

Supporting information for

Preparation and study of an f,f,f',f'' covalently linked tetranuclear hetero-trimetallic complex – a Europium, Terbium, Dysprosium triad

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Experimental procedures

1.Dy₂TbEu. The complex **2.Dy₂·6NaO₃SCF₃** (0.020 g, 9.2 μmol) was added to a solution containing **3.Tb·3NaO₃SCF₃** (0.013 g, 11 μmol), benzyl isocyanide (0.0013 g, 11 μmol), **4.Eu·3NaO₃SCF₃** (0.013 g, 11 μmol) and Na₂SO₄ (0.132 g, 0.9 mmol) in ethanol (5 cm³). The reaction mixture was stirred at room temperature for 6 days. The solids were removed by filtration and the filtrate evaporated. The crude product was washed with diethyl ether (5 x 20 cm³), redissolved in methanol and precipitated by addition of diethyl ether to give an off-white solid. The product was purified by dialysis using a 1000 Da membrane. The water was changed every 12 hours for 4 days. After removal of the solvent the product was obtained as an off-white powder. ¹H NMR pD≈6 δ 256.4, 240.4, 202.9, 187.8, 110.9, 102.9, 71.3, 57.1, 49.8, 48.4, 29.5, 29.0, 28.2, 27.2, 26.9, 26.4, 18.5, 12.6, 11.0, 10.2, 9.15, 8.67, 8.52, 7.44, 7.17, 0.84, 0.42, 0.32, 0.24, 0.13, -0.32, -3.75, -3.90, -4.72, -5.93, -6.15, -6.87, -7.17, -7.52, -8.25, -8.46, -8.71, -9.02, -9.55, -9.85, -10.9, -12.3, -12.9, -14.3, -14.9, -15.3, -16.0, -17.7, -18.3, -18.9, -67.4, -77.3, -78.5, -80.2, -101.1, -110.2, -114.5, -122.7, -365.4, -376.7, -379.6, -393.5. No dysprosium peaks observed at this pD.

nano-ESI-FTMS MS. Calculated for C₈₂H₁₁₆N₂₂O₂₇EuTbDy₂+2H₂O+2CH₃OH+NH₄⁺ = 2595.65, found: *m/z* = 2595.34. Calculated for C₈₂H₁₁₆N₂₂O₂₇EuTbDy₂+3H₂O+CH₃OH-C₇H₁₀+H⁺ = 2473.56, found: *m/z* = 2473.89.

2.Dy₂. Prepared as reported in ref 1. ¹H NMR (500 MHz, D₂O) δ 373.94, 354.78, 285.33, 271.54, 172.69, 127.81, 116.60, 88.24, -84.88, -157.32, -161.65, -177.39, -204.33, -216.18, -278.84, -346.91. MALDI-TOF MS Calculated for C₃₆H₅₃Dy₂N₉O₁₂+Na⁺ = 1151.23, found: *m/z* = 1151.41. Calculated for C₃₆H₅₃Dy₂N₉O₁₂K⁺ = 1167.20, found: *m/z* = 1166.42

3.Tb. Compound **H₃,3²** (0.15 g, 0.33 mmol) and terbium(III) trifluoromethanesulfonate (0.21 g, 0.35 mmol) were dissolved in methanol (4 cm³) and stirred at 50 °C for 2 d. The solvent was evaporated and the solid redissolved in water (10 cm³). The pH of the solution was adjusted to 12 using NaOH_{aq} and the precipitate was removed by centrifugation. The supernatant was purified by dialysis and evaporated to yield a pale yellow solid. ¹H NMR δ (minor isomer) 260.3, 243.0, 205.4, 190.4, 112.4, 104.3, (84.0), 72.4, 58.3, 50.8, 49.6, 18.9, 7.6, 7.4, (-59.8), (-63.2), -68.5, -78.1, -79.5, -81.4, (-96.6), (-100.2), -102.5, -111.7, -115.9, -124.2, (-196.5), (-212.7), -371.1, -382.6, -385.4, -399.3. ESI-QP MS Calculated for C₁₈H₂₈N₅O₉Tb+H⁺ = 618.13, found: *m/z* = 618.9.

