

Invisible Strings. The first single crystal of the cTSAP form of [Eu(DOTA)(H₂O)]⁻ has an electronic structure similar to one of the reported cSAP forms

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Supporting Information

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Contents

1. Crystal pictures	S2
2. Single-crystal luminescence spectroscopy setup	S3
3. Crystallographic Information.....	S4
4. ORTEP representations of Sr[Eu(DOTA)(H ₂ O)]NO ₃ and Y[Eu(DOTA)(H ₂ O)]Cl ₂	S5
5. Emission spectra of Gd[Eu(DOTA)(H ₂ O)]Cl ₂ , Y[Eu(DOTA)(H ₂ O)]Cl ₂ , Sr[Eu(DOTA)(H ₂ O)]NO ₃ and Ba[Eu(DOTA)(H ₂ O)]X	S8
6. Emission spectrum of Na[Eu(DOTA)(H ₂ O)] - ⁵ D ₀ → ⁷ F ₁ transition.....	S10
7. Excitation spectra.....	S11
8. Time-resolved luminescence decay	S12
9. Curve fitting for crystal field parameter determination	S14
1. AlignIt Link and Guide.....	S19
10. Comparative scale of symmetry deviation values, σ _{ideal} , for nine-coordinated ideal polyhedra	S22
11. References	S23

1. Crystal pictures

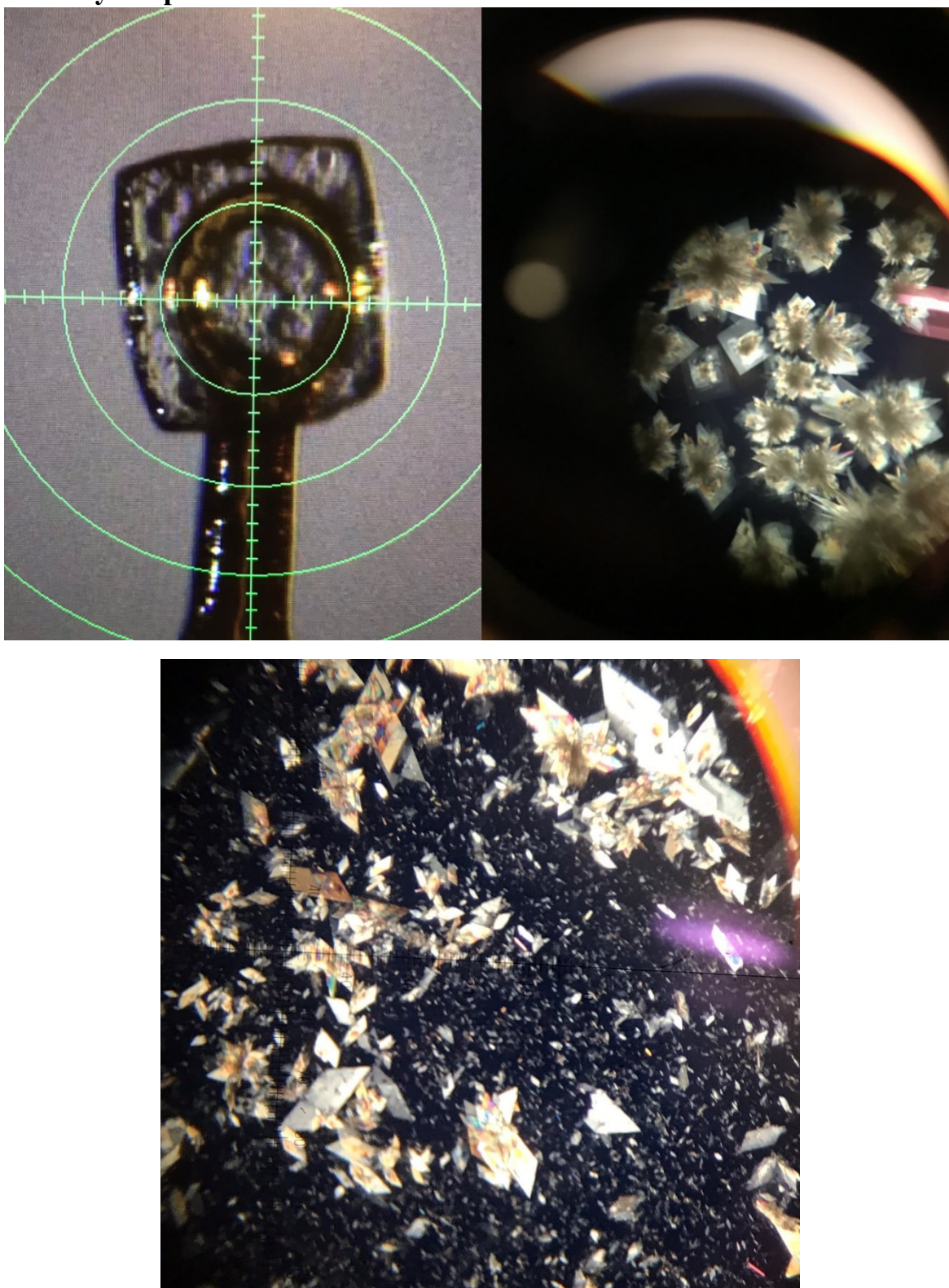


Figure S1. Crystal pictures of (top, left) $\text{Y}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$, (top, right) For $\text{Gd}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$, (bottom) $\text{Sr}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{NO}_3$

