Electronic Supporting Information For:

Rare-earth cation effects on three-dimensional metal-organic rotaxane framework (MORF) self assembly

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**General Considerations**

For this study, all reagents were purchased commercially (Aldrich, Acros, or Fisher) and used without further purification. Powder X-ray diffraction (PXRD) data was collected on a Rigaku R-Axis Spider diffractometer with an image plate detector using a graphite monochromator with CuKα radiation (λ = 1.5418 Å) at room temperature. The RINT_XRD XG program was used for data collection.

The single crystals used to obtain the X-ray diffraction structures grew as colorless prisms unless otherwise indicated. Diffraction grade crystals were obtained by use of slow solution diffusion methods as described below. The .cif documents are available as a separate supporting information file, and provide details regarding the specific crystal used for analysis, along with the structure in question.

The procedure used to obtain diffraction grade crystals was as follows: 7.5 μL of a 2.0 M aqueous solution of M(NO₃)₃ (M = Nd, Eu, Sm or Tb) was placed on the bottom of a small vial. A small amount of a pure solvent mixture (DMF/water, 1/1, v/v; 200 μL) was then slowly added via pipette along the inner wall of the vial to create a layering effect. A mixture, which consisted of 75 μL of a 0.05 M solution of terephthalic acid (2·2H⁺) in DMF, 37.5 μL of a 0.20 M solution of tetramethylammonium hydroxide pentahydrate (NMe₄·OH·5H₂O) in water, 15 μL of a 0.05 M solution of 1⁺ in DMF, and 90 μL of DMF and 142.5 μL of water (all premixed), was carefully added as the upper layer by dripping it slowly along the inner wall making an effort not to disturb the other two layers. The resulting three-layer set of clear solutions was allowed to stand.

After 5 days, presumably as the result of slow diffusive mixing, colorless prisms of

\[ [1^+\cdot(2)_{5.5}\cdot\text{Nd}_{2}\cdot4\text{H}_2\text{O}]\cdot(2)_{0.5}\cdot17\text{H}_2\text{O} \quad (\text{MORF-Nd}), \]
\[ [1^+\cdot(2)_{5}\cdot\text{Sm}_{2}\cdot2\text{H}_2\text{O}]\cdot14.5\text{H}_2\text{O}\cdot\text{DMF} \quad (\text{MORF-Sm}), \]
\[ [1^+\cdot(2)_{5}\cdot\text{Eu}_{2}\cdot3\text{H}_2\text{O}]\cdot16\text{H}_2\text{O} \quad (\text{MORF-Eu}), \quad \text{and} \quad [1^+\cdot(2)_{5}\cdot\text{Tb}_{2}\cdot2\text{H}_2\text{O}]\cdot10\text{H}_2\text{O}\cdot0.5\text{DMF} \]
(MORF-Tb)), were obtained. These crystals proved suitable for single crystal X-ray diffraction analysis (*vide infra*).

The data crystals were cut from a cluster of crystals and had the approximate dimensions given in the .cif documents. The data were collected on a Rigaku Saturn724+ (2 x 2 bin mode) CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). The data were collected using ω-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 SIR97² and refined by full-matrix least-squares on F² 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 Δ(|F₀|² - |Fₐ|²) values. The utility ROTAX⁴ in the program WinGX⁵ was used to look for possible twins. The function, w(|F₀|² - |Fₐ|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; these are available from the Cambridge Crystallographic Centre free of charge by quoting ref. numbers 824439, 824438, 881834 and 881835. The documents also contain details of crystal data, data collection, and structure refinement.
All samples used for the luminescence studies (*vide infra*) were prepared by rinsing the crystals in question with a 1:1 solution of DMF and water to remove unreacted precursors and other possible impurities from the surface. The crystals were then re-suspended in acetonitrile, and the actual samples used for the luminescence microscopic analysis were prepared by drop casting these crystals suspended onto a 1 x 1 cm Al₂O₃ single crystal (purchased from MTI). Luminescence images were recorded with an Olympus BX60 fluorescence microscope with a CCD camera (SPOT 2 Diagnostic Instruments) using a 20x objective. Samples were excited using the UV lines of a 100 W mercury arc lamp. Images were acquired with automatic exposure timing recording only the green and red channels to minimize the fluorescence from the organic components of the crystal complex. Photoluminescence spectra were acquired using a Fluorolog-3 (Horiba Jobin-Yvon). All samples were excited at 310 nm using a band pass of 5 nm. All emission spectra were acquired with a 500 nm long wavelength pass filter. The corresponding spectrum for the sample of MORF-Nd was taken with an integration time of 0.5 seconds, an emission slit width of 5 nm, and a step size of 1 nm. The emission for the MORF-Eu sample was recorded using an integration time of 1 second, an emission slit width of 0.5 nm, and a step size of 0.25 nm.
Synthetic routes to MORF-M complexes (M = Nd, Eu, Sm or Tb)

The synthetic procedure used to obtain crystalline samples of the MORFs (i.e., MORF-M, M = Nd, Sm, Eu or Tb) were similar and involved the three-phase layering technique described above. The MORF-Eu (i.e., \([\text{1}\text{4}\text{+}\text{•}(2)\text{•Eu}_2\text{•3H}_2\text{O}]\text{•16H}_2\text{O}\)•\text{16H}_2\text{O}\)) was also obtained on large scale using a one-pot synthesis. These two approaches, provided MORF-Eu (A) from the small scale layering method and MORF-Eu (B) from the one-pot large scale synthesis. The samples obtained via these two preparative methods were found to be congruent materials, as inferred from PXRD analyses (see subsequent discussion). Details of the bulk one-pot synthesis are provided below.