4.Eu. EuDO3A propargyl³ (106 mg, 0.19 mmol) and 2-azidopropanal (83 mg, 0.84 mmol) are dissolved in methanol. CuSO₄ 5H₂O (4.8 mg, 0.02 mmol) and sodium ascorbate (8mg, 0.04 mmol) are then added and the reaction mixture is stirred for 16 hours at RT under a nitrogen atmosphere. After removal of solvent under vacuum the so formed sticky solid is redissolved in 10 mL of water and extracted with DCM (3x10mL) and the organic phase is then discarded. Removal of water yielded a pale yellow solid that is dialysed against water using a 500MW membrane for 2 days. Removal of residual solvent yielded a white off solid (115 mg, 91% yield). ¹H NMR δ (minor isomer) (30.0), (29.8), 29.4, (28.5), 27.1, 26.8, 26.3, (12.5), (10.8), (10.2), (9.63), 8.50, 6.99, 6.26, 3.68, 3.34, (-1.54), (-2.74), (-3.27), -4.81, (-6.42), -6.95, -7.22, -7.56, (-8.03), -8.56, -8.78, -9.08, -9.83, (-10.9), -12.3, -13.0, -14.4, -14.9, -16.1, (-16.7), (-17.2), -18.4, -18.9. HR-ESI-TOF MS Calculated for C₂₀H₃₀EuN₇O₇+CH₃OH+Na⁺ = 688.1575, found: *m/z* = 688.1573.

NMR

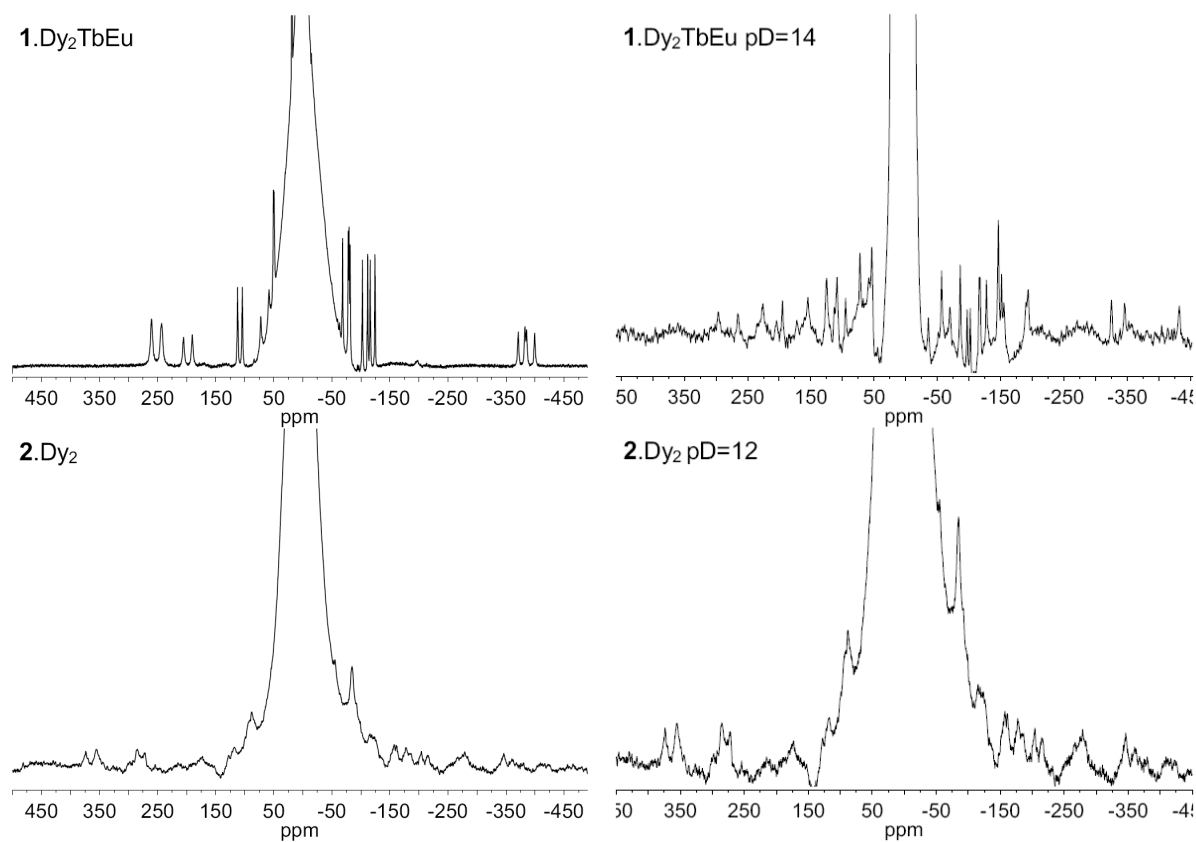


Figure S1. Paramagnetic ^1H NMR spectra of **1.Dy₂TbEu** and **2.Dy₂** in D_2O .

