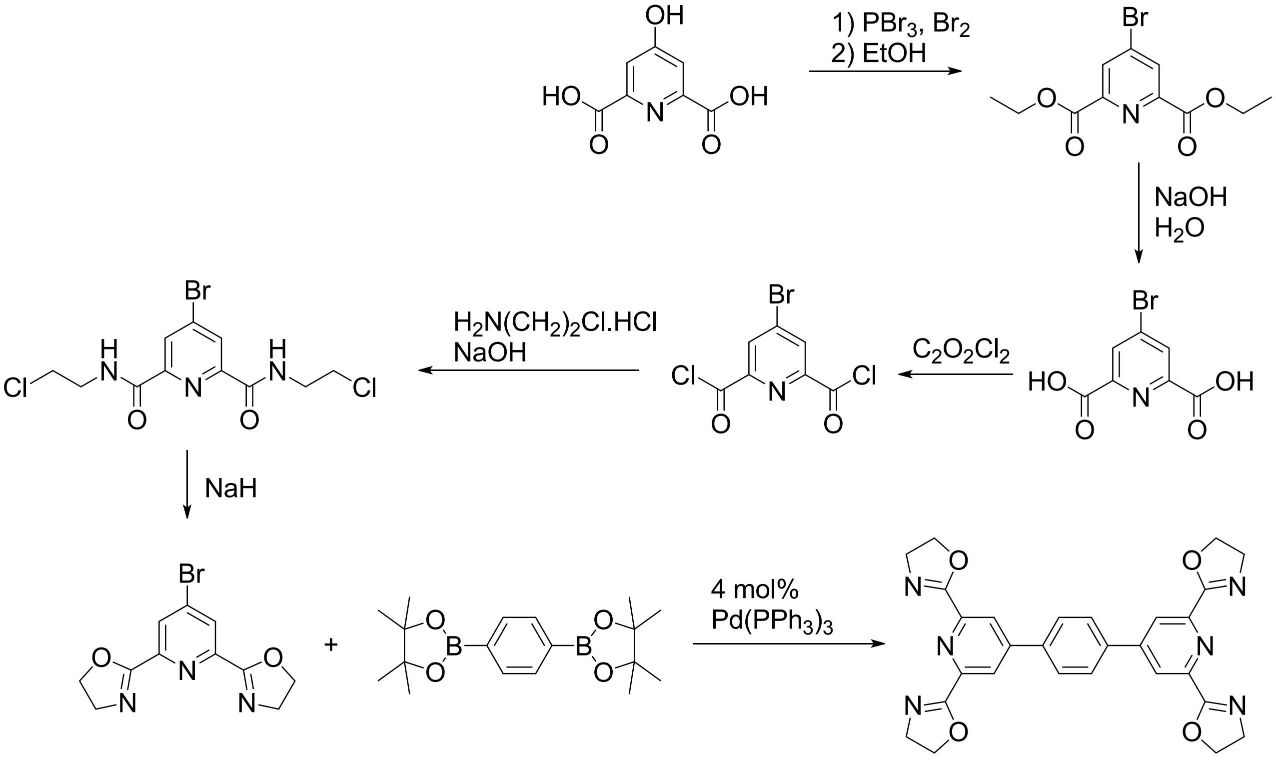
Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information



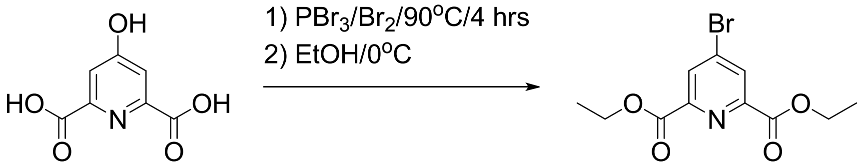
Scheme S1. Synthesis procedure of the ligand DitopicPyboxPh.

Experimental details

All commercially available materials were used as received without any further purification. Lanthanide salts and deuterated solvents were kept under dry and inert conditions in a glovebox. All solvents were of at least HPLC grade, dried by standard methods, and stored in a glovebox. All measurements were performed at room temperature, unless otherwise stated. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Electrospray ionization (ESI) spectra were obtained from a Finnigan LCQ quadrupole Ion trap mass spectrometer. High resolution mass spectra were recorded on a Shimdazu LCMS-IT-TOF Liquid Chromatograph Mass Spectrometer. Samples for mass spectra had a concentration of about 5 x 10^{-5} M Eu(III) and were filtered through a 0.2 µm syringe filter prior to injecting into the spectrometer. SEM images were obtained on a JEOL FESEM JSM6700F instrument with an accelerating voltage of 15 kV using an in-lens detector at a working distance of 7 mm. Samples for SEM were sputtered with gold using a JEOL JFC-1200 Fine Coater. A typical sputtering time for the coating was about 50 sec per sample. Elemental analysis was performed by X-ray photoelectron spectroscope on a Thermo Fischer Scientific Theta Probe XPs with an Al K alpha monochromatic X-ray source with survey scan pass energy of 200 eV and high resolution scan pass energy of 40 eV.

Ligand synthesis

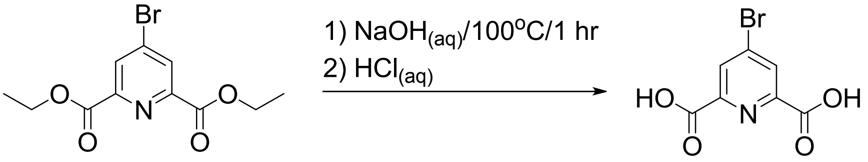
Diethyl 4-bromopyridine-2,6-dicarboxylate



To a vigorously stirred solution of bromine (10.6 mL, 206.4 mmol, 3 eq) in petroleum benzene (60 mL) was added phosphorus tribromide (19.4 mL, 206.4 mmol, 3 eq). After stirring the mixture at room temperature for one hour, phosphorus pentrabromide was obtained by evaporating the excess of petroleum benzene under reduced pressure. Chelidamic acid (12.6 g, 68.8 mmol, 1 eq) was added and the resulting solid mixture was heated at 90 °C for four hours. After cooling to room temperature chloroform (120 mL) was added and the resulting black solution was left overnight under nitrogen. The chloroform phase was separated and absolute ethanol (120 mL) was added dropwise at 0°C. All solvents were removed under reduced pressure and the residue was recrystallized from absolute ethanol. The product was obtained as a white powder (12.10 g, 40.05 mmol, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.44 (t, 6H, $^3J_{HH}$ = 7.11 Hz, C*H₃*), 4.48 (q, 4H, $^3J_{HH}$ = 7.15 Hz, C*H₂*), 8.41 (s, 2H, py*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.31, 62.84, 131.18, 135.04, 149.63, 163.67. ES+ TOF HRMS ($CHCl_3$): *m/z* 302.0031 [M + H]$^+$ (calc. for $C_{11}H_{13}BrNO_4$ 302.0028).

$C_{11}H_{12}BrNO_4$ (302.12 g/mol)	Anal. calc.	C 43.73	H 4.00	N 4.64
	Found	C 43.83	H 3.89	N 4.69

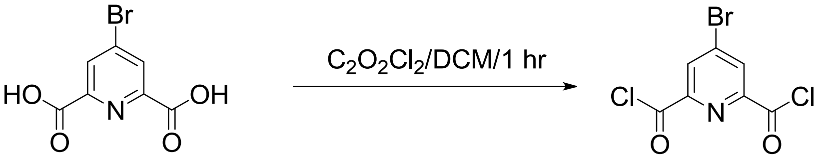
4-Bromopyridine-2,6-dicarboxylic acid



Sodium hydroxide (4 g, 99.30 mmol, 6 eq) was dissolved in water (75 mL) and to this solution diethyl 4-bromopyridine-2,6-dicarboxylate (5 g, 16.55 mmol) was added. The resulting suspension was stirred at 100 °C for one hour and allowed to cool to room temperature afterwards. The pH was adjusted to 1 using 37% aqueous hydrogen chloride solution. The resulting precipitate was filtered off, washed with water (3 x 30 mL) and dried under vacuum. The product was obtained as a white solid (3.93 g, 15.97 mmol, 97%). ^{1}H NMR (400 MHz, DMSO-d6): δ (ppm) = 8.37 (s, 2H, py*H*). ^{13}C NMR (100 MHz, DMSO-d6): δ (ppm) = 130.25, 134.26, 149.76, 164.56.