2. Single-crystal luminescence spectroscopy setup

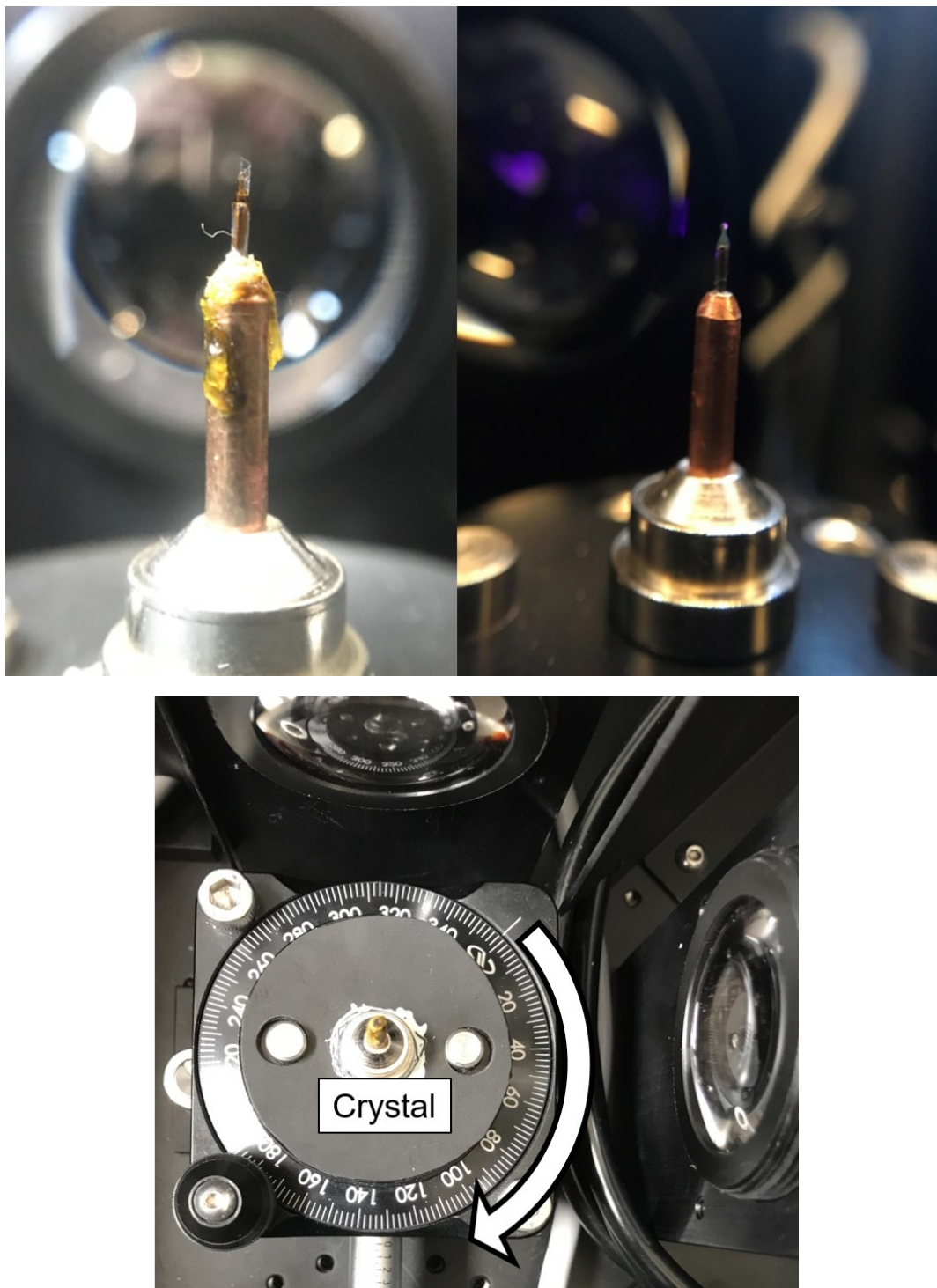


Figure S2. Single-crystal luminescence set-up. Top (left): Single crystal on diffractometer mounting loop. Top (right): Eu(III) ion containing crystal excited at 394 nm. Bottom: Setup platform

3. Crystallographic Information

Table S1. Crystallographic information

Empirical formula	$C_{16}H_{44.8}Cl_{2.52}Eu_{0.96}N_4O_{19}Y$	$C_{16}H_{49}Cl_{2.46}EuGdN_4O_{19}$	$C_{16}H_{34}EuN_5O_{16}Sr$
Formula weight	921.95	997.83	792.06
Temperature/K	100	100.00	100.00
Crystal system	tetragonal	tetragonal	triclinic
Space group	I422	I422	P-1
a/Å	8.8351(6)	8.8814(7)	8.9141(14)
b/Å	8.8351(6)	8.8814(7)	9.2988(15)
c/Å	41.578(4)	41.505(5)	15.741(3)
$\alpha/^\circ$	90	90	85.531(6)
$\beta/^\circ$	90	90	82.580(6)
$\gamma/^\circ$	90	90	83.711(6)
Volume/Å ³	3245.5(6)	3273.9(6)	1283.4(4)
Z	4	4	2
$\rho_{\text{calc}}/\text{cm}^3$	1.887	2.024	2.050
μ/mm^{-1}	3.912	4.188	4.585
F(000)	1853.0	1975.0	788.0
Crystal size/mm ³	0.36 × 0.312 × 0.034	0.748 × 0.61 × 0.034	0.522 × 0.375 × 0.08
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.918 to 61.974	4.69 to 72.618	2.614 to 54.206
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -60 ≤ l ≤ 60	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -69 ≤ l ≤ 69	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -20 ≤ l ≤ 20
Reflections collected	80579	46223	38046
Independent reflections	2613 [$R_{\text{int}} = 0.0931$, $R_{\text{sigma}} = 0.0261$]	4000 [$R_{\text{int}} = 0.0790$, $R_{\text{sigma}} = 0.0331$]	5667 [$R_{\text{int}} = 0.0693$, $R_{\text{sigma}} = 0.0431$]
Data/restraints/parameters	2613/0/122	4000/12/120	5667/12/376
Goodness-of-fit on F ²	1.088	1.069	1.068
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0237$, $wR_2 = 0.0542$	$R_1 = 0.0291$, $wR_2 = 0.0747$	$R_1 = 0.0364$, $wR_2 = 0.0763$
Final R indexes [all data]	$R_1 = 0.0269$, $wR_2 = 0.0554$	$R_1 = 0.0343$, $wR_2 = 0.0774$	$R_1 = 0.0422$, $wR_2 = 0.0783$
Largest diff. peak/hole / e Å ⁻³	0.73/-1.29	1.70/-3.17	1.70/-1.57
Flack parameter	0.022(13)	0.09(2)	

4. ORTEP representations of $\text{Sr}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{NO}_3$ and $\text{Y}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$

The structures $\text{Y}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$ and $\text{Gd}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$ are isostructural, therefore only the former shown.

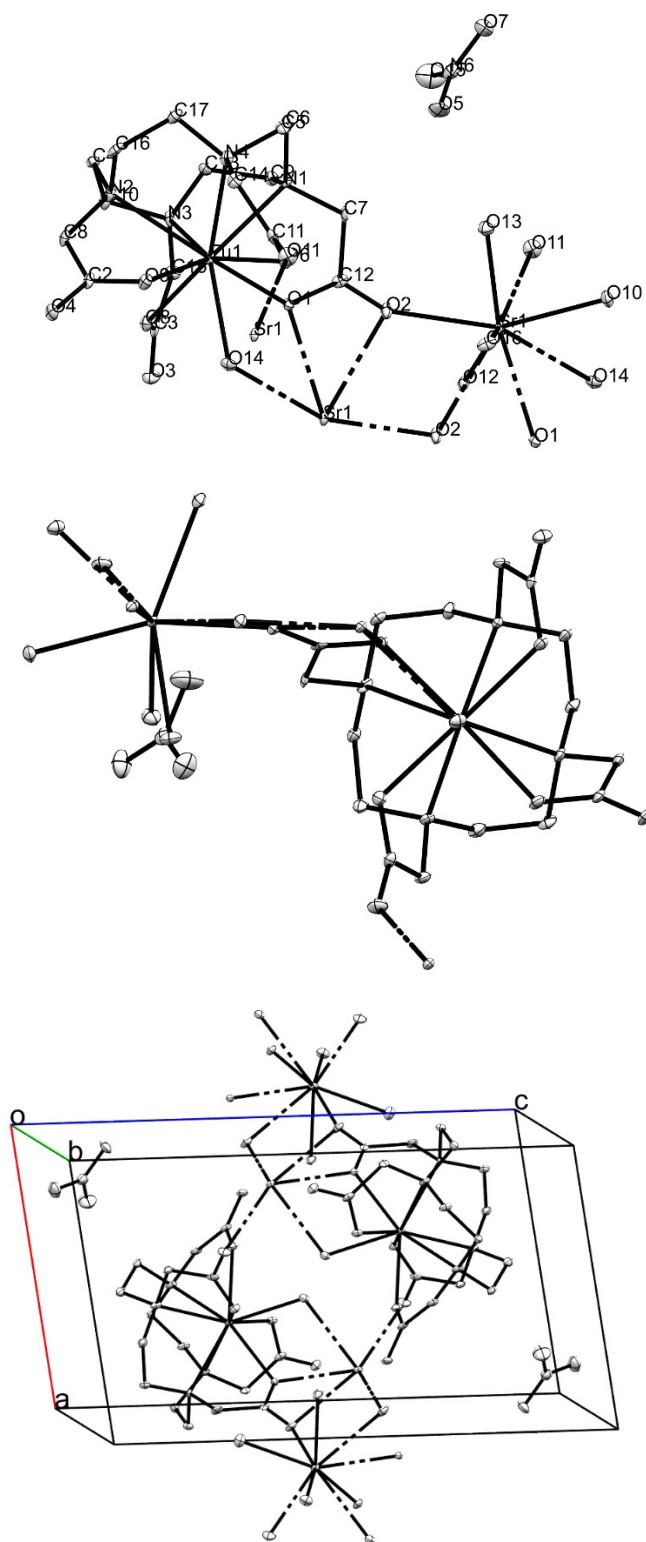


Figure S3. ORTEP representation of Sr[Eu(DOTA)(H₂O)]NO₃. Top: Labeled complex. Middle: Looking through the capping water molecule. Bottom: Unit cell packing.

