A metal-organic framework

replete with ordered donor-acceptor catenanes

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Supplementary Information

1. Synthetic Method of MOF-1011

General Method

Chemicals were purchased from commercial suppliers and used as received, unless otherwise noted. Dry solvents were obtained from an EMD Chemicals DrySolv[®] system. Thin-layer chromatography (TLC) was carried out using glass plates, precoated with silica gel 60 with fluorescent indicator (Whatman LK6F). The plates were inspected by UV light (254 nm). Column chromatography was carried out using silica gel 60F (230-400 mesh). ¹H and ¹³C NMR spectra were recorded on ARX500 (500 MHz), DRX500 (500 MHz) or AV600 (600 MHz) spectrometers with the residual solvent as the internal standard. High-resolution electrospray ionization (ESI) mass spectra were measured on a Micromass Q-Tof Ultima (SCS, University of Illinois). Elemental microanalyses of all products were performed at the University of California, Los Angeles, Department of Chemistry and Biochemistry, or at Quantitative Technologies, Inc.

MOF-1011: H₂BPP34C10DC-CAT was synthesized as previously reported.¹ Strut purity was checked by ¹H and ¹³C NMR, and ESI mass spectra. A solid mixture of H₂BPP34C10DC-CAT (10.00 mg, 5.20×10^{-6} mol) and Cu(NO₃)₂·2.5H₂O (20.00 mg, 8.60×10^{-5} mol, Aldrich Chemical Co.) was dissolved in 375 µL DMF, 375 µL EtOH, and 250 µL H₂O in a 4-mL vial. The vial was capped and placed in an isothermal oven at 85 °C for 6 d. The vial was then removed from the oven and allowed to cool to room temperature naturally. A mixture of green crystals and brown crystals was obtained. After decanting mother liquor, 2 mL DMF and 1.5 mL CHBr₃ was added to the vial. Because of the density difference of two types of crystals, brown crystals float on top of the solution, while green crystals stay at the bottom. MOF-1011, which is the brown compound, was collected and rinsed with DMF (4 × 1 mL).

Elemental Analysis (evacuated): Cu(C₈₂H₇₈N₄O₁₄)(NO₃)₃: Calcd.: C, 60.22; H, 4.94; N, 6.15. Found: C, 59.64; H, 4.50; N, 5.37.

2. MOF-1011 Single-Crystal X-Ray Diffraction Data Collection, Structure Solution, and Refinement Procedures

General Data Collection and Refinement Procedures:

Initial ω - φ scans of each specimen were taken to gain preliminary unit cell parameters and to assess the mosaicity (i.e. breadth of spots between frames) of the crystal to select the required frame width for data collection. For all cases frame widths of 0.5° were judged to be appropriate and full hemispheres of data were collected using the *Bruker APEX2*² software suite to carry out overlapping φ and ω scans at different detector (20) settings. Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration and to check for rotational twinning using *CELL_NOW*³. Data were integrated using *Bruker APEX2* V 2.1 software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. The space group determination and tests for merohedral twinning were carried out using *XPREP*⁴. In all cases the highest possible space group was chosen and no indications of merohedral twinning were observed.

The structure was solved by direct methods and refined using the *SHELXTL '97* software suite⁵. Atoms were located from iterative examination of difference F-maps following least-squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2 times Ueq of the attached carbon atoms. Structure was examined using the *Adsym* subroutine of PLATON⁶ to assure that no additional symmetry could be applied to the models.

Experimental and Refinement Details for MOF-1011:

A brown rod-shaped crystal $(0.10 \times 0.05 \times 0.05 \text{ mm}^3)$ of MOF-1011 was placed in a 0.4 mm diameter borosilicate capillary along with a small amount of mother liquor. The capillary was flame sealed and mounted on a SMART APEXII three circle diffractometer equipped with a CCD area detector and operated at 1200 W power (40 kV, 30 mA) to generate Cu *Ka* radiation ($\lambda = 1.5418$ Å) while being flash frozen to 258(2) K in a liquid N₂ cooled stream of nitrogen. Full hemispheres of data were collected using the *Bruker APEX2* software suite to carry out overlapping φ and ω scans at two different detector (20) settings (20 = 28, 60°). A total of 49428 reflections were collected, of which 12485 were unique and 8513 of these were greater than $2\sigma(I)$. The range of θ was from 2.29 to 45.09°. Analysis of the data showed negligible decay during collection. The structure was solved in the orthorhombic *Pca2*₁ space group with *Z* = 4 using direct methods. All atoms are refined isotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. Modeling the Cu atoms anisotropically leads to non-positive definite values for ellipsoids.