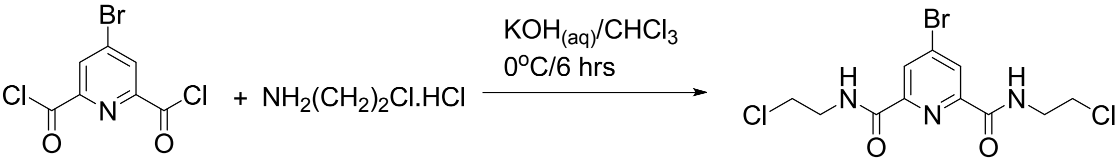
$C_7H_4BrNO_4$ (246.01 g/mol)	Anal. calc.	C 34.17	H 1.64	N 5.69
	Found	C 33.93	H 1.55	N 5.62

4-Bromopyridine-2,6-dicarbonyl dichloride



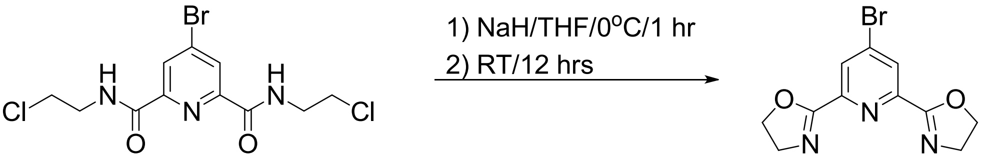
To a solution of 4-bromopyridine-2,6-dicarboxylic acid (3.13 g, 12.72 mmol, 1 eq) in dry dichloromethane (150 mL) was added oxalyl chloride (4.3 mL, 50.88 mmol, 4 eq) and a catalytic amount of dimethylformamide (8 drops). The resulting solution was stirred at room temperature for six hours and filtered through a pad of celite afterwards. The solvent was removed under reduced pressure and the product was obtained as a light purple powder (2.82 g, 9.96 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.47 (s, 2H, py*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 129.05, 132.04, 136.18, 149.93.

4-Bromo-N^2,N^6-bis(2-chloroethyl)pyridine-2,6-dicarboxamide



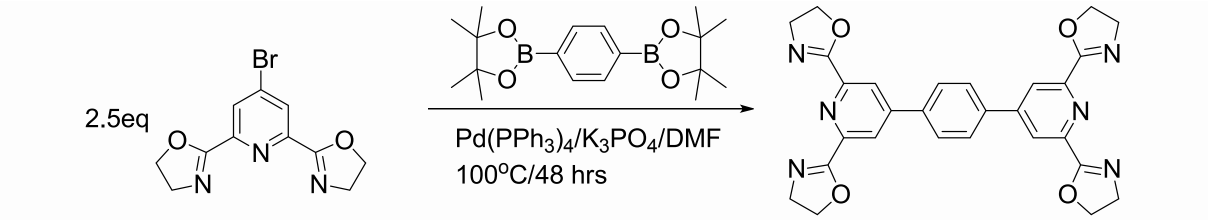
To a solution of 2-chloroethanolamine hydrochloride (2.66 g, 22.9 mmol, 2.3 eq) and potassium hydroxide (2.96 g, 52.67 mmol, 4.6 eq) in water (100 mL) was added a solution of 4-bromopyridine-2,6-dicarbonyl dichloride (2.82 g, 11.45 mmol, 1 eq) in dry dichloromethane (100 mL) dropwise at 0 °C. The resulting solution was stirred for 24 h at room temperature. Afterwards the water phase was extracted with dichloromethane (3 x 60 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Recrystallization of the solid residue from dichloromethane : methanol / 95 : 5 yielded the desired product as a white solid (3.08 g, 8.35 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.76 (t, 4H, $^3J_{HH}$ = 5.76 Hz, C*H$_2$*Cl), 3.84 – 3.89 (m, 4H, C*H$_2$*N), 8.08 (br s, 2H, N*H*), 8.52 (s, 2H, 3-py*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 41.41, 43.98, 128.89, 136.67, 149.59, 162.48. ES+ TOF HRMS ($CHCl_3$): m/z 369.9551 [M + H]$^+$ (calc. for $C_{11}H_{13}BrCl_2N_3O_2$ 370.0498).

4-Bromopyridine-2,6-bis(oxazoline)



Under N_2, to a stirred suspension of sodium hydride (60% in mineral oil, 0.48 g, 11.92 mmol, 4 eq) in dry tetrahydrofuran (50 mL) was added a solution of 4-bromo-bis(2-chloromethyl)pyridine-2,6-dicarboxamide (1.1 g, 2.98 mmol, 1 eq) in dry tetrahydrofuran (20 mL) dropwise at 0 °C. The resulting mixture was stirred overnight at room temperature and filtered afterwards. The solution was concentrated under reduced pressure and redissolved in ethyl acetate (100 mL). The organic phase was washed with water (3 x 70 mL) and the solvent was removed under reduced pressure. After recrystallization from absolute ethanol the product was obtained as a white solid (0.51 g, 1.69 mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.12 (t, 4H, $^3J_{HH}$ = 9.81 Hz, C*H$_2$*O), 4.54 (t, 4H, $^3J_{HH}$ = 9.81 Hz, C*H$_2$*N), 8.34 (s, 2H, py*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.23, 68.70, 125.86, 145.57, 148.11, 162.78. ES+ TOF HRMS ($CHCl_3$): m/z 296.0043 $[M + H]^+$ (calc. for $C_{11}H_{11}BrN_3O_2$ 296.0035).

1,4-Bis(2,6-bis(4,5-dihydrooxazol-2-yl)pyridin-4-yl)benzene (DitopicPyboxPh)



A mixture of 4-bromopyridine-2,6-bis(oxazoline) (0.5 g, 1.69 mmol, 2.5 eq), 1,4-benzenediboronic acid bis(pinacol) ester (0.22 g, 0.68 mmol, 1 eq), $Pd(PPh_3)_4$ (31 mg, 4 mol%), and K_3PO_4 (0.72 g, 3.40 mmol, 5 eq) was degassed and backfilled with N_2 for three times. To this dry and degassed dimethylformamide (25 mL) was added. The resulting mixture was stirred at 100 °C for 48 hours. After cooling to room temperature the solvent was removed under reduced pressure. The solid residue was extracted with chloroform (3 x 60 mL) and the combined organic phases were washed with water (3 x 50 mL), dried over Na_2SO_4 and filtered. Addition of ethyl ether (50 vol%) led to precipitation of an off-white solid which was filtered off and washed with hexane, ethanol, and ether. After drying under vacuum the desired product was obtained as a white solid (0.35 g, 0.57 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.17 (t, 8H, $^3J_{HH}$ = 9.35 Hz, C*H$_2$*O), 4.59 (t, 8H, $^3J_{HH}$ = 9.35 Hz, C*H$_2$*N), 7.91 (s, 4H, Ar*H*), 8.48 (s, 4H, py*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.22, 68.61, 123.28, 128.11, 138.01, 147.63, 148.91, 163.74. ES+ TOF HRMS ($CHCl_3$): m/z 509.1313 $[M + H]^+$ (calc. for $C_{28}H_{25}N_6O_4^+$ 509.1932).

