

We Are Never Ever Getting (back to) Ideal Symmetry: Structure and luminescence from a ten-coordinated Europium(III) sulfate crystal

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1. Images of crystals

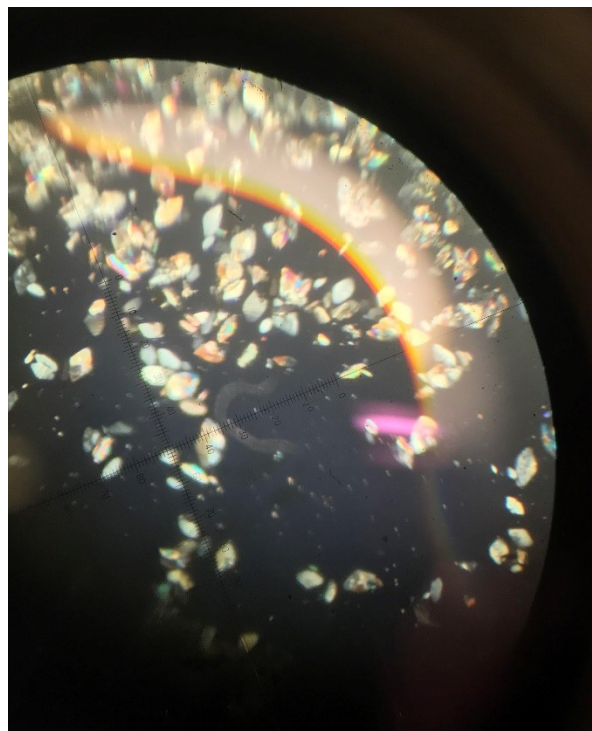


Figure S1. Top: Picture of $\text{K}_5\text{Na}[\text{Eu}_2(\text{SO}_4)_6]$ crystals through a microscope lens. Bottom: Picture of $\text{K}_5\text{Na}[\text{Eu}_2(\text{SO}_4)_6]$ crystals excited with a 405 nm laser pen.

2. Crystallization of $\text{K}_5\text{Na}[\text{Eu}_2(\text{SO}_4)_6]$

All chemicals were used as received. 98% $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ from STREM Chemicals, $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (MERCK) and KCl (MERCK). A stock solution was made by adding 2.01 g (0.0033 mol) $\text{Eu}(\text{CF}_3\text{SO}_3)_3$, 1.42 g (0.0066 mol) and 24.85 g KCl (0.333 mol) to a 250 ml volumetric flask and dissolved by adding demineralized water to the 250 ml mark. A solution of HSO_4^- was made by dissolving 6.90 g (0.05 mol) NaHSO_4 in demineralized water in a 25 ml volumetric flask. The solution was diluted by transferring 3.0 ml of the NaHSO_4 solution to a sample vial with a micropipette and adding 2.0 ml of demineralized water. In a new vial was 3 ml of the $\text{Eu}(\text{III})$ stock solution and 1 ml of the diluted HSO_4^- solution mixed. Blocks of rhombohedral crystals formed overnight (see Figure S1).

3. Crystallographic Information

Single Crystal X-ray diffraction data were collected on a Bruker D8 VENTURE diffractometer equipped with Mo K α high brilliance I μ S radiation X-ray tube ($\lambda = 0.71073 \text{ \AA}$), a multilayer X-ray mirror, a PHOTON 100 CMOS detector, and an Oxford Cryo Systems low temperature device. The diffractometer was controlled using the SAINT program as implemented in the APEX2¹ software package. The structure was solved using Olex2² with the ShelXT solution program³ using direct methods and refined with the ShelXL refinement package⁴ using least-squares minimization. Non-hydrogen atoms were refined anisotropically.

Empirical formula	Eu ₂ K ₅ NaO ₂₄ S ₆	F(000)	1040.0
Formula weight	1098.79	Crystal size/mm ³	0.287 × 0.162 × 0.102
Temperature/K	120	Radiation	MoK α ($\lambda = 0.71073$)
Crystal system	Monoclinic	2 Θ range for data collection/ $^\circ$	5.05 to 80.486
Space group	C2/m	Index ranges	-15 ≤ h ≤ 15, -26 ≤ k ≤ 26, -12 ≤ l ≤ 12
a/ \AA	9.1004 (9)	Reflections collected	20809
b/ \AA	16.1318 (15)	Independent reflections	2620 [R _{int} = 0.0309, R _{sigma} = 0.0172]
c/ \AA	7.6365 (7)	Data/restraints/parameters	3385/0/95
β / $^\circ$	110.614 (2)	Goodness-of-fit on F ²	1.144
Volume/ \AA^3	1049.30 (17)	Final R indexes [I>2 σ (I)]	R ₁ = 0.0137, wR ₂ = 0.0340
Z	2	Final R indexes [all data]	R ₁ = 0.0147, wR ₂ = 0.0343
ρ_{calc} /cm ³	3.478	Largest diff. peak/hole / e \AA^{-3}	0.87/-1.31
μ /mm ⁻¹	7.650		

4. Powder X-ray Diffraction Spectrum

Powder X-ray diffraction was performed on crushed single crystals. The samples were measured on a low background silica sample holder and data was collected on a Bruker D8 Advance diffractometer fitted with suitable optics and a Cu X-ray tube.

