7O_{36}Cu_6$	
Formula weight	3169.01	
Temperature	100(2) K	
Wavelength	0.90000 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 11.499(2) Å	α = 70.32(3)°.
	b = 31.249(6) Å	β = 86.31(3)°.
	c = 33.737(7) Å	γ = 84.32(3)°.
Volume	11352(4) $Å^3$	
Z	2	
Density (calculated)	0.927 Mg/m^3	
Absorption coefficient	0.605 mm^{-1}	
F (000)	3264	
Crystal size	0.18 x 0.13 x 0.09 mm^3	
Theta range for data collection	1.62 to 26.51°	
Index ranges	-10<=h<=11, -30<=k<=30, -33<=l<=33	
Reflections collected	42032	
Independent reflections	22362 [R (int) = 0.0585]	
Completeness to theta = 26.51°	96.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9475 and 0.8988	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22362 / 0 / 1698	
Goodness-of-fit on F^2	1.194	
Final R indices [I>2sigma (I)]	R1 = 0.1160, wR2 = 0.3199	
R indices (all data)	R1 = 0.1370, wR2 = 0.3366	
Extinction coefficient	0.0094(7)	
Largest diff. peak and hole	0.588 and –0.420 e. $Å^{-3}$	

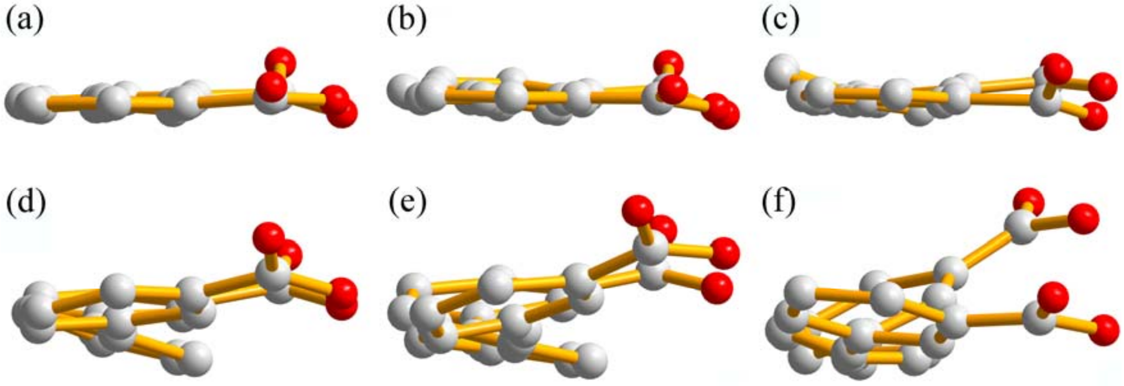

Fig. S1 Six crystallographically independent dicarboxylates in **1**, from (a) to (f). The dihedral angles between the carboxylate groups in an approximate *cis*-conformation range from 0–30°.

