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Luminescent lanthanide (Eu(III)) cross-linked supramolecular metallo co-polymeric hydrogels: The effect of ligand symmetry

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General methods and materials

All reagents and solvents were purchased from commercial suppliers and used without further purification. Dry solvents were prepared following standard procedures[1] or by solid-phase solvent purification. Synthesis was completed, unless stated, under inert atmospheres of N_2 or Ar. Flash chromatography was carried out using a TeledyneIsco CombifFlash Rf 200 automated purification system; pre-packed normal phase, amine or C-18 silica cartridges were used supplied by TeledyneIsco RediSep® or Grace Technologies. Thin-layer chromatography (TLC) was conducted using MerckMillipore Kiesegel 60 F_{254} silica or alumina plates and visualised under λ = 254 nm; amine containing compounds were visualised using Ninhydrin in EtOH. Melting points were determined using an Electrothermal IA900 digital apparatus. Infrared spectra were recorded (in cm^{-1}) using a PerkinElmer Spectrum One FT-IR Spectrometer fitted with a universal ATR sampling accessory from solid samples under 70 N compression. Elemental analysis for % carbon, hydrogen and nirogen was carried out at the Microanalytical Laboratory, School of Chemistry and Chemical Biology, University College Dublin. Microwave-assisted reactions were carried out in a Biotage Initiator Eight EXP microwave reactor using 2-5 mL or 10-20 mL sealed vials.

NMR Spectroscopy

NMR spectra were recorded using a Bruker DPX-400 Avance spectrometer or Agilent DD2/LH spectrometer at frequencies of 400.13 MHz and 100.6 MHz for ^{1}H-NMR and ^{13}C-NMR, respectively; or a Bruker AV-600 spectrometer at frequencies of 600.1 MHz and 150.2 MHz for ^{1}H-NMR and ^{13}C-NMR, respectively. All spectra were recorded in commercially sourced per-deuterated solvents and referenced to residual proton signals of those solvents. Recorded free-induction decay signals were Fourier-transformed and processed using MestreNova v.6 without apodization and chemical shifts expressed in parts per million (ppm / δ) and coupling constants (J) in Hz.

Mass Spectrometry

Mass spectrometry was completed in the departmental mass spectrometery service of the School of Chemistry, Trinity College Dublin. Electrospray mass spectrometry was completed using a Mass Lynz NT V 3.4 on a Waters 600 controller with 996 photodiode array detector. HPLC grade solvents were used throughout and accurate molecular weights determined *via* a peak-matching method against enkephaline standard reference (m/z = 556.2771); all accurate masses were reported within ± 5 ppm of the calculated mass. MALDI Q-ToF mass spectra were recorded on a MALDI Q-TOF Premier (Waters Corporation, Micromass MS

Technologies, Manchester, UK) and high-resolution mass spectrometer was performed using Glu-Fib as an internal reference (*m/z* = 1570.677).

Photophysical measurements

All photophysical measurements were taken in spectroscopic grade solvents (Sigma-Aldrich®) and were used in quartz cells purchased from HellmaAnalytics with path length 10mm. Spectroscopic solutions were prepared from stock solutions using Pipetman® Classic micropipettes (Gilson, Inc).

UV-visible absorption and luminescence spectroscopy

UV-visible absorption spectra were recorded using a Varian Cary 50 spectrophotometer, a spectroscopic window of 450 – 200 nm was used for all spectra with applied baseline correction from blank solvent. Luminescence spectra (fluorescence and time-gated emission) were recorded using a Varian Cary Eclipse spectrophotometer and reported in arbitrary units; spectral windows of 570 – 720 nm was applied for Eu(III) emission. Time-gated emission spectra were recorded over an average integration time for 0.1 seconds. The temperature was kept constant throughout the measurements at 298 K by using a thermostated unit block.