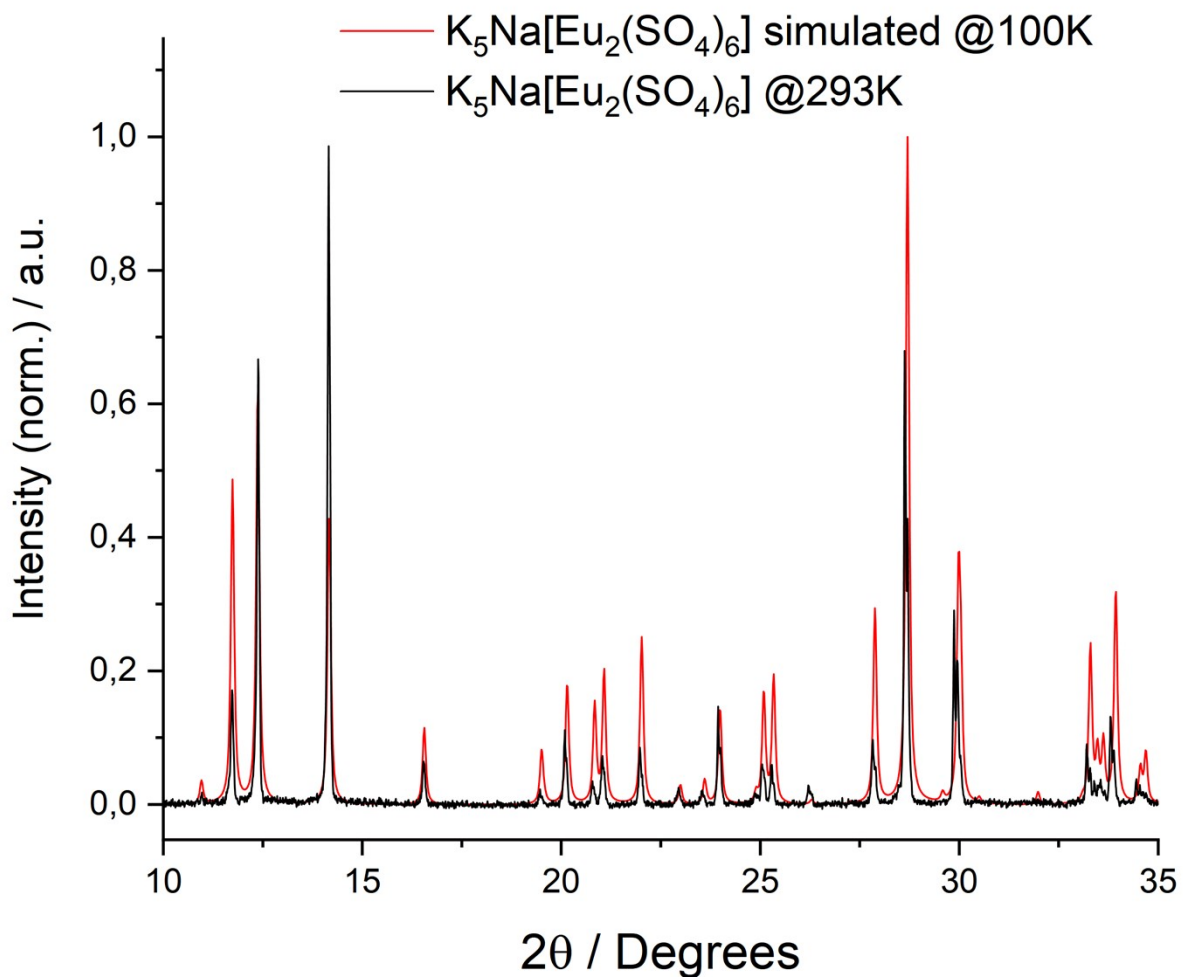


Figure S2. Powder X-Ray Diffractograms. Black: $\text{K}_5\text{Na}[\text{Eu}_2(\text{SO}_4)_6]$ at 293 K, red: $\text{K}_5\text{Na}[\text{Eu}_2(\text{SO}_4)_6]$ simulated from single crystal structure recorded at 100 K.

