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Supporting information for article:

Crystal structure and optical properties of a two-sited Eu^{III} compound: an Eu^{III} ion coordinated by two $[Eu^{III}(DOTA)]^{-}$ complexes (DOTA is 1,4,7,10-tetrazacyclododecane-1,4,7,10-tetraacetate)

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S1. $[Eu(\mu O)_5(OH_2)_2(OH)][Eu(DOTA)(H_2O)]_2$ crystals

Crystals of $[Eu(\mu O)_5(OH_2)_2(OH)][Eu(DOTA)(H_2O)]_2$ (**1-H)** precipitates as plated flowers, where ultrathin plates grow from the same origin.

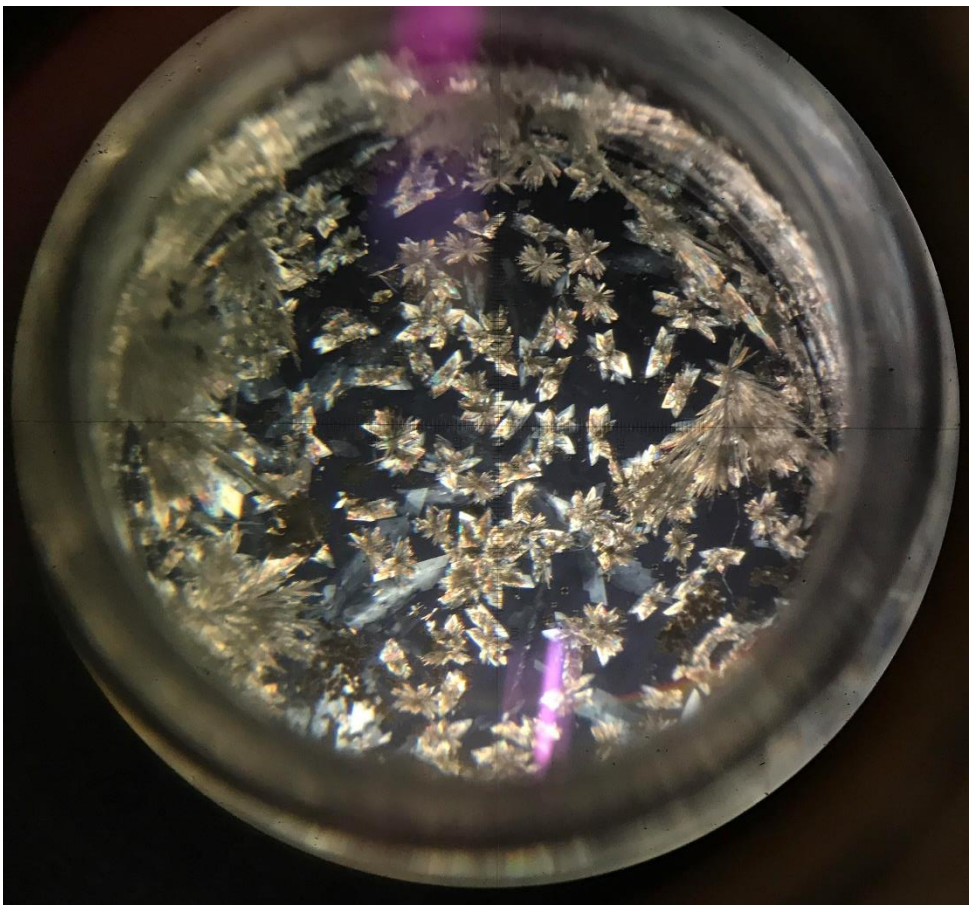


Figure S1 Crystals of $[Eu(\mu O)_5(OH_2)_2(OH)][Eu(DOTA)(H_2O)]_2$ (**1-H**). The picture is taken through a microscope lens.

S2. Setup for single crystal measurements

Setup for measuring single crystals in PTI QuantaMaster8075. The crystal is sitting on a magnetic sample mount used for single crystal X-ray diffraction measurements. The sample mount is placed on a rotation platform. The position of the crystal was manually adjusted to the excitation beam.

