Electronic Supporting Information For:

Multi Component Self-Assembly: Supramolecular Organic Frameworks Containing Metal-Rotaxane Subunits (RSOFs)

Han-Yuan Gong, Brett M. Rambo, Cory A. Nelson, Won Cho, Vincent M. Lynch, Xiaoyang Zhu, Moonhyun Oh, and Jonathan L. Sessler

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. 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. Thermogravimetric analysis (TGA) measurement was carried out using a Shimadzu TGA-50 instrument in a nitrogen atmosphere at a heating rate of 10 °C/min over the temperature range of 25-850 °C. The nitrogen gas adsorption isotherm was measured in the gaseous state at 77K using a BELSORP II-mini volumetric adsorption setup.

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 files, and provide details regarding the specific crystal used for analysis, along with the structure in question.

The specific conditions used to obtain diffraction grade crystals were as follows: 7.5 μL of a 2.0 M aqueous solution of M(NO₃)₃ (M = Y, Gd, Er, Tm or Lu) 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 solution was allowed to stand. After 5 days, presumably as the result of slow diffusive mixing, colorless prisms of RSOF-M (M = Y, Gd, Er, Tm or Lu) (i.e., \([1^{4+}(2)\cdot Y_{2}\cdot 8H_{2}O\cdot 31H_{2}O\) (RSOF-Y), \([1^{4+}(2)\cdot Gd_{2}\cdot 8H_{2}O\cdot 22H_{2}O\) (RSOF-Gd), \([1^{4+}(2)\cdot Er_{2}\cdot 8H_{2}O\cdot 19H_{2}O\) (RSOF-Er), \([1^{4+}(2)\cdot Tm_{2}\cdot 8H_{2}O\cdot 32H_{2}O\) (RSOF-Tm), and \([1^{4+}(2)\cdot Lu_{2}\cdot 8H_{2}O\cdot 22H_{2}O\) (RSOF-Lu)), 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 (\(\lambda = 0.71073 \text{ Å}\)). The data were 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; these are available from the Cambridge Crystallographic Centre free of
charge by quoting ref. numbers 824440, 824442, 824441, 838076 and 838077. 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 3x with a 1:1 solution of dimethylformamide 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 spectra for the complex of 1⁺ and 2, R Sof-Y, R Sof-
Er and R Sof-Lu (as single crystals) were taken with an integration time of 0.5 seconds, an
emission slit width of 5 nm, and a step size of 1 nm.
**Synthetic routes to RSOF-M’s (M = Y, Gd, Er, Tm or Lu)**

The synthetic procedure used to obtain crystalline samples of the ROSF-M’s (M = Y, Gd, Er, Tm or Lu) were similar and involved the three-phase layering technique described above. The RSOF-Er (*i.e.*, \([\text{1}^{+}\cdot(2)_5\cdot\text{Er}_2\cdot8\text{H}_2\text{O}]\cdot19\text{H}_2\text{O}\)) was also obtained on large scale using a one-pot synthesis. These two approaches, product A from the small scale layering method and product B from the one-pot large scale synthesis, provided congruent material, as inferred from PXRD analyses (see main text and discussion below). Details of the bulk one-pot synthesis are provided below.

Macrocycle \(\text{1}^{+}\cdot4\text{PF}_6\^-\) (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 \(2\cdot2\text{H}^+\) in DMF and 6.25 mL of an aqueous 0.20 M solution of \(\text{NMe}_4\cdot\text{OH}\cdot5\text{H}_2\text{O}\). 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 \(\text{Er(NO}_3)_3\) 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 \(\text{1}^{+}\cdot4\text{PF}_6^-\) was then added as the upper layer. Upon addition, a pink 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 201 mg of a pink solid (product B). The yield was 71% based on the presumed congruence to sample A.
**PXRD studies of RSOF-Er materials obtained using different synthetic procedures**