Macrocycle \(\text{1}\text{4}\text{+}\text{•4PF}_6\) (152 mg, 0.125 mmol), 15 mL water, and 10 mL DMF were added to a large glass vial containing a mixture consisting of 12.5 mL of a 0.05 M solution of \(2\text{•2H}^+\) in DMF and 6.25 mL of an aqueous 0.20 M solution of \(\text{NMe}_4\text{•OH•5H}_2\text{O}\). The reaction mixture was heated with stirring at 125 °C until the solution became clear. The solution was then cooled to room temperature. Into a separate vial, was then added a solution of 1.25 mL of a 0.20 M solution of \(\text{Eu(NO}_3\text{)}_3\) in water to form what would become the first layer of three separate layers within this new vial. A mixture of DMF and water (5 mL; v:v, 1/1) was then added to form what would be the middle layer. The first solution containing \(\text{1}\text{4}\text{+}\text{•4PF}_6\) was then added as the upper layer. Upon this latter addition, a white solid began to precipitate from the clear solution. After 12 hours, the solid was collected by filtration and was washed with 100 mL water and 100 mL acetonitrile. The solid was then dried under vacuum using a water aspirator. This gave 220 mg of a white solid (product MORF-Eu (B)). The yield was 84% based on the presumed congruence to sample A.
**X-Ray crystallographic study of MORF-M (M = Nd, Eu, Sm or Tb)**

Table S1. X-ray crystallographic data comparison of [1⁺•(2)₄⁺•Nd₂•4H₂O]•(2)₀.₅•17H₂O (MORF-Nd), [1⁺•(2)₃⁺•Eu₂•3H₂O]•16H₂O (MORF-Eu), [1⁺•(2)₃⁺•Sm₂•2H₂O]•14.₅H₂O•DMF (MORF-Sm), and [1⁺•(2)₃⁺•Tb₂•2H₂O]•10H₂O•0.₅DMF (MORF-Tb).

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<td>C₇₈H₉₀N₁₀Nd₂O₄₁</td>
<td>2118.13</td>
<td>0.41 × 0.28 × 0.15</td>
<td>Triclinic</td>
<td>P-1</td>
<td>11.649(2)</td>
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<td>25.515(5)</td>
<td>99.17(3)</td>
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<td>93.41(3)</td>
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*The PLATON/SQUEEZE* function was used to treat solvent distribution disorder.
X-Ray crystallographic study of MORF-Nd

In all the structures described herein, the anions are located in different chemical environments. This is illustrated by the use of different colors, both in the main text and in Figures S1-S16. In the single crystal structure of MORF-Nd (i.e., \([1^{4+} \cdot (2)_{4.5} \cdot \text{Nd}_{2} \cdot 4\text{H}_2\text{O}) \cdot (2)_{0.5} \cdot 17\text{H}_2\text{O}]\)), one anion (2), with O(11), inserts into the cavity of macrocycle 1\(^{4+}\) resulting in the formation of a pseudorotaxane structure (cf. Figure S1). This observation is distinctly different from the ‘outside’ binding mode seen in the supramolecular complex formed directly from 1\(^{4+}\) and 2 (in the absence of Nd), and is similar to what is seen in the previously reported non-MOF structures obtained with the smaller trivalent lanthanide cations, i.e., RSOF-M (M = Y, Gd, Er, Tm and Lu).\(^{10-12}\)

A very similar pseudorotaxane unit, \([1^{4+} \cdot (2)]^{2+}\), was found to act as the primary building block in all the MORFs described herein, an example of which is shown in Figure S1.

**Figure S1.** The pseudorotaxane unit \([1^{4+} \cdot (2)]^{2+}\) found in the single crystal X-ray structure of MORF-Nd (i.e., \([1^{4+} \cdot (2)_{4.5} \cdot \text{Nd}_{2} \cdot 4\text{H}_2\text{O}) \cdot (2)_{0.5} \cdot 17\text{H}_2\text{O}]\)). (a) Shown in the ellipsoid form with atom-labeling scheme for the pseudorotaxane complex \([1^{4+} \cdot (2) \cdot \text{Nd}_{2}]^{8+}\) present in MORF-Nd. Top view (b), and side views (c) and (d) of the \([1^{4+} \cdot (2) \cdot \text{Nd}_{2}]^{8+}\) pseudorotaxane structure. Displacement ellipsoids are scaled to the 50% probability level. Selected interatomic distances [Å] for possible \(\pi-\pi\) donor acceptor interactions: C(13)…C(65) 3.80(2), C(17)…C(63) 3.49(2), C(17)…C(64)
3.53(2), C(18)…C(60) 3.73(2), C(18)…C(61) 3.73(1), C(18)…C(62) 3.71(2), C(18)…C(63) 3.73(2), C(18)…C(64) 3.71(2), C(18)…C(65) 3.68(2), C(36)…C(60) 3.60(2), C(36)…C(61) 3.69(2), C(37)…C(64) 3.78(2), C(37)…C(65) 3.75(2); possible intermolecular hydrogen bonding interactions are evidenced as below: selected interatomic distances [Å]: C(1)…O(12) 2.99(1), C(9)…O(12) 3.20(1), C(20)…O(13) 3.12(1), C(28)…O(13) 3.22(1); selected interatomic angles: C(1)-H(1A)…O(12) 169.6(7)°, C(9)-H(9A)…O(12) 176.2(7)°, C(20)-H(20A)…O(13) 166.1(7)°, C(28)-H(28A)…O(13) 173.9(7)°.