The data was collected at 258K rather than lower temperature. For many extended framework structures, we believe it is more reasonable to model against data collected at elevated temperatures (258K, rather than 100K to 173K), especially for crystals mounted in a capillary with a small amount of solvents. At cryogenic temperatures it was found that free solvent in the crystal would 'freeze' into non-ordered arrays within the pore structure and the dataset did not improve.

The attempts made to model anions and solvent molecules did not succeed. This difficulty lies in the raw data with higher resolution present but weak (low intensity). A common strategy for improving X-ray data, increasing the exposure time of the crystal to X-rays did not ameliorate the quality of the high angle data in these cases, as minimal improvement in the high angle data was achieved. Additionally, diffuse scattering from the solvents in the void spaces within the crystal and solvents from the capillary used to mount the crystal contributed to the background noise and the 'washing out' of high angle data. High esd's make it impossible to determine accurate positions for anions and solvent molecules. Thus, first two unidentified peaks within void spaces which could not be assigned to any definite entity were modeled as isolated oxygen atoms O1S and O2S. Including additional unidentified peaks as isolated oxygen atoms led to unstable refinement.

Some atoms showed high Uiso before thermal constraints were applied. Atoms with similar environment (for example, O108, O111, O114, O117, O120 in the crown ethers) were set as the same temperature factor for the refinement. After some mild thermal constraints, the Uiso of all the atoms are below 0.37 in the MOF-1011.CIF, and below 0.33 in the MOF-1011 SQUEEZE.CIF. Considering the small crystal size and the poor data, the structure was expected to have elevated reliability factors. Some bond length and bond angles exceed the normal range (for example, C53-O54 is 1.786 Å). These poor lengths and angles are due to insufficient constraints and the esd's are also high.

Attempts at further refinement resulted in non positive definite Cu1 and Cu2 ellipsoids; thus Cu1 and Cu2 were refined isotropically in the updated CIF files. The first four Q peaks are very close to Cu atoms, with distances to Cu atoms less than 0.71 Å. *SHELX* does not suggest splitting either of the Cu atom positions. It is possible that these ellipsoids indicated that each copper atom occupies two positions, each at partial occupancy; however, attempts to model them with partial disorder did not succeed. The space group assignment was checked again, and *ADDSYMM* does not suggest any higher symmetry space group. In the asymmetric unit of MOF-1011, there are two sets of catenanes that are not exactly the same as each other in the crystallographic view. Although the Flack parameter is close to 0.5, we found that the crystal does not have inversion twinning.

Possible anions in the structure are PF_6^- or NO_3^- or both. PF_6^- should be easy to locate from the x-ray data if they are present, even with some disorder. From the elemental analysis we conclude that the anions in this structure are NO_3^- (three NO_3^- for every Cu atom). Nonetheless, assignment and refinement of the extended structure of MOF-1011 gave reasonable values for the more rigid parts, as judged by the resulting bond and angle metrics which are chemically reasonable. Given the size and contents of MOF-1011, with crown ethers, CBPQT⁴⁺ cyclophane, anions, and guest molecules, the final refined structures have, expectedly, elevated reliability factors in comparison with to those from small molecule crystallography. Largest diff. peak in MOF-1011 is 5.366 e.Å⁻³. Several datasets have been collected with different crystals, including data from a crystal at low temperature and data from a crystal not contained in a capillary. None of those trials gave us better data. We also understand that Cu radiation can be a problem for a crystal containing Cu. Since high-resolution data could not be obtained and we wanted to maximize the intensities, Cu radiation seemed to be a better choice than Mo. The crystal used to obtain this data was very small and we assumed that, despite the high value of the absorption coefficient for Cu, the absorption correction would not be a significant problem. Of course the glass of the capillary and the small amount of solvent included in the capillary will also contribute to the diffraction background and this becomes more important when the crystal is very small. The reported structure displays the framework of MOF-1011 as isolated in the crystalline form. MOF-1011 contains one catenane link per copper atom. The application of the SQUEEZE⁷ routine of A. Spek has been performed. However atomic co-ordinates for the "non-SQUEEZE" structures are also presented. Final (after performing SQUEEZE) full matrix least-squares refinement on F^2 converged to $R_1 = 0.1976$ (F >2 σ (F)) and $wR_2 = 0.4854$ (all data) with GOF = 1.829. For the structure where the SQUEEZE program has not been employed, final full matrix leastsquares refinement on F^2 converged to $R_1 = 0.2901$ ($F > 2\sigma(F)$) and $wR_2 = 0.6108$ (all data) with GOF = 2.544. We note that the elevated R-values are commonly encountered in MOF crystallography, for the reasons expressed above, by us and by other research groups.⁷