As can be seen from an inspection of Figure S1, products A and B 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 (trace B) and B (trace B). Also shown is the calculated PXRD spectra (trace T) based on data from a single crystal diffraction analysis of the metal rotaxane supramolecular organic framework [1\(+\)•(2)\(_5\)•Er\(_2\)•8H\(_2\)O]•19H\(_2\)O (RSOF-Er; product A).](image-url)
X-Ray crystallographic study of RSOF-M (M = Y, Gd, Er, Tm or Lu)

Table S1. X-ray crystallographic data comparison of RSOF-M (i.e., \([1^{4+}(2)_3Y_2\cdot8H_2O\cdot31H_2O]\) (RSOF-Y), \([1^{4+}(2)_3Gd_2\cdot8H_2O\cdot22H_2O]\) (RSOF-Gd), \([1^{4+}(2)_3Er_2\cdot8H_2O\cdot19H_2O]\) (RSOF-Er), \([1^{4+}(2)_3Tm_2\cdot8H_2O\cdot32H_2O]\) (RSOF-Tm), and \([1^{4+}(2)_3Lu_2\cdot8H_2O\cdot22H_2O]\) (RSOF-Lu)).

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*The PLATON/SQUEEZE function was used to treat solvent distribution disorder.
In all the structures described here, 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 S2-S9. In the single crystal structure of RSOF-Er (i.e., [${\text{1}}^{4+}$·(2)$_3$·Er$_2$·8H$_2$O]·19H$_2$O), one anion (2), with O(1), inserts into the core of macrocycle 1$^{4+}$ resulting in the formation of a pseudorotaxane structure (cf. Figure S2). This observation is distinctly different from the ‘outside’ binding mode seen in the supramolecular complex formed directly from 1$^{4+}$ and 2 (cf. Figure S3)\textsuperscript{10}.

**Figure S2.** The pseudorotaxane complex found in the single crystal X-ray structure of RSOF-Er (i.e. [${\text{1}}^{4+}$·(2)$_3$·Er$_2$·8H$_2$O]·19H$_2$O). (a) Atom-labeling scheme for the pseudorotaxane complex [${\text{1}}^{4+}$·(2)·Er]$_8^{8+}$ fragment present in [${\text{1}}^{4+}$·(2)$_3$·Er$_2$·8H$_2$O]·19H$_2$O. Top view, (b) and side views (c), (d) of the [${\text{1}}^{4+}$·(2)·Er]$_8^{8+}$ pseudorotaxane structure. Displacement ellipsoids are scaled to the 40% probability level. The entire assembly sits around a crystallographic inversion center at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. The symmetry transformation invoked by the additional "A" letter in the atom labels is (1-x,1-y,1-z). Selected interatomic distances [Å] for possible $\pi$–$\pi$ donor acceptor interactions: C(14)$\cdot$C(37) 3.703(8), C(15)$\cdot$C(38) 3.741(9), C(16)$\cdot$C(37) 3.550(9), C(17)$\cdot$C(39) 3.747(9), C(19)$\cdot$C(38) 3.771(9); Selected interatomic distances [Å] for possible intermolecular hydrogen bond interactions: C(10)$\cdot$O(9) 3.252(8) and C(2)$\cdot$O(9) 2.980(8).
In the supramolecular complex formed directly from $1^{4+}$ and $2 \cdot H^+$ ($1^{4+}:(2 \cdot H^+):(PF_6)_3 \cdot 2H_2O$), which also forms a pseudorotaxane structure in the solid state, the $\pi$-surface of anion $2 \cdot H^+$ sits parallel to that of the 2,6-di(1H-imidazol-1-yl)pyridine fragments present in $1^{4+}$ (cf. Figure S3 b3). In the case of the complex formed from the trivalent metal cation Er(III) (RSOF-Er; $[1^{4+}:(2)_2 \cdot Er_2 \cdot 8H_2O] \cdot 19H_2O$) a different ‘insertion mode’ between the macrocycle and anionic species is observed. Specifically, the $\pi$-surface of anion 2 lies parallel to that of the bridging benzene rings present in $1^{4+}$ (cf. Figure S3 a3). The conformation of $1^{4+}$ differs in the pseudorotaxane units found in these two representative structures, with yet additional differences being seen in the case of the neutral, metal-free complex formed from $1^{4+}$ and 2 (i.e., $1^{4+}:2 \cdot 10H_2O$) (cf. Figure S3 c3). These differences are illustrated in Figure S3.