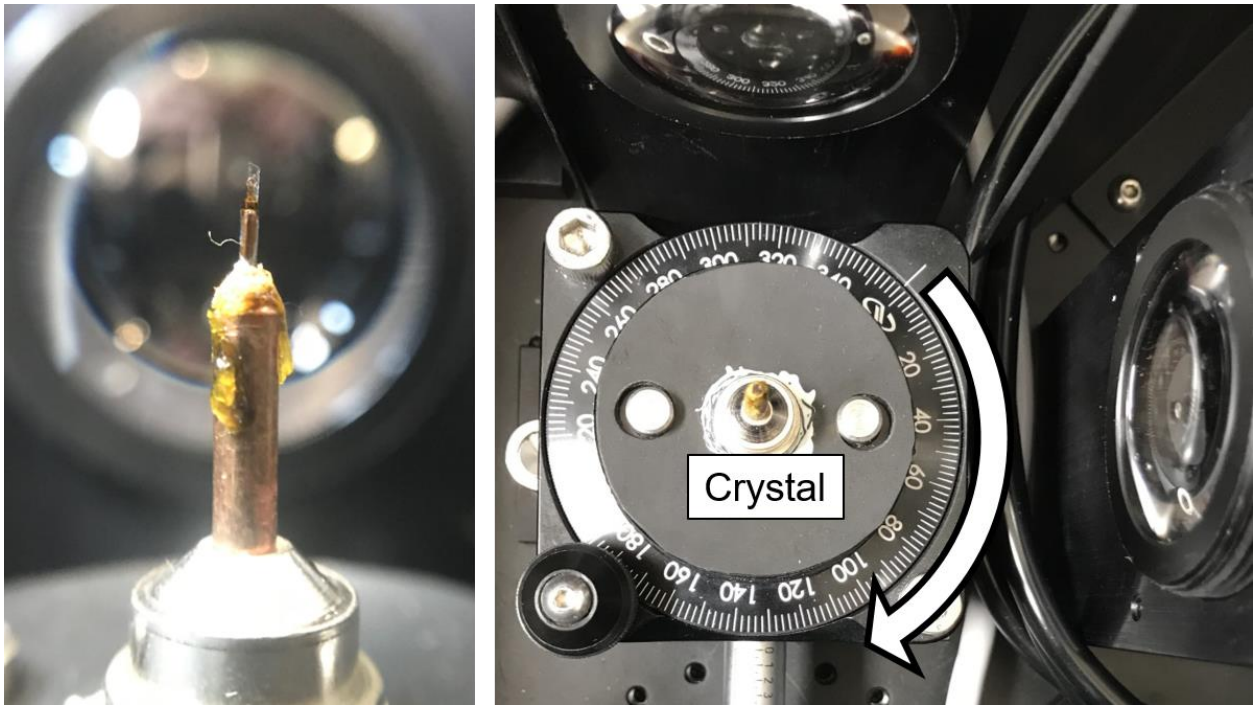
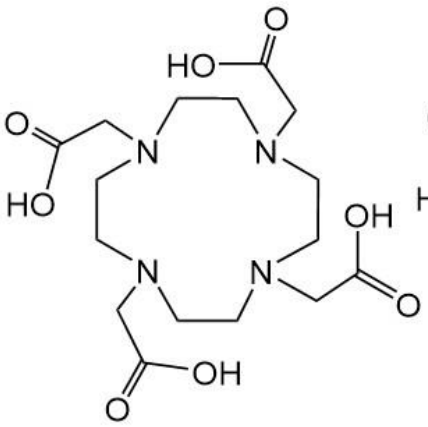
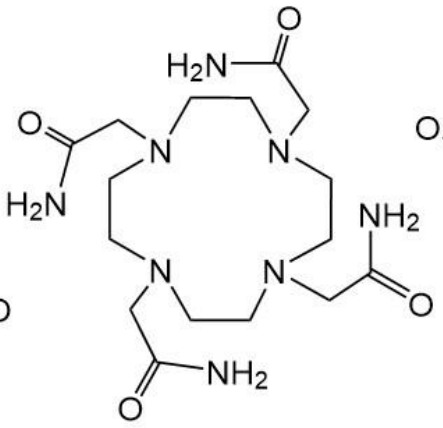


Figure S2 Setup for single crystal measurements on PTI QuantaMaster8075.

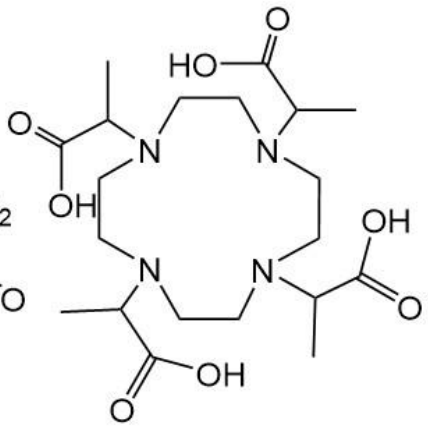
S3. Macrocyclic ligands



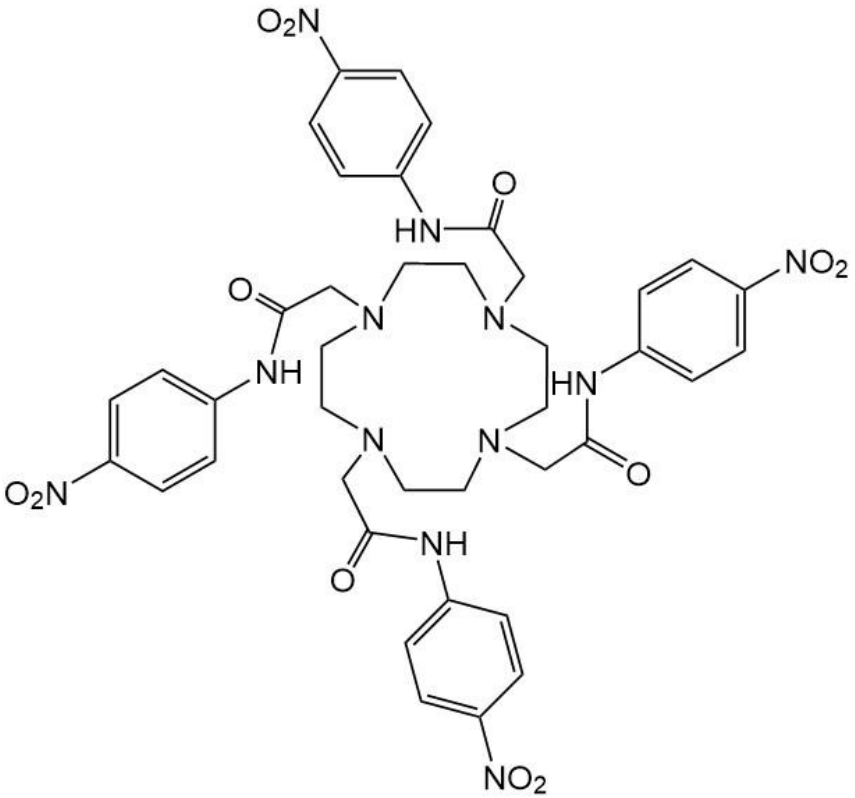
DOTA



DOTAM



DOTMA



L = 2,2',2'',2'''-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(*N*-(4-nitrophenyl)acetamide)