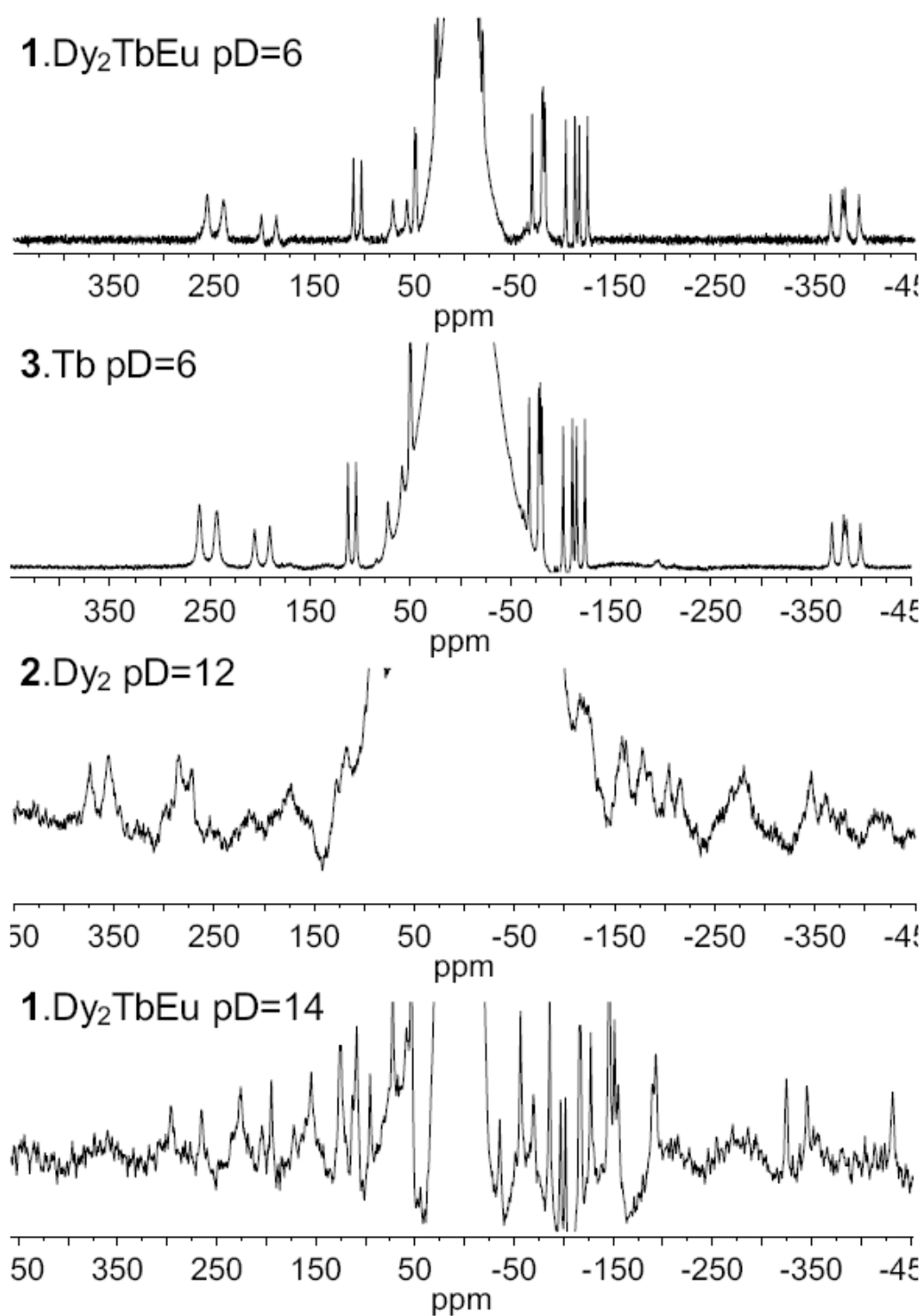


Figure S2. Influence of pH on the paramagnetic ¹H NMR spectra of **1**.Dy₂TbEu, **2**.Dy₂ and **3**.Tb in D₂O.

