Electronic Supporting Information For:

Anion-Directed Assembly of a Three-Dimensional Metal-organic Rotaxane Framework

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Materials and Methods

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**General Considerations**

All solvents were dried before use according to standard protocols. For this study, all reagents were purchased commercially (Aldrich, Acros, or Fisher) and used without further purification. PXRD (powder X-ray diffraction) data was collected on a Rigaku R-Axis Spider diffractometer with an image plate detector using a graphite monochromator with CuKα radiation (\(\lambda = 1.5418\) Å) at room temperature. The RINT_XRD XG program was used for data collection. TGA measurements were carried out using a Shimadzu TGA-50 under a nitrogen atmosphere at a heating rate of 5 °C /min in the temperature range of 22-200 °C and 1 °C /min above 200 °C. The nitrogen adsorption isotherm was measured in the gaseous state at 77 K using a BELSORP II-mini volumetric adsorption setup. The nitrogen adsorption isotherm was measured after pre-treatment under a dynamic vacuum at 200 °C.

The single crystals used to obtain the X-ray diffraction structure grew as colorless plates with the .cif document available as a separate supporting information file providing details regarding the specific crystal used for the analysis, along with the structure in question. Diffraction grade crystals were obtained by slow evaporation from solution using a mixture of water/acetonitrile/DMF as described below.

The specific conditions used to obtain diffraction grade crystals were as follows: Solvent (DMF/acetonitrile/water, 1/1/1, v/v/v; 3 mL) was added to a mixture consisting of 0.120 mL of a 0.025 M solution of \(\text{Cu}^{4+}\) in acetonitrile, 0.120 mL of 0.05 M solution of Zn(NO₃)₂ in water, and 0.240 mL of a 0.05 M solution of \(\text{Zn}^{2+}\cdot2\text{H}^+\) in DMF. Upon addition of 0.1 mL triethylamine (TEA), a white solid precipitated from the clear solution. After filtering the precipitate, and allowing the clear solution to evaporate slowly, colorless prisms of \(\text{Cu}^{4+}\cdot(\text{Zn}^{2+}\cdot2\text{H}^+)\cdot6\text{H}_2\text{O}\) were obtained from the latter solution after ca. 6 weeks; these crystals proved suitable for single crystal X-ray diffraction analysis.
The data crystals were cut from a cluster of crystals and had the approximate dimensions given in the .cif document. The data were collected on a Rigaku Mercury2 (2x2 bin mode) CCD diffractometer using a graphite monochromator with MoKα radiation (\(\lambda = 0.71073\) Å). The data was collected using \(\omega\)-scans with a scan range of 1° at low temperature using an Oxford Cryostream low temperature device. Data reduction was performed using DENZO-SMN.\(^1\) The structures were solved by direct methods using SIR97\(^2\) and refined by full-matrix least-squares on F\(^2\) with anisotropic displacement parameters for the non-H atoms using SHELXL-97.\(^3\) The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 x Ueq of the attached atom (1.5 x Ueq for methyl hydrogen atoms). The refinement showed some of the typical warning signs of twinning. In particular, there were many reflections with large, positive \(\Delta(|F_o|^2 - |F_c|^2)\) values. The utility ROTAX\(^4\) in the program WinGX\(^5\) was used to look for possible twins. The function, \(w(|F_o|^2 - |F_c|^2)^2\), was minimized. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below and in the .cif documents.\(^6\) Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).\(^7\) All ellipsoid figures were generated using SHELXTL/PC.\(^8\) Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in the .cif documents available from the Cambridge Crystallographic Centre via quoting ref. number 797584. The document also contains details of crystal data, data collection and structure refinement.
Synthetic routes to MORF-1

To obtain the 3D metal-organic rotaxane framework structure of this report, several different methods were used. All were one-pot gave congruent material, as inferred from PXRD analyses. These methods differed in terms of the choice of base, the specific solvents employed, and the reaction stoichiometry.

