

Long Story Short: Donor Set Symmetry in Eu(DOTA) Crystals Determines the Electronic Structure

Supporting Information

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1. Crystal pictures and solid-state setup

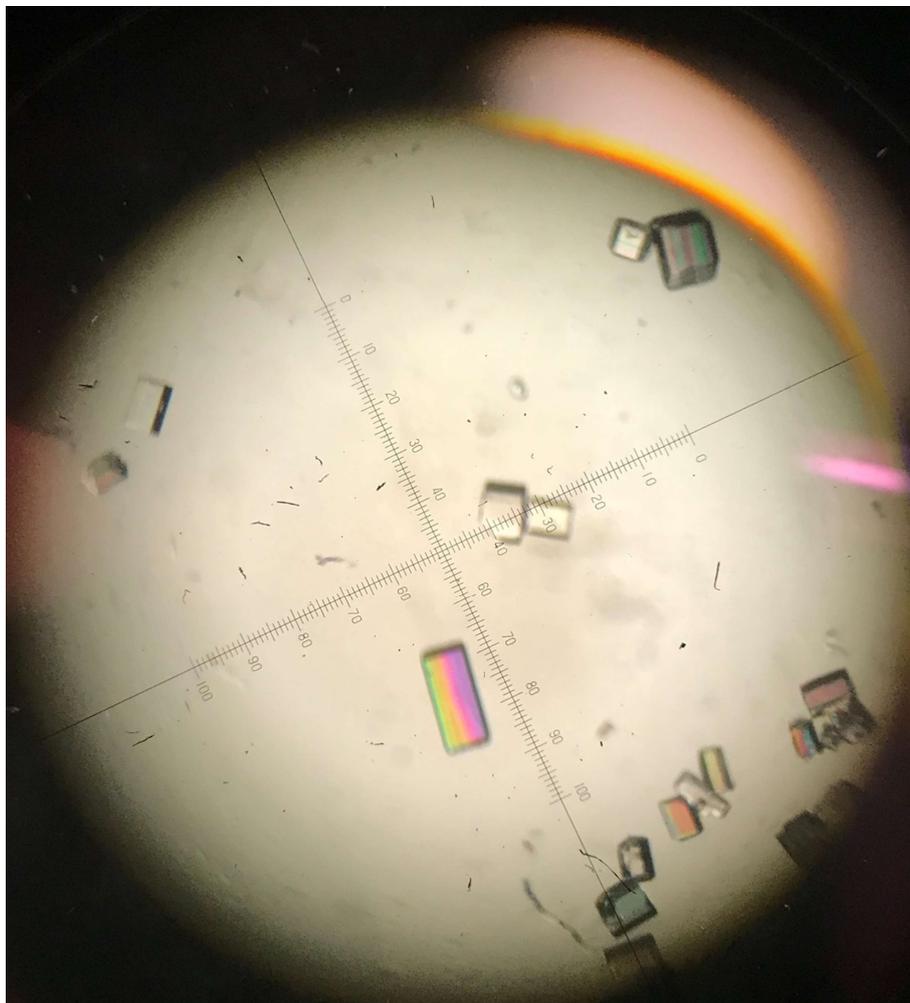


Figure S1. Crystals of [Eu(H₂DOTA)(H₂O)]Cl (2)



Figure S2. Excitation of a single crystal in solid-state setup measurement.

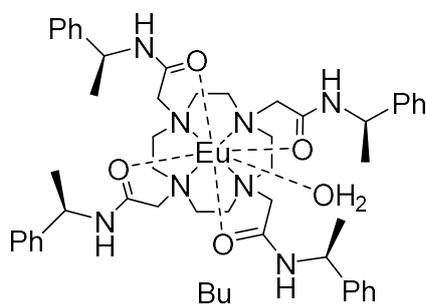


Figure S3. Position of loop platform in the spectrometer.