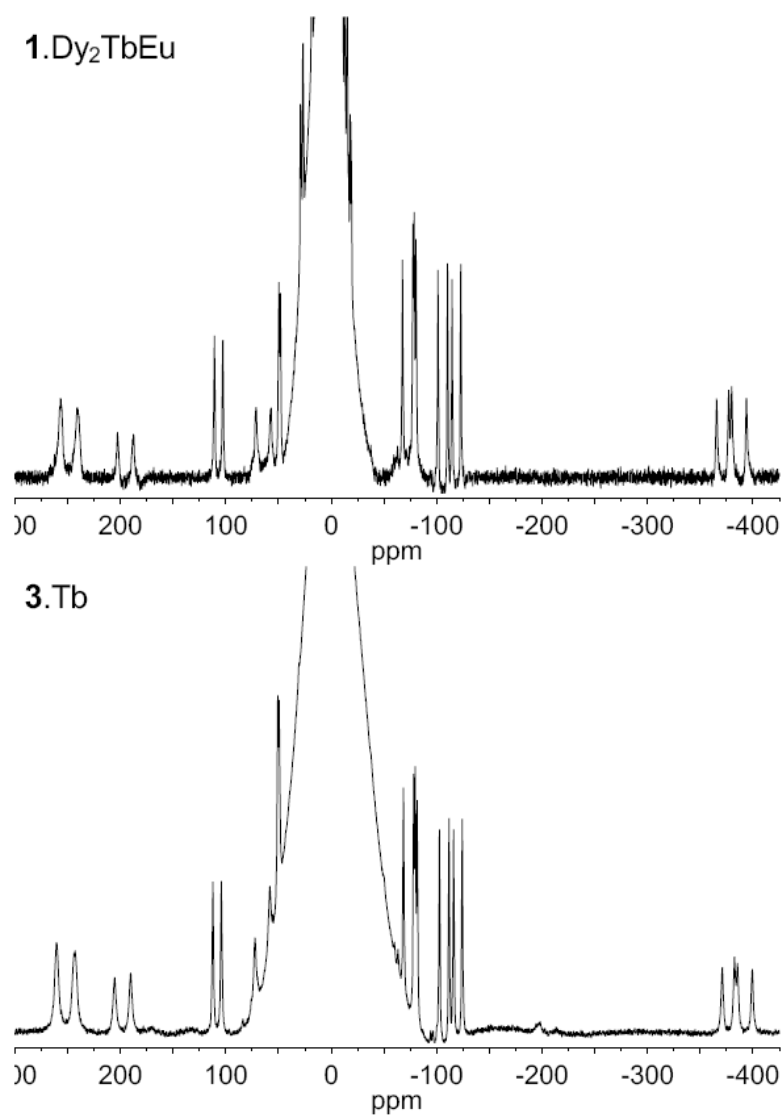


Figure S3. Paramagnetic ^1H NMR spectra of **1.Dy₂TbEu** and **3.Tb** in D_2O .