5. Excitation and emission spectrum of $\text{K}_5\text{Na}[\text{Eu}_2(\text{SO}_4)_6]$

Steady-state measurements were performed on powdered samples using a PTI QuantaMaster8075 from Horiba Scientific with a xenon arc lamp as excitation source. Excitation spectra were recorded with emission detected at 614 nm with excitation and emission slits at 1.5 and 8.0 nm, respectively. Emission spectra were recorded with excitation at 394 nm with excitation and emission slits at 8.0 and 1.5 nm respectively. Measurements on single crystals were done at room temperature. A dried powder sample was measured in a dimethyl tetrahydrofuran glass in a NMR tube in a cold-finger setup containing liquid nitrogen. A constant nitrogen flow in the sample chamber was used to avoid ice formation.

Time-resolved luminescence measurements were performed on the same systems, but with a xenon flash lamp as the excitation source. The point of excitation was 394 nm, and the emission was detected at 614 nm. Excitation slit was set at 8.0 nm and emission slit at 5.0 nm. Lifetime traces were fitted to either a mono-exponential decay model using the Origin 2017 software package.⁵

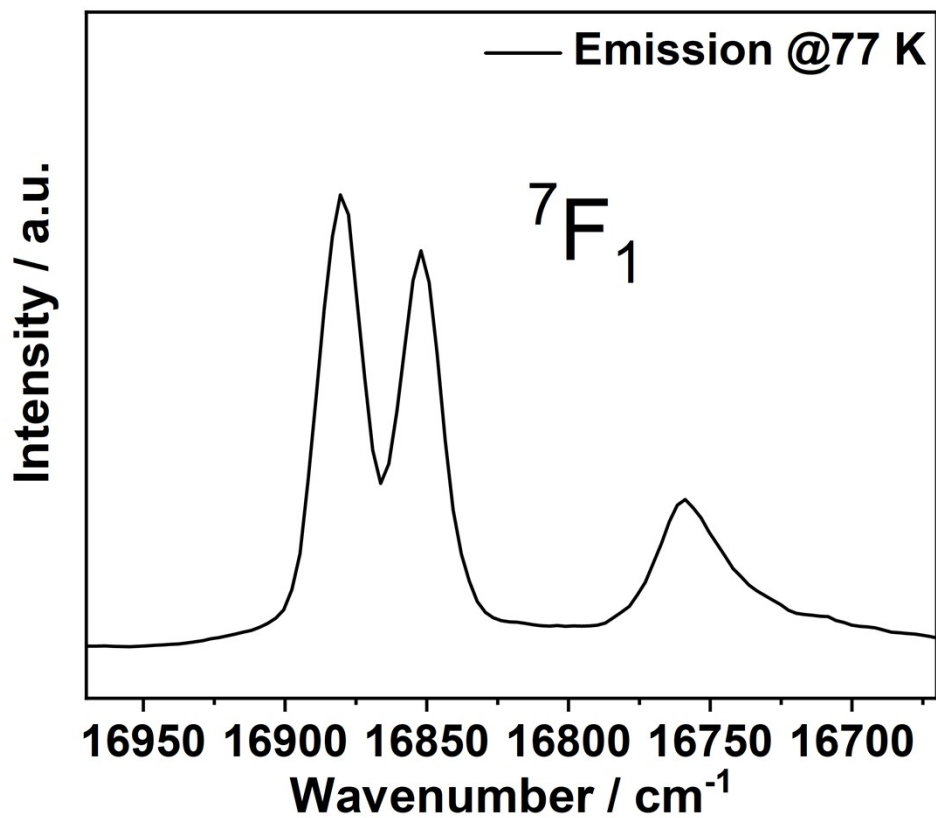


Figure S3. Normalized high spectrum (ex. 394 nm) of $K_5Na[Eu_2(SO_4)_6]$ powder in dimethyl tetrahydrofuran glass at 77K. Emission slit = 1.0 nm