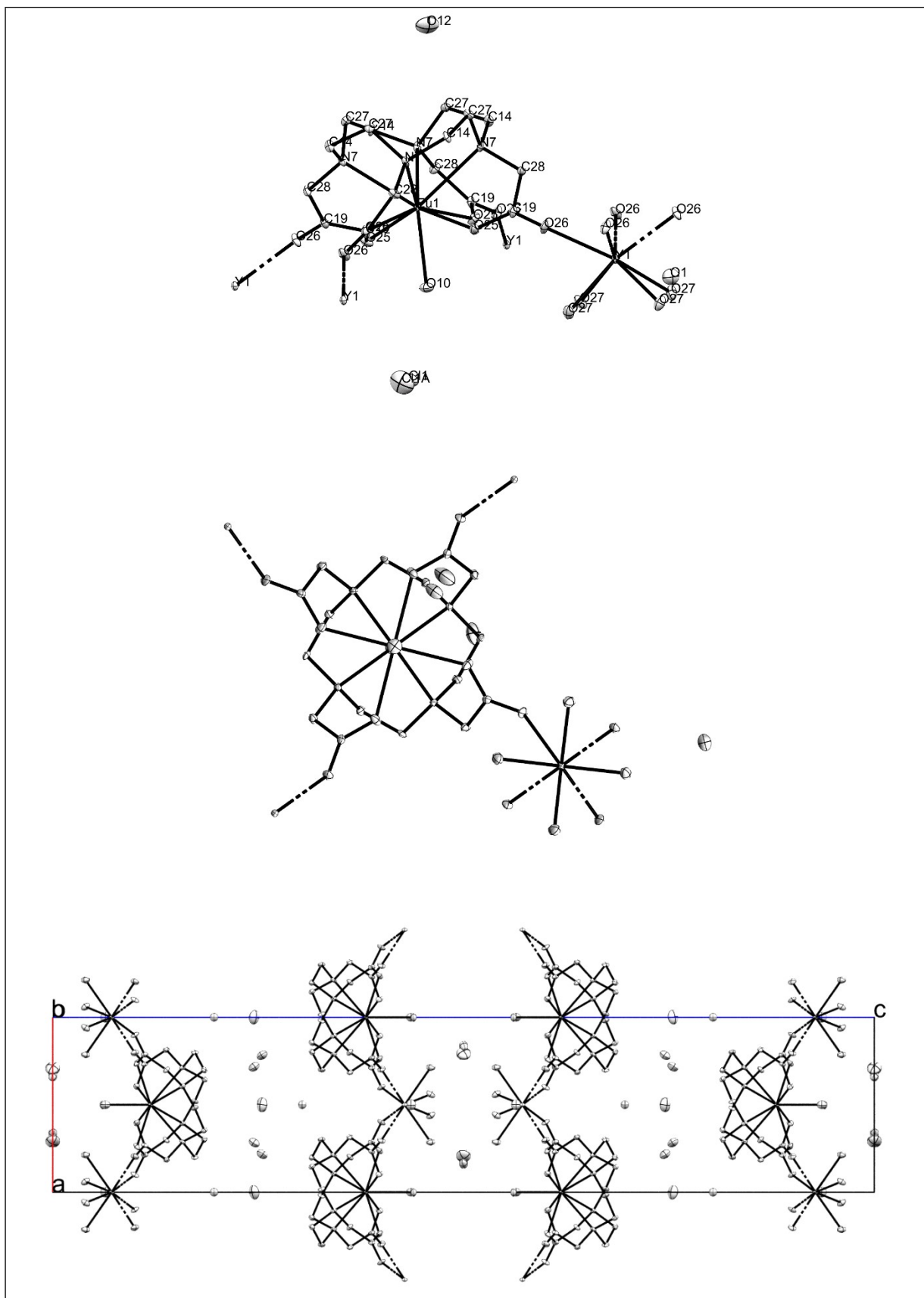
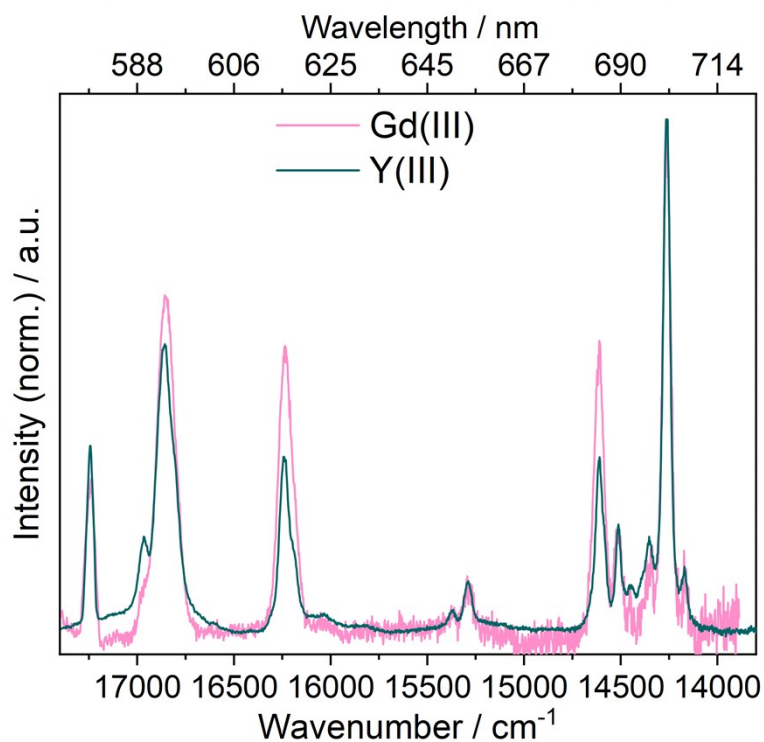


Figure S4. Figure S3. ORTEP representation of $\text{Y}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$. Top: Labelled complex. Middle: Looking through the capping water molecule. Bottom: Unit cell packing.

5. Emission spectra of $\text{Gd}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$, $\text{Y}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$, $\text{Sr}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{NO}_3$ and $\text{Ba}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{X}$



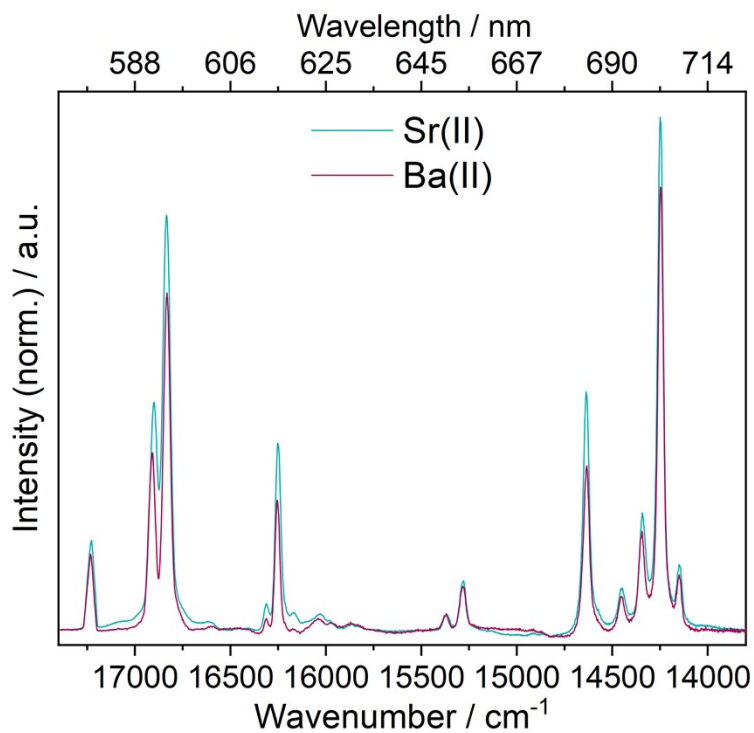


Figure S5. Normalised emission spectra of (top) $\text{Y}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$ and $\text{Gd}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$, (bottom) $\text{Sr}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{NO}_3$ and $\text{Ba}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{X}$. Ex. = 394 nm. Slits (ex.) = 8 nm, (em.) = 1.5 nm.