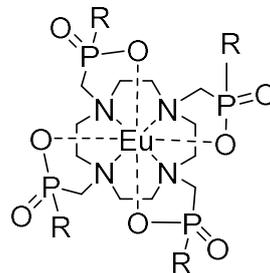
2. Crystallographic Information

Name	2	Name	3
Empirical formula	C ₃₂ H ₆₄ Cl ₂ Eu ₂ N ₈ O ₂₂	Empirical formula	C ₃₀ H _{58.64} B ₂ ClEuN ₆ O _{17.32} P ₂
CCDC number	2170386	CCDC number	2170385
Formula weight	1287.73	Formula weight	1051.56
Temperature/K	100	Temperature/K	100
Crystal system	Orthorhombic	Crystal system	Triclinic
Space group	P2 ₁ 2 ₁ 2 ₁	Space group	P-1
a/Å	9.1540(11)	a/Å	10.8019(10)
b/Å	15.8407(17)	b/Å	13.0077(13)
c/Å	15.8615(17)	c/Å	16.9777(16)
α/°	90	α/°	97.955(4)
β/°	90	β/°	96.588(3)
γ/°	90	γ/°	113.624(3)
Volume/Å ³	2300.0(4)	Volume/Å ³	2126.1(4)
Z	2	Z	2
ρ _{calc} /cm ³	1.859	ρ _{calc} /cm ³	1.643
μ/mm ⁻¹	2.907	μ/mm ⁻¹	1.691
F(000)	1296.0	F(000)	1078.0
Crystal size/mm ³	0.354 × 0.313 × 0.212	Crystal size/mm ³	0.413 × 0.271 × 0.084
Radiation	MoKα (λ = 0.71073)	Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.138 to 61.01	2θ range for data collection/°	3.49 to 66.282
Index ranges	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -22 ≤ l ≤ 22	Index ranges	-16 ≤ h ≤ 16, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26
Reflections collected	40965	Reflections collected	123351
Independent reflections	7028 [R _{int} = 0.0422, R _{sigma} = 0.0292]	Independent reflections	16216 [R _{int} = 0.0542, R _{sigma} = 0.0323]
Data/restraints/parameters	7028/0/317	Data/restraints/parameters	16216/0/586
Goodness-of-fit on F ²	1.083	Goodness-of-fit on F ²	1.044
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0153, wR ₂ = 0.0376	Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0250, wR ₂ = 0.0554
Final R indexes [all data]	R ₁ = 0.0158, wR ₂ = 0.0378	Final R indexes [all data]	R ₁ = 0.0328, wR ₂ = 0.0583
Largest diff. peak/hole / e Å ⁻³	0.35/-0.58	Largest diff. peak/hole / e Å ⁻³	1.61/-0.81
Flack parameter	0.011(4)		