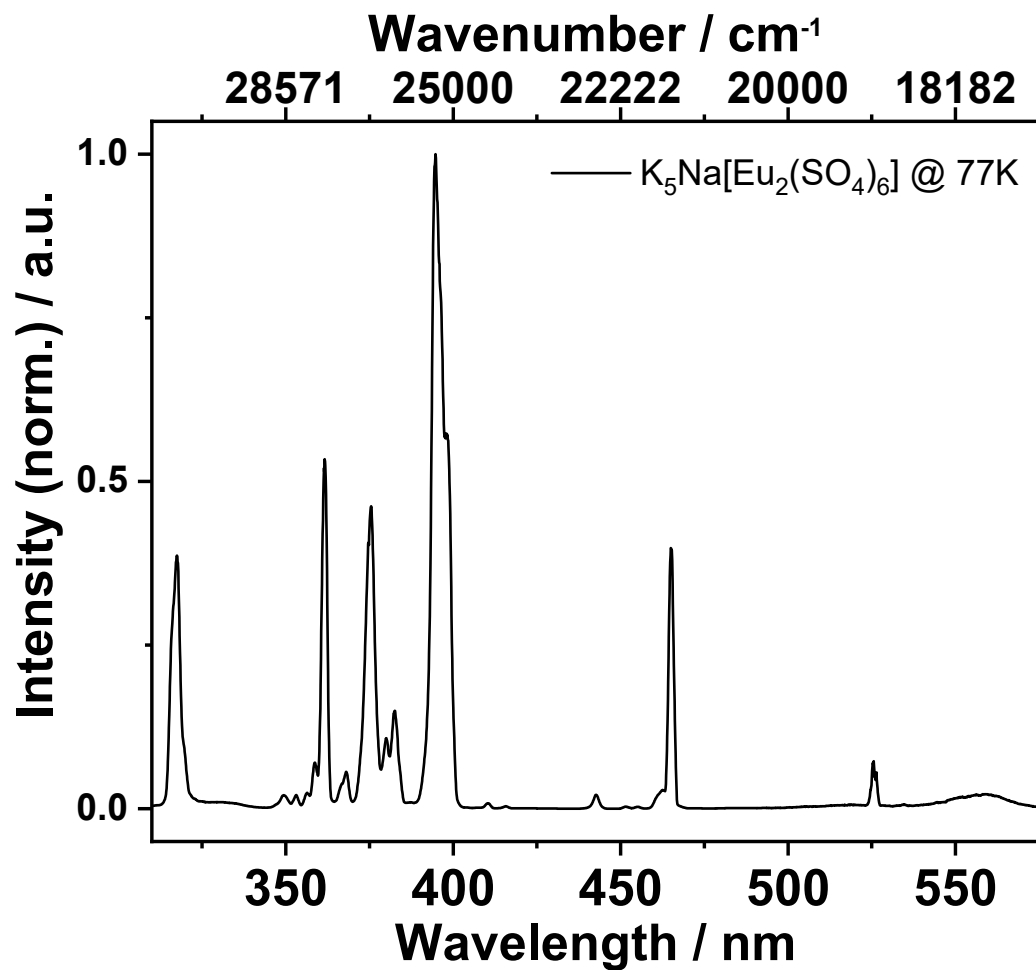


Figure S4. Normalized excitation spectrum (*em.* 614 nm) of $K_5Na[Eu_2(SO_4)_6]$ powder in dimethyl tetrahydrofuran glass at 77K. Excitation slit = 1.5 nm.

6. The full width at half-maximum

(FWHM) in emission (slit width = 1.5 nm)

Table S1. Line width
K₅Na[Eu₂(SO₄)₆]

of transition bands in

Transition	FWHM / cm ⁻¹
⁵ D ₀ → ⁷ F ₀ (Full)	41
⁵ D ₀ → ⁷ F ₁ (Peak 1)	63
⁵ D ₀ → ⁷ F ₁ (Peak 2)	50
⁵ D ₀ → ⁷ F ₂ (Peak 1)	35
⁵ D ₀ → ⁷ F ₂ (Peak 2)	32
⁵ D ₀ → ⁷ F ₂ (Full)	88
⁵ D ₀ → ⁷ F ₃ (Full)	245
⁵ D ₀ → ⁷ F ₄ (Peak 1)	27
⁵ D ₀ → ⁷ F ₄ (Peak 2)	26
⁵ D ₀ → ⁷ F ₄ (Peak 3)	33
⁵ D ₀ → ⁷ F ₄ (Full)	166