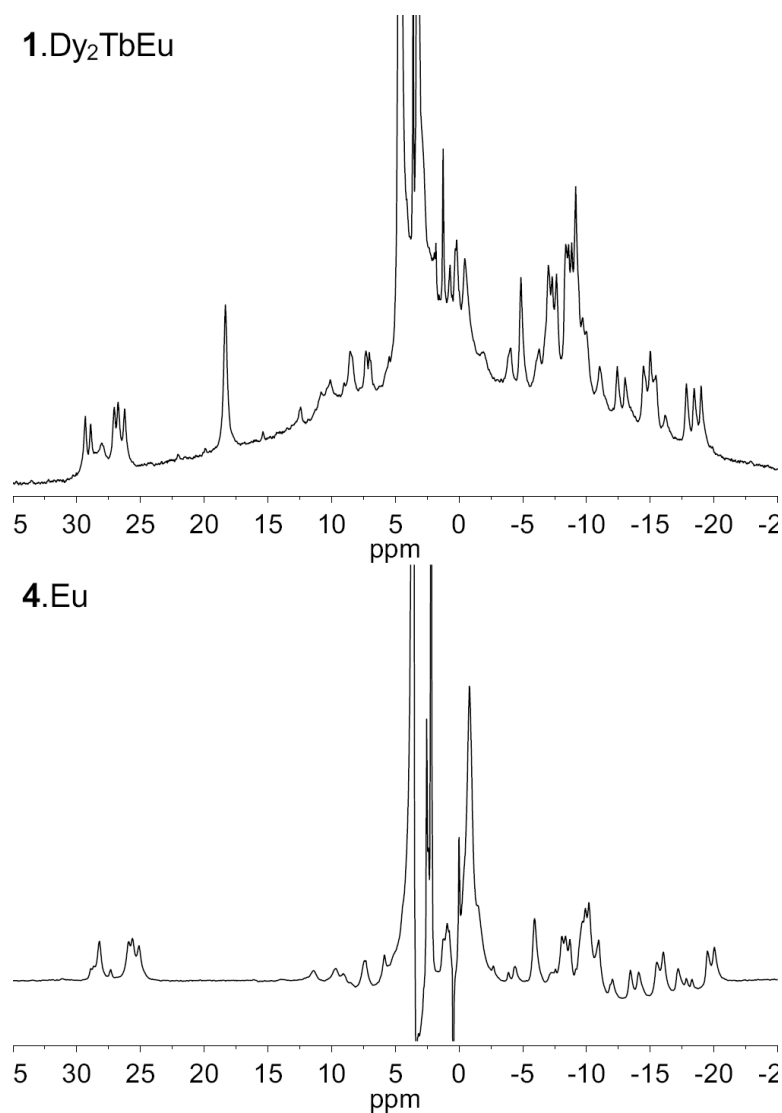


Figure S4. Paramagnetic ¹H NMR spectra of **1.Dy₂TbEu** and **4.Tb** in D₂O. Not the evident differences in the peaks around 30 and -20 ppm.

Luminescence

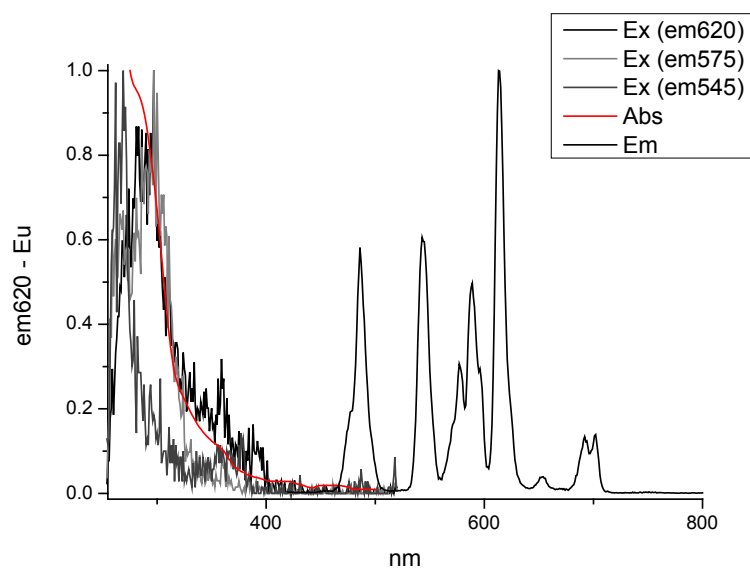


Figure S5. Absorption, emission and excitation spectra of **1**.Dy₂TbEu DMSO. The excitation spectrum changes with emission wavelength.

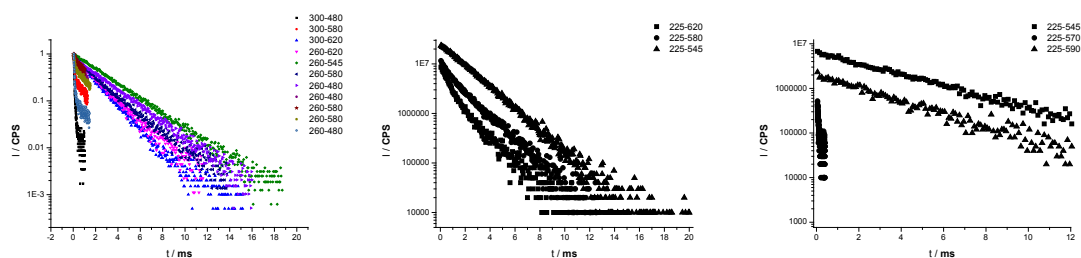


Figure S6. Luminescence lifetimes of **1**.Dy₂TbEu in DMSO, H₂O and D₂O. The lifetimes observed are highly dependent on excitation and emission wavelength.

