Excited State Properties of Lanthanide(III) Complexes with a Nonadentate Bispidine Ligand

Laura Abad-Galán, Patrick Cieslik, Peter Comba, Michael Gast, Olivier Maury, Lucca Neupert, Amandine Roux, and Hubert Wadepohl
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S1. Experimental Section

All chemicals were purchased from Merck (Sigma Aldrich Chemie GmbH), Tokyo Chemical Industry Co. Ltd., Fisher Scientific GmbH and abcr GmbH. Analytical grade solvents were used without further purification and all reactions were carried out in air if not mentioned otherwise.

NMR spectra were recorded on a Bruker Avance I 200, a Bruker Avance II 400 or a Bruker Avance III 600. NMR chemical shifts are referenced on the solvents and two-dimensional correlation spectra were used to assign the signals. Mass spectra were recorded on a Bruker ApexQe FT-ICR instrument. Ultra-Performance Liquid Chromatography was performed on a Waters UPLC-SQD2 instrument (solvents: A: H\textsubscript{2}O (0.1% TFA), B: MeCN; gradient 0-7 min 10-100% B, ionization method: APCI pos.). Elemental Analyses were performed on a CHN-O-vario EL by the micro analytical lab, Heidelberg University. X-ray data were collected at low temperature on Bruker D8 Venture (Mo K\alpha or Cu K\alpha radiation, T = 100 K) or Agilent Supernova diffractometers (Mo K\alpha radiation, T = 120 K) (see below for details). The plots of the solids state
structures were performed using the programs POV-ray and ORTEP.\textsuperscript{[1]} UV/vis spectra were recorded with a Jasco V-570 UV-vis-NIR spectrometer in water with the thermostat JASCO ETC50ST set at 20°C and Quartz cuvettes with a length of 1 cm were used for the measurements.

**S1.1. Ligand synthesis**

Piperidone \( P^{[2]} \), tert-butyl 6-(bromomethyl)picolinate \( 7^{[3]} \) and 6’-methyl-2,2’-bipyridin carboxylic acid \( 9^{[4]} \) were synthesized according to literature procedure.

**Bispidone 1**: Piperidone \( P \) (10.2 g, 21.8 mmol, 1.0 equiv.) was suspended in EtOH (130 ml) and heated to 50°C. To this suspension, 2,4-dimethoxybenzylamine (3.80 ml, 4.20 g, 25.1 mmol, 1.2 equiv.) and formaldehyde (3.70 ml, 37% in water, 1.61 g, 50.1 mmol, 2.3 equiv.) were added dropwise and simultaneously by syringe in a period of 5 min. The reaction mixture was refluxed for 16h. After cooling to room temperature, the solvent was removed under reduced pressure, the remaining solid was dissolved in EtOH (15 ml). Layering with diethyl ether yielded 1 as colorless solid (6.87 g, 10.6 mmol, 48%).

1: \(^1\text{H}-\text{NMR} \ (400 \text{ MHz}, \text{CDCl}_3): \delta = 8.50 \ (\text{ddd}, J = 5.0, 2.0, 1.0 \text{ Hz}, 2\text{H, H}_\text{py}), 8.13 \ (d, J = 8.0 \text{ Hz}, 2\text{H, H}_\text{py}), 7.50 \ (\text{td}, J = 7.5, 2.0 \text{ Hz}, 2\text{H, H}_\text{py}), 7.22 - 7.19 \ (m, 2\text{H, H}_\text{Bn}), 7.16 \ (\text{ddd}, J = 7.4, 5.0, 1.0 \text{ Hz}, 2\text{H H}_\text{py}), 7.04 \ (d, J = 8.5 \text{ Hz}, 1\text{H, H}_\text{DMB}), 6.86 - 6.82 \ (m, 2\text{H, H}_\text{py}), 6.66 \ (d, J = 2.5 \text{ Hz}, 1\text{H, H}_\text{Bn}), 6.46 \ (dd, J = 8.0, 2.5 \text{ Hz}, 1\text{H, H}_\text{Bn}), 5.00 \ (d, J = 1.0 \text{ Hz}, 2\text{H, CH}_\text{py}), 4.01 \ (s, 3\text{H, OMe}), 3.86 \ (s, 3\text{H, OMe}), 3.67 \ (s, 6\text{H, CO}_2\text{Me}), 3.47 \ (s, 2\text{H, CH}_2\text{DMB}), 3.38 \ (s, 2\text{H, CH}_2\text{Bn}), 3.06 \ (d, J = 12.5 \text{ Hz}, 2\text{H, CH}_2\text{ax,eq}), 2.37 \ (d, J = 12.5 \text{ Hz}, 2\text{H, CH}_2\text{ax,eq}) \text{ ppm}; \ ^{13}\text{C}-\text{NMR} \ (101 \text{ MHz}, \text{CDCl}_3) \delta = 204.62, 168.94, 161.54, 160.04, 158.83, 149.36, 136.49, 133.89, 133.64, 131.28, 129.03, 128.64, 128.44, 127.87, 125.34, 123.31, 118.13, 104.37, 99.24, 69.83, 62.64, 60.06, 56.52, 56.16, 56.02, 55.36, 52.70 ppm; HRMS (ESI): \textit{m/z} \text{ calcld for C}_{37}\text{H}_{39}\text{N}_4\text{O}_7+: 651.2813 \ [\text{M+H}]^+: \text{ found: 651.2816}; \text{ elemental analysis calcld}\ (%)\text{ for C}_{37}\text{H}_{43}\text{N}_4\text{O}_7:\text{ C 68.29, H 5.89, N 8.61}; \text{ found: C 68.13, H 6.07, N 8.42.}

**Bispidol 2**: Bispidone 1 (6.87 g, 10.6 mmol, 1.0 equiv.) was suspended in 180 ml of a 1,4-dioxane-water mixture (3:1) and cooled to -5°C. A solution of sodium borohydride (201 mg, 5.30 mmol, 0.5 equiv.) in 90 ml of the same solvent mixture was added with a dropping funnel in a period of 20 min. The reaction mixture was allowed to warm up to 0°C and stir at this temperature for 16h. The pH value was set to 1 by adding concentrated sulfuric acid and the
solution was stirred for 20 min. The volume was reduced to 50 ml under reduced pressure and an aqueous solution of sodium hydroxide (20 wt%) was added to adjust the pH value to 9. The resulting slurry was stirred for 1h at room temperature before adding DCM (100 ml). The leftover solid was filtered off and the liquid layers separated. Afterwards the aqueous phase was extracted with DCM (3x50 ml), the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtrated and the solvent removed under reduced pressure. 2 was used in the next step without further purification.

2-1.5 1,4-dioxane: HRMS (ESI): m/z calcld for C$_{37}$H$_{41}$N$_4$O$_7$+: 653.2970 [M+H]$^+$; found: 653.2971; elemental analysis calcld (%) for C$_{43}$H$_{52}$N$_4$O$_{10}$: C 65.80, H 6.68, N 7.14; found: C 66.01, H 6.64, N 7.36.

Bispidin 3: To a solution of 2 (6.82 g) in 25 ml of DCM was added 25 ml of trifluoroacetic acid (TFA). The resulting purple mixture was refluxed for 16h. After cooling to room temperature, solvent was removed in vacuo, the residue dissolved in MeOH (50 ml) which, to remove leftovers of TFA, was again removed under reduced pressure. MeOH (100 ml) was added and the suspension refluxed for 10 min, followed by hot filtration. After reducing the volume to 25 ml, ether diffusion resulted in colorless crystals of 3 as TFA salt (3.24 g, 5.25 mmol, 24% over two steps).