6. Emission spectrum of Na[Eu(DOTA)(H₂O)] - ⁵D₀ → ⁷F₁ transition

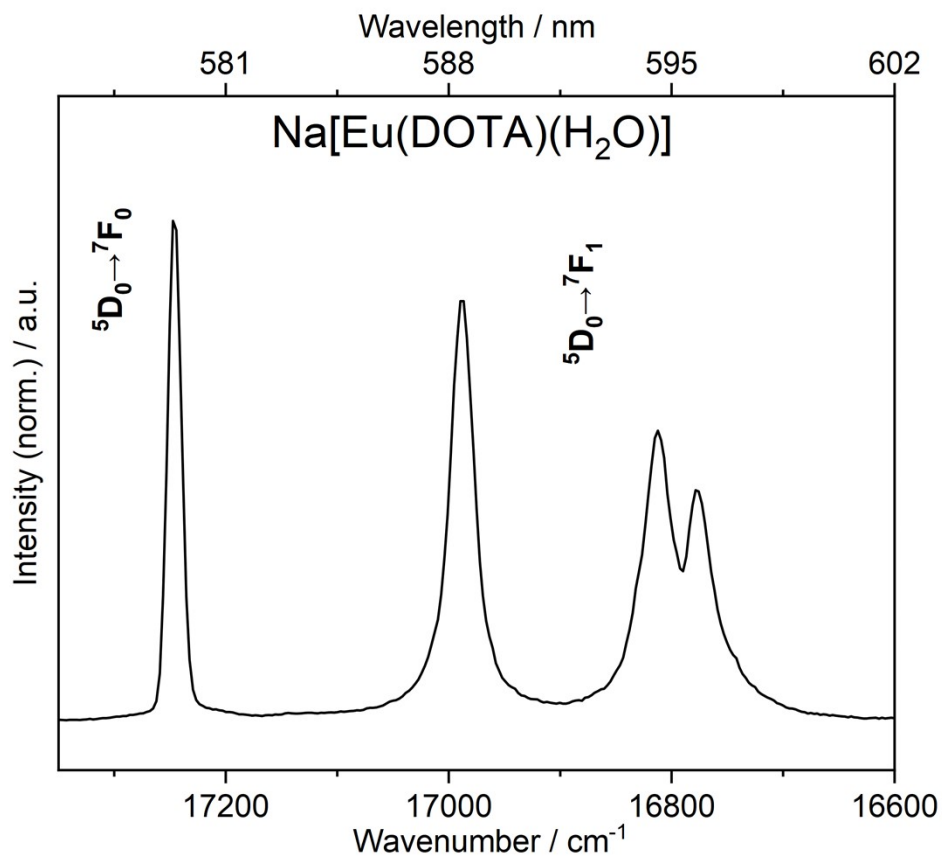


Figure S6. Normalised emission spectrum of Na[Eu(DOTA)(H₂O)]. Ex. = 394 nm. Slits (ex.) = 8 nm, (em.) = 1.0 nm.

7. Excitation spectra

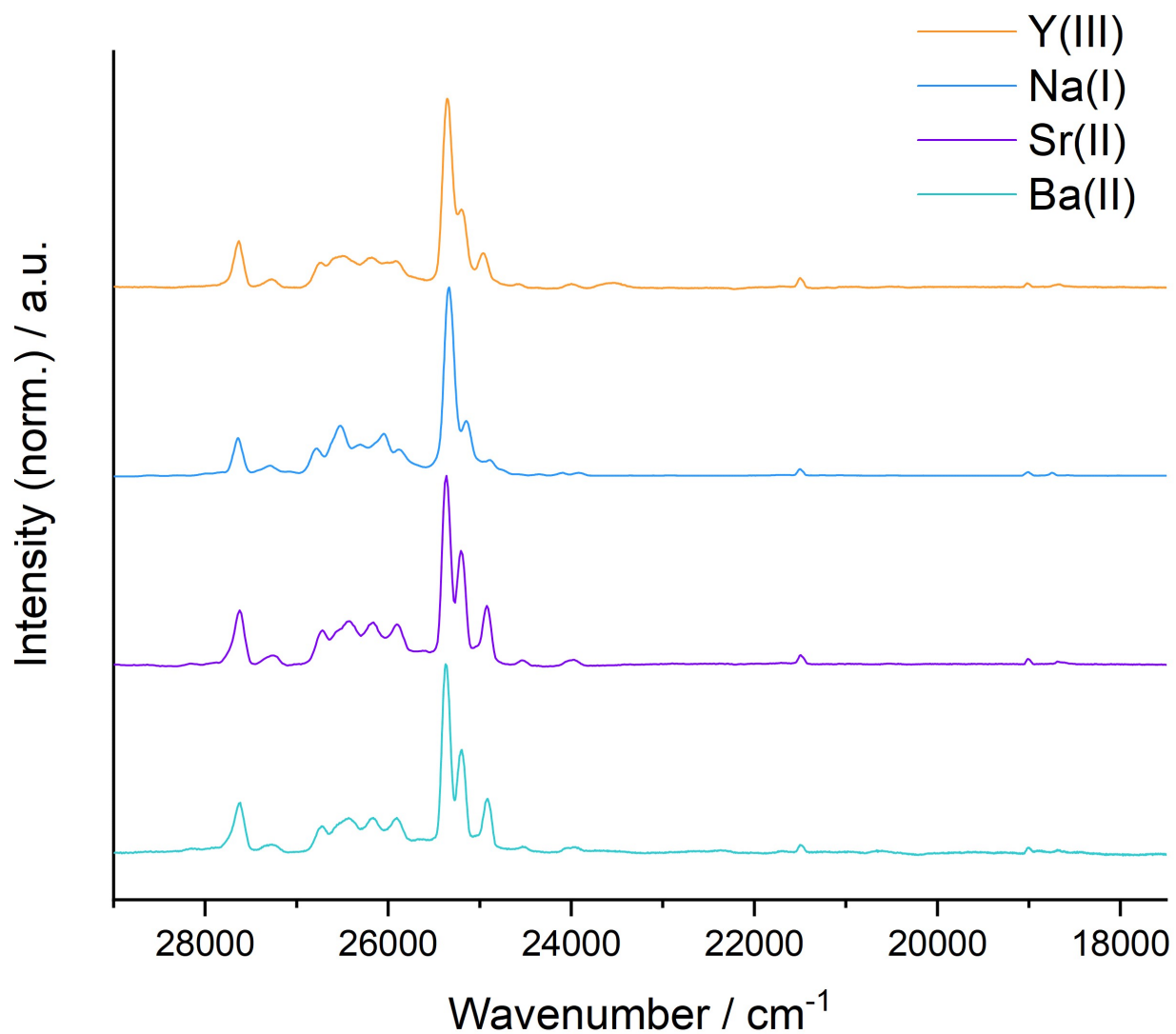


Figure S7. Normalised excitation spectra of $\text{Y}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$, $\text{Na}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]$, $\text{Sr}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{NO}_3$ and $\text{Ba}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{X}$. Em. = 614 nm. Slits (em.) = 8 nm, (ex.) = 1.5 nm.