In the structure of MORF-Nd (i.e., [1^{4+}•(2)_{4.5}•Nd_{2}•4H_{2}O]•(2)_{0.5}•17H_{2}O), the pseudorotaxane units are “expanded” as the result of additional anions (2) being present outside of 1^{4+} (cf. Figure S2 and discussion below).

![Figure S2](image)

**Figure S2.** Two interpenetrated structures (a_{1,3} and b_{1,3}) found in the single crystal structure of MORF-Nd (i.e., [1^{4+}•(2)_{4.5}•Nd_{2}•4H_{2}O]•(2)_{0.5}•17H_{2}O). In both cases, the molecular box 1^{4+} interacts with the inserted anions 2 to form a pseudorotaxane structure. Note the presence of additional molecules of 2.

In the structure of MORF-Nd, the cations (Nd^{3+}) adopt two different binding modes, both with coordination number of 9 with the ligands including the anions and water molecules (cf. Figure S3).
Figure S3. Experimentally determined structure displayed in stick forms of the two
complexation modes of Nd³⁺ in the single crystal structure of MORF-Nd (i.e.,
[14•(2)2•Nd•4H₂O]•(2)0•17H₂O). Selected interatomic distances [Å] for metal cation Nd³⁺
complexation mode 1 (shown in figure a): O(1)···Nd(1) 2.602(7), O(2)···Nd(1) 2.466(7),
O(3)···Nd(1) 2.425(8), O(5)···Nd(1) 2.652(8), O(6)···Nd(1) 2.616(7), O(7)···Nd(1) 2.458(8),
O(11)···Nd(1) 2.482(6), O(1W)···Nd(1) 2.678(7) and O(2W)···Nd(1) 2.623(8); selected
interatomic angles for these contacts are: O(1)···Nd(1)···O(2) 53.9(2)°, O(1)···Nd(1)···O(3)
85.5(3)°, O(1)···Nd(1)···O(5) 137.7(2)°, O(1)···Nd(1)···O(6) 126.3(2)°, O(1)···Nd(1)···O(7)
101.0(2)°, O(1)···Nd(1)···O(1W) 69.7(2)°, O(1)···Nd(1)···O(2W) 72.5(3)°, O(2)···Nd(1)···O(5)
97.7(2)°, O(2)···Nd(1)···O(3) 76.7(3)°, O(2)···Nd(1)···O(6) 73.2(2)°, O(2)···Nd(1)···O(7) 138.8(2)°,
O(2)···Nd(1)···O(1W) 71.3(2)°, O(2)···Nd(1)···O(2W) 118.1(3)°, O(3)···Nd(1)···O(6) 72.9(2)°,
O(6)···Nd(1)···O(5) 50.2(2)°, O(5)···Nd(1)···O(1W) 71.6(2)°, O(1W)···Nd(1)···O(7) 69.1(2)°,
O(7)···Nd(1)···O(2W) 72.5(3)°, O(2W)···Nd(1)···O(3) 71.6(3)°, O(11)···Nd(1)···O(3) 74.5(3)°,
O(11)···Nd(1)···O(5) 74.1(2)°, O(11)···Nd(1)···O(6) 71.4(2)°, O(11)···Nd(1)···O(7) 80.0(2)°,
O(11)···Nd(1)···O(1W) 136.8(2)° and O(11)···Nd(1)···O(2W) 78.5(2)°. Selected interatomic
distances [Å] for metal cation Nd³⁺ complexation mode 2 (shown in figure b): O(9)···Nd(2)
2.626(9), O(10)···Nd(2) 2.517(8), O(13)···Nd(2) 2.561(6), O(14)···Nd(2) 2.707(7), O(15)···Nd(2)
2.392(8), O(17)···Nd(2) 2.514(9), O(18)···Nd(2) 2.566(7), O(3W)···Nd(2) 2.66(1) and
O(4W)···Nd(2) 2.48(1); selected interatomic angles for these contacts are: O(9)···Nd(2)···O(10)
51.3(3)°, O(9)···Nd(2)···O(13) 75.9(2)°, O(9)···Nd(2)···O(14) 119.1(2)°, O(9)···Nd(2)···O(15)
134.1(3)°, O(9)···Nd(2)···O(3W) 90.0(3)°, O(9)···Nd(2)···O(18) 70.5(3)°, O(9)···Nd(2)···O(17)
73.2(3)°, O(10)···Nd(2)···O(13) 76.5(2)°, O(10)···Nd(2)···O(14) 122.6(2)°, O(10)···Nd(2)···O(15)
83.9(3)°, O(10)···Nd(2)···O(3W) 71.9(3)°, O(10)···Nd(2)···O(18) 107.0(3)°, O(10)···Nd(2)···O(17)
123.8(3)°, O(13)···Nd(2)···O(14) 50.1(2)°, O(14)···Nd(2)···O(15) 73.8(2)°, O(15)···Nd(2)···O(3W)
83.8(3)°, O(3W)···Nd(2)···O(18) 67.9(3)°, O(18)···Nd(2)···O(17) 53.2(3)°, O(17)···Nd(2)···O(13)
83.1(2)°, O(4W)···Nd(2)···O(13) 128.5(3)°, O(4W)···Nd(2)···O(14) 78.5(3)°, O(4W)···Nd(2)···O(15)
80.9(3)°, O(4W)···Nd(2)···O(3W) 79.6(3)°, O(4W)···Nd(2)···O(18) 72.2(3)° and O(4W)···Nd(2)···O(17)
81.5(3)°.
In the framework structure, the monomer \([((1^{4+})_2 \cdot (2)_9 \cdot \text{Nd}_4 \cdot 8\text{H}_2\text{O})]\) includes two macrocycles (1^{4+}), nine anions (2), and four metal cations (Nd^{3+}) \textit{(cf. Figure S4)}. One molar equiv of free anion 2, which provides charge balance, was found located outside of the framework as noted above. Unless otherwise indicated, the free molecules of 2 and the free solvent molecules (water) have been deleted for clarity since they are not involved in framework construction.