3-TFA: $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 8.67 (s, 2H, H$_{Py}$), 7.76 – 7.55 (m, 2H, H$_{Py}$), 7.25 – 7.22 (m, 2H, H$_{Py}$), 7.20 – 7.15 (m, 1H, H$_{Bn}$), 7.12 (t, J = 7.5 Hz, 2H, H$_{Py}$), 7.06 (s, 2H, H$_{Bn}$), 6.61 (d, J = 7.5 Hz, 2H, H$_{Bn}$), 4.75 (s, 1H, CH$_{OH}$), 4.53 (d, J = 8.0 Hz, 2H, CH$_{py}$), 3.70 (d, J = 3.2 Hz, 2H, CH$_{2,ax,eq}$), 3.66-3.56 (m, 2H, CH$_{2,Bn}$), 3.54 (s, 6H, CO$_2$Me) 3.32 (s, 2H, CH$_{2,ax,eq}$) ppm; HRMS (ESI): m/z calcld for C$_{28}$H$_{31}$NaO$_5$+: 503.2289 [M+H]$^+$; found: 503.2286; elemental analysis calcld (%) for C$_{30}$H$_{31}$F$_3$NaO$_7$: C 58.44, H 5.07, N 9.09; found: C 58.52, H 5.19, N 9.22. No $^{13}$C-NMR-data available due to solubility issues.

Bispidin 4: To a suspension of 3 (3.24 g, 5.25 mmol, 1.0 equiv.) in MeCN (100 ml) was added Na$_2$CO$_3$ (3.34 g, 31.5 mmol, 6.0 equiv.) and 1.64 g of tert-butyl 6-(bromomethyl)-picolinate 7 (6.04 mmol, 1.2 equiv.) and refluxed for 16h. After cooling to room temperature, the solvent was removed under reduced pressure and 50 ml of water and DCM were added to dissolve the solids. The layers were separated, and the aqueous layer extracted with DCM (2x50 ml). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and the solvent removed.
in vacuo. 4 was recrystallized from hot EtOH, yielding the pure compound as colorless solid (2.22 g, 3.20 mmol, 61%).

4·2 H2O: 1H-NMR (400 MHz, CDCl3): δ = 8.49 (d, J = 5.5 Hz, 2H, Hpy), 8.13 (d, J = 9.0 Hz, 2H, Hpy), 8.06 (d, J = 8.0 Hz, 1H, Hpa), 7.78 (t, J = 7.5 Hz, 1H, Hpa), 7.50 – 7.38 (m, 3H, Hpy,pa), 7.25 – 7.14 (m, 3H, HBn), 7.14 – 7.07 (m, 2H, Hpy), 6.85 (d, J = 7.0 Hz, 2H, HBn), 4.52 (s, 2H, CHpy), 4.49 (s, 1H, CHOH), 3.60 – 3.57 (m, 8H, CO2Me, CH2,pa), 3.42 (s, 2H, CH2,Bn), 2.59 (d, J = 12.5 Hz, 2H, CH2,ax,eq), 2.51 (d, J = 11.5 Hz, 2H, CH2,ax,eq), 1.63 (s, 9H, tBu) ppm; 13C-NMR (101 MHz, CDCl3): δ = 176.63, 172.79, 164.98, 159.63, 158.19, 150.03, 148.50, 145.97, 142.09, 137.07, 136.06, 133.05, 131.01, 128.19, 127.42, 127.31, 124.72, 123.37, 122.64, 82.25, 72.09, 69.40, 65.21, 54.74, 52.84, 52.22, 49.36, 28.37 ppm; HRMS (ESI): m/z calcd for C32H38N5O7+: 694.3241 [M+H]+; found: 694.3233; elemental analysis calcd (%) for C39H44N5O9: C 64.18, H 6.49, N 9.60; found: C 64.26, H 6.25, N 9.46.

Bispidin 5: Bispidin 4 (2.22 g, 3.20 mmol, 1.0 equiv.) and Pd/C (222 mg, 10 wt%) were added to a three-necked flask and suspended in EtOAc (140 ml). The flask was equipped with two adapters with stopcock and a reflux condenser attached to a balloon. The apparatus was flushed with nitrogen and put under vacuum three times, using a water pump. Then the same was done with H2, leaving the apparatus under H2 the third time. The reaction mixture was refluxed for 16h. After hot filtration over Celite and removing the solvent under reduced pressure, the crude product was dissolved in EtOH (10 ml). Layering with Et2O yielded 5 as colorless solid (1.52 g, 2.53 mmol, 79%).

5·0.75MeOH: 1H-NMR (400 MHz, CDCl3): δ = 8.43 – 8.38 (m, 2H, Hpy), 8.06 – 7.98 (m, 1H, Hpa), 7.93 (d, J = 7.5 Hz, 1H, Hpa), 7.80 (t, J = 8.0 Hz, 1H, Hpa), 7.56 (td, J = 7.5, 2.0 Hz, 2H, Hpy), 7.29 – 7.25 (m, 2H, Hpy), 7.11 (dd, J = 7.5, 5.0 Hz, 2H, Hpy), 4.91 (s, 1H, CHOH), 4.66 (s, 2H, CHpy), 3.67 (d, J = 3.0 Hz, 2H, CH2,pa), 3.64 (s, 6H, CO2Me), 2.94 – 2.79 (m, 4H, CH2,ax,eq), 1.62 (s, 9H, tBu) ppm; 13C-NMR (101 MHz, CDCl3): δ = 164.43, 148.88, 136.83, 136.31, 127.32, 123.30, 122.63, 122.10, 82.20, 65.04, 52.08, 51.87, 49.43, 28.26 ppm; HRMS (ESI): m/z calcd for C32H38N5O7+: 694.3241 [M+H]+; found: 694.3233; elemental analysis calcd (%) for C39H44N5O9: C 64.18, H 6.49, N 9.60; found: C 64.26, H 6.25, N 9.46.

Bispidin 6: To a suspension of 5 (927 mg, 1.54 mmol, 1.0 equiv) in MeCN (30 ml) was added Na2CO3 (976 mg, 9.21 mmol, 6.0 equiv.) and 536 mg of tert-butyl 6-(bromomethyl)-2,2'-
bipyridine] carboxylate 8 (1.54 mmol, 1.0 equiv.) and refluxed for 16h. After cooling to room temperature, the solvent was removed under reduced pressure and 20 ml of water and DCM were added to dissolve the solids. The layers were separated, and the aqueous layer extracted with DCM (2x20 ml). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and the solvent removed in vacuo. The crude product was used in the next step without further purification.