7. Time-resolved emission decay profile

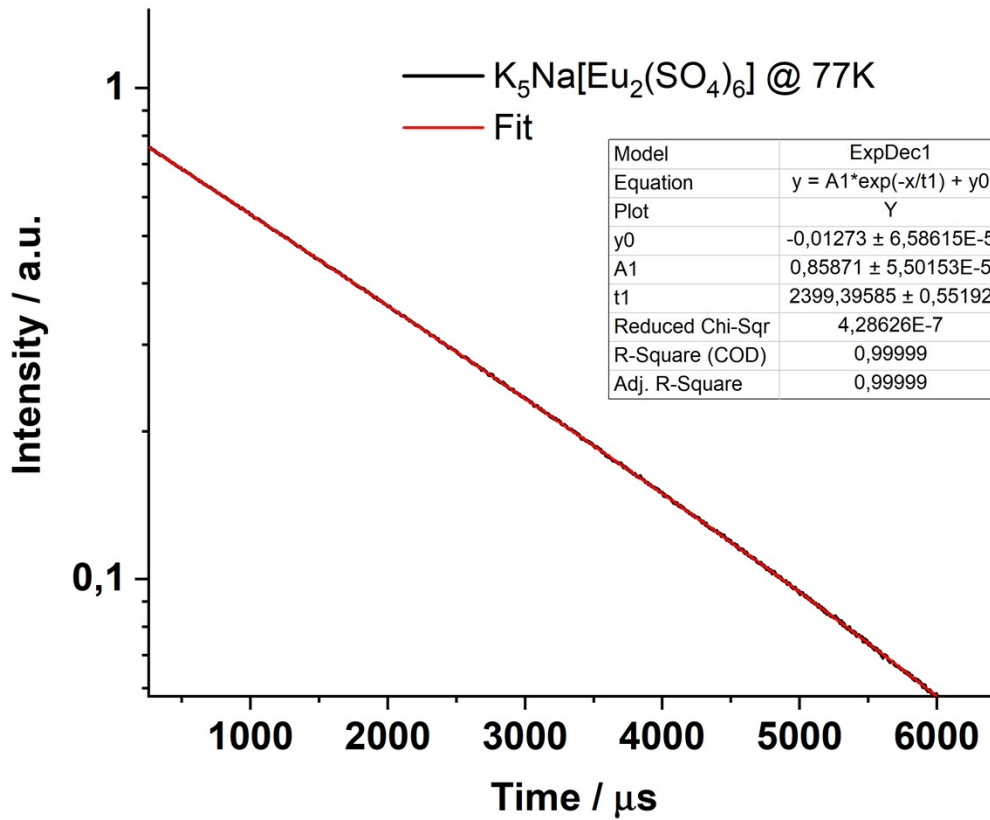


Figure S5. Lifetime decay of $K_5Na[Eu_2(SO_4)_6]$ in dimethyl tetrahydrofuran glass at 77 K.

8. Solid State Quantum Yield Measurements

Luminescence quantum yields of the crystals were recorded as relative solid state measurements using a Fluotime300 spectrophotometer with a xenon lamp for excitation (ex. 394 nm) and an integrating sphere module from Picoquant. All recorded spectra were corrected for integrating sphere absorption and detection efficiency. Solid state measurements were performed on crushed crystals between two quartz slides taped together in an integrated sphere setup. A blank sample was made by taping two silica slides together, which was measured in the integrating sphere. Absorption and emission (scattering) spectra of the blank were subtracted from corresponding sample spectra for the calculation of absolute quantum yield.

As we have data questioning absolute luminescence quantum yield determination, we chose to use the relative method in order to ensure proper instrument calibration. No suitable solid-state references can be found. Thus, reference measurement was made against a reference that was suited: Atto390. The Atto390 reference was calibrated as following: 1) a droplet of Atto390 dissolved in glycerol was measured between two silica slides in the integrating sphere setup. 2) Atto390 dissolved in glycerol was measured in a quartz cuvette. 3) the relative quantum yield of Atto390 was dissolved in glycerol, was measured against quinine sulfate in 0.1 M H₂SO₄ (Q.Y. = 58%, 22 C°) in the integrating sphere.⁶

Absorption measurements for relative quantum yields in solutions were performed on a Cary 300 absorption spectrophotometer from Agilent and a Fluotime300 spectrophotometer equipped with a xenon lamp (ex. 360 nm) from Picoquant was used to record corresponding emission spectra. All emission spectra were corrected for varying detection efficiency across wavelengths. Absorption and emission spectra of at least five solutions of varying concentration of samples were recorded and integrated emission intensity was plotted as a function of the corresponding emitter concentration (Figure S6).