Empirical formula	C164 H156 Cu2 N8 O30
Formula weight	2846.05
Temperature	258(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	$a = 30.5784(10) \text{ Å} \alpha = 90.00^{\circ}$
	$b = 13.5840(4) \text{ Å } \beta = 90.00^{\circ}$
	$c = 32.0739(8) \text{ Å } \gamma = 90.00^{\circ}$
Volume	16808.3(8)
Ζ	4
Density (calculated)	1.125 Mg/m ³
Absorption coefficient	0.864 mm ⁻¹
F(000)	5976
Crystal size	$0.10\times0.05\times0.05~mm^3$
Theta range for data collection	2.29-45.09°
Index ranges	-32<=h<=33, -12<=k<=12, -29<=l<=27
Reflections collected	49428
Independent reflections	12485 [R(int)= 0.0737]
Completeness to theta = 45.09°	97.7%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12485 / 67 / 508
Goodness-of-fit on F ²	2.544
Final R indices [I>2sigma(I)]	$R_1 = 0.2901, wR_2 = 0.5911$
R indices (all data)	$R_1 = 0.3152, wR_2 = 0.6108$
Largest diff. peak and hole	5.366 and -2.040 e.Å ⁻³

Table S1. Crystal data and structure refinement for MOF-1011

Empirical formula	C164 H156 Cu2 N8 O28
Formula weight	2814.05
Temperature	258(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	$a = 30.5784(10)$ Å $\alpha = 90.00^{\circ}$
	$b = 13.5840(4) \text{ Å } \beta = 90.00^{\circ}$
	$c = 32.0739(8) \text{ Å } \gamma = 90.00^{\circ}$
Volume	16808.3(8)
Z	4
Density (calculated)	1.112 Mg/m ³
Absorption coefficient	0.849 mm ⁻¹
F(000)	5912
Crystal size	$0.10\times0.05\times0.05~mm^3$
Theta range for data collection	$2.29 - 45.09^{\circ}$
Index ranges	-32<=h<=33, -12<=k<=12, -29<=l<=27
Reflections collected	49428
Independent reflections	12485 [R(int)= 0.0729]
Completeness to theta = 45.09°	97.7%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12485 / 67 / 500
Goodness-of-fit on F ²	1.829
Final R indices [I>2sigma(I)]	$R_1 = 0.1976, wR_2 = 0.4629$
R indices (all data)	$R_1 = 0.2215, wR_2 = 0.4854$
Largest diff. peak and hole	4.342 and -1.709 e.Å ⁻³

Table S2. Crystal data and structure refinement for MOF-1011 (SQUEEZE)



Figure S1. Ball-and-stick drawing of the asymmetric unit of MOF-1011. Hydrogen atoms, solvent molecules, and anions were excluded for clarity.

3. Experimental and Simulated Powder X-Ray Diffraction Patterns

Powder X-ray diffraction (PXRD) data were collected using a Bruker D8- Discover θ -2 θ diffractometer in reflectance Bragg-Brentano geometry. Cu *K* α radiation (λ = 1.5406 Å; 1,600 W, 40 kV, 40 mA) was focused using a planer Gobel Mirror riding the *K* α line. A 0.6 mm divergence slit was used for all measurements. Diffracted radiation was detected using a Vantec line detector (Bruker AXS) (6° 2 θ sampling width) equipped with a Ni monochromator. Sample was mounted onto a glass slide fixed on a sample holder by dropping crystals and then leveling the sample surface with a wide blade spatula. The best counting statistics were achieved by using a 0.02° 2 θ step scan from 2 – 50° with an exposure time of 0.4 s per step.



Figure S2. Comparison of the experimental PXRD pattern of as-prepared MOF-1011 (red) with the one simulated from its single crystal structure (black). The very high degree of correspondence between the patterns indicates that the bulk material has the same structure as the single crystal.

4. References

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