8. Time-resolved luminescence decay

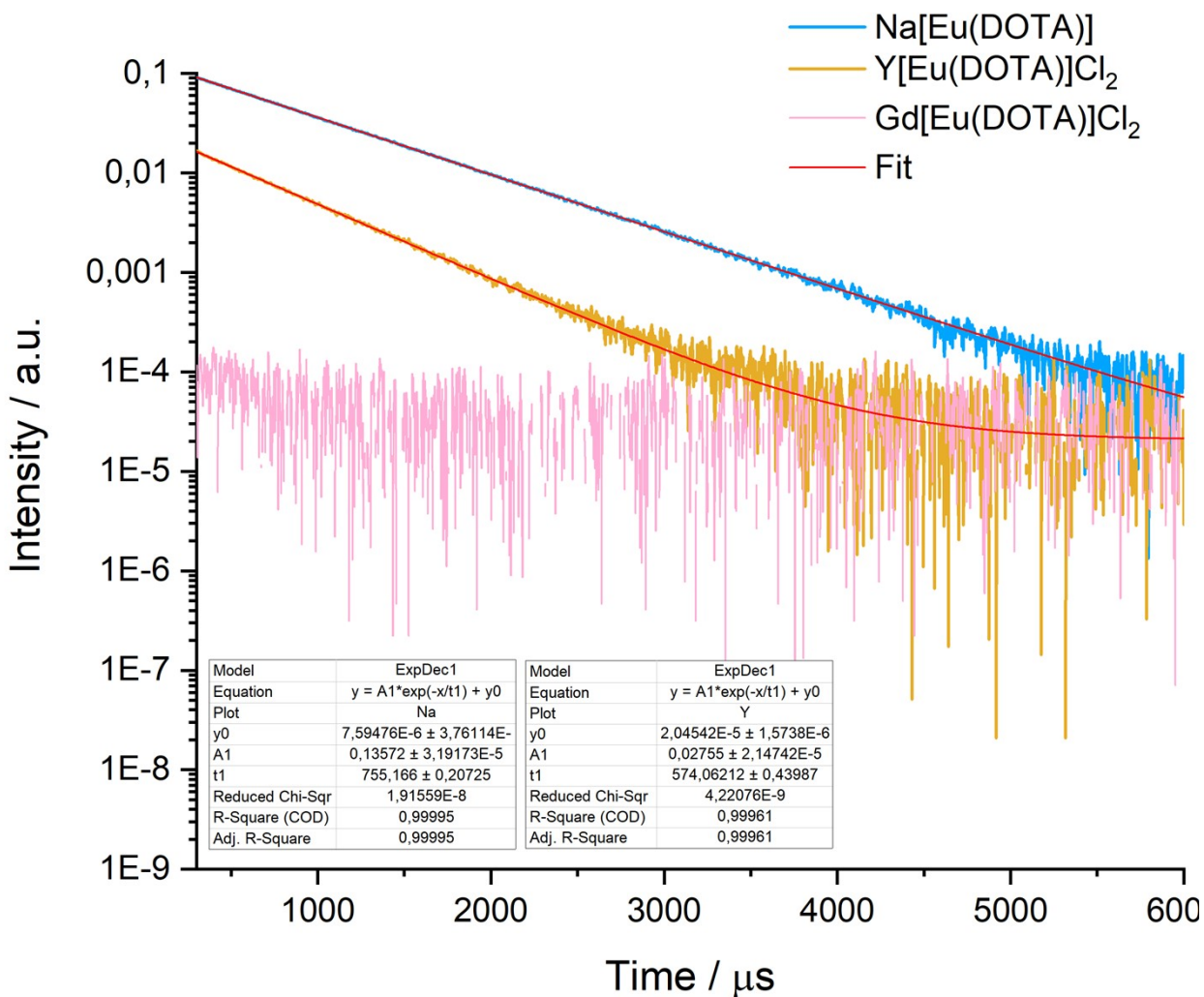


Figure S8. Time-resolved luminescence decay for Y[Eu(DOTA)(H₂O)]Cl₂, Y[Eu(DOTA)(H₂O)]Cl₂ and Na[Eu(DOTA)(H₂O)]. Ex. = 394 nm, em. = 614 nm.

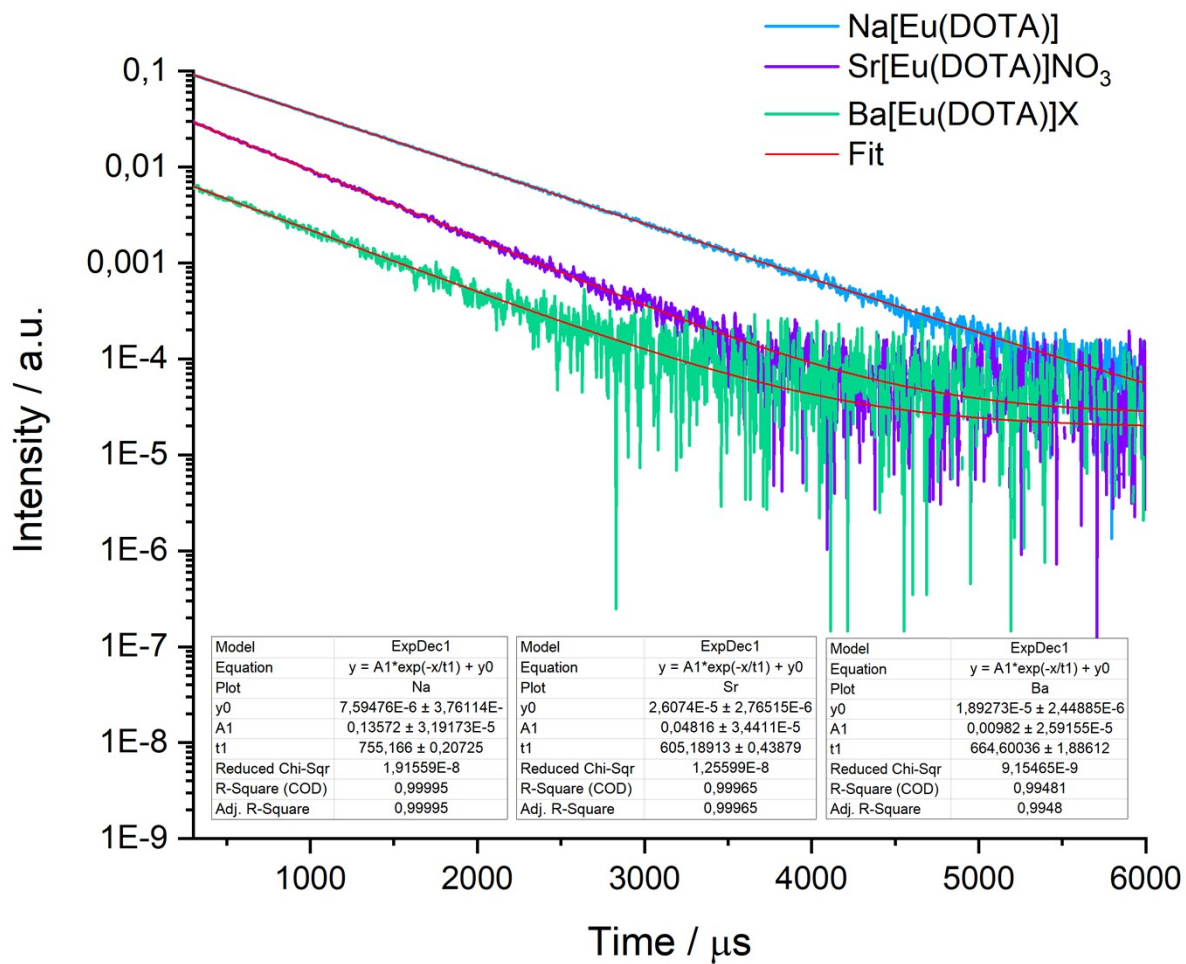


Figure S9. Time-resolved luminescence decay for Na[Eu(DOTA)(H₂O)], Sr[Eu(DOTA)(H₂O)]NO₃ and Ba[Eu(DOTA)(H₂O)]X. Ex. = 394 nm, em. = 614 nm.

9. Curve fitting for crystal field parameter determination

Table S2. Peak fitting to three Gaussian curves fit in the ${}^5D_0 \rightarrow {}^7F_1$ transition band.