Method 1: In a one-pot reaction, Zn(NO₃)₂ in water (0.120 ml of a 0.05 M solution) was added to 3 mL of DMF containing 1⁴⁺·4PF₆⁻ (0.120 mL of a 0.025 M solution), which was obtained as described previously, 9 2·2H⁺ (0.240 mL, 0.05 M), and triethylamine (TEA; 0.300 mL of a 0.02 M solution). Within 5 minutes of this addition, a white solid (product A) precipitated from the clear solution.

Method 2: In a one-pot reaction, addition of TEA (0.1 ml) to a solution containing acetonitrile (3 mL), 1⁴⁺·4PF₆⁻ (0.120 mL of a 0.025 M solution in acetonitrile), Zn(NO₃)₂ (0.120 mL of 0.05 M solution in water), and 2·2H⁺ (0.240 mL of a 0.05 M solution in DMF). This resulted in the formation of a white solid precipitate (product B) from the clear solution. Based on a visual inspection, the precipitation process was deemed complete within 5 minutes.

Method 3: In a one-pot reaction, TEA (0.1 ml) was added to a mixture containing a co-solvent mixture (DMF/acetonitrile/water, 1/1/1, v/v/v; 3 mL), 1⁴⁺·4PF₆⁻ (0.120 mL of a 0.025 M solution in acetonitrile), Zn(NO₃)₂ (0.120 mL of 0.05 M solution in water), and 2·2H⁺ (0.240 mL of a 0.05 M solution in DMF). This resulted in the precipitation of a white solid (product C). After filtering off the precipitate, and allowing the clear solution to evaporate slowly, colorless prisms of 1⁴⁺(2)₄·Zn₂·6H₂O (product D) were obtained after 6 weeks; these crystals proved suitable for an X-ray diffraction analysis.

Method 4: Macrocycle 1⁴⁺·4PF₆⁻ (605 mg, 0.5 mmol), 60 mL water, and 40 mL DMF were added to a bottle containing a mixture consisting of 40 mL of a 0.05 M solution of 2·2H⁺ in DMF
and 20 mL of an aqueous 0.20 M solution of NaOH in water. The reaction mixture was heated with stirring at a temperature of 125 °C, until the solution become clear. Upon the addition of 5 mL of a 0.20 M solution of Zn(NO₃)₂ in water, a white solid precipitated from the clear solution. After cooling the reaction and adding 200 mL acetonitrile, the solid was collected by filtration and was washed with 100 mL water and 100 mL acetonitrile. The solid was subsequently dried under vacuum using a water aspirator. This gave 702 mg of a white solid (product E). The yield was 82% based on the presumed congruence to the sample characterized by X-ray diffraction analysis; this congruence was supported by the PXRD studies detailed below.
**PXRD studies of materials obtained using different synthetic procedures**

Products A to E give rise to similar PXRD spectra, leading us to suggest that these materials possess analogous, if not identical structures.

**Figure S1.** PXRD data for solid products A (a), B (b), C (c), D (d), and E (e). Also shown is the calculated PXRD spectra (T) based on data from a single crystal diffraction analysis of the metal-organic rotaxane framework $\text{I}^{4+}(\text{2})_4\text{Zn}_2\cdot6\text{H}_2\text{O}$ (product D). Diagnostic peaks are listed in Table S1.
**Table S1.** Summary of peak information obtained from the PXRD spectra of samples (A-E), as well as that for the calculated structure (T)

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>θ</th>
<th>hkl</th>
<th>Peak intensities recorded for samples (A-E) and as predicted from a calculation (T)*</th>
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<td></td>
<td>h</td>
<td>k</td>
</tr>
<tr>
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<tr>
<td>9</td>
<td>27.8</td>
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<td>5</td>
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</table>

*Calculated peak intensities were obtained using the data obtained from a single crystal X-ray diffraction analysis.
**X-Ray crystallographic analysis of 1^{4+}·(2)_4·Zn_2·6 H_2O**