**Figure S4.** Experimentally determined structure displayed in stick forms of the monomer unit \([(1^{4+})_2 \cdot (2)_9 \cdot \text{Nd}_4 \cdot 8\text{H}_2\text{O})\] forming the framework \([(1^{4+})_2 \cdot (2)_9 \cdot \text{Nd}_4 \cdot 8\text{H}_2\text{O})_n\] in the single crystal structure of \([1^{4+} \cdot (2)_{4.5} \cdot \text{Nd}_2 \cdot 4\text{H}_2\text{O}) \cdot (2)_{0.5} \cdot 17\text{H}_2\text{O}\) (MORF-Nd).

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.
**Figure S5.** The 1D polyrotaxane sub-structure present within the single crystal X-ray structure of \([1^{+\ast}(2)_{3.5} \cdot \text{Nd}_2 \cdot 4\text{H}_2\text{O}] \cdot (2)_{0.5} \cdot 17\text{H}_2\text{O} \) (MORF-Nd).

The disparate 1D polyrotaxane chains are linked to each other *via* anionic oxygen atoms O(3 and 15) (labeled in greyish green); the result is a 2D polyrotaxanated metal-organic network (*cf.* Figure S6).

**Figure S6.** The 2D polyrotaxane network present within the single crystal X-ray structure of \([1^{+\ast}(2)_{3.5} \cdot \text{Nd}_2 \cdot 4\text{H}_2\text{O}] \cdot (2)_{0.5} \cdot 17\text{H}_2\text{O} \) (MORF-Nd).

Within the overall structure, the disparate 2D polyrotaxane networks are linked to each other *via* the anions with oxygen atoms O(7 and 5) (labeled in blue and brown); the result is a 3D polyrotaxanated metal-organic framework that is noteworthy for its polycatenated cage structure. Nine molar equivalent of anion 2 were found bound to four molar equivalent Nd(III) cations to
form a poly-anionic 3D framework with $1^{4+}$ being threaded in two different directions. This arrangement is illustrated in Figure S7.

**Figure S7.** Structure as wire frame (views $a_1$, $a_2$, $a_3$) and space filling representations (views $b_1$, $b_2$, $b_3$) of the 3D metal-organic rotaxanated framework present in $[1^{4+}\cdot(2)_{4.5}\cdot\text{Nd}_2\cdot4\text{H}_2\text{O}]\cdot(2)_{0.5}\cdot17\text{H}_2\text{O}$ (MORF-Nd).

**X-Ray crystallographic study of MORF-Eu**

The cation Eu$^{3+}$ has smaller effective ionic radius (1.066 Å or 1.120 Å with coordination numbers of 8 or 9, respectively) than Nd$^{3+}$ (1.109 Å or 1.163 Å with coordination numbers of 8 or 9, respectively), and is larger than the cations used to assemble the previously reported RSOF structures (1.019 Å for Y$^{3+}$ with a coordination number of 8; 1.053 Å for Gd$^{3+}$ with a coordination number of 8; 1.004 Å for Er$^{3+}$ with a coordination number of 8; 0.994 Å for Tm$^{3+}$ with a coordination number of 8; 0.977 Å for Lu$^{3+}$ with a coordination number of 8). Upon changing the metal cation species to Eu$^{3+}$, the aforementioned one-pot synthesis was again found to form a metal organic rotaxane framework (*i.e.*, $[1^{4+}\cdot(2)_3\cdot\text{Eu}_2\cdot3\text{H}_2\text{O}]\cdot16\text{H}_2\text{O}$; MORF-Eu). Herein the cations were found to direct the insertion of anion 2 into the cavity of $1^{4+}$ resulting in the formation of an interpenetrated structure (*cf.* Figure S8).
Figure S8. Two interpenetrated structures (views a1,3 and b1,3) found in the single crystal structure of \([1^{1+} \cdot (2)_5 \cdot \text{Eu}_2 \cdot 3\text{H}_2\text{O}] \cdot 16\text{H}_2\text{O}\) (MORF-Eu). In both cases, 1\(^{1+}\) was found to bind with anions of 2 via an inserted mode similar to what is seen in the pseudorotaxane found in the RSOFs reported previously and in the MORF-Nd of this report.

The Eu\(^{3+}\) cations were revealed to exist in two different binding modes in the resulting structure. They were found to adopt coordination numbers of 8 and 9, respectively, counting the bound anions and water molecules as ligands (cf. Figure 8).