7F_1	Peak 1 / cm^{-1}	Peak 2 / cm^{-1}	Peak 3 / cm^{-1}
Y(III)	16968	16865	16800
Na(I)	16986	16819	16794
Sr(II)	16902	16824	-

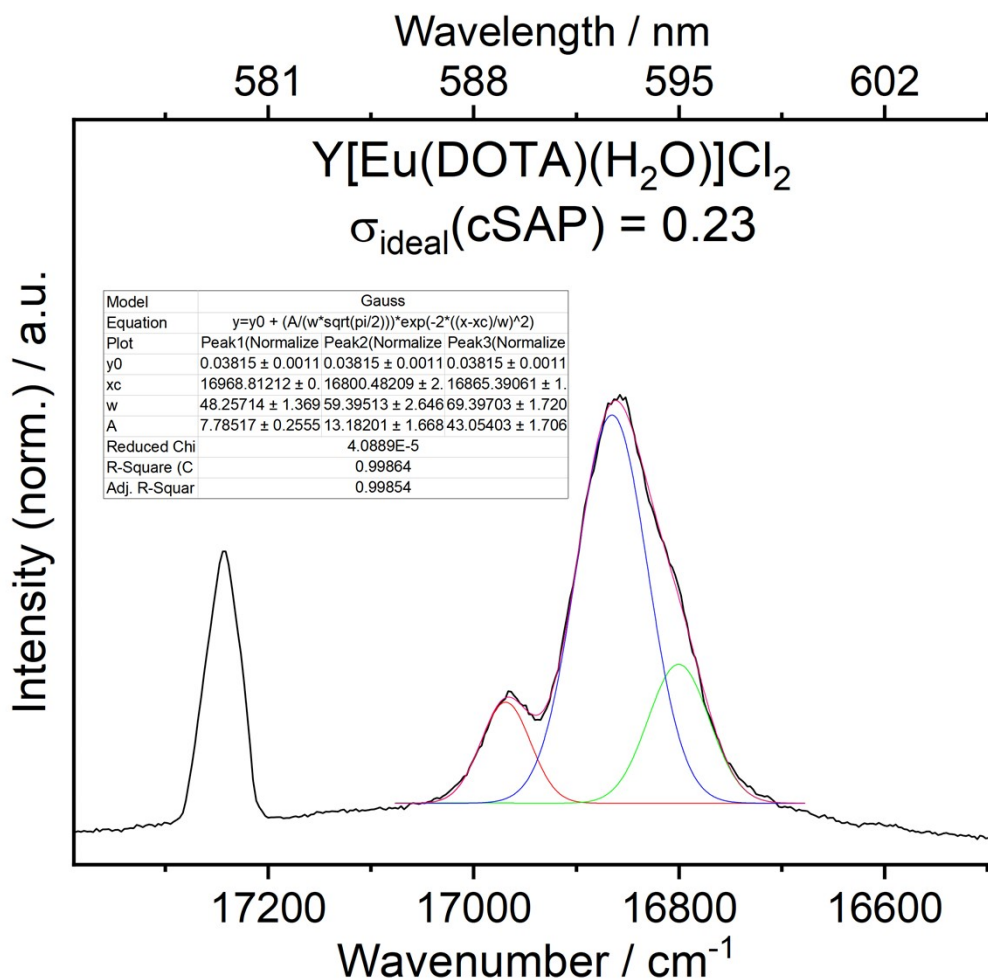


Figure S10. Peak fitting to three Gaussian curves fit in the ${}^5D_0 \rightarrow {}^7F_1$ transition band for $\text{Y}[\text{Eu}(\text{DOTA})(\text{H}_2\text{O})]\text{Cl}_2$,

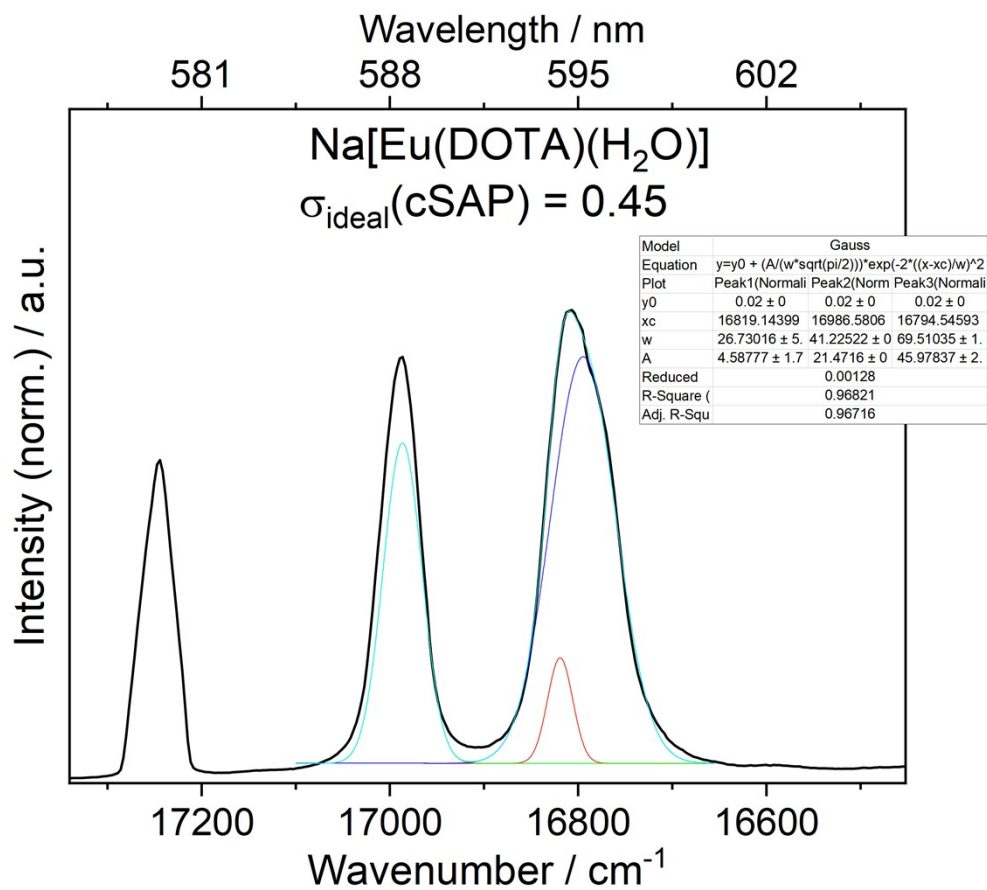


Figure S11. Peak fitting to three Gaussian curves fit in the $^5D_0 \rightarrow ^7F_1$ transition band for Na[Eu(DOTA)(H₂O)].

Table S3. Peak fitting to two Gaussian curves fit in the $^5D_0 \rightarrow ^7F_1$ transition band.

7F_1	Peak 1 / cm^{-1}	Peak 2 / cm^{-1}
Y(III)	16977	16854
Na(I)	16988	16798
Sr(II)	16902	16824

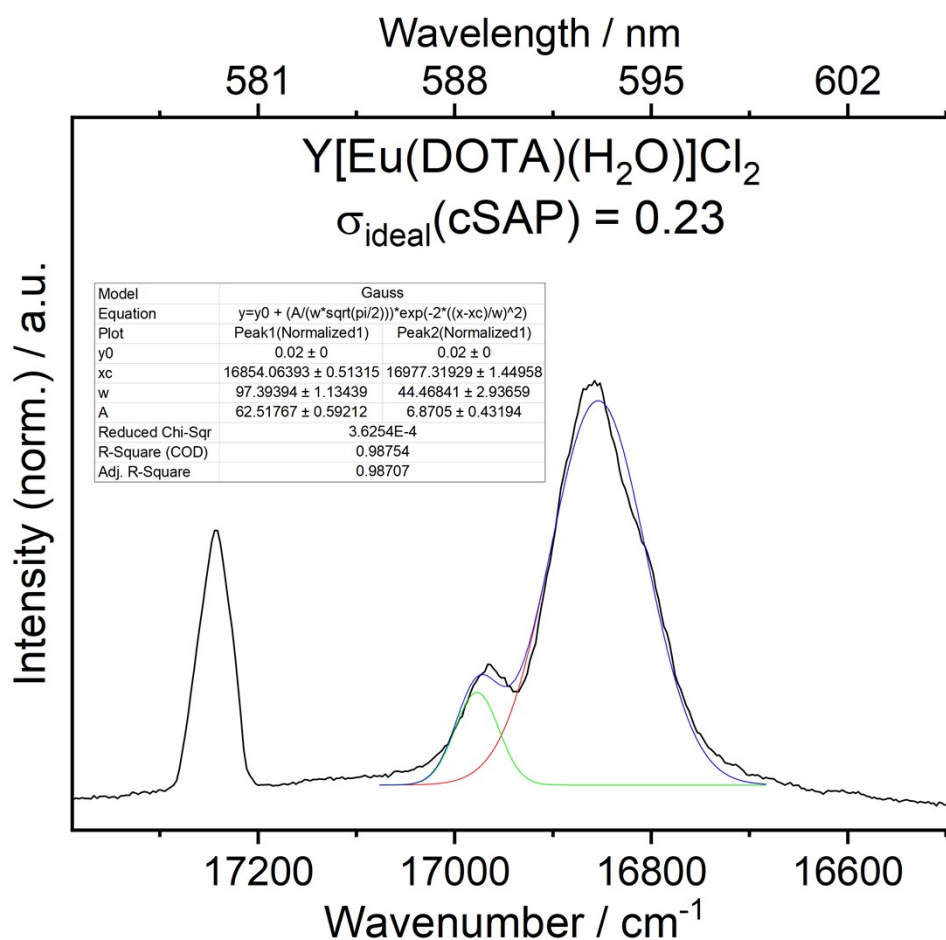


Figure S12. Peak fitting to two Gaussian curves fit in the $^5D_0 \rightarrow ^7F_1$ transition band for Y[Eu(DOTA)(H₂O)]Cl₂.