S4. Crystal structure and packing

Only one position shown for split water molecules

Unit cell of 1-H (HKLF 4 data) – CSD 2055279

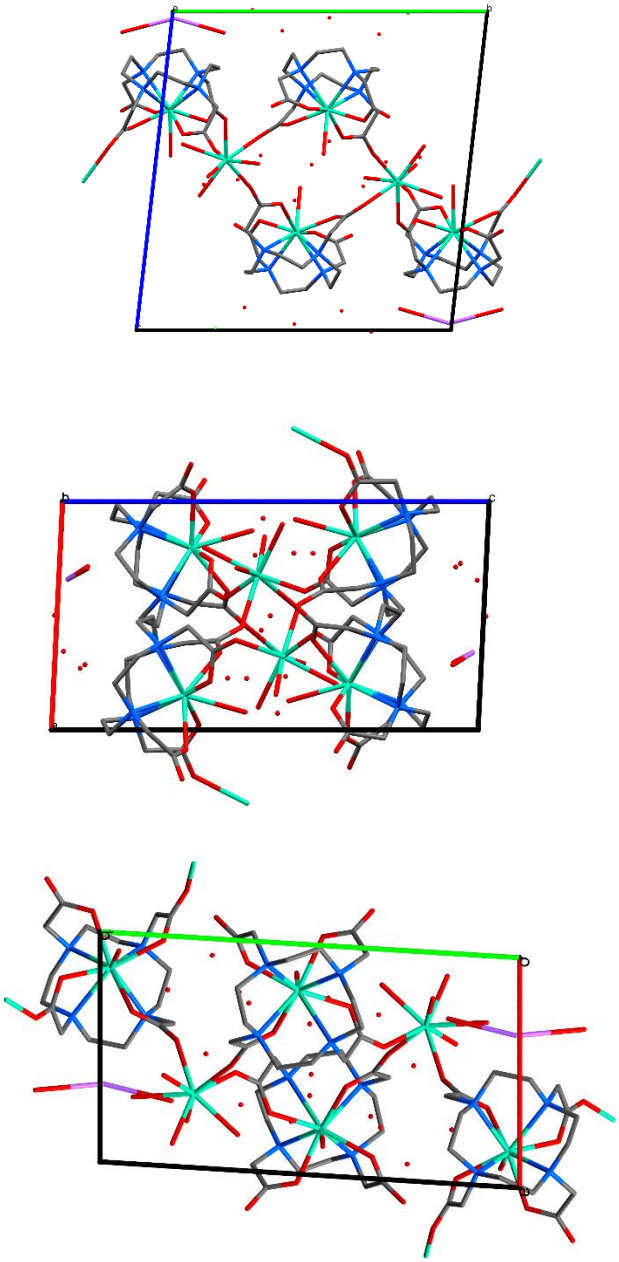


Figure S3 Unit cell viewed along cell axis. Top: along a, middle: along b, bottom, along c. Eu = teal, O, red, C = grey, N = blue, Na = purple, Cl = green. Hydrogens omitted.

S5. Crystal packing in 1-H (HKLF 4 data)

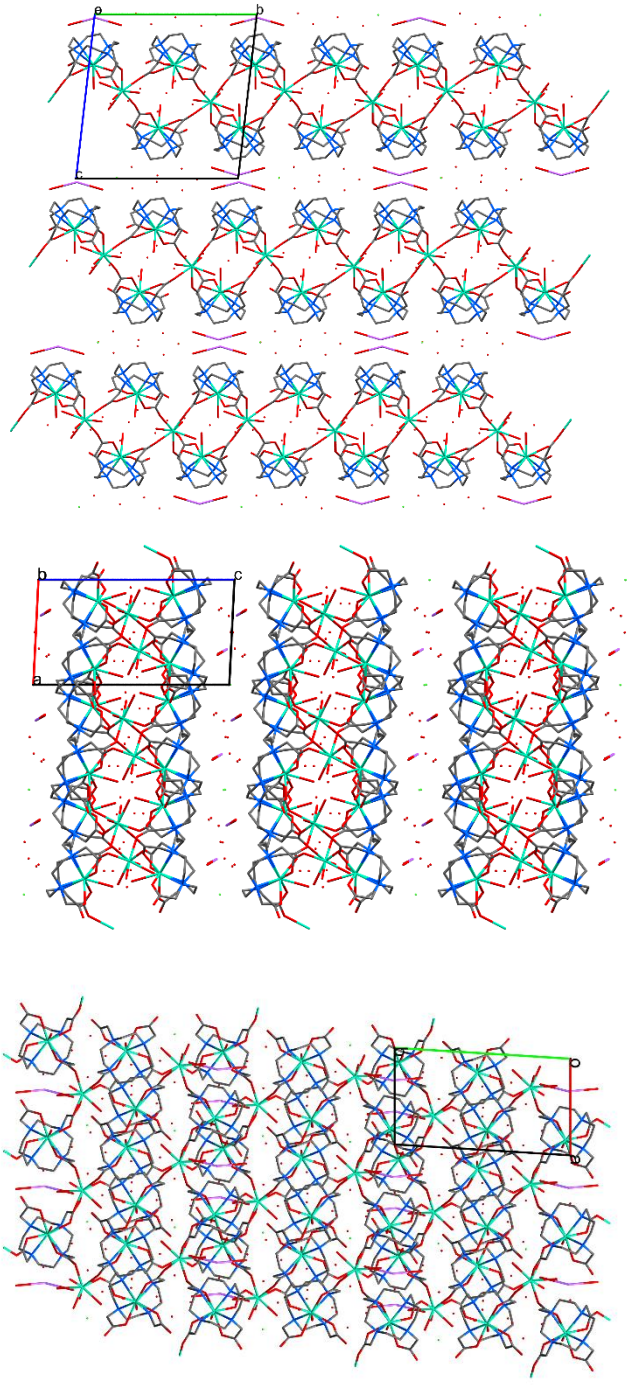


Figure S4 Crystal packing viewed along cell axis. Top: along a, middle: along b, bottom, along c. Eu = teal, O, red, C = grey, N = blue, Na = purple, Cl = green. Hydrogens omitted.