Crystal data for 1^{4+}·(2)_4·Zn_2·6H_2O: C_{86}H_{58}N_{10}O_{22}Zn_2, M_w = 1714.16, colorless plates, 0.38 × 0.25 × 0.06 mm^3, monoclinic, space group P21/c, a = 10.195(2), b = 21.342(4), c = 18.533(4) Å, β = 102.96(3) °, V = 3929.7(14) Å^3, Z = 2, ρ = 1.449 g·cm^−3, T = 223(2) K, Mo-Kα radiation (λ = 0.71073 Å), μ = 0.695 mm^−1, 6906 intensities measured in the range 3.0° ≤ 2θ ≤ 50.0°, 27304 independent intensities (R_int = 0.0622), 6906 observed intensities [I ≥ 2σ(I)], empirical absorption correction (0.821 ≤ T ≤ 1.000), R = 0.0957, wR = 0.1459 for 550 parameters refined against |F|^2 of all 6906 unique intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. The positional parameters of the hydrogen atoms associated with the water molecule in the asymmetric unit were not added to the structure model. The asymmetric unit contains one formula unit 1^{4+}·(2)_4·Zn_2·6 H_2O.

In the single crystal structure, one anion (2) with O(6) inserts into macrocycle 1^{4+} and forms a pseudorotaxane structure, which is similar to the pseudorotaxane unit in the supramolecular complex formed directly from 1^{4+} and 2.¹⁰
**Figure S3.** The pseudorotaxane complex found in the single crystal X-ray structure of 1\(^{4+}\cdot(2)\)\(_4\)·Zn\(_2\)·6H\(_2\)O. (a) Atom-labeling scheme for the pseudorotaxane complex [1\(^{4+}\cdot(2)\)·Zn\(_2\)]\(^{4+}\) fragment present in 1\(^{4+}\cdot(2)\)\(_4\)·Zn\(_2\)·6H\(_2\)O. Top view, (b) and side views (c), (d) of the [1\(^{4+}\cdot(2)\)]\(^{2+}\) pseudorotaxane structure. Displacement ellipsoids are scaled to the 25% probability level. The entire assembly sits around a crystallographic inversion center at \(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\). Selected interatomic distances [Å]: C(4)···C(31) 3.387, N(2)···C(30) 3.315, C(5)···C(29) 3.540, C(6)···O(6) 3.556, C(6)···C(27) 3.752, C(6)···C(29) 3.596, N(3)···C(28) 3.689, N(3)···C(32) 3.508, N(3)···C(32A) 3.381, C(9)···C(32) 3.578, N(4)···C(31) 3.453, C(11)···C(31) 3.754, C(11)···C(30) 3.397, C(12)···C(30) 3.592.

The inserted anionic moiety (2) is further complexed with Zn(II) cations, an interaction that serves to link this first anionic subunit with three other non-interpenetrated naphthalene dicarboxylate anions via O (2) or O (4 and 8). Thus, four anionic species are bound to one Zn(II) cation, which results in the formation of a twisted tetrahedron-like complex. In this complex, the anions are located in three different chemical environments; this is illustrated by using different colors both in the main text and in Figures S4-S8.
**Figure S4.** The twisted tetrahedron-like subunit, complex $[\text{I}^{4+} \cdot (\text{II})_4 \cdot \text{Zn}_2]$, found in the single crystal X-ray structure of $\text{I}^{4+} \cdot (\text{II})_4 \cdot \text{Zn}_2 \cdot 6\text{H}_2\text{O}$. (a) Atom-labeling scheme for the pseudorotaxane complex $[\text{I}^{4+} \cdot (\text{II})_4 \cdot \text{Zn}]^-_2$ present in $\text{I}^{4+} \cdot (\text{II})_4 \cdot \text{Zn}_2 \cdot 6\text{H}_2\text{O}$. Top view, (b) and side views (c), (d) of the $[\text{I}^{4+} \cdot (\text{II})_4 \cdot \text{Zn}_2]$ pseudorotaxane subunit structure. Displacement ellipsoids are scaled to the 25% probability level. The entire assembly sits around a crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

Selected interatomic distances: O(2) ... Zn(1) 1.949 Å, O(4A) ... Zn(1) 1.965 Å, O(6) ... Zn(1) 1.951 Å and O(8) ... Zn(1) 1.945 Å; selected interatomic angels for these contacts are: O(2) ... Zn(1) ... O(4A) 104.88º, O(2) ... Zn(1) ... O(6) 123.50º, O(2) ... Zn(1) ... O(8) 100.85º, O(4) ... Zn(1) ... O(6) 104.20º, O(6) ... Zn(1) ... O(8) 106.99º, O(8) ... Zn(1) ... O(4A) 117.39º.