$C_7H_4BrNO_4 \cdot 2H_2O$ (544.56 g/mol)	Anal. calc.	C 61.76	H 5.18	N 15.43
	Found	C 61.44	H 4.78	N 15.04

Preparation of soluble lanthanide coordination networks

Stock solutions of the ligand DitopicPyboxPh were prepared in chloroform and sonicated for 30 min to obtain a clear solution. Stock solution of $Eu(NO_3)$ x $5H_2O$ were prepared in an acetonitrile / chloroform mixture. The correct metal ion concentration of the Eu(III) stock solution was assured by titration with EDTA and xylenol orange as the indicator. The Eu(III) stock solutions were diluted to a concentration of around 5×10^{-5} M. To that the ligand stock was slowly added in ratios of 0.25 eq up to 4.0 eq dropwise to avoid the formation of insoluble aggregates. For all samples it was ensured that the final solvent mixture of acetonitrile and chloroform was in an equal volume ratio of 1:1. Both, the initial stock solutions and the final samples were prepared in a glovebox under a controlled atmosphere. All samples were left to equilibrate for 12 hours prior to the photophysical measurements. The samples in methnol and deuterated methanol were prepared according to the same procedure by replacing acetonitrile as solvent.

Spectrophotometric titrations

NMR titrations were performed in a mixture of deuterated methanol and deuterated chloroform. Due to the prominent water peak all spectra were shimmed for acetonitrile as the solvent. For the titration a stock solution of $La(CF_3SO_3)_3$ was prepared in a 1:1 (v:v) mixture of deuteratued acetonitrile and deuterated chloroform and diluted to an approximate concentration of 3 x 10^{-6} M. To 2 mL of that solution was added a ligand stock solution in deuterated chloroform stepwise in amounts of 0.25 eq. To avoid significant differences in the concentration of the samples, the amount of ligand solution added was set to 4 µL. After each addition the sample was allowed to equilibrate for 15 min. Dynamic photophysical titrations were performed by replacing Eu(III) with either Tb(III) or Sm(III). For that to 2 mL of the sample with a metal to ligand ratio of 1:1.75 was added a solution of a Tb(III) or Sm(III) stock solution in equal amounts of 0.1 eq. Prior to each photophysical measurements the samples were allowed to equilibrate for 15 min. To avoid differences in the concentration of the sample the volume of metal solution added was set to 2 µL for each titration step.

Photophysical measurements

UV-vis absorption spectra were recorded using a Shimadzu UV-2501PC UV-VIS Recording Spectrophotometer. Steady-state emission spectra were recorded using Shimadzu RF-5301PC Spectrofluorophotometer. Fluorescence spectra were corrected using a radiometric calibrated lamp, Ocean Optics HL-2000-CAL. Relative total Eu(III) emission quantum yields were calculated from steady state emission/absorption spectra using **formula 1**,[1]

$$\phi_x = \frac{A_{ref}\, I_x\, n_x^2}{A_x\, I_{ref}\, n_{ref}^2}\phi_{ref} \qquad \mathbf{(1)}$$

where ϕ is the emission quantum yield of the sample *x/*reference *ref*, *n* is the refractive index of the solvent (1.33 in water, 1.40 in acetonitrile/chloroform (1:1 / v:v)[2]), *A* is the absorbance at the excitation wavelength , and *I is* the integrated intensity of the corrected emission. $Cs_3[Eu(dipic)_3]$ (ϕ_{ref} = 24.0%, A_{279} = 0.2, 7.5 x 10^{-5} M) in Tris buffer (0.1 M) was used as the reference.[1,3] $Cs_3[Eu(dipic)_3]$ was prepared from 2,6-dipicolinic acid and Eu_2O_3 according to a previously established method.[4] The excitation wavelength was set to 279 nm for all quantum yield measurements and it was always ensured that the absorbing/emitting species in solution exhibit a linear trend between the concentration and the integrated intensity of the emitted light. The intensity of the emitted light was integrated over all observable Eu(III) $^5D_0 \rightarrow {}^7F_J$ (J = 0 – 4) emission peaks. Time-resolved emission spectroscopy measurements were carried out using an Edinburgh Instruments flash-photolysis spectrometer LP920 equipped with an Edinburgh Instruments LP920-K PMT Detector and a time-gated Andor DH720 ICCD camera. Maximum resolution of the setup is 10 ns. Samples were excited at 355 nm using a 3rd harmonic of Nd-YAG laser of an Expla NT341A OPO laser system. Excitation pulse energy was about 1mJ, beam diameter about 5mm. All photophysical measurements were performed in air since measurements under argon did not result in any changes in the obtained data. All spectra were recorded using 0.2 cm path length quartz cuvettes. All Eu(III) emission decay kinetics were recorded at 615 nm and fitted with the Edinburgh Instruments FLASH software. All data reported herein are the average of three independent measurements.

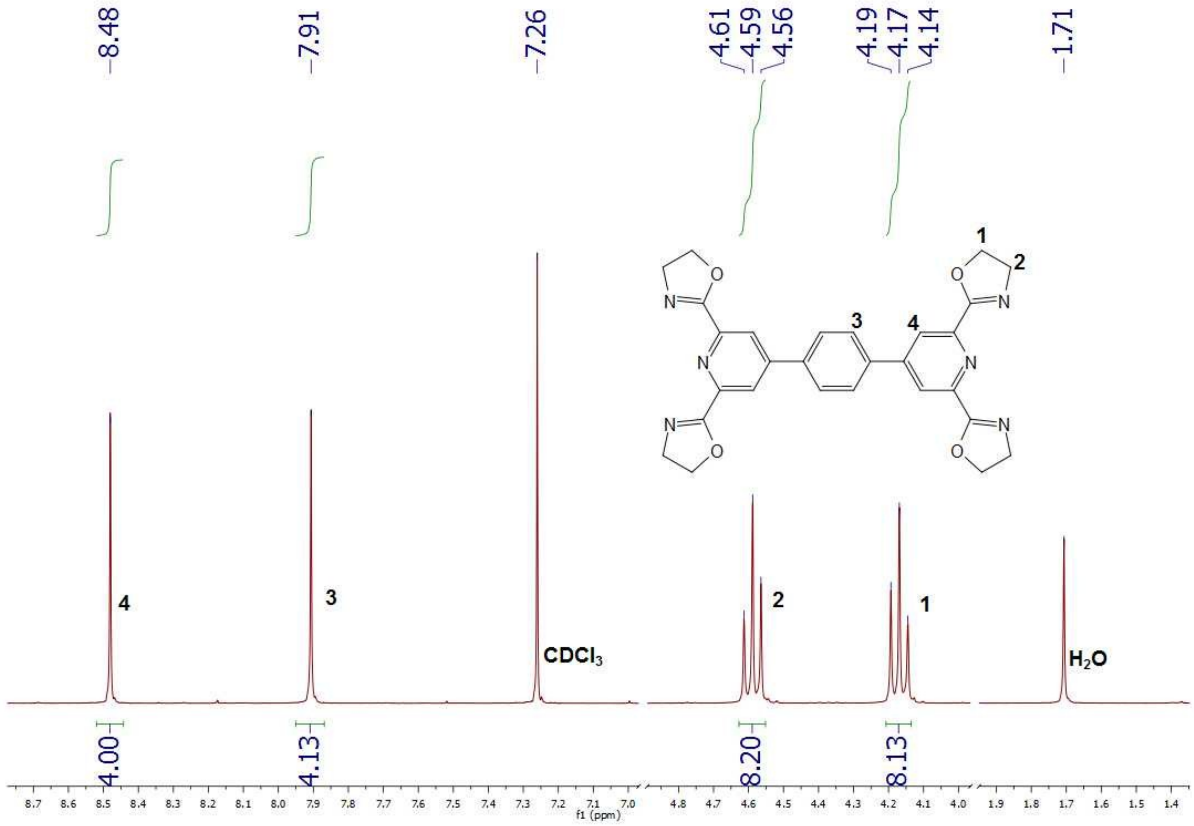


Figure S1: ^{1}H NMR spectrum of the ligand DitopicPyboxPh in CDCl$_3$.