3. Complexes

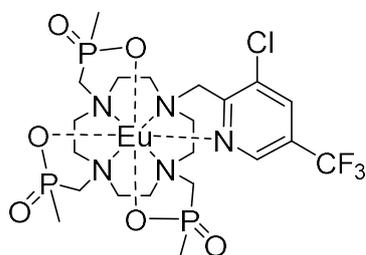


$[\text{Eu}(\text{DOTA-amide})(\text{H}_2\text{O})]^{3+}$

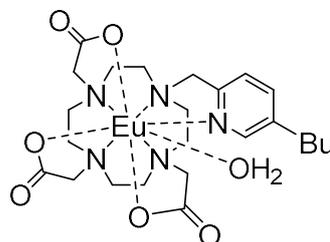


$[\text{Eu.L}^{2a}]^+$ R = CH₃

$[\text{Eu.L}^{2b}]^+$ R = CH₂Ph



$[\text{Eu.L}^3]^+$

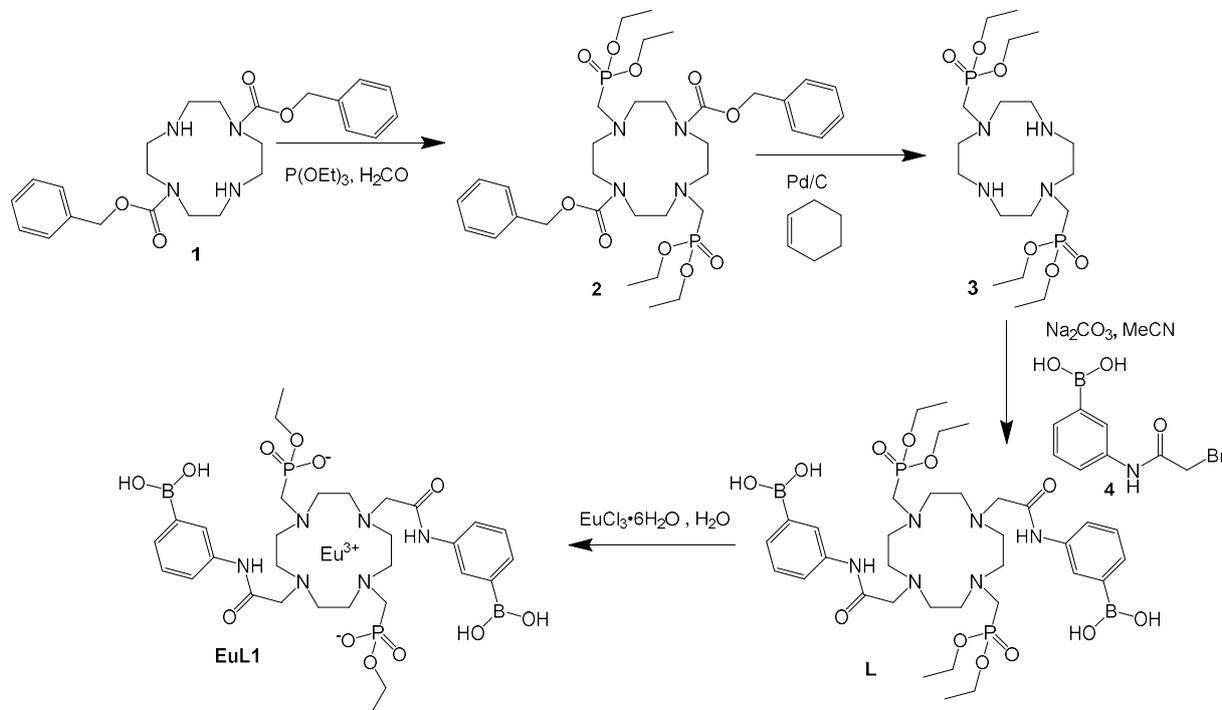


$[\text{Eu.L}^4]^+$

Figure S4. Complexes used for comparison of crystal field parameters in Table 5 (see main text). The complexes are drawn from ref 1.

4. Synthesis of the 1,7-bis(methylene-ethylphosphonate-methyl)-1,4,7,10-tetraazacyclododecane-4,10-bis(*N*-(3-boronophenyl)-acetamide) ligand

The first step was carried out according to literature.² The next step was carried out according to Manning et al.³



Scheme S1: Synthetic pathway to **DO-2P-2APB** (L in scheme).

Ligand synthesis (L) :

Dibenzyl 1,4,7,10-tetraazacyclododecane-1,7-dicarboxylate, 1

The compound was synthesized according to literature procedures.⁴

Cyclen (4.957 g, 28.77 mmol) was dissolved in chloroform (250 ml) under argon. Benzyl chloroformate (8.4 ml, 59 mmol) was added dropwise over 30 min. the resulting cloudy solution was heated to 60 °C for 2 hours after which the solvent was removed under vacuum. The solid was washed with diethyl ether (2·100 ml) and subsequently dissolved in 2 M aq. NaOH (200 ml). the product was extracted with DCM (2·200 mL). The organic phases were combined, dried over Na₂SO₄ and the solvent removed under vacuum. The product was purified using dry column chromatography using MeOH:NH₃. Yield 3.408 g (27 %).

Dibenzyl 4,10-bis((diethoxyphosphoryl)methyl)-1,4,7,10-tetraazacyclododecane-1,7-dicarboxylate, 2

The compound was synthesized following literature procedures.²

Dibenzyl 1,4,7,10-tetraazacyclododecane-1,7-dicarboxylate, 6 (1.359 g, 3.08 mmol) was dissolved in triethylphosphite (5 ml). Paraformaldehyde (278 mg, 9.25 mmol) was added and the reaction was left to stir at room temperature for 3 days after which the reaction volume was reduced by evaporation under vacuum. The compound was purified by flash column chromatography 100:3:0.1 DCM:MeOH:NEt₃. The fractions containing the product were combined and the solvent removed under vacuum. The product was then dissolved in EtOAc (50 mL) and washed with water (3·25 ml) and brine (20 ml). The organic phase was dried over MgSO₄ and the solvent evaporated under vacuum. The product was then dried on an oil pump. Yield 951 mg (42 %).