Figure S9. Experimentally determined structure shown in the stick forms representing the two complexation modes of Eu\(^{3+}\) found in the single crystal structure of \([1^{1+} \cdot (2)_5 \cdot \text{Eu}_2 \cdot 3\text{H}_2\text{O}] \cdot 16\text{H}_2\text{O}\) (MORF-Eu). Selected interatomic distances [Å] for metal cation Eu\(^{3+}\) complexation mode 1 (shown in figure a): O(1)–Eu(1) 2.43(1), O(2)–Eu(1) 2.470(6), O(3)–Eu(1) 2.306(7),
O(5)···Eu(1) 2.314(7), O(7)···Eu(1) 2.36(1), O(11)···Eu(1) 2.51(1) and O(12)···Eu(1) 2.45(1); selected interatomic angels for these contacts are: (1)···Eu(1)···O(2) 53.0(3)^{\circ}, (1)···Eu(1)···O(3) 80.3(3)^{\circ}, (1)···Eu(1)···O(7) 78.8(3)^{\circ}, (1)···Eu(1)···O(5) 82.9(3)^{\circ}, (1)···Eu(1)···O(11) 120.0(3)^{\circ}, O(1)···Eu(1)···O(12) 124.7(3)^{\circ}, O(2)···Eu(1)···O(3) 85.0(3)^{\circ}, O(2)···Eu(1)···O(7) 131.0(3)^{\circ}, O(2)···Eu(1)···O(5) 98.0(3)^{\circ}, O(2)···Eu(1)···O(11) 74.8(3)^{\circ}, O(2)···Eu(1)···O(12) 75.5(3)^{\circ}, O(3)···Eu(1)···O(7) 77.9(3)^{\circ}, O(7)···Eu(1)···O(5) 82.6(3)^{\circ}, O(5)···Eu(1)···O(11) 76.5(3)^{\circ}, O(11)···Eu(1)···O(12) 51.3(3)^{\circ}, O(12)···Eu(1)···O(3) 76.0(3)^{\circ}, O(1W)···Eu(1)···O(3) 99.4(3)^{\circ}, O(1W)···Eu(1)···O(7) 75.3(3)^{\circ}, O(1W)···Eu(1)···O(5) 88.4(3)^{\circ}, O(1W)···Eu(1)···O(11) 81.7(3)^{\circ} and O(1W)···Eu(1)···O(12) 80.1(3)^{\circ}; Selected interatomic distances [Å] for metal cation Eu^{3+} complexation mode 2 (shown in figure b): O(9)···Eu(2) 2.35(1), O(13)···Eu(2) 2.52(1), O(14)···Eu(2) 2.46(1), O(15)···Eu(2) 2.55(1), O(17)···Eu(2) 2.425(9), O(18)···Eu(2) 2.538(8), O(2W)···Eu(2) 2.453(8) and O(3W)···Eu(2) 2.463(8); selected interatomic angels for these contacts are: O(13)···Eu(2)···O(14) 51.3(3)^{\circ}, O(13)···Eu(2)···O(16) 72.0(3)^{\circ}, O(13)···Eu(2)···O(15) 119.5(3)^{\circ}, O(13)···Eu(2)···O(2W) 122.5(3)^{\circ}, O(13)···Eu(2)···O(3W) 95.1(3)^{\circ}, O(13)···Eu(2)···O(18) 70.6(3)^{\circ}, O(13)···Eu(2)···O(17) 80.9(3)^{\circ}, O(14)···Eu(2)···O(16) 77.1(3)^{\circ}, O(14)···Eu(2)···O(15) 122.9(3)^{\circ}, O(14)···Eu(2)···O(2W) 73.8(3)^{\circ}, O(14)···Eu(2)···O(3W) 74.8(3)^{\circ}, O(14)···Eu(2)···O(18) 109.1(3)^{\circ}, O(14)···Eu(2)···O(17) 131.4(3)^{\circ}, O(16)···Eu(2)···O(15) 52.2(3)^{\circ}, O(15)···Eu(2)···O(2W) 74.4(3)^{\circ}, O(2W)···Eu(2)···O(3W) 84.2(3)^{\circ}, O(3W)···Eu(2)···O(18) 73.8(3)^{\circ}, O(18)···Eu(2)···O(17) 52.1(3)^{\circ}, O(17)···Eu(2)···O(16) 80.5(3)^{\circ}, O(9)···Eu(2)···O(16) 126.5(3)^{\circ}, O(9)···Eu(2)···O(15) 74.5(3)^{\circ}, O(9)···Eu(2)···O(2W) 79.6(3)^{\circ}, O(9)···Eu(2)···O(3W) 74.9(3)^{\circ}, O(9)···Eu(2)···O(18) 84.7(3)^{\circ} and O(9)···Eu(2)···O(17) 86.0(3)^{\circ}.

The disparate rotaxane units are linked to each other via anions with oxygen atoms O(3, 5 and 7) (labeled in dark blue, grey and brown); the result is a 2D polyrotaxanated metal-organic network (cf. Figure S10).

**Figure S10.** The 2D polyrotaxane network present within the single crystal X-ray structure of [1^{3+} ·{2,Eu}_2·3H_2O]·16H_2O (MORF-Eu).
Within the overall structure, the disparate 2D polyrotaxane networks are linked to each other via the anions with oxygen atoms O(3) (labeled in dark blue); the result is a 3D polyrotaxanated metal-organic framework that provides a polycatenated cage structure. Further, 5 molar equivalent anions (2) are bound to 2 molar equivalent Eu(III) cations resulting in the formation of a poly-cationic 3D-framework with $\text{Eu}^{3+}$ being threaded in two different directions. These structural features are illustrated in Figure S11.