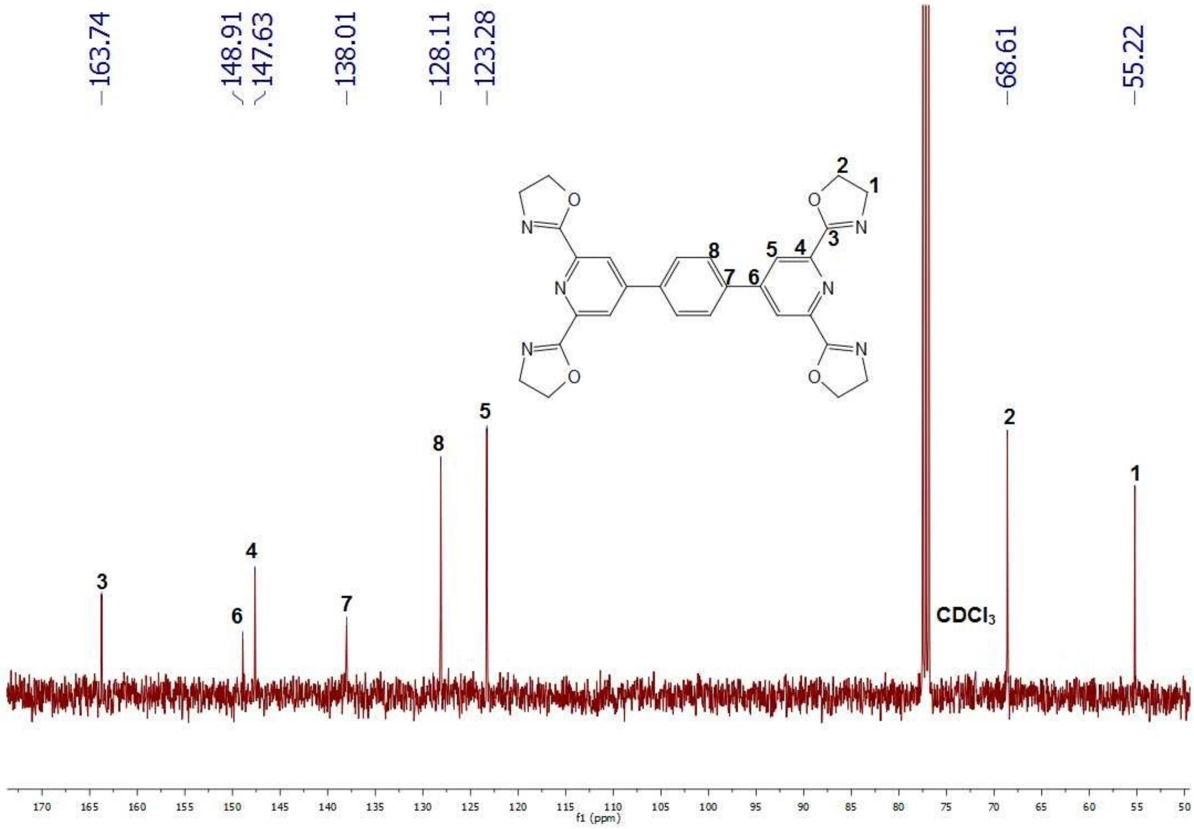


Figure S2: ^{13}C NMR spectrum of the ligand DitopicPyboxPh in CDCl$_3$.

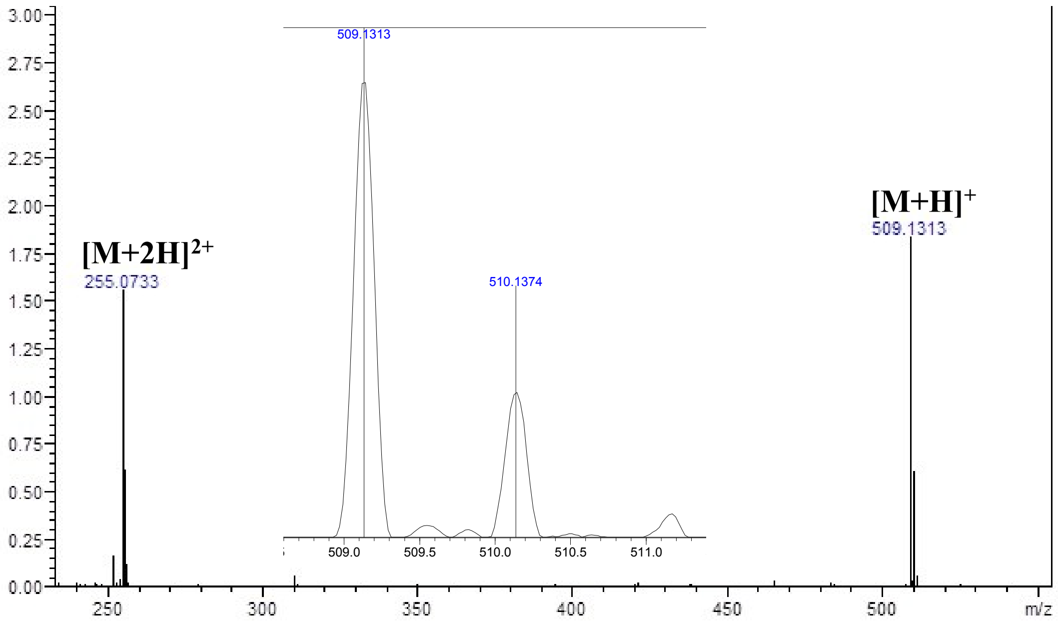


Figure S3: HRMS mass spectrum of the ligand DitopicPyboxPh in CHCl$_3$.

Table S1: Excited state lifetimes τ in different solvent mixtures, number of coordinated water molecules q, Intensity ratios (R) of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ Eu(III) transitions, and relative quantum yields of the coordination networks in different ligand to metal ratios.

Ligand to metal ratio	**τ_{MeCN} (ms)(a)**	**τ_{MeOH} (ms)(b)**	**$\tau_{MeOD\text{-}d4}$ (ms)(c)**	**q(d)**	**R(e)**	**ϕ (%)(f)**
0.25:1	1.08 ± 0.03	0.77 ± 0.05	2.00 ± 0.04	1.64	3.7	34.6 ± 2.6
0.5:1	1.23 ± 0.06	0.85 ± 0.03	1.96 ± 0.03	1.30	3.3	45.5 ± 3.4
0.75:1	1.51 ± 0.03	1.02 ± 0.04	1.96 ± 0.05	0.82	2.9	51.2 ± 3.8
1:1	1.64 ± 0.07	1.12 ± 0.05	1.96 ± 0.05	0.62	2.8	58.6 ± 4.3
1.25:1	1.72 ± 0.03	1.20 ± 0.06	1.94 ± 0.04	0.46	2.7	66.2 ± 4.7
1.5:1	1.78 ± 0.05	1.29 ± 0.03	1.94 ± 0.05	0.32	2.7	72.1 ± 5.2
1.75:1	1.80 ± 0.06	1.33 ± 0.04	1.97 ± 0.04	0.29	2.5	73.4 ± 4.1
2:1	1.83 ± 0.04	1.35 ± 0.05	1.96± 0.04	0.25	2.6	66.8 ± 4.5
2.25:1	1.85 ± 0.05	1.36 ± 0.04	2.00 ± 0.04	0.27	2.6	60.4 ± 4.2
2.5:1	1.83 ± 0.06	1.36 ± 0.06	2.00 ± 0.05	0.26	2.5	56.2 ± 3.7
2.75:1	1.84 ± 0.05	1.34 ± 0.03	2.00 ± 0.04	0.29	2.5	48.8 ± 3.2
3:1	1.83 ± 0.03	1.35 ± 0.05	2.02 ± 0.04	0.29	2.7	42.6 ± 2.7

(a)Measured in a CHCl$_3$: MeCN (1:1 / v:v) solvent mixture. (b)Measured in a CHCl$_3$: MeOH (1:1 / v:v) solvent mixture. (c)Measured in a CHCl$_3$: MeOD-d4 (1:1 / v:v) solvent mixture. (d)Calculated from lifetime measurements in MeOH and MeOD-d4 according to Horrock's equation.[5] (e)Intensity ratios (R) of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ Eu(III) transitions. (f)Relative quantum yield compared to Cs$_3$[Eu(dipic)$_3$].