Tetraethyl ((1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(methylene))bis(phosphonate), 3

The compound was synthesized following literature procedures.³

In a three necked bottle under nitrogen, Pd/C (10 %, 96 mg) was added. Ethanol (25 ml) was added followed by a solution of dibenzyl 4,10-bis((diethoxyphosphoryl)methyl)-1,4,7,10-tetraazacyclododecane-1,7-dicarboxylate, **12** (955 mg, 1.29 mmol) in ethanol (10 mL) and cyclohexene (7 ml). The reaction was heated to 78 °C. After 2 hours the heat was removed and the solution allowed to reach room temperature after which it was filtrated through a plug of celite. The solvent was removed and the compound dried on an oil pump. Yield 580 mg (95 %).

(3-(2-Bromoacetamido)phenyl)boronic acid, **4**

The compound was synthesized following literature procedure.⁵

(3-aminophenyl)boronic acid (1.24 g, 9.08 mmol) was suspended in THF (60 mL). Na₂CO₃ (1.972 g, 18.06 mmol) was added and the suspension cooled on an ice-bath. Bromoacetyl bromide (2.4 ml, 27 mmol) was added over 25 min after which the reaction was left to stir on ice for 30 min after which the ice was removed and the solution left to stir for an additional hour at room temperature. The reaction mixture was the filtrated and the solvent evaporated in vacuum leaving an orange oil. Water (7 ml) was added and the two phase solution was stirred over night after which a sticky solid had precipitated. The solid was isolated by filtration. The solid was dissolved in MeOH (2 ml) and water (8 ml) was added resulting in precipitation of a white solid. The solid was dissolved in 1 M aq. NaOH and the aqueous solution washed with diethyl ether (2·25 ml). The aqueous phase was then acidified using 1 M aq. HCl and the product was isolated by repeated extractions with diethyl ether. Evaporation of the organic solvent yielded the product, 938 g (40 %).

((4,10-bis(2-((3-boronophenyl)amino)-2-oxoethyl)-1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(methylene))bis(phosphonic acid), **L**

TMSB (0,14 ml, 1.06 mmol) was added to a suspension of (((2,2'-(4,10-bis((diethoxyphosphoryl)methyl)-1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(acetyl))bis(azanediy))bis(3,1-phenylene))diboronic acid, **14** (110 mg, 0.13 mmol) in MeCN (2 ml) under a nitrogen atmosphere. The solution was stirred at room temperature for 24 hours after which water (1 ml) was added. The solvent was then removed under vacuum. Water was added to the residue and the precipitated product isolated by filtration and dried on an oil pump. Yield 25 mg (26 %).

Complex formation of [Eu(DO-2P-2APB)(H₂O)]Cl, EuL (3**):** ((4,10-bis(2-((3-boronophenyl)amino)-2-oxoethyl)-1,4,7,10-tetraazacyclododecane-1,7-diyl)bis(methylene))bis(diethoxyphosphoryl) (**L**) (21.7 mg, 0.030 mmol) was suspended in water (0.2 mL). EuCl₃·6H₂O (11.7 mg, 0.031 mmol) was added. The pH was adjusted to 6 with 1 M aq. NaOH. The reaction mixture was stirred at room temperature for 48 hours after which the pH was adjusted to 11 with 2 M aq. NaOH. The solution was filtered through a syringe filter and subsequently freeze dried to afford the desired complex as a white solid. Yield 23 mg (93%). Crystals suitable for X-ray diffraction precipitated in the NMR tube.