**Figure S3.** Comparison of the binding modes of the supramolecular complexes between $1^{4+}$ and 2 (or $2 \cdot H^+$) in single crystal X-ray structures of RSOF-Er (i.e., $[1^{4+}:(2)_2 \cdot Er_2 \cdot 8H_2O] \cdot 19H_2O$) (a1,3), $1^{4+}:(2 \cdot H^+):(PF_6)_3 \cdot 2H_2O$ (b1,3), and $1^{4+}:2 \cdot 10H_2O$ (c1,3). The other anions and solvent molecules present in the crystalline lattice have been omitted for clarity.

In RSOF-Er, the inserted anionic moiety (2) is further complexed with Er(III) cations, an interaction that serves to link this first anionic subunit with two other non-interpenetrated
naphthalene dicarboxylate anions via O (3) or O (7). Thus, three anionic species and 4 water ligands are bound to one Er(III) cation, which results in the formation of a metal rotaxane complex (cf. Figure S4). The carboxylate anion containing O(7) (labeled blue in the framework depiction of Figure S4) lies parallel to the neighboring 2,6-di(1H-imidazol-1-yl)pyridine fragment. A strong π-π donor-acceptor interaction is inferred from the short distance (less than 3.4 Å) between the two units in question (cf. Figure S4).

**Figure S4.** The metal rotaxane subunit ([1\(^{4+}\)·(2)\(_{5}\)·Er\(_{2}\)·8H\(_{2}\)O]) found within the overall structure of RSOF-Er (i.e., [1\(^{4+}\)·(2)\(_{5}\)·Er\(_{2}\)·8H\(_{2}\)O]·19H\(_{2}\)O) as deduced from a single crystal X-ray diffraction analysis. (a) Atom-labeling scheme for this subunit. Top view, (b) and side views (c), (d) of the [1\(^{4+}\)·(2)\(_{5}\)·Er\(_{2}\)·8H\(_{2}\)O] of the metal rotaxane subunit structure. Displacement ellipsoids are scaled to the 40% 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] for possible π···π and/or anion···π donor acceptor interactions: N(3)···C(21) 3.420(8), C(5)···C(26) 3.366(9), C(6)···C(25) 3.518(9), C(7)···C(24)
The complexation mode of Er(III) is shown below in detail (Figure S5). Three anions and four water ligands bind with one Er(III) cation to give a coordination number of eight. Strong hydrogen bonding interactions with the neighboring sub-units are inferred from the structural parameters (cf. Figure S5b).