6 1.25 MeOH: ¹H-NMR (200 MHz, CDCl₃): δ = 8.98 (t, J = 4.5 Hz, 1H, H₉), 8.40 (dd, J = 4.5, 1.5 Hz, 2H, H₆), 8.32 (dd, J = 8.0, 1.0 Hz, 1H, H₈), 8.11 - 7.94 (m, 5H, H₉), 7.80 (t, J = 7.5 Hz, 1H, H₆), 7.63 (t, J = 7.5 Hz, 1H, H₆), 7.55 - 7.43 (m, 3H, H₉), 7.13 - 7.03 (m, 2H, H₈), 6.73 - 6.65 (m, 1H, H₆), 4.97 (s, 2H, CHpy), 4.48 (d, J = 6.0 Hz, 1H, CHOH), 3.58 (s, 2H, CH₂,pba), 3.52 (d, J = 4.0 Hz, 8H, CO₂Me, CH₂,pba), 2.45 (s, 4H, CH₂,ax/eq), 1.63 (s, 9H, tBu), 1.60 (s, 9H, tBu) ppm; UPLC-MS (APCI): m/z calcd for C₄₈H₅₄N₇O₉+: 872.399 [M+H]+; found: 872.530 (peak intensity 100%; retention time: 4.00 min). HRMS (ESI): m/z calcd for C₄₈H₅₄N₇O₉+: 872.3978 [M+H]+; found: 872.3968; m/z calc. for C₄₉H₅₃N₇NaO₉+: 894.3797 [M+Na]+; found: 894.3787; elemental analysis calcd (%) for C₄₉.25H₅₈N₇O₁₀.25: C 64.86, H 6.41, N 10.75; found: C 64.80, H 6.27, N 10.66. No ¹³C-NMR-data available due to solubility issues.

Bispidin L²: To a solution of the crude of 6 (1.42 g, 1.0 equiv.) in 15 ml of DCM was added 15 ml of trifluoroacetic acid (TFA). The resulting purple mixture was refluxed for 16h and the solvent removed in vacuo. To remove leftovers of TFA, the residue was dissolved in EtOAc (20 ml) and the solvent removed under reduced pressure. EtOH (10 ml) and 10 ml of diethyl ether were added to the solid. The formed precipitate was collected via filtration. The TFA salt of L² was obtained as colorless solid (679 mg, 688 µmol, 45% over two steps).

L².125TFA.2MeOH.0.5MeCN: ¹H-NMR (600 MHz, CD₃OD): δ = 8.70 (s, 1H, H₉), 8.43 (t, J = 8.0 Hz, 2H, H₆), 8.33 - 8.25 (m, 3H, H₈), 8.27 - 8.23 (m, 2H, H₉), 8.07 (s, 1H, H₆), 7.76 - 7.61 (m, 3H, H₈), 7.33 - 7.19 (m, 2H, H₉), 7.07 (s, 2H, H₆), 6.57 (s, 1H, H₆), 5.39 - 5.36 (m, 2H, CHpy), 4.85 (s, 1H, CHOH), 4.75 (s, 2H, CH₂,bpic), 4.17 (s, 2H, CH₂,ax/eq), 3.78 (d, J = 12.5 Hz, 2H, CH₂,pic), 3.59 (s, 6H, CO₂Me), 3.52 - 3.46 (m, 2H, CH₂,ax/eq) ppm; ¹³C-NMR (151 MHz, CD₃OD): δ = 208.86, 200.12, 170.61, 168.18, 167.38, 162.85, 157.35, 156.32, 155.53, 151.58, 150.98, 150.91, 149.42, 140.73, 139.76, 138.97, 138.90, 138.71, 126.59, 126.14, 125.28, 121.31, 72.36, 70.79, 62.73, 55.09, 53.98, 53.29, 51.28 ppm; HRMS (ESI): m/z calcd for C₄₉H₅₈N₇O₁₀.25: 758.2580 [M-H]-; found: 758.2580; m/z calcd for C₄₂H₃₇F₃N₇O₁₁-: 872.2509

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[M+TFA-H]; found: 872.2506. elemental analysis calcd (%) for C_{45.5}H_{47.75}F_{3.75}N_{7.5}O_{13.5}: C 55.37, H 4.88, N 10.64; found: C 55.28, H 4.73, N 10.65.

tert-butyl 6'-methyl-2,2'-bipyridin carboxylate 10: 6'-methyl-2,2'-bipyridin carboxylic acid 9 (2.52 g, 11.8 mmol, 1.0 equiv.) was dissolved in 100 ml of DCM. To this solution were added 4.22 ml of tert-butyl 2,2,2-trichloroacetimidate (5.15 g, 23.6 mmol, 2.0 equiv.) and a catalytic amount of Boron trifluoride diethyl etherate (0.24 ml, 276 mg, 2.97 mmol, 20 µl/mmol acid) and the mixture was let to stir for 16h at room temperature. Sodium carbonate (approx. 150 mg) was added to quench the reaction, the solvent was removed in vacuo and the remaining solid extracted with 200 ml of n-hexane. The extraction process was repeated three times, before removing the solvent in vacuo yielded 10 as colorless solid (1.36 g, 5.00 mmol, 43%).

\[^1\text{H}-\text{NMR} (400 \text{MHz, CDCl}_3): \delta = 8.64 (d, J = 9.0 \text{ Hz, 1H, } C_{ar}), 8.40 (d, J = 8.0 \text{ Hz, 1H, } C_{ar}), 8.03 (dt, J = 8.0, 1.0 \text{ Hz, 1H, } C_{ar}), 7.91 (td, J = 8.0, 1.0 \text{ Hz, 1H, } C_{ar}), 7.73 (dd, J = 9.0, 7.0 \text{ Hz, 1H, } C_{ar}), 7.20 (d, J = 7.5 \text{ Hz, 1H, } C_{ar}), 2.65 (s, 3H, CH}_3), 1.66 (s, 9H, tBu) \text{ ppm; } ^{13}\text{C-NMR} (101 \text{ MHz, CDCl}_3): \delta = 164.28, 157.87, 154.65, 148.88, 137.80, 137.54, 124.71, 124.00, 118.99, 82.22, 28.28, 27.83 \text{ ppm.}\]

tert-butyl 6'-(bromomethyl)-(2,2'-bipyridine)-6-carboxylate 8: To a solution of 10 (1.99 g, 7.34 mmol, 1.0 equiv.) in CCl\(_4\) (80 ml) was added N-Bromosuccinimide (1.31 g, 7.34 mmol, 1.0 equiv.) and Azobisisobutyronitrile (199 mg, 1.22 mmol, 10 wt%). The resulting suspension was refluxed for 6h, cooled to room temperature, filtrated and the solvent removed in vacuo. Product 8 was obtained as colorless solid after purification with column chromatography (SiO\(_2\), gradient from 100% petroleum ether to 15% ethyl acetate) in 30% yield (777 mg, 2.22 mmol).

\[^1\text{H}-\text{NMR} (200 \text{ MHz, CDCl}_3): \delta = 8.64 (dd, J = 8.0, 1.3 \text{ Hz, 1H, } C_{ar}), 8.52 (dd, J = 8.0, 1.0 \text{ Hz, 1H, } C_{ar}), 8.06 (dd, J = 7.5, 1.0 \text{ Hz, 1H, } C_{ar}), 7.93 (t, J = 7.5 \text{ Hz, 1H, } C_{ar}), 7.84 (t, J = 8.0 \text{ Hz, 1H, } C_{ar}), 7.48 (dd, J = 7.5, 1.0 \text{ Hz, 1H, } C_{ar}), 4.63 (s, 2H, CH\(_2\)), 1.67 (s, 9H, tBu) \text{ ppm; } ^{13}\text{C-NMR} (151 \text{ MHz, CDCl}_3): \delta = 164.06, 156.19, 148.82, 138.54, 138.13, 138.11, 125.13, 124.32, 124.21, 123.49, 121.24, 82.47, 33.79, 28.28 \text{ ppm; HRMS (ESI): } m/z \text{ calcd for } C_{16}H_{17}BrN_2O_2+: 371.0366 [M+Na]^+; \text{ found: 371.0363}; \text{ elemental analysis calcd} (%) \text{ for } C_{16}H_{17}BrN_2O_2: C 55.03, H 4.91, N 8.02; \text{ found: C 54.73, H 4.85, N 8.55.}\]
S1.2. Complex syntheses

General procedure: The lanthanide(III) salt (68.7 µmol, 1.0 equiv.) was dissolved in 2 ml of a MeOH-water mixture (1:1) and was combined with a solution of L² TFA (60.0 mg, 68.7 µmol, 1.0 equiv.) in the same amount of MeOH-water (1:1). The mixture was stirred for 10 min at 50°C and cooled down to room temperature and let to stir for 16h at ambient temperature. The solvent was removed in vacuo before MeOH was added. The solid was filtered off and the remaining solution layered with diethyl ether, which produced the complexes as colorless crystals.