S6. Powder X-ray diffraction

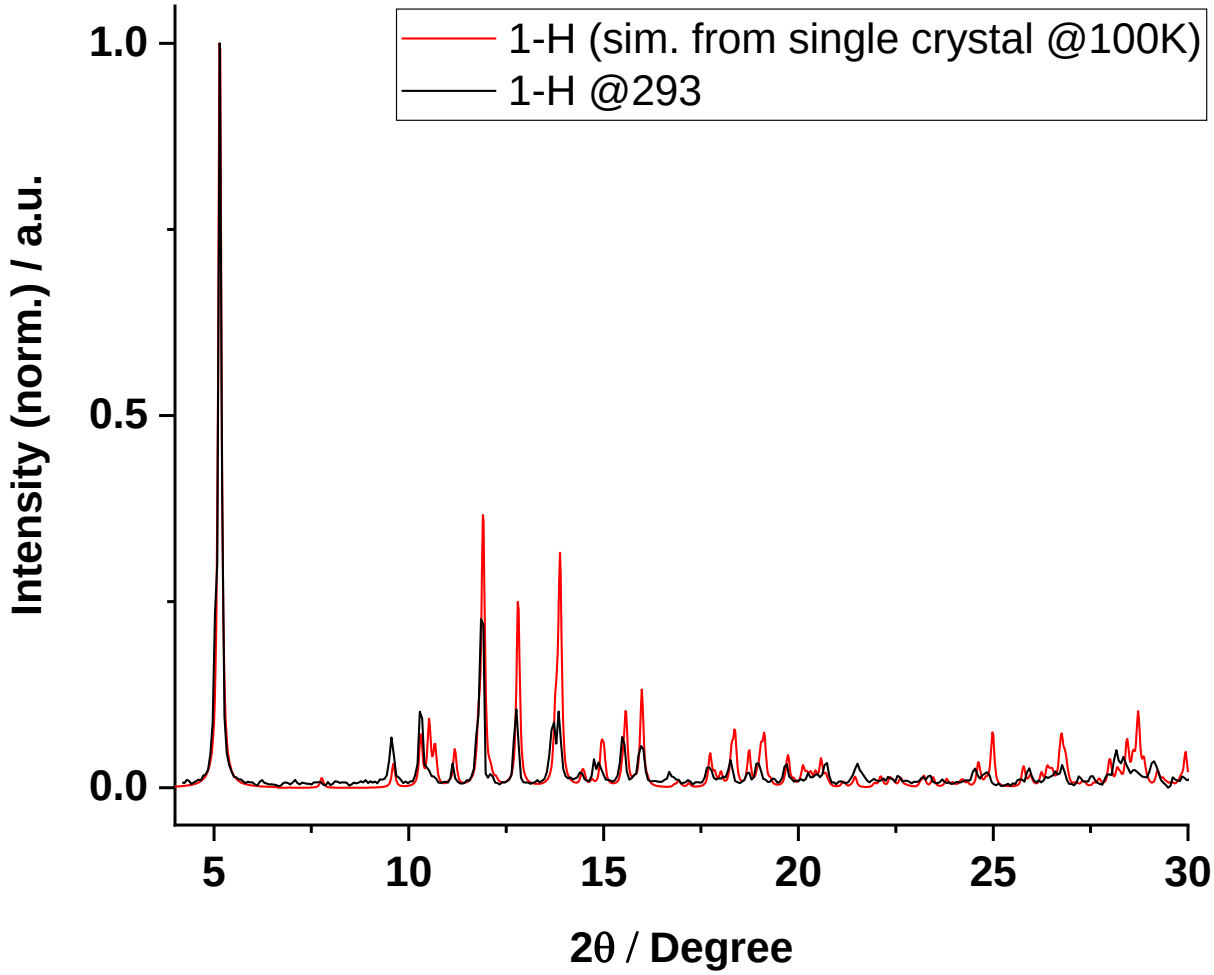


Figure S5 Powder X-ray diffraction pattern (293 K) and simulated powder diffraction pattern from single crystal structure (100 K).