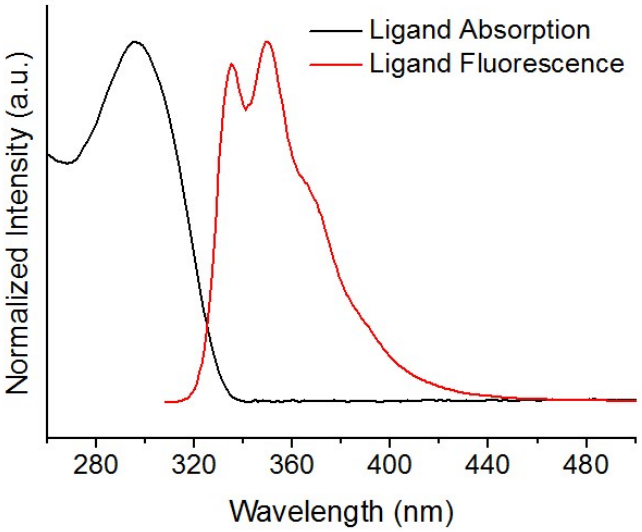


Figure S4: Absorption and fluorescence ($\lambda_{ex} = 300$ nm) spectra of the uncoordinated ligand DitopicPyboxPh.

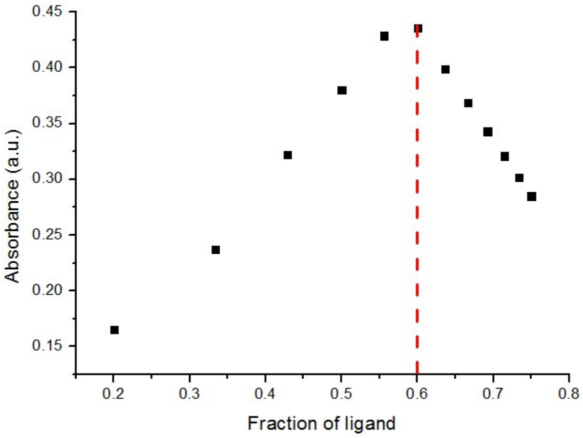


Figure S5: A Job plot from UV-vis absorption measurements at different proportions of ligand and metal ions at a constant concentration of 3 x 10^{-4} mol/L and a wavelength of 340 nm.

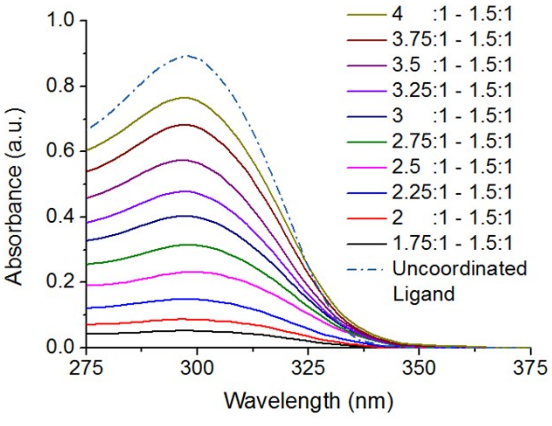


Figure S6: Absorption spectra of the Eu(III) coordination polymers with ligand to metal ratios 1.75:1 – 4:1 after subtraction of the absorption spectrum of the ligand to metal ratio 1.5:1 sample. Spectrum of the uncoordinated ligand is shown as well.

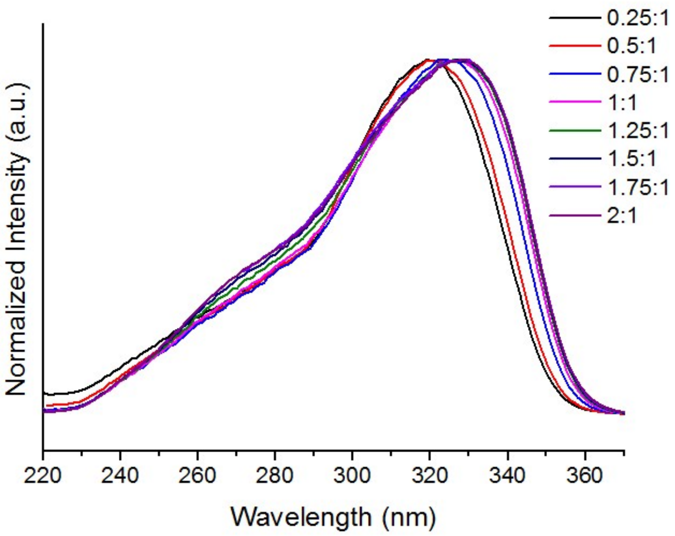


Figure S7: Excitation spectra of a solution containing $Eu(NO_3)_3$ and the ditopic ligand in chloroform / acetonitrile in different ligand to metal ratios, 0.25:1 – 2:1 (λ_{em} = 615 nm).

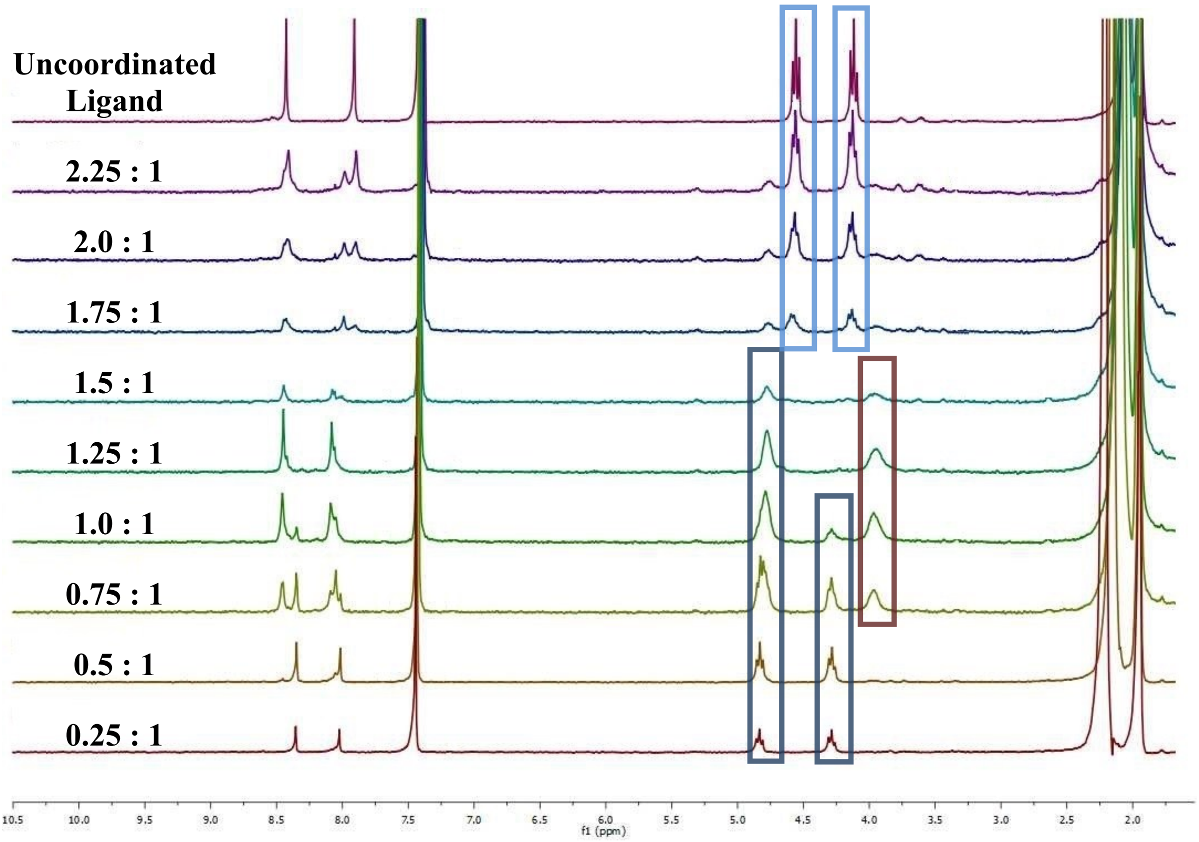


Figure S8: ^1H NMR titration of $La(CF_3SO_3)$ against the DitopicPyboxPh in a mixture of $CDCl_3$ and MeCN-d_3 (1:1 / v:v) in different ligand to metal ratios. Highlighted are the triplet signals of the ligand oxazline protons CH_2O and CH_2N respectively.