\([\text{Eu}^{III}L^2]C_3F_3O_2\): The general procedure for the synthesis of complexes was followed using 22.7 mg of Eu(OAc)₃·H₂O. The complex was obtained in 68% yield (50.9 mg, 46.9 µmol).

\([\text{Eu}L^2]C_3O_2C_3F_3·3.5 H_2O\): HRMS (ESI), calcd for C₄₀H₃₅EuN₇O₉+: 910.1709 [M]+; found: 910.1715; elemental analysis calcd (%) for C₄₂H₄₂EuF₃N₇O₁₅.5: C 46.46, H 3.90, N 9.03; found: C 46.69, H 4.11, N 8.84.

\([\text{Gd}^{III}L^2]NO_3\): The general procedure for the synthesis of complexes was followed using 31.1 mg of Gd(NO₃)₃·6H₂O. The complex was obtained in 50% yield (44.5 mg, 34.4 µmol).

\([\text{Gd}L^2]NO_3·6H_2O·TFA·1.5HNO_3\): HRMS (ESI): m/z calcd for C₄₀H₃₅GdN₇O₉+: 915.1737 [M]+; found: 915.1737; elemental analysis calcd (%) for C₄₀H₄₉.5F₃GdN₉.5O₂₄.5: C 39.00, H 3.86, N 10.29; found: C 38.94, H 3.90, N 10.53.

\([\text{Tb}^{III}L^2]NO_3\): The general procedure for the synthesis of complexes was followed using 23.8 mg of Tb(NO₃)₃·6H₂O. The complex was obtained in 57% yield (43.8 mg, 39.2 µmol).

\([\text{Tb}L^2]NO_3·6H_2O·0.5HNO_3\): HRMS (ESI): m/z calcd for C₄₀H₃₅N₇O₅Tb+: 916.1750 [M]+; found: 916.1750; elemental analysis calcd (%) for C₄₁H₄₉.5N₈.5O₁₉.₅Tb: C 42.96, H 4.28, N 10.65; found: C 43.19, H 4.07, N 10.66.

\([\text{Yb}^{III}L^2]NO_3\): The general procedure for the synthesis of complexes was followed using 31.1 mg of Yb(NO₃)₃·3H₂O. The complex was obtained in 36% yield (33.7 mg, 25.1 µmol).

\([\text{Yb}L^2]NO_3·7H_2O·2HNO_3·TFA\): HRMS (ESI): m/z calcd for C₄₀H₃₅N₇O₅Yb+: 931.1885 [M]+; found: 931.1890; elemental analysis calcd (%) for C₄₂H₅₅F₃N₁₀O₂₆Yb: C 37.62, H 3.76, N 10.45; found: C 37.61, H 3.89, N 10.36.
S2. Photophysical measurements

Emission spectra were measured using Horiba-Jobin–Yvon Fluorolog-3 fluorimeter. The steady-state luminescence was excited by unpolarized light from a 450 W xenon continuous wave (CW) lamp and detected at an angle of 90° for measurements of dilute solutions (10 mm quartz cuvette) by using a Hamamatsu R928. Spectra were corrected for both excitation source light-intensity variation and emission spectral responses. For the visible emission spectra a 450 nm long-pass filter was used to filter out the second order diffraction of the excitation peak at 626 nm ($\lambda_{exc}$=313 nm). Near-infrared spectra were recorded at an angle of 45° using a liquid-nitrogen-cooled, solid indium/gallium/arsenic detector (850–1600 nm). Luminescence quantum yields Q for [EuL2][CF3CO2] and [TbL2][NO3] in water were measured in diluted solutions with an absorbance lower than 0.1, by using the following Equation 1:

$$\frac{Q_x}{Q_r} = \frac{A_r(\lambda)}{A_x(\lambda)} \cdot \frac{n_x^2}{n_r^2} \cdot \frac{D_x}{D_r} \quad (1)$$

where $A(\lambda)$ is the absorbance (or optical density) at the excitation wavelength, $n$ the refractive index of the solvent and D the integrated luminescence intensity. “r” and “x” stand for reference and sample, respectively. Here, the reference is quinine bisulfate in 0.5 M sulfuric acid (Φf = 0.55 in 0.5 M sulfuric acid). Excitations of reference and sample compounds were performed at the same wavelength. The reported results are the average of 4–5 independent measurements at various absorbances (comprised between 0.01–0.1) for both sample and reference. The plot of the integrated luminescence intensity vs. absorbance gives straight line with excellent correlation coefficients and the slope S can be determined for both sample (x) and reference (r). Equation 1 becomes Equation 2:

$$\frac{Q_x}{Q_r} = \left[ \frac{S_x}{S_r} \right] \cdot \frac{n_x^2}{n_r^2} \quad (2)$$

Solid samples were placed in a 0.5 mm diameter quartz tube that was cool down in a liquid nitrogen Dewar (77K) insert directly in the sample chamber of the spectrofluorometer. The interference signals due to scattered excitation light were suppressed by a 400 nm high pass filter placed at the entry of emission monochromator. Quantum yields in the solid state were measured with the use of an integrating sphere coated with BenFlect. Luminescence decay plots were obtained by pulsed excitation using a FL-1040 UP xenon lamp and lifetimes were obtained by an exponential least-squares fitting using Origin.
S2.1. Calculation of the Eu\textsuperscript{III} radiative lifetime and intrinsic quantum yield.

The radiative decay of the Eu\textsuperscript{3+} complex was calculated following Equation 1.

\[
\frac{1}{\tau_r} = A_{MD,0} n^3 \left( \frac{\tau_T}{I_{MD}} \right)
\] (2.1)

Where \(A_{MD,0}\) is the spontaneous emission probability of the \(7F_1 \leftrightarrow 5D_0\) transition with a constant value of 14.65 s\textsuperscript{-1}, \(I_T/I_{MD}\) is the ratio of the total integrated area to the magnetic dipole transition of the Eu\textsuperscript{3+} emission spectrum\textsuperscript{[6]} and \(n\) is the refractive index of the medium, considered 1.5 in the solid state.\textsuperscript{[7]}

The photoluminescence quantum yield (\(\Phi\)) is the ratio of the number of emitted photons to the number of photons absorbed and therefore, describes the efficiency of the whole sensitisation process. For the lanthanoid ions two different values of quantum yield are normally calculated. The intrinsic quantum yield (\(\Phi_{Ln}^I\)) describes the contribution of radiative decay from the lanthanoid excited states, considering the radiative and non-radiative rates, following Equation 1.8:

\[
\Phi_{Ln}^I = \frac{k_r}{k_r + k_r} = \frac{\tau_{abs}}{\tau_{r}}
\] (2)

As the intrinsic quantum yield depends directly on the radiative decay, this value is difficult to estimate. However, the overall quantum yields (\(\Phi_{Ln}^O\)), which describes the overall efficiency of sensitised emission, was obtained experimentally with the use of an integrating sphere or by dilute method.