S7. Luminescence lifetimes

Lifetime 1-H single crystal

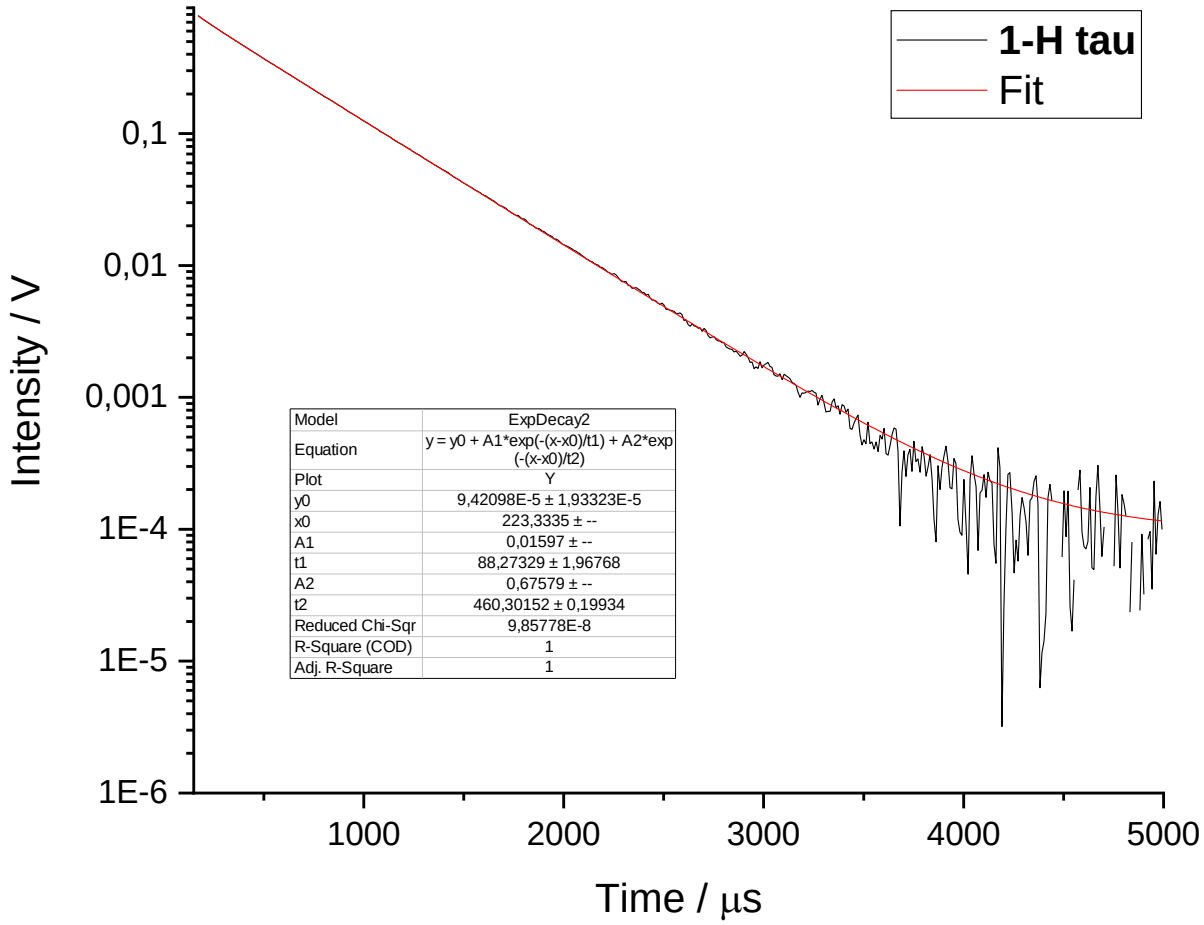


Figure S6 Lifetime of **1-H** fitted to a bi-exponential decay curve. Ex = 395, em = 614 nm. Ex slit = 8 nm, em slit = 8 nm. Recorded at room temperature.