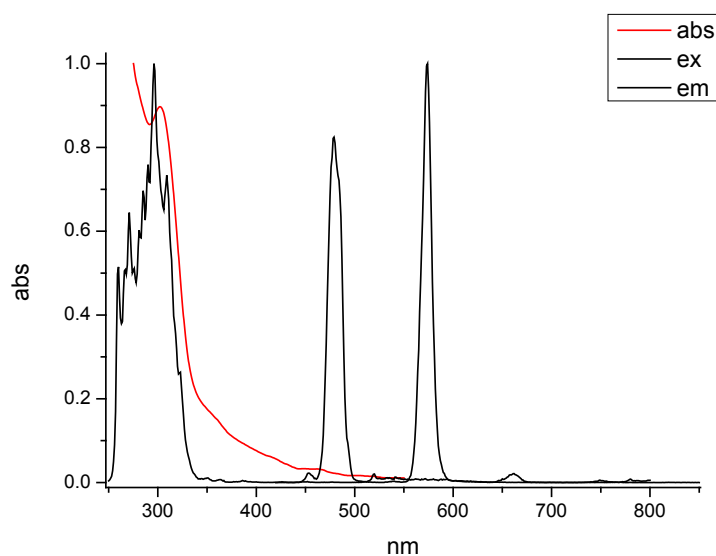


Figure S7. Absorption, emission and excitation spectra of **2.Dy₂** DMSO.

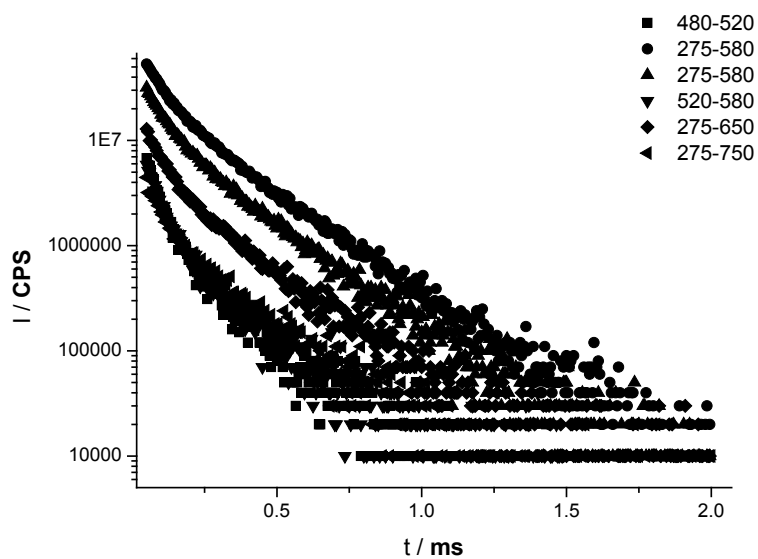


Figure S8. Luminescence lifetimes of **2.Dy₂** in DMSO. The initial slope in the curves are due to scattered light, only the tail was used to determine the lifetime.

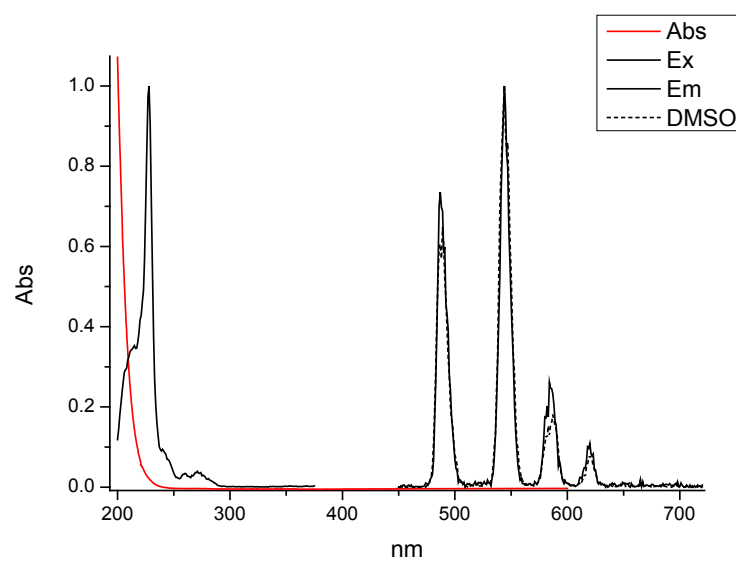


Figure S9. Absorption, emission and excitation spectra of **3.Tb** in D₂O and DMSO.