The two different quantum yields are related according to equation 3:

\[
\Phi_{Ln}^O = \Phi_{ISC} \times \Phi_{ET} \times \Phi_{Ln}^I = \Phi_{sens} \times \Phi_{Ln}^n
\]

Where the efficiency of energy transfer (\(\Phi_{ET}\)) and intersystem crossing (\(\Phi_{ISC}\)) combined are defined by the sensitisation efficiency (\(\Phi_{sens}\)).
S2.2. Photophysical spectra

Figure S1. Molar absorptivity of a 10 µM aqueous solution of ligand L² at 25°C.
Figure S2. Deconvolution of the phosphorescence band for [GdL₂][NO₃] with a delay of 0.1 ms (blue trace) in a mixture EtOH:MeOH (4:1) at 77K.

Model Gauss

Equation \( y = y_0 + \left( \frac{A}{w \sqrt{\pi/2}} \right) \exp\left( -2 \left( \frac{x-x_c}{w} \right)^2 \right) \)

Plot Peak1(D)  Peak2(D)  Peak3(D)  Peak4(D)

\( y_0 \quad 0.00493 \pm 0.0014 \quad 0.00493 \pm 0.0014 \quad 0.00493 \pm 0.0014 \quad 0.00493 \pm 0.0014 \)

\( x_c \quad 22496.41551 \pm 8.80005 \quad 21137.2209 \pm 13.39809 \quad 19813.32217 \pm 20.77559 \quad 18538.21834 \pm 96.36332 \)

\( w \quad 707.00054 \pm 14.49209 \quad 1152.78799 \pm 35.39342 \quad 1023.64352 \pm 60.41034 \quad 2009.26974 \pm 155.45238 \)

\( A \quad 438.37655 \pm 13.72501 \quad 1318.01079 \pm 43.47234 \quad 705.07003 \pm 120.68623 \quad 1204.2221 \pm 122.92478 \)

Reduced Chi-Sqr 2.21621E-4

R-Square (COD) 0.99812

Adj. R-Square 0.99803
Figure S3. Excitation ($\lambda_{em} = 614$ nm) (a) and emission spectra ($\lambda_{exc} = 313$ nm) (b) of $[\text{EuL}_2][\text{CF}_3\text{CO}_2]$ in water at room temperature (black trace) and in EtOH/MeOH (4:1) at 77 K (blue trace).

Figure S4. Excitation ($\lambda_{em} = 614$ nm) (a) and emission spectra ($\lambda_{exc} = 313$ nm) (b) of $[\text{EuL}_2][\text{CF}_3\text{CO}_2]$ in the solid state at room temperature (black trace) and at 77 K (blue trace).
Figure S5. Emission spectra ($\lambda_{exc} = 313$ nm) of [EuL$^2$][CF$_3$CO$_2$] in solid state (black trace) and solution (blue trace) at 77K.
Figure S6. Deconvolution of all emission bands for [EuL²][CF₃CO₂] in the solid state at 77K.

J₀ and J₁

Model Gauss

Equation \( y = y_0 + \frac{A}{w \sqrt{\pi/2}} \exp\left(-2 \times \frac{(x-x_c)^2}{w^2}\right) \)

Plot Peak1(Subtracted_Data Y1) Peak2(Subtracted_Data Y1) Peak3(Subtracted_Data Y1) Peak4(Subtracted_Data Y1)

\( y_0 \) 0.00521 ± 0.00143 0.00521 ± 0.00143 0.00521 ± 0.00143 0.00521 ± 0.00143
\( xc \) 16756.63421 ± 0.7925116856.34278 ± 0.7834616959.60332 ± 1.3558417250.81318 ± 14.45672
\( w \) 52.2021 ± 1.73243 48.86136 ± 1.73421 73.08347 ± 3.08177 12.80378 ± 46.10431
\( A \) 13.93777 ± 0.41841 14.88976 ± 0.48182 15.44479 ± 0.58007 0.51094 ± 0.49116

Reduced Chi-Sqr 6.16929E-5

R-Square (COD) 0.99116

Adj. R-Square 0.98885

J₂

Model Gauss
Equation \( y = y_0 + \frac{A}{(w\sqrt{\pi/2})} \cdot \exp(-2\cdot((x-xc)/w)^2) \)

| Plot       | Peak1(Subtracted_Data Y1) | Peak2(Subtracted_Data Y1) | Peak3(Subtracted_Data Y1) | Peak4(Subtracted_Data Y1) | Peak5(Subtracted_Data Y1) |
|------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| y0         | 0.0098 ± 0.00128          | 0.0098 ± 0.00128          | 0.0098 ± 0.00128          | 0.0098 ± 0.00128          | 0.0098 ± 0.00128          |
| xc         | 16292.81098 ± 1.4422      | 16279.49105 ± 0.216961    | 16213.2187 ± 1.31637      | 16140.83343 ± 7.55694     |
| w          | 60.62677 ± 1.56605        | 23.2107 ± 0.69655         | 33.00317 ± 3.50229        | 88.4314 ± 24.54899        |
| A          | 28.85852 ± 1.51851        | 21.55023 ± 1.21017        | 6.30756 ± 1.08349         | 6.26327 ± 1.49091         |

Reduced Chi-Sqr 6.28357E-5

R-Square (COD) 0.99855

Adj. R-Square 0.99813

\( J_3 \)

Model Gauss

Equation \( y = y_0 + \frac{A}{(w\sqrt{\pi/2})} \cdot \exp(-2\cdot((x-xc)/w)^2) \)

| Plot       | Peak1(Subtracted_Data Y1) | Peak2(Subtracted_Data Y1) | Peak3(Subtracted_Data Y1) | Peak4(Subtracted_Data Y1) | Peak5(Subtracted_Data Y1) | Peak6(Subtracted_Data Y1) | Peak7(Subtracted_Data Y1) |
|------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| y0         | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  |
| xc         | 15430.60624 ± 0.28942     | 15376.54188 ± 1.80896     | 15304.3866 ± 0.73599      | 15271.1054 ± 1.69972      |
| w          | 26.07277 ± 0.55628        | 46.9736 ± 4.20522         | 20.37161 ± 1.56702        | 18.19263 ± 4.04192        |
| A          | 2.57036 ± 0.06422         | 1.03699 ± 0.08242         | 0.6082 ± 0.0419           | 0.20921 ± 0.04047         |

Reduced Chi-Sqr 1.55613E-6

R-Square (COD) 0.99735

Adj. R-Square 0.99558

\( J_4 \)

Model Gauss

Equation \( y = y_0 + \frac{A}{(w\sqrt{\pi/2})} \cdot \exp(-2\cdot((x-xc)/w)^2) \)

| Plot       | Peak1(Subtracted_Data Y1) | Peak2(Subtracted_Data Y1) | Peak3(Subtracted_Data Y1) | Peak4(Subtracted_Data Y1) | Peak5(Subtracted_Data Y1) | Peak6(Subtracted_Data Y1) | Peak7(Subtracted_Data Y1) |
|------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| y0         | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  | -2.73985E-4 ± 3.49256E-4  |
| xc         | 15430.60624 ± 0.28942     | 15376.54188 ± 1.80896     | 15304.3866 ± 0.73599      | 15271.1054 ± 1.69972      |
| w          | 26.07277 ± 0.55628        | 46.9736 ± 4.20522         | 20.37161 ± 1.56702        | 18.19263 ± 4.04192        |
| A          | 2.57036 ± 0.06422         | 1.03699 ± 0.08242         | 0.6082 ± 0.0419           | 0.20921 ± 0.04047         |
Figure S7. Deconvolution of all emission bands for [EuL²][CF₃CO₂] in solution at 77K.