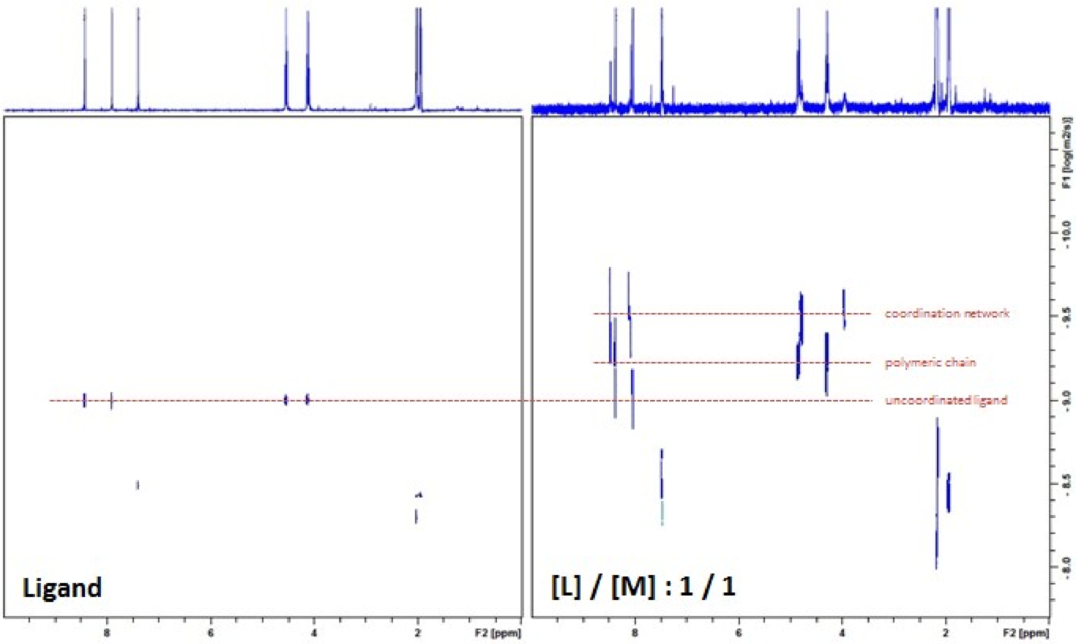


Figure S9: DOSY two-dimensional diffusion ordered NMR spectra (500 MHz, $CDCl_3$/MeCN-d_3 = 1/1, v/v, 295 K) of the uncoordinated ligand (left) and a sample in a ligand to La(CF_3SO_3) ratio of 1:1 (right) at a concentration of 0.5 mmol/L.

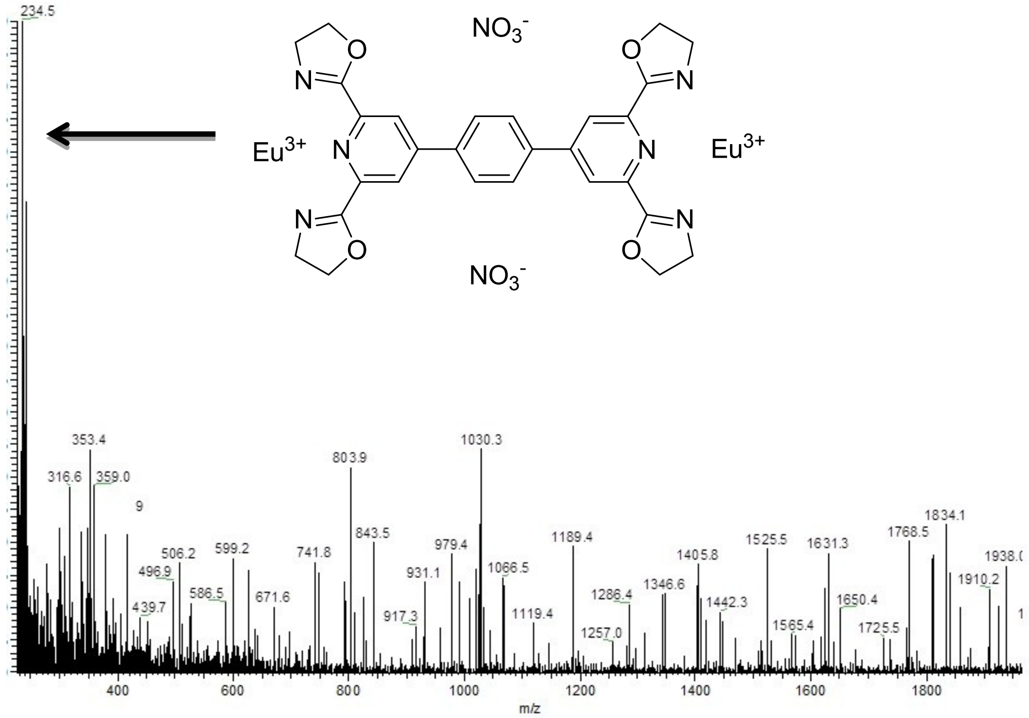


Figure S10: ESI spectrum in a chloroform/acetonitrile (1/1, v/v) solution of the sample in a ligand to metal ratio of 1.5:1.

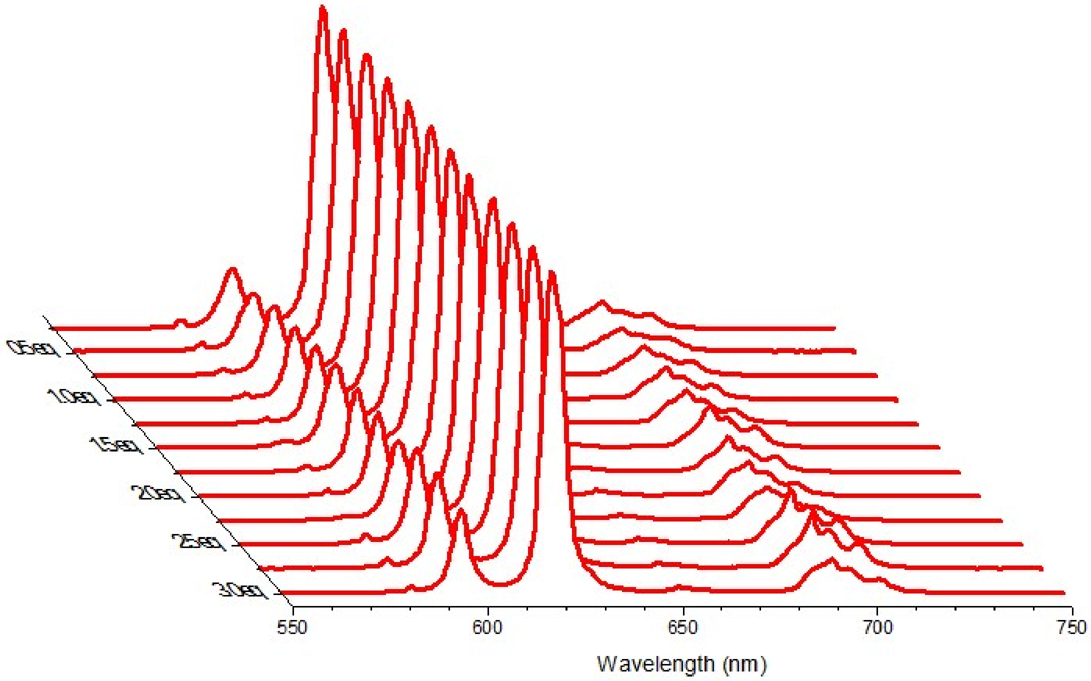


Figure S11: Steady-state Eu(III) emission spectra of all samples (λ_{ex} = 355 nm).