![Figure S11](image)

**Figure S11.** Views of the structure as wire frame ($a_{1-4}$) and space filling representations ($b_{1-4}$) of the 3D metal organic rotaxane framework present in $[\text{1}^{4+}\cdot(2)_5\cdot\text{Eu}_2\cdot3\text{H}_2\text{O}]\cdot16\text{H}_2\text{O}$ (MORF-Eu).

**X-Ray crystallographic study of MORF-Sm and MORF-Tb**

The MORF structures generated from Sm$^{3+}$ and Tb$^{3+}$ were found to contain similar structural frameworks, as described below. In both structures (*i.e.*, $[\text{1}^{4+}\cdot(2)_3\cdot\text{Sm}_2\cdot2\text{H}_2\text{O}]\cdot14.5\text{H}_2\text{O}\cdot\text{DMF}$ (MORF-Sm), and $[\text{1}^{4+}\cdot(2)_5\cdot\text{Tb}_2\cdot2\text{H}_2\text{O}]\cdot10\text{H}_2\text{O}\cdot0.5\text{DMF}$ (MORF-Tb)), the cations adopt two different binding modes but retain a coordination number of 8, including the anions and water molecules (*cf.* Figures S12 and S13).
Figure S12. Experimentally determined structure displayed in stick forms of the two complexation modes of Sm$^{3+}$, as found in the single crystal structure of [1$^{4+}$·(2)$_2$.Sm$_2$.2H$_2$O]14.5H$_2$O •DMF (MORF-Sm). Selected interatomic distances [Å] for metal cation Eu$^{3+}$ complexation mode 1 (shown in figure a): O(1)···Sm(1) 2.564(5), O(2)···Sm(1) 2.486(6), O(3)···Sm(1) 2.505(5), O(4)···Sm(1) 2.539(5), O(5)···Sm(1) 2.320(5), O(7)···Sm(1) 2.323(7), O(11)···Sm(1) 2.323(5), O(1W)···Sm(1) 2.430(6); selected interatomic angels for these contacts are: O(1)···Sm(1)···O(2) 52.2(2)$^\circ$, O(2)···Sm(1)···O(11) 72.8(2)$^\circ$, O(11)···Sm(1)···O(7) 77.5(2)$^\circ$, O(7)···Sm(1)···O(5) 83.4(2)$^\circ$, O(5)···Sm(1)···O(1) 80.2(2)$^\circ$, O(3)···Sm(1)···O(4) 52.0(2)$^\circ$, O(3)···Sm(1)···O(1) 69.4(2)$^\circ$, O(3)···Sm(1)···O(2) 71.4(2)$^\circ$, O(3)···Sm(1)···O(11) 97.5(2)$^\circ$, O(3)···Sm(1)···O(7) 140.2(2)$^\circ$, O(3)···Sm(1)···O(5) 86.4(2)$^\circ$, O(4)···Sm(1)···O(1) 118.2(2)$^\circ$, O(4)···Sm(1)···O(2) 114.8(2)$^\circ$, O(4)···Sm(1)···O(11) 84.2(2)$^\circ$, O(4)···Sm(1)···O(7) 88.2(2)$^\circ$, O(4)···Sm(1)···O(5) 78.4(2)$^\circ$, O(1W)···Sm(1)···O(1) 71.7(2)$^\circ$, O(1W)···Sm(1)···O(2) 80.3(2)$^\circ$, O(1W)···Sm(1)···O(11) 99.6(2)$^\circ$, O(1W)···Sm(1)···O(7) 78.4(2)$^\circ$ and O(1W)···Sm(1)···O(5) 92.8(2)$^\circ$; Selected interatomic distances [Å] for metal cation Sm$^{3+}$ complexation mode 2 (shown in figure b): O(9)···Sm(2) 2.353(5), O(13)···Sm(2) 2.343(5), O(15)···Sm(2) 2.473(6), O(16)···Sm(2) 2.508(6), O(17)···Sm(2) 2.544(5), O(18)···Sm(2) 2.420(5), O(19)···Sm(2) 2.324(5), O(2W)···Sm(2) 2.406(6); selected interatomic angels for these contacts are: O(17)···Sm(2)···O(18) 52.5(2)$^\circ$, O(17)···Sm(2)···O(9) 105.7(2)$^\circ$, O(17)···Sm(2)···O(16) 74.3(2)$^\circ$, O(17)···Sm(2)···O(15) 75.0(2)$^\circ$, O(17)···Sm(2)···O(19) 80.5(2)$^\circ$, O(17)···Sm(2)···O(13) 128.6(2)$^\circ$, O(18)···Sm(2)···O(9) 83.4(2)$^\circ$, O(18)···Sm(2)···O(16) 112.1(2)$^\circ$, O(18)···Sm(2)···O(15) 126.8(2)$^\circ$, O(18)···Sm(2)···O(19) 