Luminescence lifetime measurements

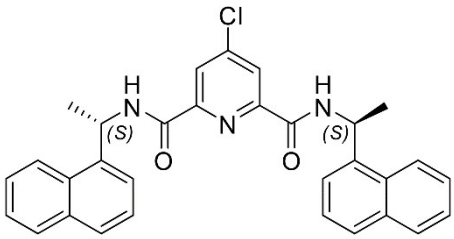
Luminescence lifetime measurements of Eu(III)-centred emission was recorded using a Varian Cary Eclipse spectrophotometer as a time-resolved measurement at 298 K. Excitation was made at the maximum absorbance (*ca.* 281 – 310 nm*)* and, following a gate time, the decay in intensity of the $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III) was monitored. Final lifetimes were averaged from at least five measurements at different gate times between 0.02 – 0.04 ms. The recorded decay curves were fitted to mono- or bi-exponential decay functions using Origin® 8.5.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out either in at the School of Pharmacy, Queen's University Belfast using a DSC 2920 Modulated DSC (TA Instruments) or in the School of Chemistry, Trinity College Dublin using a DSC 8000 (Perkin Elmer). Samples were prepared in DSC pans provided by TA Instruments and PerkinElmer, respectively, and heat flows measured against a reference pan. Both instruments were fitted with recirculating coolers and programs run with heating and cooling rates of 5 °C/min and 10°C/min, respectively. The temperature extremes were held isothermally between each heating and

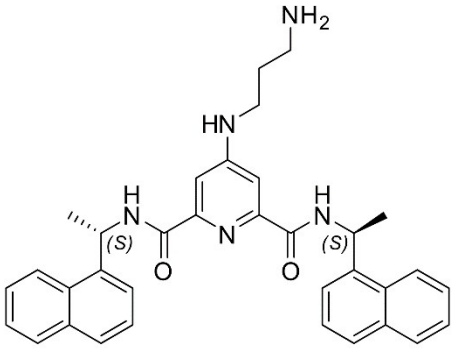
cooling run. T_g values were estimated at the centre point by tangent extrapolation methods using TA Universal Analysis or Pyris® software associated with the respective instruments.

4-Chloro-*N,N'*-bis((*S*)-1-(naphthalen-1-yl)ethyl)pyridine-2,6-dicarboxamide - **3(*S,S*)**



Chelidamic acid monohydrate was heated (0.40 g, 1.99 mmol) in $SOCl_2$ (5 mL) with cat. DMF (3 drops) at 50 ^oC for 18 hours until complete dissolution. Excess $SOCl_2$ was distilled under reduced pressure. The residue dried under high vacuum then dissolved into THF (50 mL) and treated with *(S)*-1-(1-naphthyl)ethylamine (0.64 mL, 3.99 mmol) and TEA (0.56 mL, 3.99 mmol) at 0 ^oC. After 30 minutes the reaction was allowed to warm to RT and stirred for 48 hours. Solvent was removed *in vacuo* then residues redissolved into CH_2Cl_2 (150 mL). This solution was washed with sat. aq. $NaHCO_3$ (2 x 50 mL), brine (50 mL) and the organic phase dried over $MgSO_4$, filtered and concentrated *in vacuo*. Trituration under MeOH and filtration of resultant solids yielded **1(*S,S*)** as a white solid (0.615 g, 1.21 mmol, 61%); m.p. 129.9 – 131.2 ^oC ; HRMS (*m/z*) (ES^+) Calculated for $C_{31}H_{27}ClN_3O_2$ *m/z* = 508.1766 $[M + H]^+$. Found *m/*z =507.1714; ^1H NMR (400 MHz, $CDCl_3$) δ : 8.34 (2H, s, pyridyl-CH), 8.13 (2H, br. d, *J* = 5.9 Hz, naph-CH), 7.85 (2H, br. d, *J* = 7.5 Hz, naph-CH), 7.63 (2H, d, *J* = 7.7 Hz, naph-CH), 7.55 – 7.49 (4H, m, naph-CH), 7.49 – 7.39 (4H, m, naph-CH), 6.12 – 5.89 (2H, m, pyr-CH), 1.67 (6H, d, *J* = 6.6 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 161.3, 150.0, 147.7, 137.8, 133.9, 130.9, 128.9, 128.6, 126.7, 126.0, 125.5, 125.2, 123.1, 122.7, 45.4, 20.8 ; IR ν_{max} (cm^{-1}): 3281, 2976, 1644, 1599, 1510, 1373, 1334, 1232, 1173, 1118, 1081, 998, 900, 860, 800, 777, 765, 681.