Lifetime of 1-H **powder**

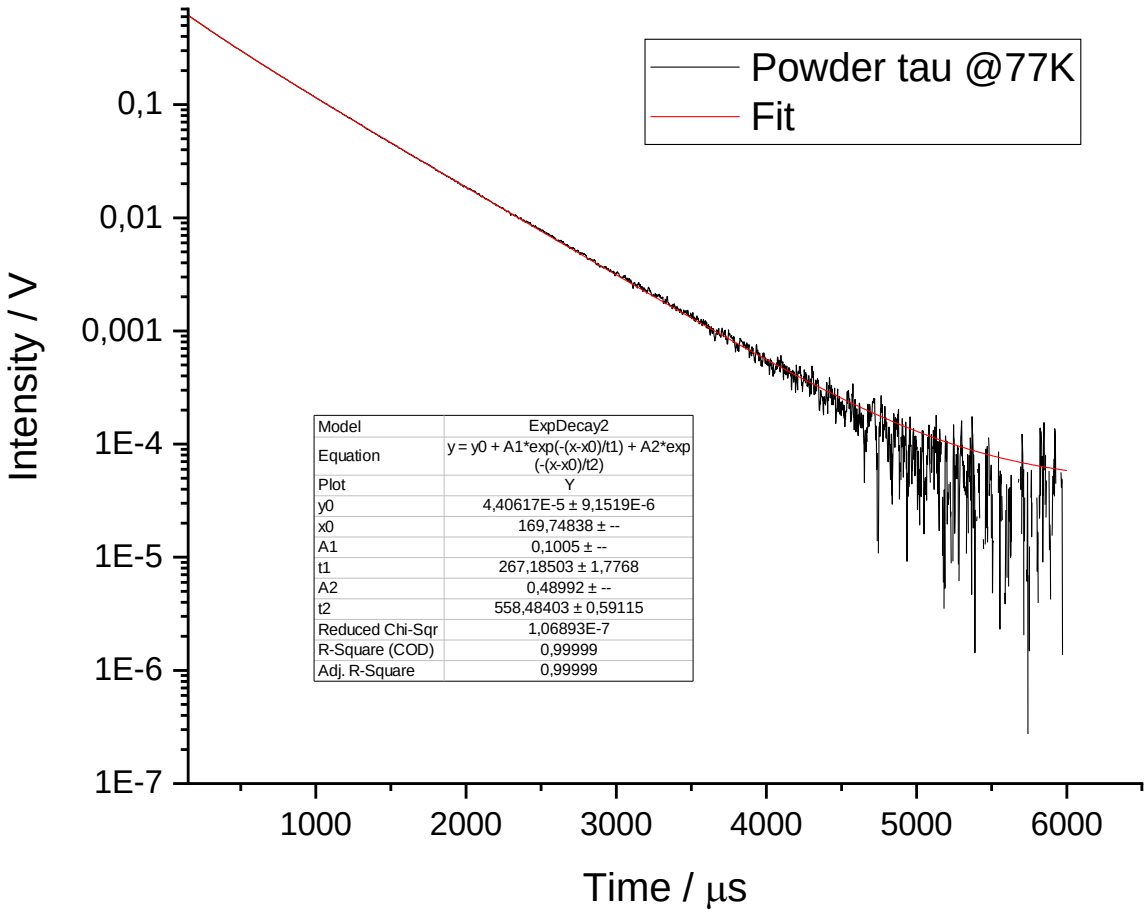
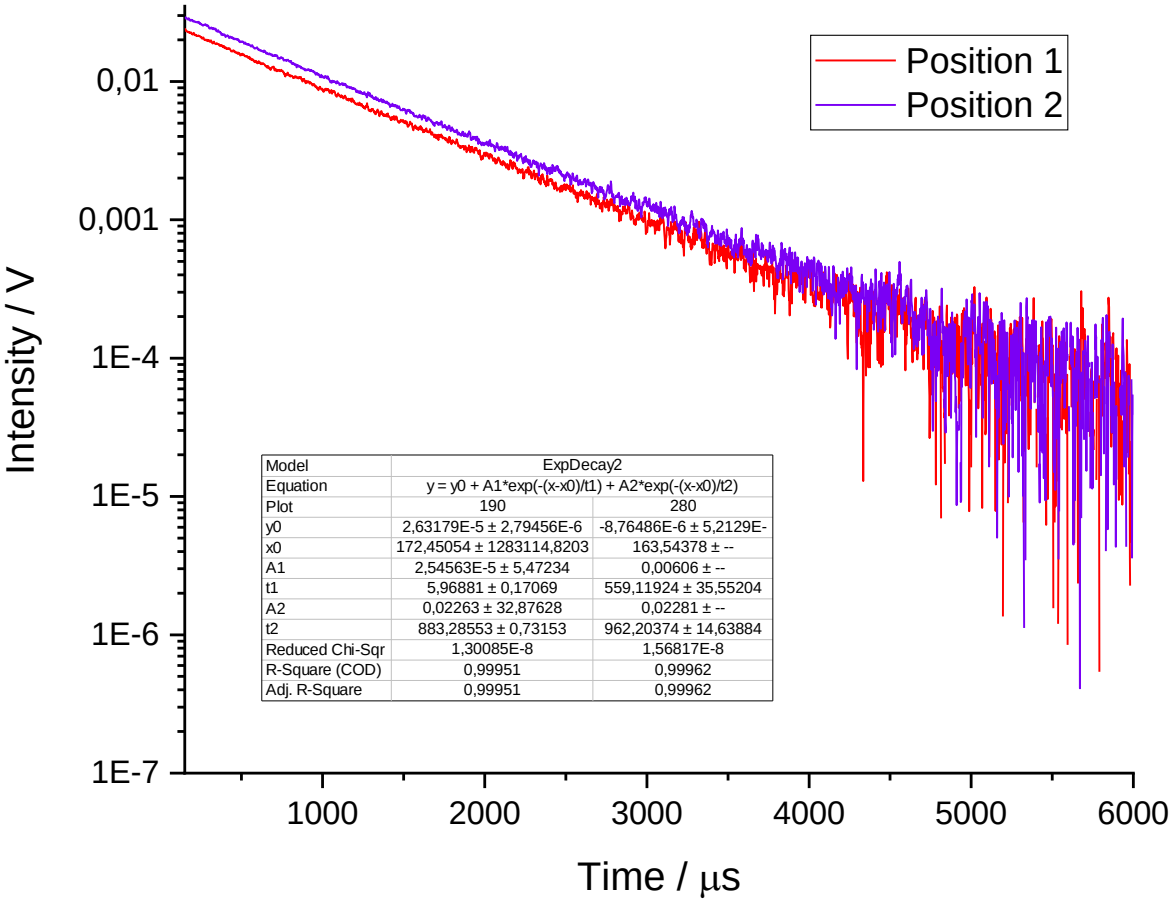


Figure S7 Lifetime of **1-H** powder fitted to a bi-exponential decay curve. Ex = 395, em = 614 nm. Ex slit = 8 nm, em slit = 8 nm.

Lifetime of 1-D single crystal



Model	ExpDecay2	
Equation	y = y0 + A1*exp(-(x-x0)/t1) + A2*exp(-(x-x0)/t2)	
Plot	190	280
y0	2,63179E-5 ± 2,79456E-6	-8,76486E-6 ± 5,2129E-
x0	172,45054 ± 1283114,8203	163,54378 ± --
A1	2,54563E-5 ± 5,47234	0,00606 ± --
t1	5,96881 ± 0,17069	559,11924 ± 35,55204
A2	0,02263 ± 32,87628	0,02281 ± --
t2	883,28553 ± 0,73153	962,20374 ± 14,63884
Reduced Chi-Sqr	1,30085E-8	1,56817E-8
R-Square (COD)	0,99951	0,99962
Adj. R-Square	0,99951	0,99962

Figure S8 Lifetime of **1-D** at position 1 and 2 fitted to a bi-exponential decay curve. Ex = 395, em = 614 nm. Ex slit = 8 nm, em slit = 8 nm. Recorded at room temperature.