85.0(2)$^\circ$, O(18)···Sm(2)···O(13) 78.7(2)$^\circ$, O(2W)···Sm(2)···O(9) 88.6(2)$^\circ$, O(2W)···Sm(2)···O(16) 90.8(2)$^\circ$, O(2W)···Sm(2)···O(15) 79.8(2)$^\circ$, O(2W)···Sm(2)···O(19) 93.6(2)$^\circ$, O(2W)···Sm(2)···O(13) 73.5(2)$^\circ$, O(15)···Sm(2)···O(16) 52.0(2)$^\circ$, O(16)···Sm(2)···O(9) 72.9(2)$^\circ$, O(9)···Sm(2)···O(13) 80.6(2)$^\circ$, O(13)···Sm(2)···O(19) 80.2(2)$^\circ$ and O(19)···Sm(2)···O(15) 77.8(2)$^\circ$. 
Figure S13. Experimentally determined structure displayed in the stick forms of the two complexation modes of Tb$^{3+}$, as found in the single crystal structure of [1$^{4+}$·(2)$_{10}$·M$_{2}$·2H$_2$O]·10H$_2$O·0.5DMF (MORF-Tb). Selected interatomic distances [Å] for metal cation Tb$^{3+}$ complexation mode 1 (shown in figure a): O(1)···Tb(1) 2.497(9), O(2)···Tb(1) 2.41(1), O(3)···Tb(1) 2.42(1), O(4)···Tb(1) 2.47(1), O(5)···Tb(1) 2.27(1), O(7)···Tb(1) 2.23(1), O(11)···Tb(1) 2.23(1), O(1W)···Tb(1) 2.37(1); selected interatomic angels for these contacts are: O(1)···Tb(1)···O(2) 51.6(3)$^\circ$, O(2)···Tb(1)···O(11) 73.1(4)$^\circ$, O(11)···Tb(1)···O(7) 78.4(4)$^\circ$, O(7)···Tb(1)···O(5) 81.2(4)$^\circ$, O(5)···Tb(1)···O(1) 81.0(3)$^\circ$, O(3)···Tb(1)···O(4) 53.7(3)$^\circ$, O(3)···Tb(1)···O(1) 70.0(3)$^\circ$, O(3)···Tb(1)···O(2) 73.0(3)$^\circ$, O(3)···Tb(1)···O(11) 98.3(3)$^\circ$, O(3)···Tb(1)···O(7) 137.1(4)$^\circ$, O(3)···Tb(1)···O(5) 85.8(3)$^\circ$, O(4)···Tb(1)···O(1) 121.1(3)$^\circ$, O(4)···Tb(1)···O(2) 116.7(3)$^\circ$, O(4)···Tb(1)···O(11) 82.7(3)$^\circ$, O(4)···Tb(1)···O(7) 83.7(4)$^\circ$, O(4)···Tb(1)···O(5) 79.2(3)$^\circ$, O(1W)···Tb(1)···O(1) 70.8(4)$^\circ$, O(1W)···Tb(1)···O(2) 80.6(4)$^\circ$, O(1W)···Tb(1)···O(11) 101.2(4)$^\circ$, O(1W)···Tb(1)···O(7) 80.5(4)$^\circ$ and O(1W)···Tb(1)···O(5) 91.1(4)$^\circ$; selected interatomic distances [Å] for metal cation Tb$^{3+}$ complexation mode 2 (shown in figure b): O(9)···Tb(2) 2.25(1), O(13)···Tb(2) 2.29(1), O(15)···Tb(2) 2.42(1), O(16)···Tb(2) 2.47(1), O(17)···Tb(2) 2.46(1), O(18)···Tb(2) 2.39(1), O(19)···Tb(2) 2.22(1), O(2W)···Tb(2) 2.35(1); selected interatomic angels for these contacts are: O(17)···Tb(2)···O(18) 53.2(3)$^\circ$, O(17)···Tb(2)···O(9) 103.9(3)$^\circ$, O(17)···Tb(2)···O(16) 73.3(3)$^\circ$, O(17)···Tb(2)···O(15) 73.8(3)$^\circ$, O(17)···Tb(2)···O(19) 84.3(4)$^\circ$, O(17)···Tb(2)···O(13) 129.6(3)$^\circ$, O(18)···Tb(2)···O(9) 84.0(4)$^\circ$, O(18)···Tb(2)···O(16) 114.4(3)$^\circ$, O(18)···Tb(2)···O(15) 125.4(3)$^\circ$, O(18)···Tb(2)···O(19) 83.6(4)$^\circ$, O(18)···Tb(2)···O(13) 77.8(3)$^\circ$, O(2W)···Tb(2)···O(9) 88.6(4)$^\circ$, O(2W)···Tb(2)···O(16) 88.5(4)$^\circ$, O(2W)···Tb(2)···O(15) 80.0(4)$^\circ$, O(2W)···Tb(2)···O(19) 93.3(4)$^\circ$, O(2W)···Tb(2)···O(13) 75.0(4)$^\circ$, O(15)···Tb(2)···O(16) 51.7(4)$^\circ$, O(16)···Tb(2)···O(9) 74.3(4)$^\circ$, O(9)···Tb(2)···O(13) 79.1(4)$^\circ$, O(13)···Tb(2)···O(19) 78.8(4)$^\circ$ and O(19)···Tb(2)···O(15) 78.6(4)$^\circ$.