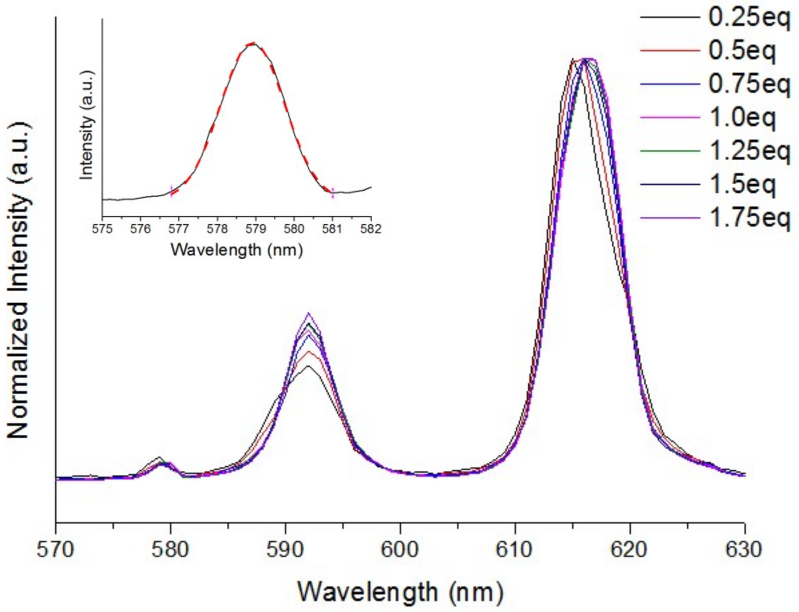


Figure S12: Comparison of the intensity ratios (R) of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ Eu(III) transitions for different ligand concentrations and Gaussian fit for a typical $^5D_0 \rightarrow {}^7F_0$ transition (inset).

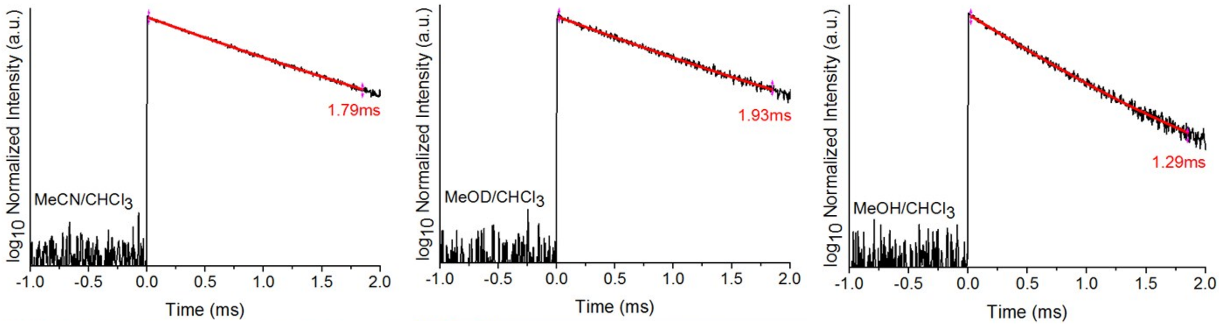


Figure S13: Typical Eu(III) excited state decay curves and mono-exponential fitting curves in different solvent systems (λ_{ex} = 355 nm, recorded at 615 nm).

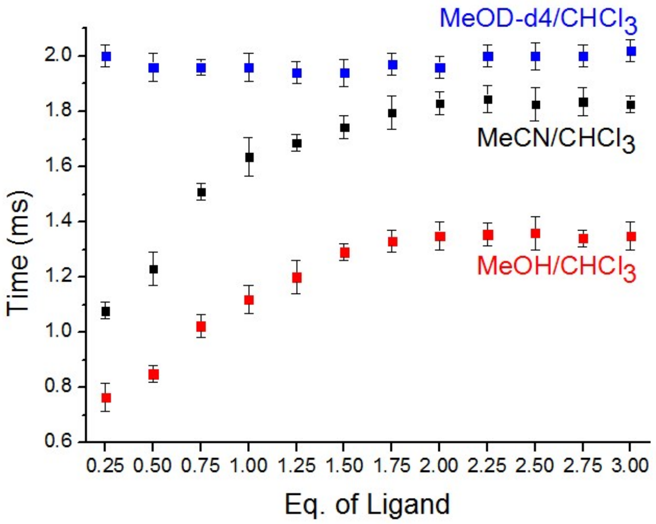


Figure S14: Comparison of Eu(III) excited state decay curves in different solvent systems for all samples with error bars (λ_{ex} = 355 nm, recorded at 615 nm).

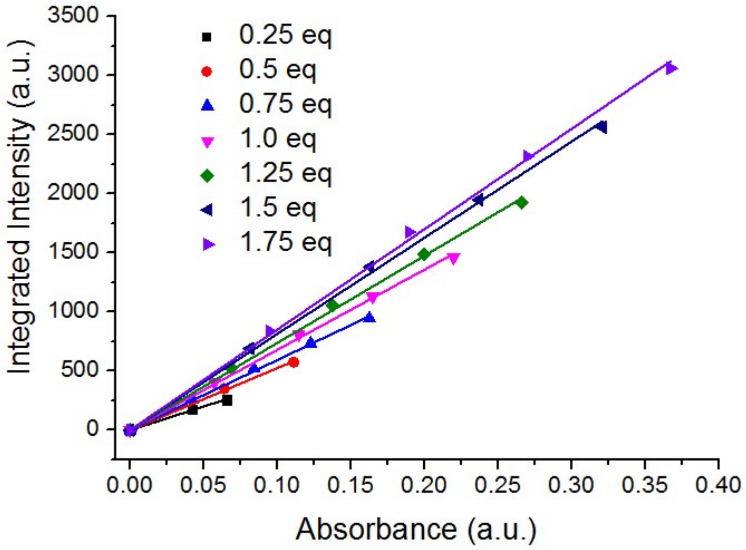


Figure S15: Concentration dependence of integrated emission intensity ($^5D_0 \rightarrow {}^7F_J$ (J = 0 – 4)) on absorbance for different metal to ligand ratios and their linear fits used for quantum yield calculations.

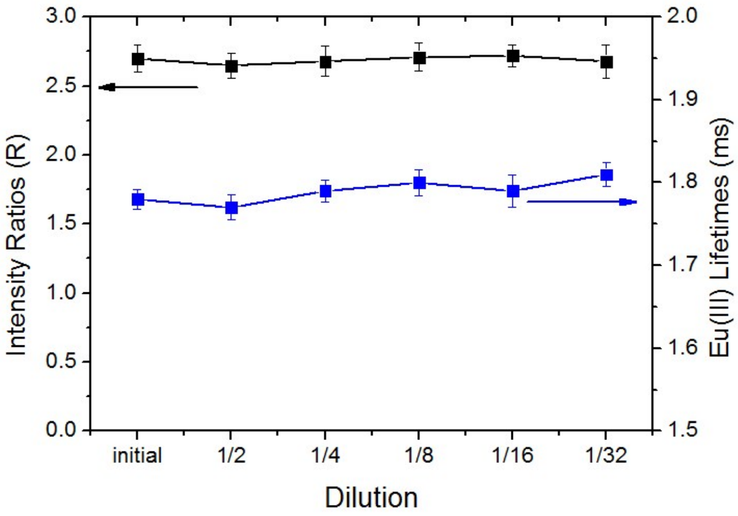
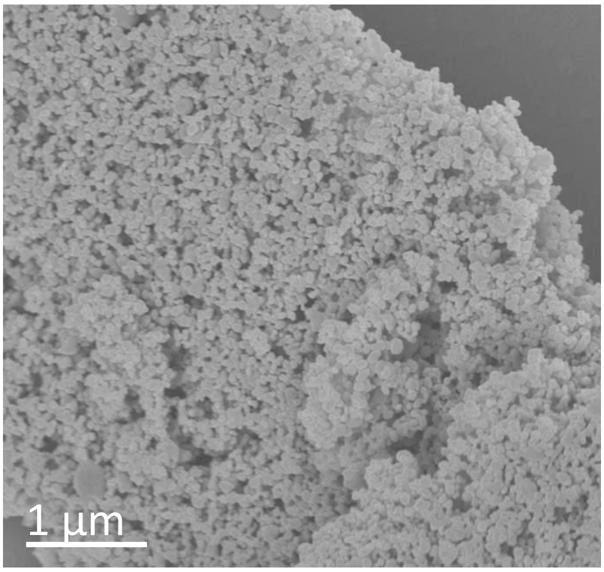