J₀ and J₁

Model Gauss
Equation \( y = y_0 + \frac{A}{w \sqrt{\pi/2}} \exp\left(-2\left(\frac{x-x_c}{w}\right)^2\right) \)
Plot Peak1(D) Peak2(D) Peak3(D) Peak4(D)

\begin{align*}
y_0 & \quad 0.00463 \pm 3.87826E-4 & 0.00463 \pm 3.87826E-4 & 0.00463 \pm 3.87826E-4 & 0.00463 \pm 3.87826E-4 \\
x_c & \quad 14673.56066 \pm 0.87749 & 14482.18432 \pm 0.55211 & 14395.97174 \pm 2.68322 & 14335.87813 \pm 3.70865 \\
w & \quad 49.32199 \pm 1.86443 & 42.52471 \pm 1.18555 & 49.76473 \pm 4.06007 & 51.24004 \pm 5.5015 \\
A & \quad 12.30888 \pm 0.44653 & 18.48036 \pm 0.47202 & 17.66043 \pm 2.10208 & 13.69531 \pm 2.09437 \\
\end{align*}

Reduced Chi-Sqr 1.01908E-4
R-Square (COD) 0.99184
Adj. R-Square 0.98928
Model Gauss

Equation \( y = y_0 + \frac{A}{w\sqrt{2\pi}} \exp\left(-\frac{(x-xc)^2}{w^2}\right) \)

| Plot | Peak1(D) | Peak2(D) | Peak3(D) | Peak4(D) | Peak5(D) |
|------|----------|----------|----------|----------|----------|
| y0   | 0.0056 ± 4.32261E-4 | 0.0056 ± 4.32261E-4 | 0.0056 ± 4.32261E-4 | 0.0056 ± 4.32261E-4 | 0.0056 ± 4.32261E-4 |
| xc   | 16285.4257 ± 0.5994 | 16262.1891 ± 0.03315 | 16198.90025 ± 0.24453 | 16121.17837 ± 2.11137 | 16035.8783 ± 0.54365 |
| w    | 45.10216 ± 0.6592 | 19.1081 ± 0.11923 | 26.42281 ± 0.52548 | 54.37717 ± 5.07157 |
| A    | 12.25008 ± 0.29576 | 18.93015 ± 0.24987 | 3.62621 ± 0.06582 | 1.20732 ± 0.10054 |

Reduced Chi-Sqr 1.53451E-5
R-Square (COD)0.99946
Adj. R-Square 0.99942

Model Gauss

Equation \( y = y_0 + \frac{A}{w\sqrt{2\pi}} \exp\left(-\frac{(x-xc)^2}{w^2}\right) \)

| Plot | Peak1(D) | Peak2(D) | Peak3(D) | Peak4(D) |
|------|----------|----------|----------|----------|
| y0   | 0.00503 ± 1.65182E-4 | 0.00503 ± 1.65182E-4 | 0.00503 ± 1.65182E-4 | 0.00503 ± 1.65182E-4 |
| xc   | 15427.28662 ± 0.1015115374.98366 ± 0.6909915300.54547 ± 0.3934615264.40497 ± 0.74952 |
| w    | 22.79775 ± 0.20417 | 41.86389 ± 1.64366 | 20.40546 ± 0.85613 | 21.00288 ± 1.66873 |
| A    | 1.61615 ± 0.01551 | 0.58349 ± 0.02314 | 0.33569 ± 0.01329 | 0.18318 ± 0.01411 |

Reduced Chi-Sqr 7.01061E-7
R-Square (COD)0.99651
Adj. R-Square 0.99651
Model Gauss

Equation \[ y = y_0 + \frac{A}{w \sqrt{\pi/2}} \exp\left(-\frac{2 ((x - x_c)/w)^2}{w}\right) \]

| Plot | Peak1(D)         | Peak2(D)         | Peak3(D)         | Peak4(D)         | Peak5(D)         | Peak6(D)         |
|------|------------------|------------------|------------------|------------------|------------------|------------------|
| y0   | 0.015 ± 3.94328E-4 | 0.015 ± 3.94328E-4 | 0.015 ± 3.94328E-4 | 0.015 ± 3.94328E-4 | 0.015 ± 3.94328E-4 | 0.015 ± 3.94328E-4 |
| xc   | 14663.67838 ± 0.15603 | 14483.76113 ± 0.10552 | 14407.287 ± 0.17899 | 14365.15098 ± 0.4037 | 14333.59811 ± 0.54319 | 14240.54675 ± 0.27295 |
| w    | 31.28212 ± 0.32654 | 27.92744 ± 0.21943 | 29.74217 ± 0.39117 | 21.75611 ± 0.79265 | 22.2205 ± 1.17889 | 28.20475 ± 0.86402 |
| A    | 7.11224 ± 0.06965 | 8.76882 ± 0.06412 | 7.70096 ± 0.08922 | 3.85546 ± 0.1942  | 1.12597 ± 0.05512 | 5.08835 ± 0.17918 |

Reduced Chi-Sqr 2.11107E-5

R-Square (COD) 0.99541

Adj. R-Square 0.99512

**Figure S8.** Excitation (\(\lambda_{em} = 545\) nm) (a) and emission spectra (\(\lambda_{exc} = 313\) nm) (b) of \([\text{TbL}^2][\text{NO}_3]\) in water at room temperature.
Figure S9. Excitation ($\lambda_{\text{em}} = 545$ nm) (a) and emission spectra ($\lambda_{\text{exc}} = 313$ nm) (b) of [TbL$_2$][NO$_3$] in the solid state at room temperature (black trace) and at 77K (blue trace).

Figure S10. Excitation ($\lambda_{\text{em}} = 980$ nm) (a) and emission spectra ($\lambda_{\text{exc}} = 313$ nm) (b) of [YbL$_2$][NO$_3$] in water at room temperature (black trace) and in a mixture EtOH:MeOH at 77K (red trace).
Figure S11. Excitation ($\lambda_{\text{em}} = 980$ nm) (a) and emission spectra ($\lambda_{\text{exc}} = 313$ nm) (b) of $[\text{Yb}L^2][\text{NO}_3]$ in the solid state at room temperature (black trace) and at 77K (red trace).

Figure S12. Deconvolution of the emission band for $[\text{Yb}L^2][\text{NO}_3]$ in a mixture EtOH:MeOH (4:1) at 77K.
Figure S13. Deconvolution of the emission band for [Yb²⁺][NO₃] in the solid state at 77K.

Model Gauss

Equation \( y = y_0 + \frac{A}{w \sqrt{\pi/2}} \exp(-2*((x-xc)/w)^2) \)

Plot

|       | Peak1(D) | Peak2(D) | Peak3(D) | Peak4(D) |
|-------|----------|----------|----------|----------|
| y₀    | 0.01909 ± 0.00312 | 0.01909 ± 0.00312 | 0.01909 ± 0.00312 | 0.01909 ± 0.00312 |
| xc    | 10211.98992 ± 0.30077 | 10034.25922 ± 2.21744 | 9892.14657 ± 1.42143 | 9769.61801 ± 0.63626 |
| w     | 34.95313 ± 0.61794 | 103.82437 ± 5.05282 | 70.05391 ± 3.44219 | 71.4209 ± 1.39299 |
| A     | 43.09133 ± 0.69724 | 37.68103 ± 1.66675 | 33.6894 ± 1.54144 | 69.63636 ± 1.25299 |

Reduced Chi-Sqr 4.22761E-4

R-Square (COD) 0.99327

Adj. R-Square 0.99235
Figure S14. Determination of the quantum yield of [TbL₂][NO₃] (green) and [EuL₂][CF₃CO₂] (red) in H₂O, and the reference quinine sulfate in a 1N aqueous solution of sulfuric acid (blue). The straight lines correspond to the linear fit.