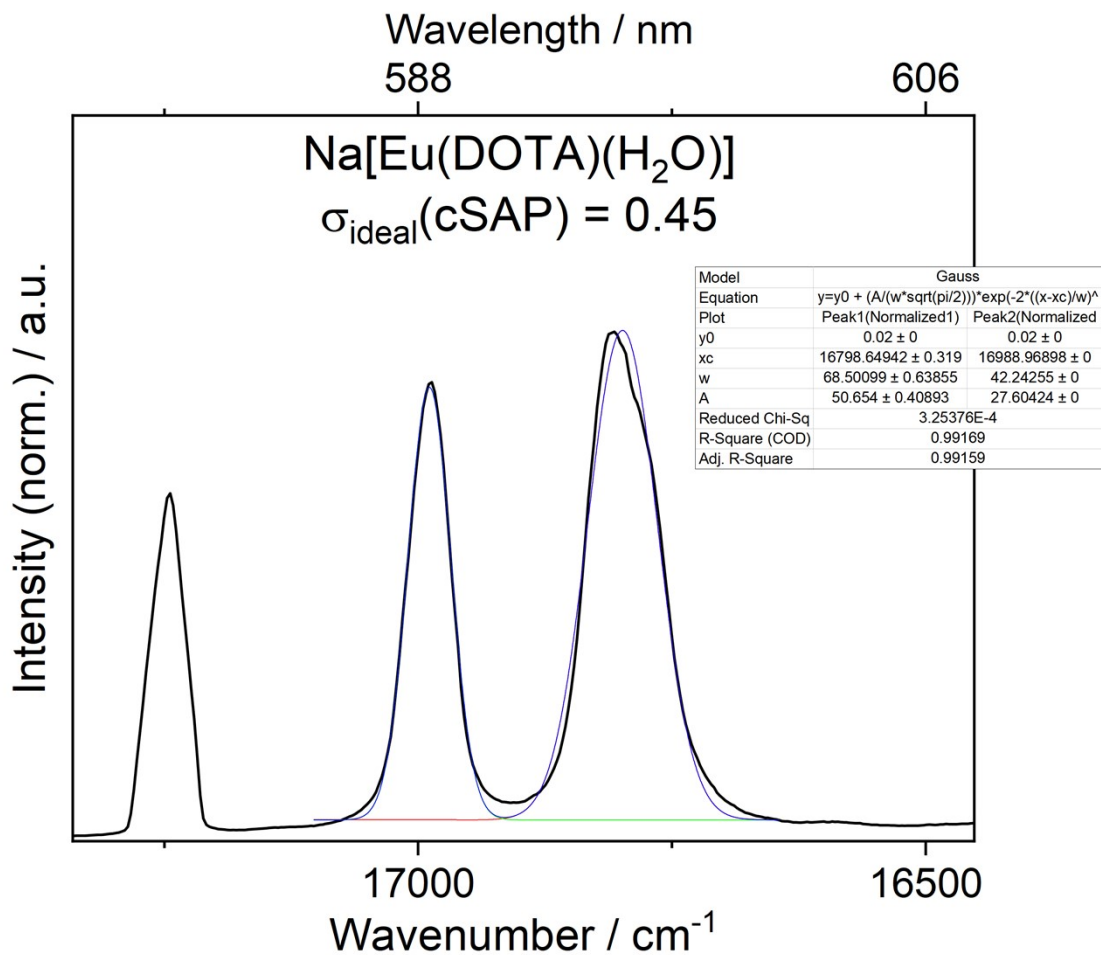


Figure S13. Peak fitting to two Gaussian curves fit in the $^5D_0 \rightarrow ^7F_1$ transition band for Na[Eu(DOTA)(H₂O)].

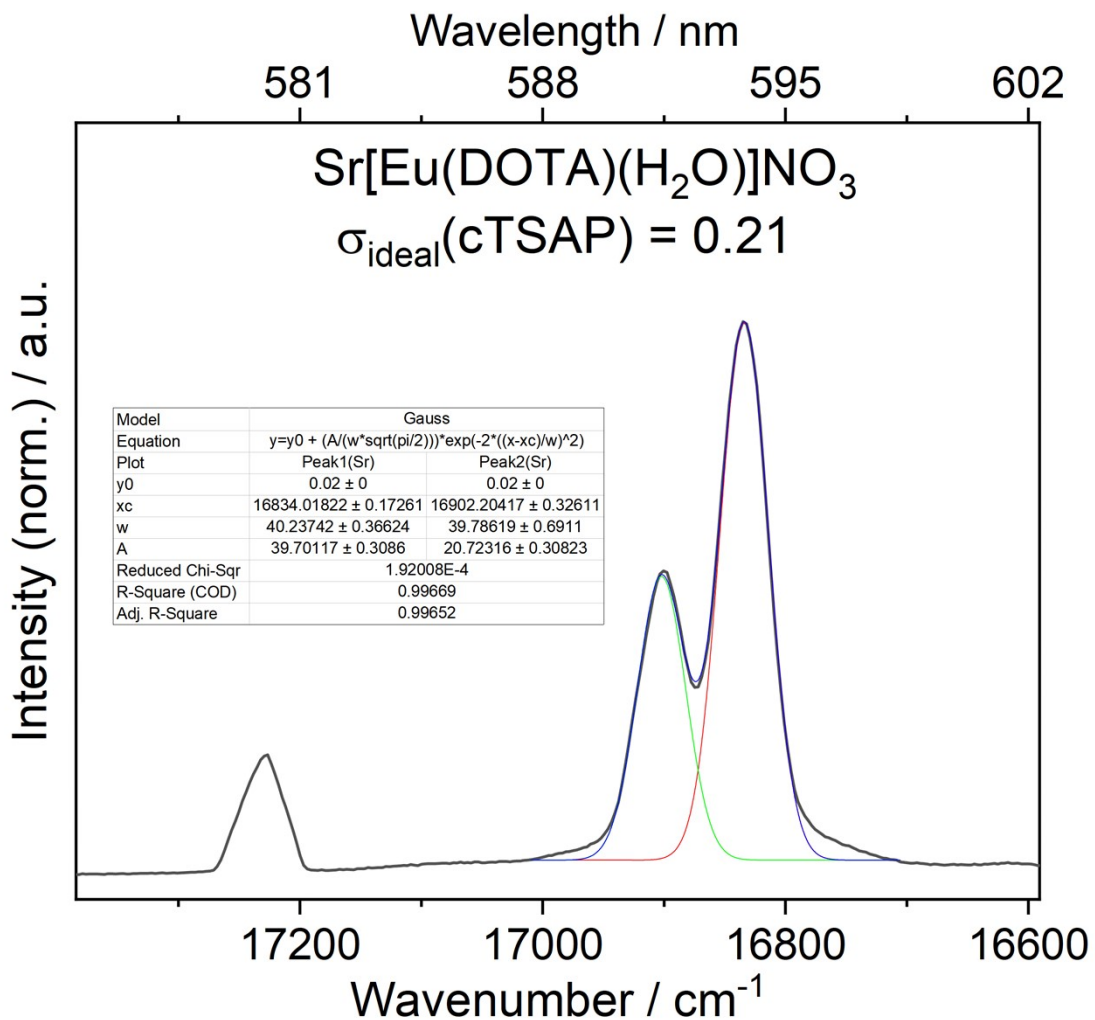


Figure S14. Peak fitting to two Gaussian curves fit in the $^5D_0 \rightarrow ^7F_1$ transition band for Sr[Eu(DOTA)(H₂O)]NO₃

1. AlignIt Link and Guide

[Link to AlignIt:](https://github.com/AndyNano/AlignIt.git)

<https://github.com/AndyNano/AlignIt.git>

Files used to calculate symmetry deviation value, σ_{ideal} , are available with Supporting Information in three zip folders. One containing examples files used in the guide below. One containing coordinates for of cSAP, cTSAPc, cTSAPcc, TTP, Muff, Hoop, TCup and HBPY with central atoms used for making the symmetry deviation scale. One containing the coordinates for calculating the symmetry deviation of **Y(III)**, **Gd(III)** and **Sr(II)** and model structures.