5. Excitation spectra

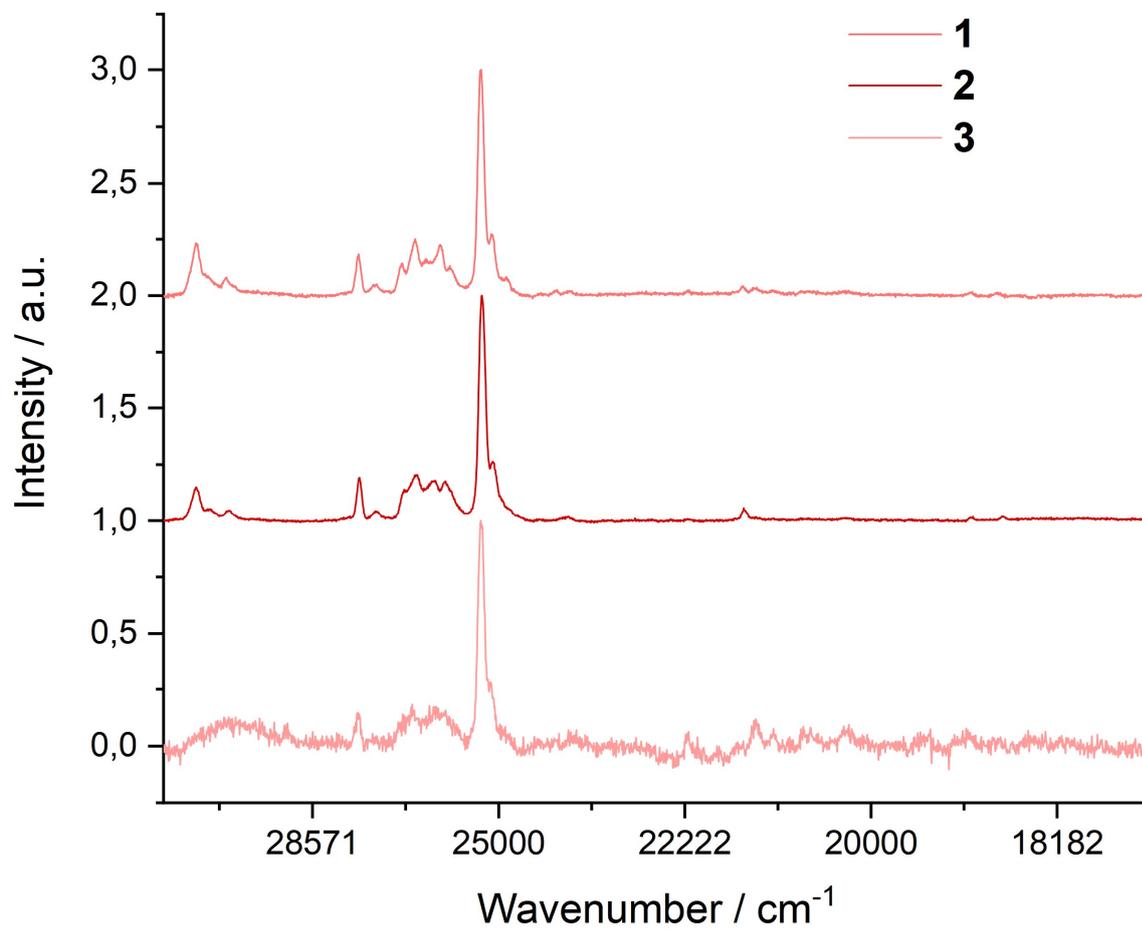


Figure S5. Excitation spectra measured on single crystals. Emission = 614 nm. Excitation slit = 1.5 nm, emission slit = 8 nm.