In MORF-M (M = Sm or Tb), the monomer unit [(1$^{4+}$)$_{2}$·(2)$_{10}$·M$_{2}$·4H$_2$O] (M = Sm or Tb) was found to form with two anions (2) inserting into the cavity of 1$^{4+}$ resulting in the formation of interpenetrated structures with threading taking place in two different directions (cf. Figure 13).

Figure S14. Experimentally determined structure displayed in stick form of the monomer unit [(1$^{4+}$)$_{2}$·(2)$_{10}$·M$_{2}$·4H$_2$O] (M = Sm or Tb) that makes up the framework [(1$^{4+}$)$_{2}$·(2)$_{10}$·M$_{2}$·4H$_2$O]$_{n}$ (M
= Sm or Tb), as found in the single crystal structure of $[1^{4+}\cdot(2)_3\cdot\text{Sm}_2\cdot2\text{H}_2\text{O}]\cdot14.5\text{H}_2\text{O}\cdot\text{DMF}$ (MORF-Sm), or $[1^{4+}\cdot(2)_3\cdot\text{Tb}_2\cdot2\text{H}_2\text{O}]\cdot10\text{H}_2\text{O}\cdot0.5\text{DMF}$ (MORF-Tb).

Another way to consider the structure, is to view it along the polyrotaxane-like chain formed from anion 2 with O(11). This view is shown in Figure S15; the anion 2 is shown with it and the O(11) oxygen atoms labeled in green.

![Figure S15](image)

**Figure S15.** The 1D polyrotaxane sub-structure present within the single crystal X-ray structure of MORF-M (M = Sm or Tb).

The disparate 1D polyrotaxane chains are linked to each other *via* anionic oxygen atoms O(5, 7 and 19) (labeled in grey, purple, and brown, respectively); the result is a 2D polyrotaxanated metal-organic network (*cf.* Figure S16).
Figure S16. The 2D polyrotaxane network present within the single crystal X-ray structure of MORF-M (M = Sm or Tb).

Within the overall structure, the individual 2D polyrotaxane networks are linked to each other via the anions with oxygen atoms O(1) (labeled in blue); the result is a 3D polyrotaxanated metal-organic framework that provides for a polycatenated cage structure. Further, ten molar equivalents of anion 2 were found bound to four molar equivalents of the Nd(III) cations, resulting in the formation of a poly-anionic 3D framework with $\text{1}^{4+}$ being threaded in two different directions. This is illustrated in Figure S17.

Figure S17. View of the structure as wire frame (a$_{1,3}$) and space filling representations (b$_{1,3}$) of the 3D metal-organic rotaxanated framework present in MORF-M (M = Sm or Tb).
**Solid state photoluminescence spectra study for MORF-M (M = Nd or Eu)**

Luminescence microscopy and photoluminescence spectra have been carried out for the two complexes (i.e., MORF-Nd and MORF-Eu) shown in this report. These results were compared to previously obtained data on RSOF structures, which included RSOF-M (M = Er, Y, Lu). Across this set only the MORF-Eu showed strong fluorescence properties that are not ligand-based (cf. Figure S18 to 19).

In the case of MORF-Nd, weak peaks ascribable to the lanthanide cations were observed in the photo luminescence spectra upon excitation at 310 nm. The sample displayed weak green luminescence (as revealed by luminescence microscopy photos). The actual spectra were dominated by a broad band that tails off from 450 to 750 nm, and which has its origin in the interaction between $\text{Eu}^{2+}$ and 2 (cf. Figure S18). The result is both a spectrum and optical aspect that are similar under conditions of luminescence microscopy and photoluminescence spectroscopy to what was seen in the previous reported study of RSOF-M (M = Er, Y, Lu).

**Figure S18.** Solid photoluminescence spectrum (a) and luminescence microscopy photos of crystalline sample of $[\text{Eu}^{2+} \cdot 2\cdot \text{Eu} \cdot 3\text{H}_2\text{O}] \cdot 16\text{H}_2\text{O}$ (MORF-Eu) under white light (b) and luminescence under UV excitation (c). Image was acquired with automatic exposure timing using only green and red exposure to minimize the fluorescence from the crystal complex. Selected peak position (nm) and relative intensity of the photoluminescence spectrum (panel (a)) are as follows: 77.8%; 542 nm, 100%; 582 nm, 55.7%; 610 nm, 54.8%.

Completely different solid photoluminescence spectrum and luminescence microscopy photos were obtained when $[\text{Eu}^{2+} \cdot 2\cdot \text{Eu} \cdot 3\text{H}_2\text{O}] \cdot 16\text{H}_2\text{O}$ (MORF-Eu) was studied (cf. Figure S19). These
results provided evidence that the multi-component self-assembly systems shown in this report are strongly cation dependent, not only structurally, but with respect to the optical properties as well (e.g., photoluminescence spectrum properties).

Figure S19. The solid photoluminescence spectrum (a) and luminescence microscopy photos of crystalline sample of $[1^{+}\cdot(2)_5\cdot\text{Eu}_2\cdot2\text{H}_2\text{O}]$ (MORF-Eu) under white light (b) and luminescence under UV excitation (c). Image was acquired with automatic exposure timing using only green and red exposure to minimize the fluorescence from the crystal complex. Selected peak positions (nm) and relative intensities of the photoluminescence spectrum (panel (a)) are: (a): 590 nm, 32.3%; 614 nm, 100%; 651 nm, 2.41%; 687.5 nm, 9.95%; 697 nm, 21.9%; 700.5 nm, 32.2%.
PXRD studies of RSOF-Er materials obtained using different synthetic procedures

As can be seen from an inspection of Figure S20, the two separate products of MORF-Eu (A) and MORF-Eu (B) gave rise to similar PXRD spectra, leading us to suggest that these materials possess analogous, if not identical structures.

Figure S20. PXRD data for solid products MORF-Eu (A; trace A) and MORF-Eu (B; trace B). Also shown is the simulated PXRD spectra (trace T) based on data from a single crystal diffraction analysis of the metal-organic rotaxanated framework \([\text{1}^{4+}\cdot(2)_5\cdot\text{Eu}_2\cdot3\text{H}_2\text{O}]\cdot16\text{H}_2\text{O}\) (MORF-Eu (A)).
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.