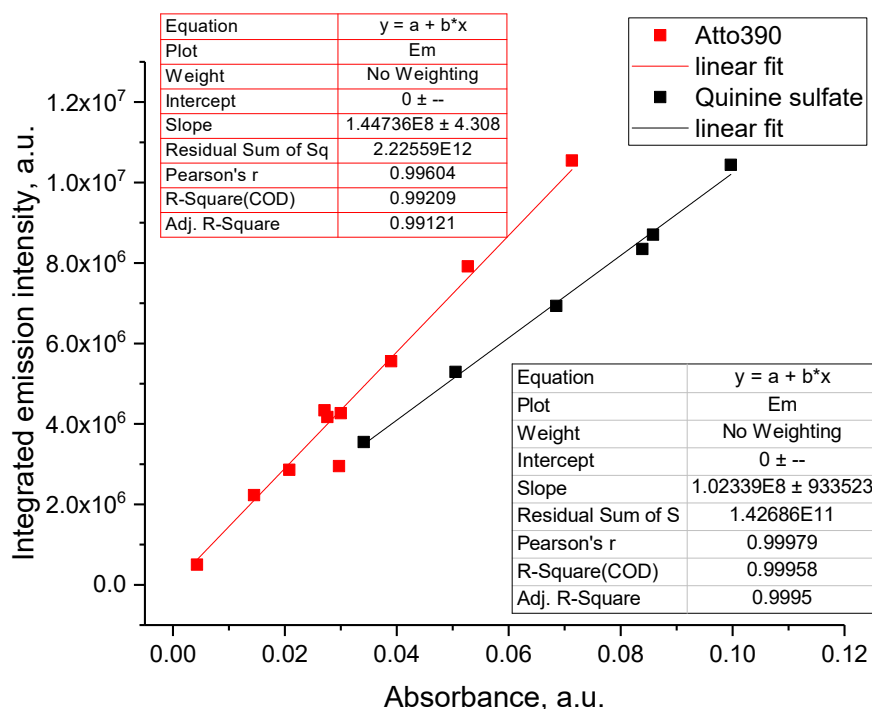


Figure S6. Integrated fluorescence intensity as a function of corresponding sample absorption (at 360 nm) for the Atto390 in glycerol and a reference compound (quinine sulfate).

Quantum yield of the molecules in solution (QY) was calculated as:

$$QY = QY_{ref} \left(\frac{Grad}{Grad_{ref}} \right) \left(\frac{n^2}{n_{ref}^2} \right),$$

where QY_{ref} is a quantum yield of the reference compound, $Grad$ and $Grad_{ref}$ are the slopes of the linear fits in the Figure S6 and n is the refractive index of the solvent for the molecule-of-interest and the reference (n_{ref}). Using this equation the quantum yield of Atto390 in glycerol was calculated to be 93%, which is in a good agreement with a reported quantum yield of Atto390 in water (PBS, pH = 7) of 90% (Atto-tec, Product catalog, 2020). Similar, however slightly lower quantum yield values were also obtained in the absolute quantum yield measurements of Atto390 in glycerol and water in the integrating sphere (Q.Y. = 77% and Q.Y. = 84%, respectively), most likely due to the significantly longer integration time necessary for the measurement and therefore unavoidable bleaching.

9. Link to AlignIt and comparison files

Link to AlignIt: <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 bcSAP, bcDod, Sdod, PP, PAP and OBPY with central atoms used for making the symmetry deviation scale. One containing the coordinates for calculating the symmetry deviation of $\text{Eu}(\text{O})_{10}$ with both of $\text{Th}(\text{O})_{10}$, $\text{U}(\text{O})_{10}$ and model structures.

Guide to using AlignIt

This guide is intended for anyone who wishes to use AlignIt to calculate SCVs for any desired polyhedron. The guide is intended to start from a .cif as to provide the complete process from crystal structure to σ_{ideal} .

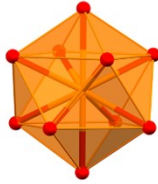



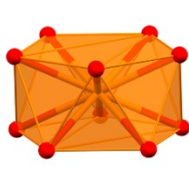
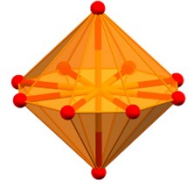
In order to run the program Anaconda and Mercury⁷ (licensed) is needed to treat the data.