Figure S16: Solution concentration dependency of the $^5D_0 - {}^7F_2$ / $^5D_0 - {}^7F_1$ emission intensity ratios (R) and Eu(III) lifetimes of a sample (initial concentration of 0.1 mmol/L) at ligand to metal ratio of 1.5:1.



C	64.0 at%
O	27.0 at%
N	8.9 at%
Eu	1.3 at%
C : Eu ratio	49
Ligand : Eu	1.75 : 1

$$Ligand = \frac{XPS\ C:Eu\ ratio}{Carbon\ atoms\ ligand} = \frac{49}{28}$$

Figure S17: SEM image (left) and elemental analysis by XPS (right) of the precipitate formed from solutions at higher concentrations in a ligand to metal ratio of 1.5:1.

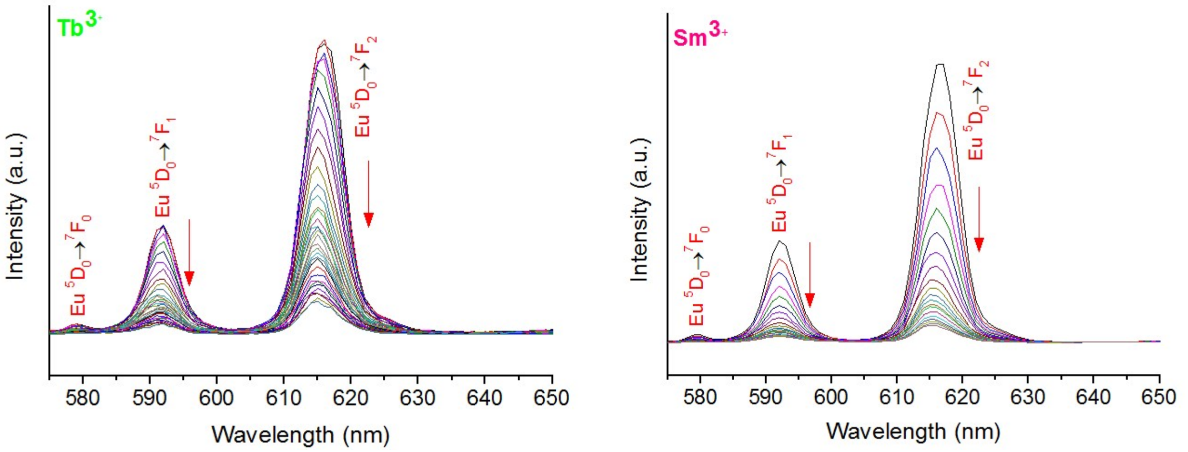


Figure S18: Steady-state emission spectra of a typical titration experiment of an Eu(III) sample with increasing amounts of Tb(III) and Sm(III) (λ_{ex} = 300 nm).

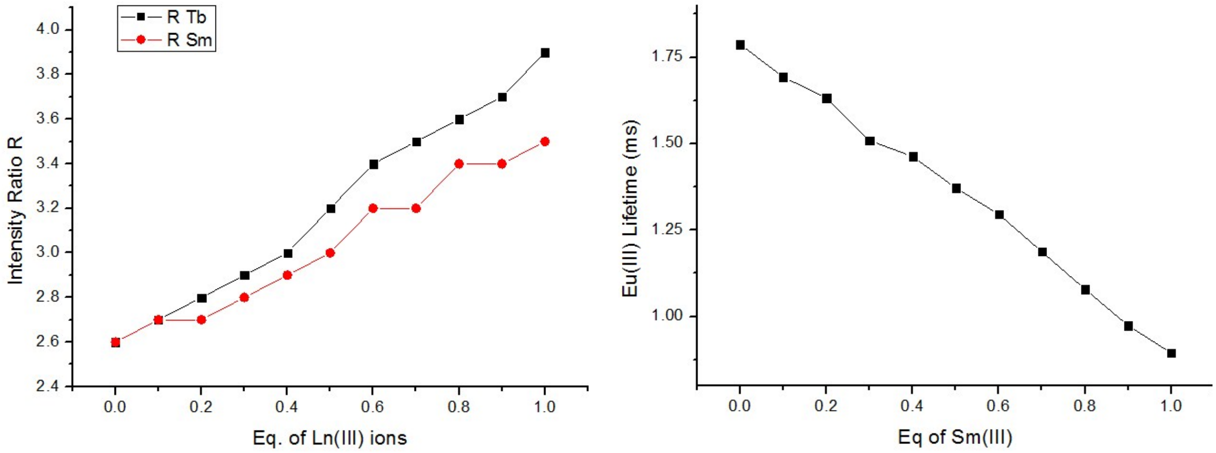


Figure S19: Changes of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ Eu(III) intensity ratios during titrations with Tb(III) and Sm(III) (left), changes of Eu(III) excited state lifetimes during titration against Sm(III) metal ions (right).

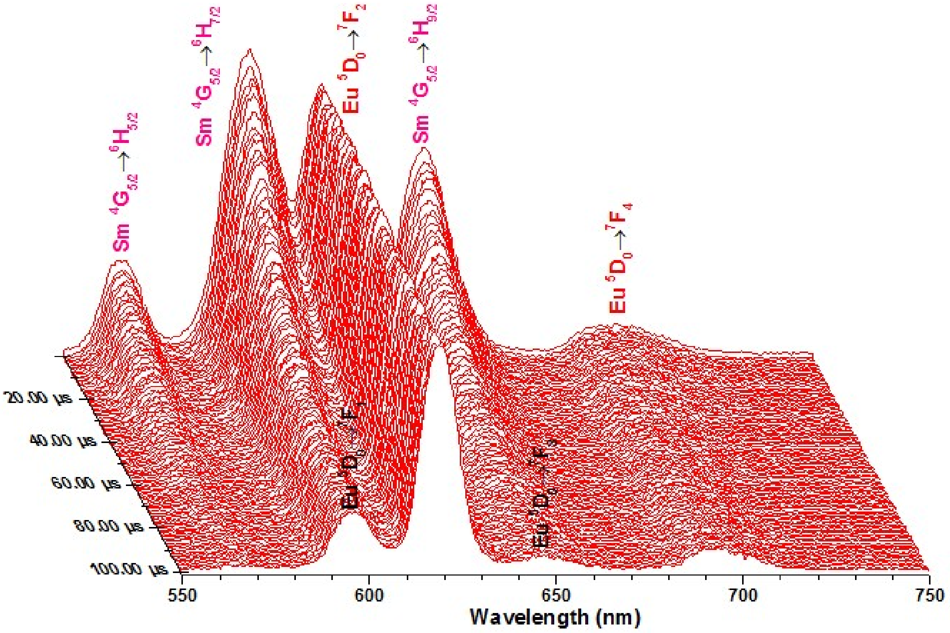


Figure S20: Time-gated emission spectra of a mixed Eu(III) and Sm(III) coordination network in a 1 : 1.5 / Eu(III) : Sm(III) ratio measured between 1 µs and 100 µs ($\lambda_{ex} = 355$ nm, band with 2nm).

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