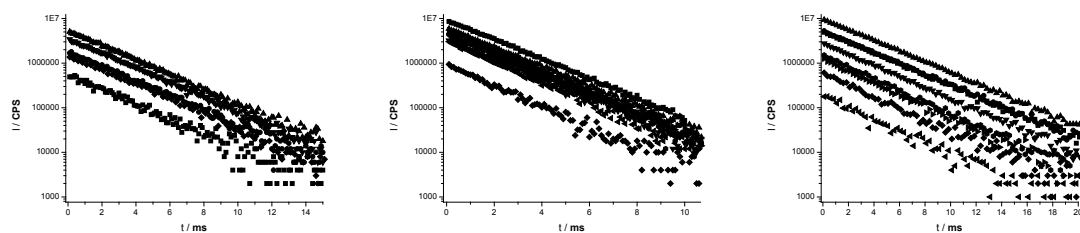


Figure S10. Luminescence lifetimes of **3.Tb** in DMSO, H₂O and D₂O exciting at 260 nm and monitoring in each of the Tb bands.

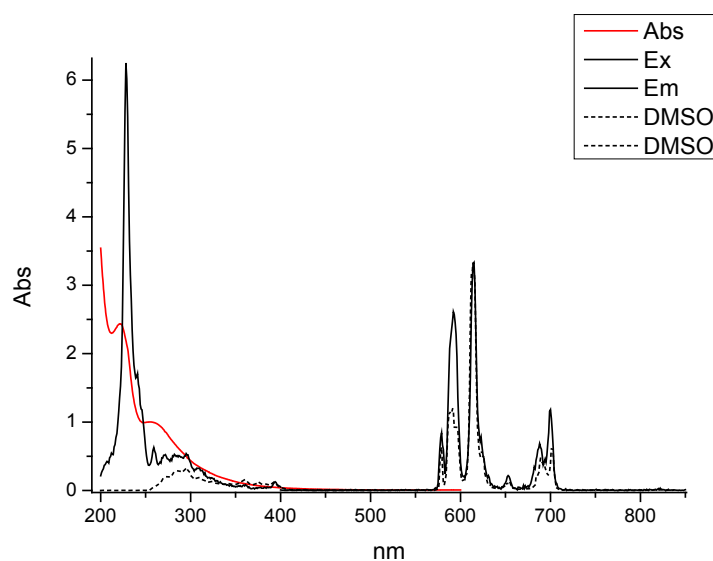


Figure S11. Absorption, emission and excitation spectra of **10.Eu** D2O and DMSO.

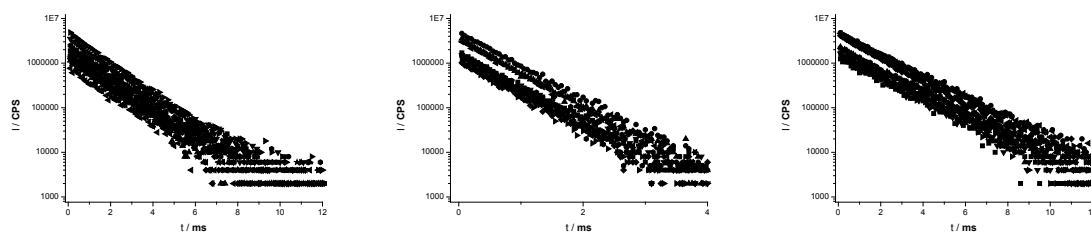


Figure S12. Luminescence lifetimes of **4.Eu** DMSO, H2O and D2O exciting at 260 nm and 300 nm and monitoring in each of the Eu bands