Figure S15. Quantum yield measurement of [EuL₂][CF₃CO₂] in solid state via integrated sphere (blue trace: blank, black trace: sample).
**Figure S16.** Quantum yield measurement of $[\text{TbL}_2][\text{NO}_3]$ in solid state via integrated sphere (blue trace: blank, black trace: sample).

**Figure S17.** Lifetime measurement ($\lambda_{\text{exc}}= 313$ nm, $\lambda_{\text{em}}= 613$ nm) of $[\text{EuL}_2][\text{CF}_3\text{CO}_2]$ in water at room temperature, data points in black and exponential decay fit of the data in red.
**Figure S18.** Lifetime measurement ($\lambda_{\text{exc}} = 313$ nm, $\lambda_{\text{em}} = 613$ nm) of $[\text{EuL}_2][\text{CF}_3\text{CO}_2]$ in D$_2$O, data points in black and exponential decay fit of the data in red.

**Figure S19.** Lifetime measurement ($\lambda_{\text{exc}} = 313$ nm, $\lambda_{\text{em}} = 613$ nm) of $[\text{EuL}_2][\text{CF}_3\text{CO}_2]$ in the solid state at room temperature, data points in black and exponential decay fit of the data in red.
Figure S20. Lifetime measurement ($\lambda_{\text{exc}} = 313$ nm, $\lambda_{\text{em}} = 542$ nm) of $[\text{TbL}_2\text{][NO}_3\text{]}$ in water at room temperature, data points in black and exponential decay fit of the data in red.

Figure S21. Lifetime measurement ($\lambda_{\text{exc}} = 313$ nm, $\lambda_{\text{em}} = 542$ nm) of $[\text{TbL}_2\text{][NO}_3\text{]}$ in D$_2$O, data points in black and exponential decay fit of the data in red.
Figure S22. Lifetime measurement ($\lambda_{\text{exc}} = 313$ nm, $\lambda_{\text{em}} = 542$ nm) of [TbL$^2$][NO$_3$] in the solid state at room temperature, data points in black and exponential decay fit of the data in red.

Figure S23. Lifetime measurement ($\lambda_{\text{exc}} = 313$ nm, $\lambda_{\text{em}} = 980$ nm) of [YbL$^2$][NO$_3$] in water at room temperature, data points in black and exponential decay fit of the data in red.
Figure S24. Lifetime measurement ($\lambda_{\text{exc}} = 313$ nm, $\lambda_{\text{em}} = 980$ nm) of [YbL$_2$][NO$_3$] in the solid state at room temperature, data points in black and exponential decay fit of the data in red.

S3. X-ray crystallographic data

Crystal data and details of the structure determinations are compiled in Table S1. Intensity data were collected at low temperature on an Agilent Supernova (Mo K$\alpha$ radiation, compound [TbL$_2$][NO$_3$]-solv) or a Bruker D8 Venture (Mo K$\alpha$ or Cu K$\alpha$ radiation, all other compounds) diffractometer, both equipped with microfocus X-ray tubes and multilayer optics. Data were corrected for air and detector absorption, Lorentz and polarization effects$^{[8]}$ and scaled essentially by application of appropriate spherical harmonic functions.$^{[8, 9]}$ Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling procedure) and augmented by a spherical correction. The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors (compound [TbL$_2$][NO$_3$]-solv,$^{[10]}$ or by intrinsic phasing (all other structures, ShelXT)$^{[11]}$ and refined by full-matrix least squares methods based on $F^2$ against all unique reflections.$^{[11a, 12]}$ All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and refined with a riding model. Split atom models were used to refine disordered groups and/or solvent molecules.$^{[13]}$ When found necessary, suitable geometry and adp restraints or constraints were applied.$^{[10b, 14]}$ The OLEX2 crystallographical
gui was employed to coordinate refinement.\textsuperscript{15} Due to severe disorder and fractional occupancy, electron density attributed to solvent of crystallization (methanol and diethyl ether) was removed from the structure of [TbL\textsuperscript{2}][NO\textsubscript{3}]-solv with the BYPASS procedure,\textsuperscript{16} as implemented in PLATON (squeeze/hybrid).\textsuperscript{17} Partial structure factors from the solvent masks were included in the refinement as separate contributions to $F_{\text{calc}}$. Disordered methanol in the structure of [YbL\textsuperscript{2}][NO\textsubscript{3}] was treated with averaged positions, only, leading to unrealistically long atom-atom distances in this part of the structure.

[GdL\textsuperscript{2}][NO\textsubscript{3}] crystallizes in monoclinic space group P2\textsubscript{1}/c and has four non-coordinating water molecules in the unit cell, allocated through hydrogen bonding between nitrate anions. [TbL\textsuperscript{2}][NO\textsubscript{3}] crystallizes as a solvate with methanol and probably diethyl ether. The solvent molecules are highly disordered and could not be successfully refined as discrete molecules. The nitrate anion is also twofold disordered. Hence, no meaningful statement can be made about intermolecular interactions. [YbL\textsuperscript{2}][NO\textsubscript{3}] also crystallizes in orthorhombic space group Pccn. Beside one disordered methanol molecule, there is no other solvent molecule present in the unit cell. The nitrate anion acts as bridging element between two unit cells, by hydrogen bonding to the C9 hydroxyl residue. The presence of water in the crystal packing is also supported by TGA measurements (see below).
Table S1. Crystallographic data of the [Ln^2][X] complexes (Ln = Gd, Tb, Yb; X = NO₃).