S8. Refractive Index Influence on Lifetime Calculations

Table S1 Values used for estimations

	Value
Q.Y. (assumed)	0.1
Refractive index – H_2O	1.0
Refractive index – Lu_2O_3	1.33

Table S2 Experimental luminescence lifetimes

Compound	**τ**	**k_{obs}**	**τ_0**	**k_{Lm}(exp)**	**k_{nr}(exp)**
$[Eu(DOTA)(D_2O)]^-$ in **1-D**	962	0.001040	9620	0.000104	0.000936
[**Eu.L**$(D_2O)]^{3+}$	769	0.001300	7690	0.00013	0.001170
$[Eu(DOTA)(D_2O)]^-$	2174	0.000460	21740	4.6E-05	0.000414
$[Eu(DOTAM)(D_2O)]^{3+}$	2439	0.000410	24390	4.1E-05	0.000369

Table S3 Modelled luminescence lifetimes

Compound	**$\tau_{solution}$**	**$\tau_{crystal}$**	**k_{obs}**	**k_{Lm}(exp)**	**k_{nr}(exp)**
$[Eu(DOTA)(D_2O)]^-$ in **1-D**	1030.74		0.000970	0.000035	
[**Eu.L**$(D_2O)]^{3+}$	823.95		0.001214	0.000043	
$[Eu(DOTA)(D_2O)]^-$		1811.33	0.000552		0.000138
$[Eu(DOTAM)(D_2O)]^{3+}$		2032.12	0.000492		0.000123

S9. Absorption and excitation

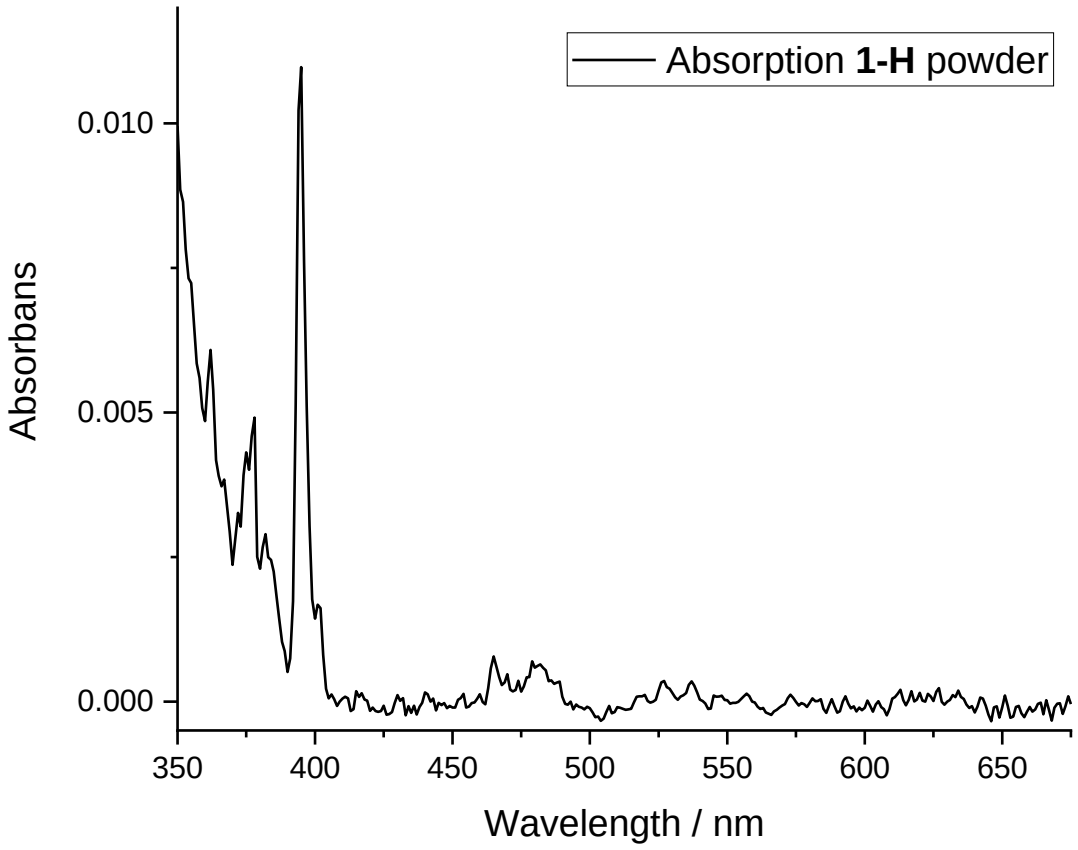


Figure S9 Absorption spectrum of **1-H** powder. Emission = 614 nm. Slits: ex = 8 nm.