- 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 and number the atoms. See example_file1.xyz for format.
- 6) Open the .xyz file in Notepad and create a new text document for overlaying structures.
- 7) In the new document:
 - Write the total number of atoms (for two ten-vertex polyhedral this is 22)
 - 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_file2.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_file2.xyz Eu2 is the central metal in the bcSAP polyhedron.
 - Save the text document as a .xyz file.
- 8) Open the new file .xyz, which contains both the real polyhedron and in Mercury. It should show two polyhedral 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 7).
- 9) 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_file2.xyz), so atoms closest to each other has the same place in the file. If not, relabel and rearrange the atoms in Notepad, save and reopen the .xyz file.
- 10) 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_file3.xyz for format.
 - 11) 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. Eu_coord_to_compare_to_bcsap.xyz. See example_file4.xyz. Note that the number of atoms is changed to 10. Remove any excess spacing between the atoms and coordinates.
 - Go to the overlay .xyz file (example_file3.xyz) and copy the coordinates of the second structure into a new Notepad document. Save as comparison file for that structure, e.g. Bcsap_coord_to_compare_to_eu.xyz. See example_file5.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.
 - 12) Save all the compare files in the same directory together with the AlignIt program.
 - 13) Open Jupyter Notebook and go to the directory where the compare files are located and open AlignIt .
 - 14) Go to ‘Define which structures σ_{ideal} should be calculated on’.
 - 15) 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_file5.xyz” and the real structure file is “example_file4.xyz”.
 - 16) Adjust the scaling by the relation between the bond lengths in the ideal structure (2.635 Å) and the average bond length obtained in step 5. E.g. for the Eu(O)₁₀ moiety the average M-O bond length is 2.53404 Å, which makes the scaling 1.0398.
 - 17) Go to Cell > Run All
 - 18) The σ_{ideal} value is returned under the matrix.

10. AlignIt σ_{ideal} values in comparative scale

Table S2. σ_{ideal} values calculated with AlignIt with two decimal points

						
	bcSAP <i>D_{4d}</i>	bcDod <i>D₂</i>	SDod <i>D₂</i>	PP <i>D_{5h}</i>	PAP <i>D_{5d}</i>	OBPy <i>D_{8h}</i>
bcSAP	0	2.31	7.93	16.45	14.87	16.14
bcDod	2.31	0	10.48	14.95	8.62	14.26
SDod	7.93	10.48	0	10.76	13.97	24.17
PP	16.45	14.96	10.76	0	6.55	22.22
PAP	14.87	8.62	13.97	6.55	0	15.87
OBPy	16.14	14.26	24.17	22.22	15.88	0

^a Coordinates for the SDod model are reported by Ruiz-Martínez *et al.*⁸. Coordinates for bcSAP, bcDod, PP, PAP and OBPy were created in Mercury (bcSAP and bcDod from description by Al-Karaghoulí *et al.*^{7,9}). ^b Values in bold are calculated with AlignIt, and values in parenthesis are calculated using SHAPE by Lluenell *et al.*¹⁰

11. Effect of rotational alignment

Comparison between the two approaches, SHAPE and AlignIt, is difficult, however, to some degree the difference between structures can be evaluated visually. Figure S8 shows overlays of bcSAP and bcDod next to bcDod and SDod. According to the CShM values obtained by SHAPE bcDod is as similar to bcSAP as to SDod. If the same comparison is made with AlignIt, bcSAP is significantly closer in shape to bcDod than SDod.