Titration with *iso*-phthalate

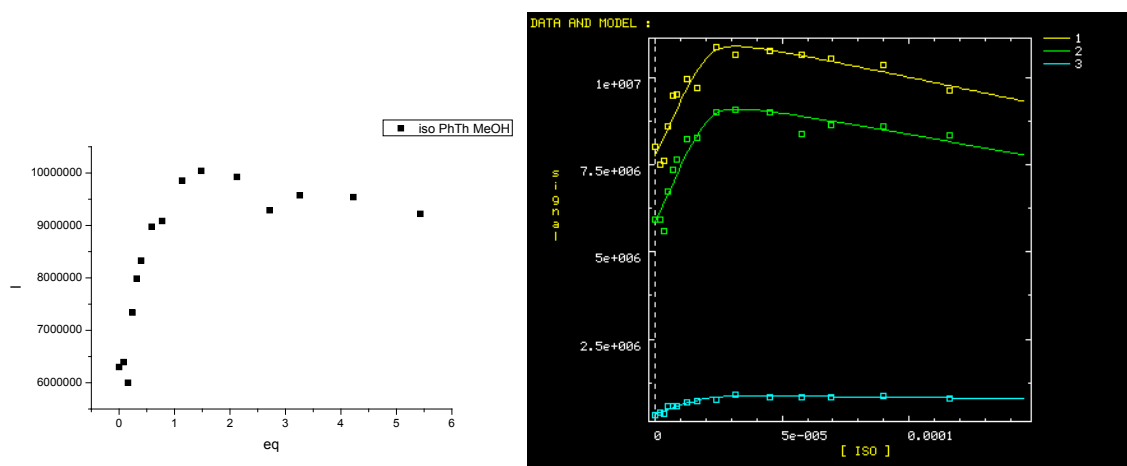


Figure S13. left: Titration of **2.Dy₂** ([**2.Dy₂**]= $2.13 \cdot 10^{-5}$) in methanol with *iso*-phthalate. right: fit of the observed data using Dynafit.⁴

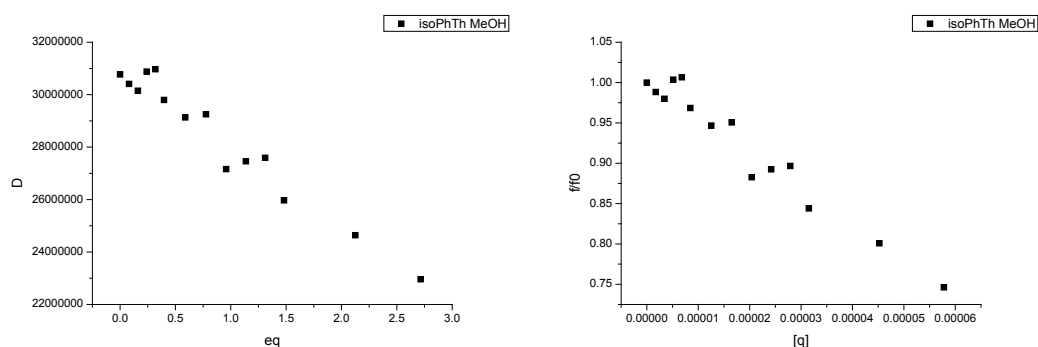


Figure S14. left: Titration of **1.Dy₂TbEu** with isophthalate. right: Stern-Volmer plot of the titration data.

Dynafit script:

[task]

task = fit

data = equilibria

[mechanism]

Dy + ISO <=> complex1 : K1 assoc

complex1 + ISO <=> complex2 : K2 assoc

[constants]

K1 = 10e5 ??

K2 = 1000 ?

[concentrations]

Dy = 2.13E-05

[responses]

Dy = 26000 , complex1 = 20000 , complex2 = 1000 ?

[equilibria]

variable ISO

file C:\Users\TJS\Documents\Kemi\Oxford\Dy2TbEu\f1.txt | response Dy = 6e5 ? , complex1 = 9e6 ? , complex2 = 1000 ?

file C:\Users\TJS\Documents\Kemi\Oxford\Dy2TbEu\f2.txt | response Dy = 1.35e4 ? , complex1 = 4.1e6 ? , complex2 = 1000 ?

file C:\Users\TJS\Documents\Kemi\Oxford\Dy2TbEu\f3.txt | response Dy = 2.2e4 ? , complex1 = 4.1e7 ? , complex2 = 1000 ?

[output]

directory C:\Users\TJS\Documents\Kemi\Oxford\Dy2TbEu\result

[end]

References

- 1: Placidi, M. P.; Natrajan, L. S.; Sykes, D.; Kenwright, A. M.; Faulkner, S. *Helvetica Chimica Acta* **2009**, *92*, 2427.
- 2: Schmitt-Willich, H.; Platzek, J.; Graske K.-D.; Raduechel B., Method for producing metal complex carboxylic acid amides, Patent#DE19961052386 19961204.
- 3: Jauregui, M.; Perry, W. S.; Allain, C.; Vidler, L. R.; Willis, M. C.; Kenwright, A. M.; Snaith, J. S.; Stasiuk, G. J.; Lowe, M. P.; Faulkner, S. *Dalton Transactions* **2009**, 6283.
- 4: Kuzmic, P., *Anal. Biochem.* **1996**, *237*, 260-273.