6. Time-resolved decay profiles

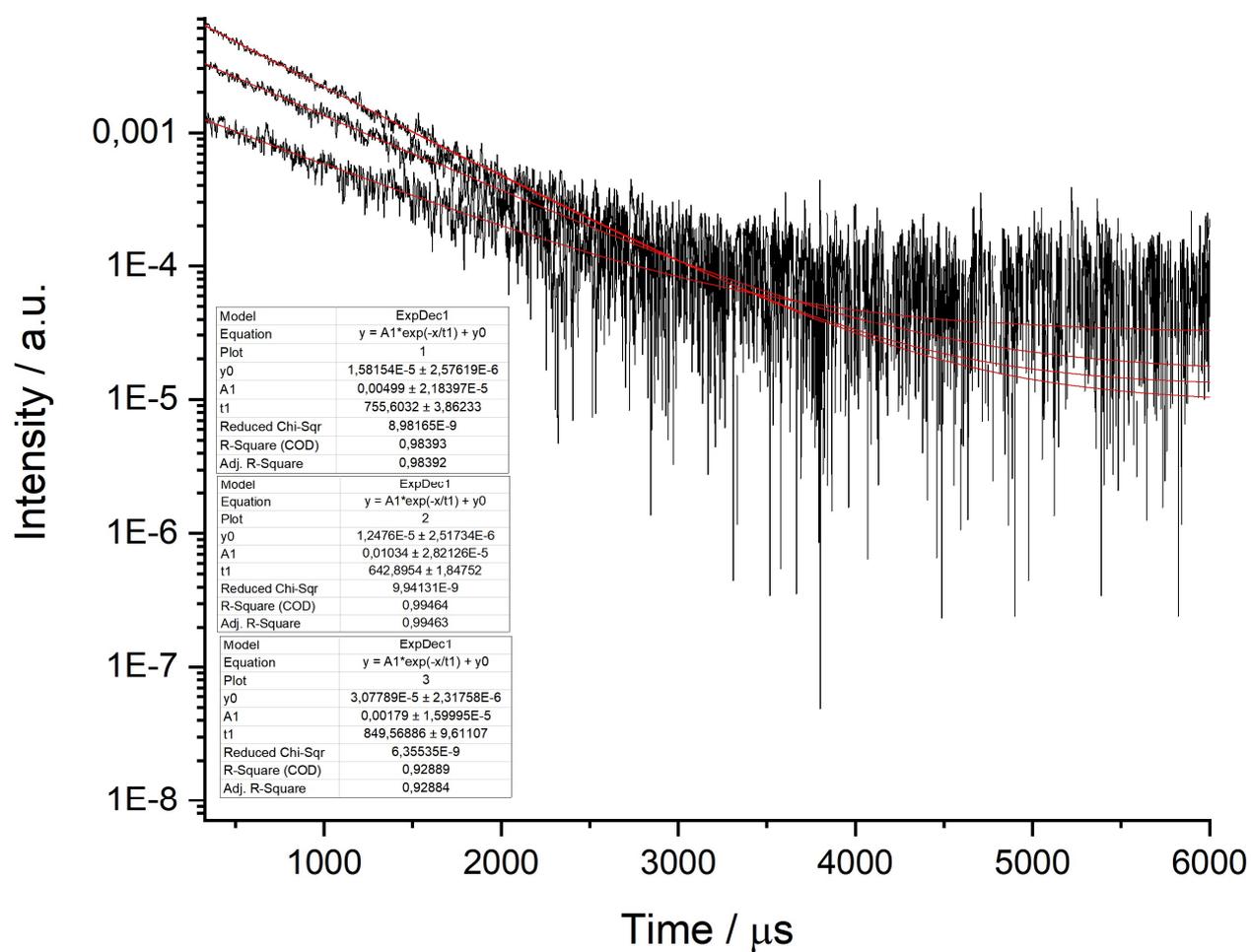


Figure S6. Time-resolved decay profiles measured on single crystals. Excitation = 394 nm, emission = 614 nm. Excitation slit = 8 nm, emission slit = 5 nm.

7. AlignIt Link and Guide

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

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

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 SAP, SAP2 and SAP-PB 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 the SAP2 structure and cSAP is used here as an example.

In order to run the program Anaconda and Mercury⁶ (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 $\sigma_{ideal} = 0.32$

8. Comparative scale, σ_{ideal} , for nine-coordinated polyhedra

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

Table S1. Symmetry deviation values for comparative nine-coordination scale

X/Z						
σ_{ideal}	<i>C_{4v}</i>	<i>D_{3h}</i>	<i>C_{2v}</i>	<i>C_{2v}</i>	<i>C_{3v}</i>	<i>D_{7h}</i>
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

			
	<i>cSAP</i>	<i>cTSAPc</i>	<i>cTSAPcc</i>
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.⁷

9. References

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