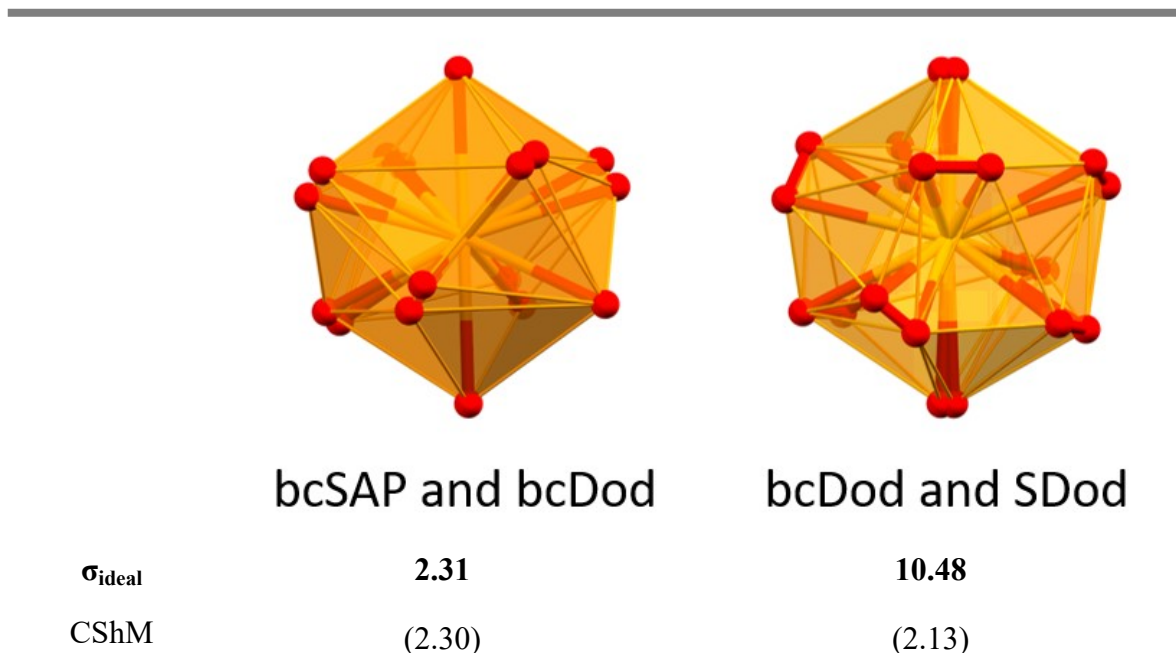


Figure S8. Overlay illustration from Mercury. Left: Ideal bcSAP polyhedra overlay with ideal bcDod polyhedra. Right: Ideal bcDod polyhedra overlay with ideal SDod polyhedra.

Generally, all values calculated by AlignIt are larger than values obtained through SHAPE for the same polyhedra, which is again attributed to the different optimization processes. The only very obvious variance is the two calculated CShM values for $\text{Eu}(\text{O})_{10}$ in relation to bcDod with a difference of 3.82 in comparison value (Table 2). Based on the values obtained with SHAPE, the $\text{Eu}(\text{O})_{10}$ moiety should be almost equally close to bcSAP and bcDod. However, for applications of AlignIt, the rotational optimization is calculated by Mercury to find the most optimal overlay of two molecules, which makes it possible to visually evaluate the resemblance. $\text{Eu}(\text{O})_{10}$ in $\text{K}_5\text{Na}[\text{Eu}_2(\text{SO}_4)_6]$ overlays with bcSAP and bcDod ideal models are shown in Figure S9.

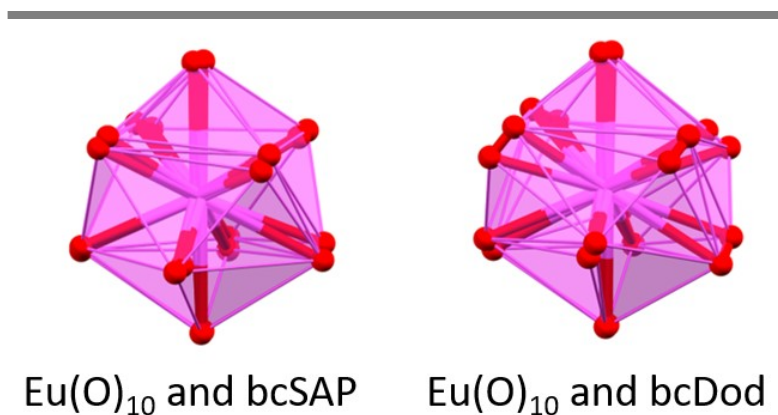


Figure S9. Overlay illustration from Mercury. Left: Eu(O)₁₀ in K₅Na[Eu₂(SO₄)₆] overlay with ideal bcSAP polyhedra. Right: Eu(O)₁₀ in K₅Na[Eu₂(SO₄)₆] overlay with ideal bcDod polyhedra.

To use Mercury overlay, the polyhedra have to consist of the same atoms, so for overlays the ideal polyhedra have same chemical composition as Eu(O)₁₀. From Figure S9 it is clear that the deviations are smaller between Eu(O)₁₀ and bcSAP than between Eu(O)₁₀ and bcDod.

12. SHAPE CShM values of Eu(O)₁₀

Continues Shape Measurement values of Eu(O)₁₀ in relation to ideal structures obtained with SHAPE.⁸ The pre-fix *J* refer to Johnson type polyhedra, where all edges are the same length.¹¹

Code	Label	Name	Point Group Symmetry (from SHAPE)	CShM with Eu(O) ₁₀
1	DP-10	Decagon	D _{10h}	36.984
2	EPY-10	Enneagonal pyramid	C _{9v}	24.727
3	OBPY-10	Octagonal bipyramid	D _{8h}	15.169
4	PPR-10	Pentagonal prism	D _{5h}	12.015
5	PAPR-10	Pentagonal antiprism	D _{5d}	13.390
6	JBCCU-10	Johnson-Bicapped cube	D _{4h}	10.378
7	JBCSAPR-10	Johnson-Bicapped square antiprism	D _{4d}	3.183
8	JMBIC-10	Johnson-Metabidiminished icosahedron	C _{2v}	8.158
9	JATDI-10	Johnson-Augmented tridiminished icosahedron	C _{3v}	20.131
10	JSPC-10	Johnson-Sphenocorona	C _{2v}	2.893
11	SDD-10	Staggered dodecahedron	D ₂	5.865
12	TD-10	Tetradecahedron	C _{2v}	5.123
13	HD-10	Hexadecahedron	D _{4h}	8.214

13. References

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