|                | [Gd^2][NO₃]        | [Tb^2][NO₃]-solv | [Yb^2][NO₃]       |
|----------------|---------------------|-------------------|-------------------|
| ID             | mo_PC04_0m          | co_pc14_sq       | cu_PC11_widea     |
| Empirical formula | GdH₄GdNa₃O₁₇       | TbH₄TbNa₃O₁₃     | YbH₄YbNa₃O₁₃     |
| Formula weight [g·mol⁻¹] | 1067.09            | 1010.72          | 1024.84          |
| Temperature [K] | 100(1)             | 120(1)           | 100(1)           |
| Radiation [Å]  | 0.71073            | 0.71073          | 1.54178          |
| Crystal system | monoclinic         | orthorhombic     | orthorhombic     |
| Space group    | P2₁/c              | Pccn             | Pccn             |
| a [Å]          | 15.9057(6)         | 31.3732(3)       | 17.0277(7)       |
| b [Å]          | 10.5906(4)         | 17.3497(3)       | 31.3789(11)      |
| c [Å]          | 25.3868(10)        | 15.84078(13)     | 15.8854(6)       |
| β [°]          | 104.748(2)         |                   |                   |
| V [Å³]         | 4135.5(3)          | 8622.38(17)      | 8487.7(6)        |
| Z              | 4                  | 8                 | 8                 |
| ρcalc [g·cm⁻³] | 1.714              | 1.557             | 1.604             |
| μ [mm⁻¹]       | 1.692              | 1.714             | 4.717             |
| Transmission factors: min/max | 0.6717/0.7454 | 0.6157/1.0000 | 0.5127/0.7538 |
| F_000          | 2164               | 4080              | 4120              |
| Crystal size [mm] | 0.19 x 0.06 x 0.04 | 0.24 x 0.07 x 0.06 | 0.32 x 0.12 x 0.07 |
| 2θ range [°]  | 4.2 .. 52.8        | 2.2 .. 34.2       | 5.9 .. 150.7     |
| Index ranges  | -19 ≤ h ≤ 19, -13 ≤ k ≤ 13, -31 ≤ l ≤ 31 | -47 ≤ h ≤ 48, -26 ≤ k ≤ 27, -24 ≤ l ≤ 24 | -16 ≤ h ≤ 21, -38 ≤ k ≤ 39, -19 ≤ l ≤ 19 |
| Reflections, collected | 60500              | 374660            | 90788             |
| Reflections, unique | 8461 [Rint = 0.0838] | 17562 [Rint = 0.0763] | 8635 [Rint = 0.0779] |
| Reflections, observed [I≥2σ(I)] | 6661              | 12400             | 6914              |
| Data / Restraints / Parameters | 8461 / 0 / 618 | 17562 / 500 / 752 | 8635 / 21 / 584 |
| Goodness-of-fit on F² | 1.032              | 1.044             | 1.041             |
| Final R indices [F≥4σ(F)] | R(F) = 0.0322, wR(F²) = 0.0606 | R(F) = 0.0462, wR(F²) = 0.0894 | R(F) = 0.0705, wR(F²) = 0.1966 |
| R indices (all data) | R(F) = 0.0509, wR(F²) = 0.0664 | R(F) = 0.0735, wR(F²) = 0.0983 | R(F) = 0.0838, wR(F²) = 0.2073 |
| Largest diff peak and hole [e·Å⁻³] | 0.65/-0.72         | 2.635/-1.894     | 1.73/-1.86       |

Deposition number CCDC | 2006149 | 2005937 | 2006148
Table S2. Continuous shape measures (CShM) for the [LnL$_2$]$^+$ complex cations (Ln = Eu, Gd, Tb, Yb).

| Structure                        | [EuL$_2$]$^+$ | [GdL$_2$]$^+$ | [TbL$_2$]$^+$ | [YbL$_2$]$^+$ |
|---------------------------------|---------------|---------------|---------------|---------------|
| Enneagon (EP-9, D$_{3h}$)       | 31.961        | 32.307        | 34.625        | 34.621        |
| Octagonal pyramid (OPY-9, C$_{8v}$) | 23.803        | 23.944        | 23.823        | 24.403        |
| Heptagonal bipyramid (HBPY-9, D$_{7h}$) | 16.055        | 15.595        | 15.736        | 15.861        |
| Johnson triangular cupola J3 (JTC-9, C$_{2v}$) | 13.224        | 13.415        | 14.226        | 14.682        |
| Capped cube J8 (JCCU-9, C$_{6v}$) | 6.796         | 7.158         | 6.701         | 6.986         |
| Spherical-relaxed capped cube (CCU-9, C$_{6v}$) | 5.361         | 5.686         | 5.235         | 5.511         |
| Capped square antiprism J10 (JCSAPR-9, C$_{4v}$) | 2.788         | 2.749         | 2.877         | 2.504         |
| Spherical capped square antiprism (CSAPR-9, C$_{4v}$) | 1.682         | 1.615         | 1.748         | 1.380         |
| Tricapped trigonal prism J51 (JCTCTPR-9, D$_{3h}$) | 2.788         | 2.787         | 3.064         | 3.050         |
| Spherical tricapped trigonal prism (TCTPR-9, D$_{3h}$) | 2.433         | 2.320         | 2.141         | 2.069         |
| Tridiminished icosahedron J63 (JTDIC-9, C$_{3v}$) | 13.200        | 12.874        | 11.844        | 12.027        |
| Hula-hoop (HH-9, C$_{2v}$)      | 9.376         | 9.770         | 9.554         | 10.274        |
| Muffin (MFF-9, C$_{3v}$)        | 2.051         | 1.995         | 2.093         | 1.828         |

[a] The counterion of [EuL$_2$][CF$_3$CO$_2$] could not be identified due to the presence of numerous Fourier peaks which could be attributed to disordered water, chlorine and/or methanol. The geometry of the cation could however be established and refined satisfactorily. [b] J indicates a Johnson polyhedron with all edges the same length and regular faces.

S4. NMR spectroscopy of intermediates

![NMR spectrum](image_url)

Figure S25. $^1$H-NMR spectrum (600.13 MHz, CD$_3$OD, 295K) of ligand L$_2$. 
Figure S26. $^{13}$C-NMR spectrum (150.91 MHz, CD$_3$OD, 295K) of ligand L$^2$.

Figure S27. $^1$H-NMR spectrum (399.89 MHz, CD$_2$Cl$_2$, 295 K) of bispidone 1.
Figure S28. $^{13}$C-NMR spectrum (100.56, CD$_2$Cl$_2$, 295 K) of bispidone 1.

Figure S29. $^1$H-NMR spectrum (600.13 MHz, CDCl$_3$, 295K) of bispidine 3.
Figure S30. $^1$H-NMR spectrum (399.89 MHz, CDCl$_3$, 295 K) of bispidine 4.

Figure S31. $^{13}$C-NMR spectrum (100.56, CDCl$_3$, 295 K) of bispidine 4.
Figure S32. $^1$H-NMR spectrum (399.89 MHz, CDCl$_3$, 295 K) of bispidine 5.

Figure S33. $^{13}$C-NMR spectrum (100.56, CDCl$_3$, 295 K) of bispidone 5.
Figure S34. $^1$H-NMR spectrum (200.18 MHz, CDCl$_3$, 300 K) of bispidine 6.

Figure S35. $^1$H-NMR spectrum (399.89 MHz, CDCl$_3$, 295 K) of tert-butyl 6'-methyl-2,2’bipyridin carboxylate 10.
**Figure S36.** $^{13}$C-NMR spectrum (100.55 MHz, CDCl$_3$, 295K) of tert-butyl 6'-methyl-2,2'bipyridin carboxylate 10.

**Figure S37.** $^1$H-NMR spectrum (200.13 MHz, CDCl$_3$, 300K) of tert-butyl 6'-(bromomethyl)-2,2'bipyridin carboxylate 8.
Figure S38. $^{13}$C-NMR spectrum (150.91 MHz, CDCl3, 295K) of tert-butyl 6'-methyl-2,2’bipyridin carboxylate 10.
S5. Mass spectrometry

Figure S39. HR-MS (ESI neg. MeOH/DCM) spectrum of bispidine L² and detected compound peaks.

Figure S40 HR-MS (ESI pos. H₂O/MeOH) spectrum of [EuL²][CF₃CO₂].
Figure S41. HR-MS (ESI pos. H₂O/MeOH) spectrum of [GdL²][NO₃].

Figure S42. HR-MS (ESI pos. H₂O/MeOH) spectrum of [TbL²][NO₃].
S6. Thermogravimetric Analysis.

Water in the crystal packing has been investigated by TGA measurements on a Mettler Toledo TGA/DSC1 STARe System of analogues Ho\textsuperscript{III}, Ce\textsuperscript{III} and Er\textsuperscript{III} complexes. TGA spectra show mass loss of a single water at temperatures between 28-50°C. A qualitative statement can be made for the complexes discussed herein.
S7. References

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