**Figure S5.** Partial view of the experimentally determined structure of RSOF-Er (i.e., [1\(^{4+}\)·(2)\(_{2}\)·Er\(_{2}\)·8H\(_{2}\)O·19H\(_{2}\)O) displayed in stick forms, demonstrating the complexation geometry about a single Er\(^{3+}\) center (a) and the relationship to neighboring Er\(^{3+}\) centers (b). The symmetry transformations invoked by the Er\(^{3+}\)(1a) and Er\(^{3+}\)(1b) for Er\(^{3+}\)(1) are (2.5-x,-1/2+y,1.5-z) and (1/2+x, 1.5-y, -1/2+z), respectively. Presumed intermolecular hydrogen bonding linkages between one Er\(^{3+}\) cation and neighboring rotaxane subunits present in the structure are labeled with red dashed lines. Selected interatomic distances about the Er\(^{3+}\) center [Å]: O(1)···Er(1) 2.315(5), O(5)···Er(1) 2.293(4), O(9)···Er(1) 2.361(4), O(10)···Er(1) 2.499(4), O(1W)···Er(1) 2.350(5), O(2W)···Er(1) 2.360(4), O(3W)···Er(1) 2.337(5) and O(4W)···Er(1) 2.345(5); selected interatomic angles about the Er\(^{3+}\) center: O(9)···Er(1)···O(1) 75.9(2)°, O(9)···Er(1)···O(1W)
86.1(2)°, O(9)···Er(1)···O(2W) 82.9(1)°, O(9)···Er(1)···O(3W) 89.8(2)°, O(9)···Er(1)···O(4W) 132.3(2)°, O(10)···Er(1)···O(1) 120.2(1)°, O(10)···Er(1)···O(1W) 70.7(2)°, O(10)···Er(1)···O(2W) 124.2(1)°, O(10)···Er(1)···O(3W) 77.2(2)°, O(10)···Er(1)···O(4W) 78.6(1)°, O(5)···Er(1)···O(1) 83.0(2)°, O(5)···Er(1)···O(1W) 102.2(2)°, O(5)···Er(1)···O(2W) 76.8(1)°, O(5)···Er(1)···O(3W) 97.1(2)°, O(5)···Er(1)···O(4W) 73.1(2)°, O(1)···Er(1)···O(2W) 70.3(2)°, O(2W)···Er(1)···O(1W) 73.5(2)°, O(1W)···Er(1)···O(4W) 78.7(2)°, O(4W)···Er(1)···O(3W) 77.1(2)°, O(3W)···Er(1)···O(1) 72.2(2)° and O(9)···Er(1)···O(10) 53.7(1)°. Selected interatomic distances [Å] for presumed intermolecular hydrogen bonding interactions: O(1W)···O(8A) 2.635(8), O(2W)···O(7A) 2.644(7) and O(4W)···O(4B) 2.664(7).

A different view of the structure of RSOF-Er (i.e., [1⁺·(2)·Er₂·8H₂O]·19H₂O) is shown in Figure S6. This presentation is designed to facilitate visualization of the 1D pseudo-polyrotaxane chains present within the overall structure. These rotaxane units involve interactions between anion 2 (labeled with green color) through with O(5) with O(1W) and O(2W) (shown in magenta) on neighboring rotaxane units; here, anions which branch off from the chain via O(7) are labeled in dark blue.
**Figure S6.** The 1D pseudo-polyrotaxane sub-structure present within the single crystal X-ray structure of RSOF-Er (i.e., [I^{4+}·(2)Er_2·8H_2O]·19H_2O).

It is important to note that the individual pseudo-polyrotaxane chains are oriented in two directions within the overall 3-D SOF structure. This results in 2D pseudo-polyrotaxane network as shown in Figure S7 (same color scheme as Figure S6).

![Partial view of the experimentally determined structure of [I^{4+}·(2)Er_2·8H_2O]·19H_2O (RSOF-Er) displayed in stick form so as to illustrate the 2D network that is presumably stabilized as the result of intermolecular hydrogen bonds between anion 2 (labeled with green color) through O(5) and O(1W) and O(2W) (shown in magenta) on the neighboring rotaxane units.](image)

The pseudo-polyrotaxane subunits described above are linked to each other through a series of hydrogen bonding interactions between the anionic species (2) via O(9) (shown in dark blue color) and O(4W) on the neighbor rotaxane network layers (cf. Figure S8).
**Figure S8.** Partial view of the experimentally determined structure of $[\text{1}^{4+}\cdot(\text{2})_5\cdot\text{Er}_2\cdot8\text{H}_2\text{O}]\cdot19\text{H}_2\text{O}$ (RSOF-Er) shown in stick form. This view is designed to illustrate the 2D network that is presumably stabilized via the interactions between the anionic species (2) (labeled in green) through O(5) and O(1W) and O(2W) (shown in magenta) on the neighboring rotaxane units. Hydrogen bonds between the anionic species (2) through O(9) (dark blue) and O(4W) on the neighboring rotaxane network layers are also shown.