Guide to using AlignIt

This guide is intended for anyone who wishes to use AlignIt to calculate σ_{ideal} for any desired polyhedron. The guide is intended to start from a .cif file as to provide the complete process from crystal structure to σ_{ideal} . Comparison between a SAP Eu(O)₉ structure and cSAP is used here as an example.

In order to run the program Anaconda and Mercury¹ (licensed) is needed to treat the data.

- 1) Open the first .cif file in Mercury, and save as a .xyz file.
- 2) Open the .xyz file in Notepad or another text file-reading program.
- 3) Isolate the atoms included in the polyhedral of interest and delete all other atoms. If it is not obvious, which atoms constitutes the polyhedron it can be helpful to label each atom in Notepad, save the .xyz file and reopen it in Mercury.
- 4) Once the polyhedron is isolated, open the .xyz file in Mercury and measure the M-O distances and find the average bond length. This information is needed later.
- 5) Rearrange the atoms so the metal atom is listed first and the ligating atoms next starting from the capping atom. Number the atoms in all structures used for comparison using the same convention. See example_file1.xyz for format. Here the capping atom is O1 and the rest are labelled clockwise looking down the capping atom. It is important to arrange the atoms in the same order as in the model structures.
- 6) In order not to introduce artificial orientation preference in the rotational optimization, all atoms are changed to oxygen atoms. See example_file2.xyz. As .xyz files are mere coordinates, the type of atoms is irrelevant for the symmetry deviation analysis.
- 7) Open the .xyz file in Notepad and create a new text document for overlaying structures.
- 8) In the new document:
 - Write the total number of atoms (for two nine-vertex polyhedral this is 20)
 - Copy and paste in the coordinates of the two structure (e.g. first the real and then the ideal model) into the new document. See example_file3.xyz for format. If the two central atoms are not the same element, then rename one of the atoms to be the same element as the first but with a different number, e.g. in example_file3.xyz Eu2 is the central metal in the cSAP polyhedron.

- Save the text document as a .xyz file.
- 9) Open the new file .xyz, which contains both the real polyhedron and the ideal polyhedron in Mercury. It should show two polyhedra with the same central atom.
- If the two polyhedra are on top of each other or appear connected, open either of the .xyz files that contains the coordinates of only one structure in Mercury. Go to Edit > Transform Molecules > Inversion & Translation tap > Choose a translation > Click Transform until the polyhedron is moved sufficiently.
 - Save the new translation and insert the new coordinated into the two polyhedra file from 8).
- 10) Select the two polyhedral and go to Calculate > Overlay Molecules > Overlay
- If these does not contain the same elements, the program cannot calculate the overlay.
 - Without closing the Automatic Molecule Overlay dialog box, tick the 'Label atoms' box on the bottom right of the window.
 - Ensure that the ligand atoms in the two polyhedral have the same numbering (see for example_file3.xyz), so atoms closest to each other has the same place in the file. If not, relabel and rearrange the atoms in Notepad to have the same ordering. Save and reopen the .xyz file to check that the ordering of the atoms in the real structure is the same as the model.
- 11) Still not closing the Automatic Molecule Overlay dialog box, Go to File > Save as... and save the coordinates of the overlay in a new .xyz document. See example_file4.xyz for format. Check that atoms with the same numbering are the closest, e.g. the nearest atom to O1 in the real structure should be O1 in the model structure. If not, relabel and rearrange until it is.
- 12) Open the overlay .xyz file in Notepad.
- Copy the coordinates of (only) the ligands belonging to the first polyhedra into a new Notepad document and save this as the comparison coordinates for that structure, e.g. sap2_to_csap.xyz. See example_file5.xyz. Note that the number of atoms is changed to 9. Remove any excess spacing between the atoms and coordinates.
 - Go to the overlay .xyz file (example_file4.xyz) and copy the coordinates of the second structure into a new Notepad document. Save as comparison file for that structure, e.g. csap_to_sap2.xyz. See example_file6.xyz.
 - The central atom is not included in the comparison file because AlignIt places the center of the coordinates in origo. The close distance between two central atoms that nearly overlap will result in an artificially large σ_{ideal} value.
- 13) Save all the compare files in the same directory together with the AlignIt program.
- 14) Open Jupyter Notebook and go to the directory where the compare files are located and open AlignIt.
- 15) Go to 'Define which structures σ_{ideal} should be calculated on'.

- 16) Write the names of the files containing the ideal structure coordinates and the real structure coordinates. In the example, the ideal structure file is “example_file6.xyz” and the real structure file is “example_file5.xyz”.










```
ideal_structure_name = " example_file6.xyz "  
disordered_structure_name = " example_file5.xyz "  
scaling = 0.9965
```

- 17) Adjust the scaling by the relation between the bond lengths in the ideal structure (2.50 Å) and the average bond length obtained in step 4. E.g. for the Eu(O)₉ moiety the average M-O bond length is 2.5088 Å, which makes the scaling 0.9965. The scaling ratio is multiplied to the disordered structure.
- 18) Go to Cell > Run All
- 19) The σ_{ideal} value is returned under the matrix and a .txt file appears in the Results_AlignIt folder (see example_file7.txt). For this comparison $\sigma_{\text{ideal}} = 0.32$

10. Comparative scale of symmetry deviation values, σ_{ideal} , for nine-coordinated ideal polyhedra

For all models, only oxygen atoms were used to induce preferred orientation in the overlay process.

Table S4. Symmetry deviation values for comparative nine-coordination scale

X/Z						
σ_{ideal}	cSAP C_{4v}	TTP D_{3h}	MFF C_{2v}	Hoop C_{2v}	TCup C_{3v}	HBPy D_{7h}
cSAP	0	0.97 (0.97)	13.51 (0.96)	20.15 (11.85)	16.71 (16.03)	26.89 (21.31)
TTP	0.97	0	9.42 (1.92)	21.18 (11.64)	15.85 (15.24)	23.25 (21.90)
MFF	13.64	9.41	0	14.61 (9.96)	20.40 (14.06)	24.92 (18.30)
Hoop	20.40	22.25	14.41	0	19.79 (12.69)	14.49 (13.25)
TCup	16.86	15.98	20.47	20.38	0	21.52 (20.30)
HBPy	26.83	23.25	25.02	13.67	21.43	0
						
cSAP	0		2.00 (1.99)		2.00	
cTSAPc	2.00		0		7.95 (0.00)	
cTSAPcc	2.00		7.95		0	

Values in bold above the diagonal are calculated using AlignIt where X is set as ideal, Z as distorted. Below the diagonal, the relation is reversed. Values in parenthesis are calculated using SHAPE.²

11. References

- (1) Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M. et al. Mercury 4.0: from visualization to analysis, design and prediction. *Journal of Applied Crystallography* **2020**, 53 (1), 226.
- (2) Llunell, M.; Casanova, D.; Cirera, J.; Alemany, P.; Alvarez, S. SHAPE, version 2.1. *Universitat de Barcelona, Barcelona, Spain* **2013**, 2103.