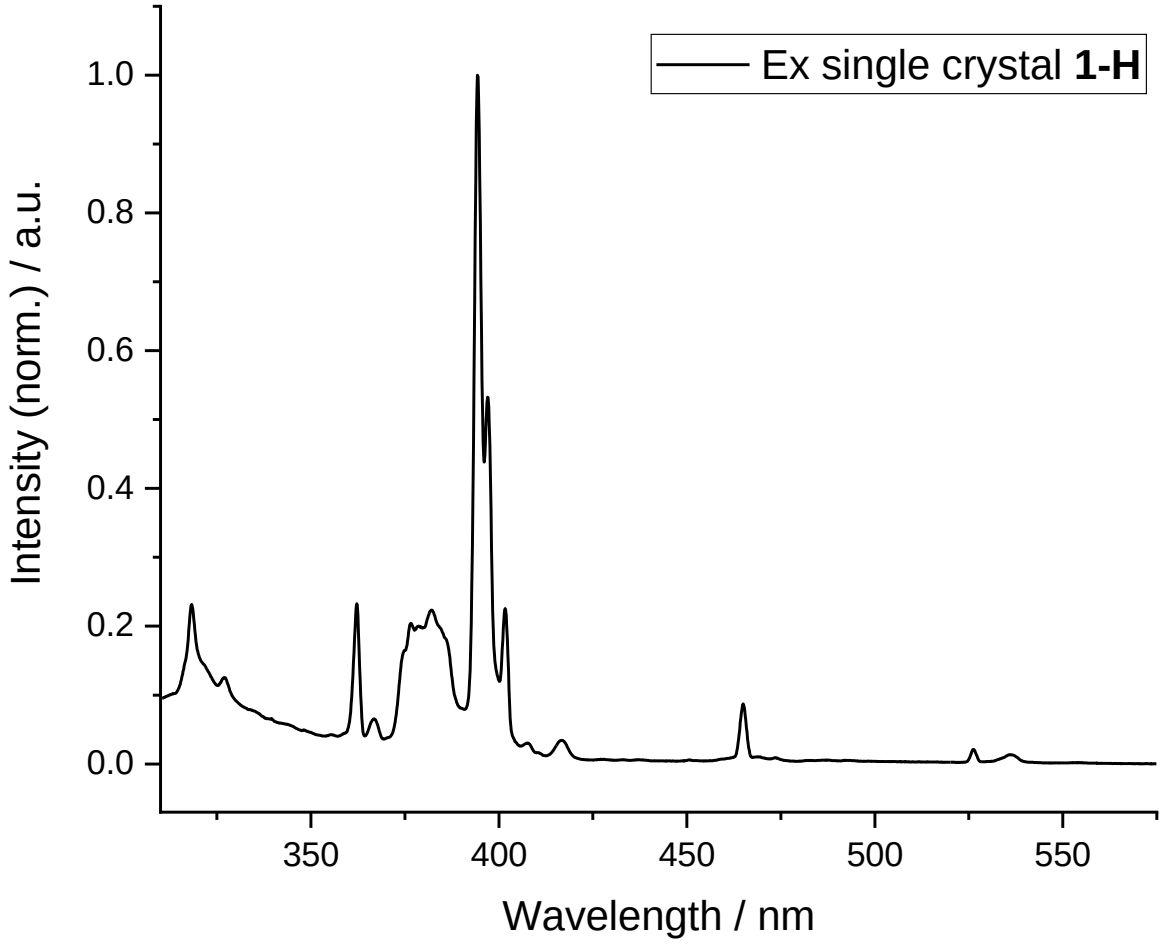


Figure S10 Excitation spectrum of **1**-**H** single crystal. Emission = 614 nm. Slits: ex = 1.5 nm, em = 8 nm. Recorded at room temperature.

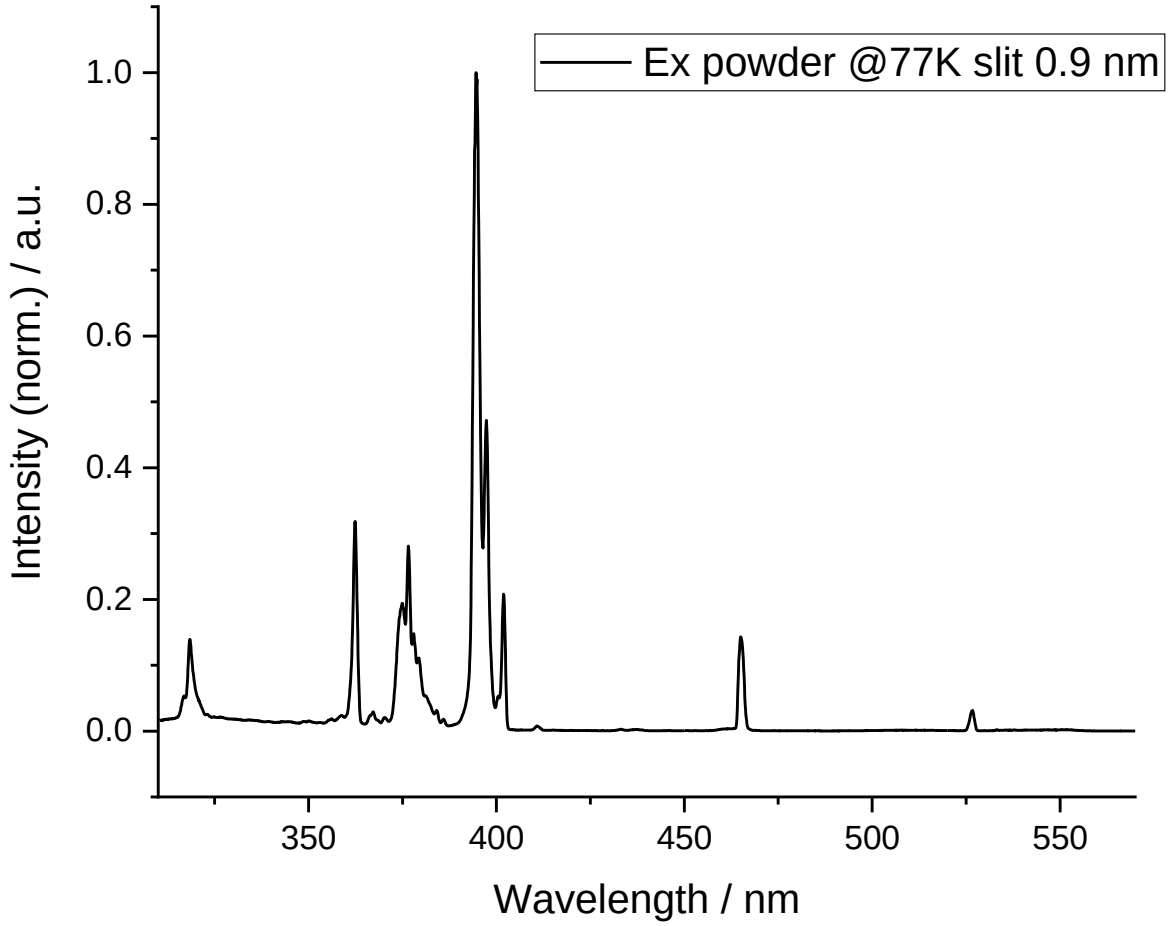


Figure S11 Excitation spectrum of **1**-**H** powder. Emission = 614 nm. Slits: ex = 0.9 nm, em = 8 nm.