Figure S9 shows the packing diagrams for $[\text{1}^{4+}\cdot(\text{2})_5\cdot\text{Er}_2\cdot8\text{H}_2\text{O}]\cdot19\text{H}_2\text{O}$ (RSOF-Er). All the anions (2) are bound to the Er(III) cation and result in the formation of a metal rotaxane with $1^{4+}$ being threaded by a salt-like structure. Within the overall structure, the disparate $[\text{1}^{4+}\cdot(\text{2})_5\cdot\text{Er}_2\cdot8\text{H}_2\text{O}]$ rotaxane units are linked to each other to form a 2D rotaxane network via intermolecular hydrogen bonding interactions between the anionic oxygen atoms O(5 and 6) (labeled in green) and O(1W), and also O(2W) on the neighboring rotaxane units. The connection between the anionic species (shown in dark blue) and the neighboring rotaxane network layers through O(9) and O(4W), respectively, in conjunction with the previously described interactions leads to the overall 3D metal-rotaxane containing supramolecular organic framework observed in the single crystal structure of RSOF-Er).
**Figure S9.** Framework (a) and space-filling (b) views of the packing diagram for the 3D metal-rotaxane containing supramolecular framework, RSOF-Er, as determined from the single crystal X-ray structure of $[1^{4+}(2)_5\cdot Er_2\cdot 8H_2O]\cdot 19H_2O$.

The other four RSOFs of this report (i.e., $[1^{4+}(2)_5\cdot Y_2\cdot 8H_2O]\cdot 31H_2O$ (RSOF-Y), $[1^{4+}(2)_5\cdot Gd_2\cdot 8H_2O]\cdot 22H_2O$ (RSOF-Gd), $[1^{4+}(2)_5\cdot Tm_2\cdot 8H_2O]\cdot 32H_2O$ (RSOF-Tm), and $[1^{4+}(2)_5\cdot Lu_2\cdot 8H_2O]\cdot 22H_2O$ (RSOF-Lu)) displayed similar structures, packing modes, and lattice cell parameters as RSOF-Er (i.e., $[1^{4+}(2)_5\cdot Er_2\cdot 8H_2O]\cdot 19H_2O$). They were also found to form similar 3D metal-rotaxane containing supramolecular frameworks in the solid state as determined from single crystal X-ray diffraction analyses. They are thus not discussed further here. However, full details of the structures may be obtained from the .cif documents, which may be obtained from the Cambridge Crystallographic Data Centre by quoting CCDC Nos. 824440, 838076, 824442, 838077, and 824441.

**Analysis of RSOF-Er and its properties**

Thermogravimetric analysis (TGA) of the representative bulk sample, i.e., $[1^{4+}(2)_5\cdot Er_2\cdot 8H_2O]\cdot 19H_2O$ (RSOF-Er), revealed a weight decrease corresponding to the loss of
the free and bound solvent (H$_2$O). The TGA measurement was carried out by increasing the temperature from 25 °C to 850 °C at a ramping rate of 10 °C/min, and the observed weight loss compared to that expected for the theoretical loss of water molecules, as discussed in the text proper.

The nitrogen gas adsorption isotherm was determined at 77 K (Figure S10). The study revealed features consistent with a low porosity material that displays multilayer adsorption behavior.