Another way to consider the structure, is to view it along the polyrotaxane-like chains formed from anion 2 with O(2). This view is shown in Figure S5, with the O (2) oxygen atoms labeled in dark blue.
**Figure S5.** The 1D polyrotaxane sub-structure present within the single crystal X-ray structure of $\text{1}^{4+}$·$(\text{2})_4$·$\text{Zn}_2$·$\text{6H}_2\text{O}$.

It is important to note that the tetrahedral subunits are oriented in two directions within the overall 3-D MOF structure. This is illustrated by the partial structure shown in Figure S6.

**Figure S6.** Schematic representation (a) and single crystal structure (b) of the subunit $[(\text{1}^{4+})_2$.$(\text{2})_8$·$\text{Zn}_4]$ present in $\text{1}^{4+}$·$(\text{2})_4$·$\text{Zn}_2$·$\text{6H}_2\text{O}$.

Figure S7 shows the packing diagrams for $\text{1}^{4+}$·$(\text{2})_4$·$\text{Zn}_2$·$\text{6H}_2\text{O}$ as viewed along the crystallographic $a$ and $c$ axes in $\text{1}^{4+}$·$(\text{2})_4$·$\text{Zn}_2$·$\text{6H}_2\text{O}$. As can be noted from an inspection of this figure, there are two parallel polyrotaxane chains oriented in two different directions within the overall structure.
**Figure S7.** Schematic representation of the 1D polyrotaxane subunits, [(1$^{4+}$)$_2$·(2)$_8$·Zn$_4$], present in the overall structure (a), and packing diagrams of 1$^{4+}$·(2)$_4$·Zn$_2$·6H$_2$O as viewed along the crystallographic $a$ axis (b) and $c$ axis (c). Shadings of different colors are meant to illustrate chains oriented in different directions.

Within the overall structure, the disparate 1D polyrotaxane chains are linked to each other via anionic oxygen atoms O(4 and 8) (labeled in green); the result is a 3D polyrotaxanated metal-organic framework, as well as a polyrotaxane cage structure. All the anions (2) are bound to Zn(II) cation and form a poly-anionic diamond-like 3D framework with 1$^{4+}$ thread being threaded in two different directions. This is illustrated in Figure S8.
Figure S8. Schematic illustration (a) and real structure as wire frame (b) and space filling representations (c) of the polycatenated cage present in $1^{4+} \cdot (2)_4 \cdot Zn_2 \cdot 6H_2O$.

Analysis of MORF-1 and its properties

Thermogravimetric analysis (TGA) of MORF-1 showed a weight loss corresponding to the loss of the 6 H$_2$O of crystallization per macrocyclic subunit (exp. 6.5%; calcd. 6.3%), as can be seen from an inspection of Figure 5. The sample analyzed after this latter weight loss retained the original structure as inferred from comparative PXRD. The on-set of thermal decomposition was inferred to occur at ca. 300 °C on the basis of the TGA analysis.

No discernable change was seen for the material analyzed after thermal treatment to ca. 200 °C. On this basis we conclude that the key rotaxane feature present in MORF-1 is thermally
stable (i.e., crystallinity is retained after removal of the co-crystallized solvent, water), as noted in the main text.

A nitrogen adsorption isotherm was determined at 77 K after removal of the waters of crystallization (Figure S9). It revealed features consistent with a low porosity material that displays multilayer adsorption behavior.

![Nitrogen adsorption isotherm](image)

**Figure S9.** Nitrogen adsorption isotherm at 77 K for $\text{1}^{\text{4+}} \cdot (2)_4 \cdot \text{Zn}_2$.

**References:**


(6) $R_w(F^2) = \{w(|F_o|^2 - |F_c|^2)^2/w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.

$R(F) = (|F_o| - |F_c|)/|F_o|$ for reflections with $F_o > 4(|F_o|)$.

$S = [w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.