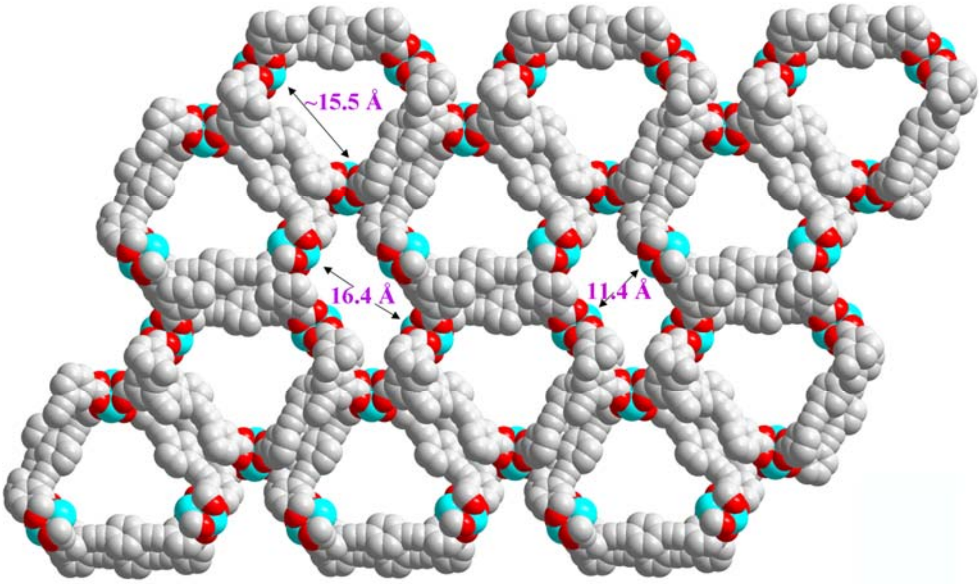

Fig. S2 A packing view of **1**, showing that the average distance between the inner metal ions of the paddle-wheel units within the MOM is ~15.5 Å, while the two distances between the metal centers across the rectangular channel are 11.4 Å and 16.4 Å. All hydrogen atoms and solvent molecules are omitted for clarity (copper, blue; carbon, gray; oxygen, red).

Fig. S3 A photograph of the bulk crystalline sample of **1**.

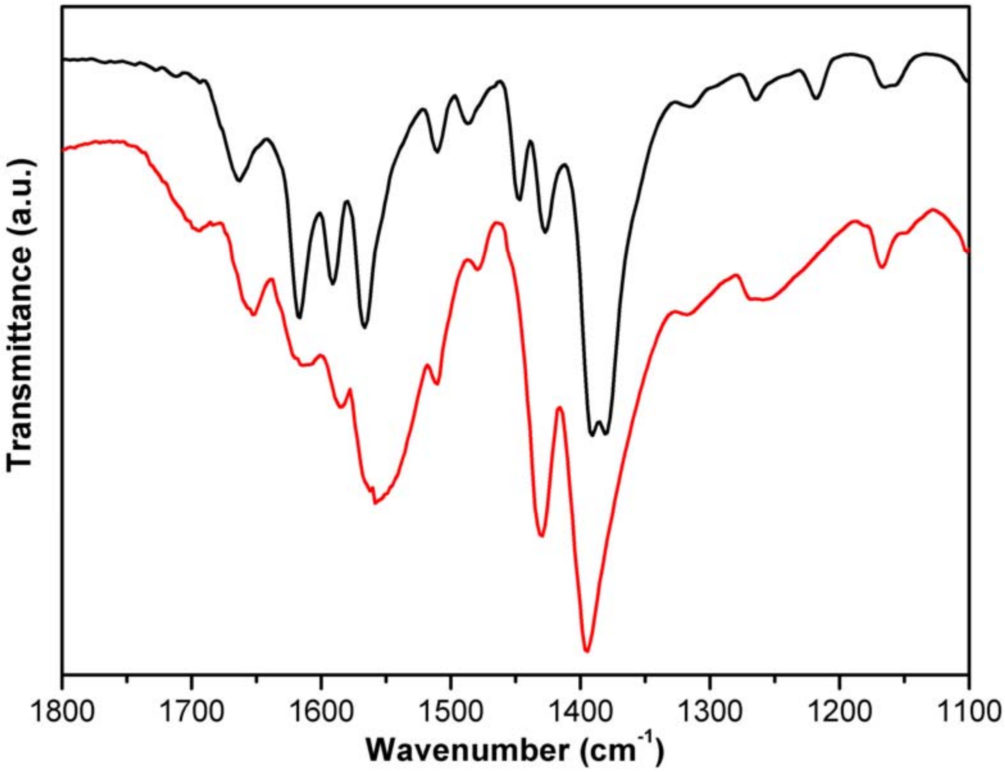

Fig. S4 IR spectra of the activated sample **1a** (red), and the precipitated sample from the pyridine-containing mixed solvent system (black).