![Nitrogen adsorption isotherm at 77 K](image)

**Figure S10.** Nitrogen adsorption isotherm at 77 K for [1$^{4+}$·(2)$_3$:Er$_2$:8H$_2$O]·19H$_2$O (RSOF-Er).

Luminescence microscopic and photoluminescence spectral analyses were carried out for three of the crystalline complexes, namely [1$^{4+}$·(2)$_3$:Y$_2$:8H$_2$O]·31H$_2$O (RSOF-Y), [1$^{4+}$·(2)$_3$:Er$_2$:8H$_2$O]·19H$_2$O (RSOF-Er) and [1$^{4+}$·(2)$_3$:Lu$_2$:8H$_2$O]·22H$_2$O (RSOF-Lu), produced in the context of this study (*cf.* Figure S11 to 14).

As a control, crystalline samples of 1$^{4+}$·(2)$_2$:10H$_2$O were produced and analyzed. Upon photoexcitation at 310 nm, these crystals gave rise to a broad emission band that tailed off from 325 to 750 nm. The sample also looked green under conditions of luminescent spectroscopy. Since no metal cations were present in the sample, it is postulated that the interaction between 1$^{4+}$ and 2 is responsible for both the sloping background seen in the fluorescence spectra and the green appearance of the crystals in the microscopy images.
**Figure S11.** Solid photoluminescence spectrum (a) with (red) and without (black) a 500 nm long wave pass filter, (b) luminescence microscopy photos of crystalline sample of $\text{1}^{4+}$-$\text{(2)}_2$-$\text{10H}_2\text{O}$ under white light, and (c) under UV excitation. 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.

Under identical detection conditions, similar luminescence microscopy photos were observed for all three of the RSOFs studied here; namely $[\text{1}^{4+}$-$\text{(2)}_5$-$\text{Er}_2$-$\text{8H}_2\text{O}]$-$\text{19H}_2\text{O}$ (RSOF-Er), $[\text{1}^{4+}$-$\text{(2)}_5$-$\text{Y}_2$-$\text{8H}_2\text{O}]$-$\text{31H}_2\text{O}$ (RSOF-Y) and $[\text{1}^{4+}$-$\text{(2)}_5$-$\text{Lu}_2$-$\text{8H}_2\text{O}]$-$\text{22H}_2\text{O}$ (RSOF-Lu). In particular, the photoluminescence spectra of all the three RSOF structures revealed a broad peak similar to that observed in the complex of $\text{1}^{4+}$-$\text{(2)}_2$-$\text{10H}_2\text{O}$. However, distinctive peaks ascribable to the different trivalent rare earth cations were seen in the case of the Y(III) and Lu(III) samples, as can be seen by inspection of Figure 7 in the main text and Figures S22-24 below.
**Figure S12.** Solid state photoluminescence spectrum (a) and luminescence microscopy photos of a crystalline sample of $[\text{I}^{4+} \cdot (2)_5 \cdot \text{Er}_2 \cdot 8\text{H}_2\text{O}] \cdot 19\text{H}_2\text{O}$ (RSOF-Er) recorded under white light (b) and UV excitation (c). 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.

**Figure S13.** The solid photoluminescence spectrum (a) and luminescence microscopy photos of a crystalline sample of $[\text{I}^{4+} \cdot (2)_5 \cdot \text{Y}_2 \cdot 8\text{H}_2\text{O}] \cdot 31\text{H}_2\text{O}$ (RSOF-Y) under white light (b) and UV excitation (c). 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. Note the peak at 543 nm.
**Figure S14.** The solid photoluminescence spectrum (a) and luminescence microscopy photos of crystalline sample of \([\text{[1}^{4+} \cdot (2)_5 \cdot \text{Lu}_2 \cdot 8\text{H}_2\text{O}] \cdot 22\text{H}_2\text{O} \text{ (RSOF-Lu)}\] under white light (b) and luminescence under UV excitation (c). 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. Selected peak positions (nm) and relative intensities of the photoluminescence spectra normalized to the largest feature (a): 531 nm, 84.4%; 542 nm, 78.4%; 590 nm, 41.5%; 614 nm, 100%.

**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.