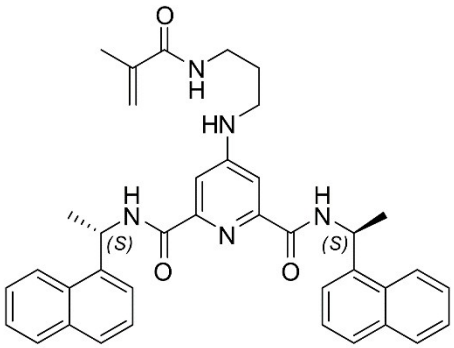
4-(3-Aminopropylamino)-N,N'-bis((S)-1-(naphthalen-1-yl)ethyl)pyridine-2,6-dicarboxamide – **4(*S,S*)**



Compound **3(*S,S*)** was suspended in 1,3-diaminopropane as solvent and refluxed for 18 hours. Upon completion by TLC reaction mixtures were poured into iced-water (3 mL) precipitating beige solids which were isolated by filtration and washed with excess H_2O and dried *in vacuo*. Crude mixtures were eluted on silica (RediSep® 40g, 10 CV DCM followed by gradient elution 0 → 15 % CH_3OH in DCM), product containing fractions were concentrated to give pure products as a white solid. Yield: 45 %; m.p. 172 – 174 ^oC; HRMS (*m/z*) (ES^-) Calculated for $C_{34}H_{34}N_5O_2$ *m/z* = 544.2713. Found *m/z* = 544.3138. $[M + H]^+$. ^1H NMR (600 MHz, $CDCl_3$, broad signals possible aggregation) δ 8.10 (m, 3H, aryl-CH), 7.79

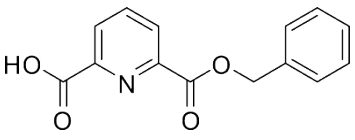
(m, 4H, aryl-CH), 7.42 (m, 8H, aryl-CH), 5.96 (app. s, 1H, aliphatic-CH), 3.15 (m, 4H, CH_2), 2.07 (m, 2H, CH_2), 1.55 (app. s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.70, 155.70, 149.10, 138.72, 133.89, 130.81, 128.88, 128.11, 127.28, 126.45, 125.98, 125.78, 125.63, 125.44, 125.24, 123.23, 122.89, 122.61, 121.40, 46.51, 45.30, 30.92, 29.70, 24.74, 21.24. IR ν_{max} (cm^{-1}): 3285, 3048, 2934, 1654, 1605, 517, 1309, 1467, 1241 1144, 1116, 873, 9899, 777.

4-(3-Methacrylamido-propylamino)-N,N'-bis((S)-1-(naphthalen-1-yl)ethyl)pyridine-2,6-dicarboxamide - **1(*S,S*)**



To a solution of **4(*S,S*)** (0.250 g, xx mmol, 1 equiv.) in CH_2Cl_2 (20 mL) at 0 °C methacrylic anhydride (0.2 mL, 1.26 mmol, 3.4 equiv.) was added and the reaction stirred at RT for 24 hours. The reaction mixture was subsequently diluted with CH_2Cl_2 (50 mL) and washed with H_2O (100 mL) and NaCl (sat. aq., 100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford a crude oily liquid which was eluted in silica (RediSep®, 5% CH_3OH in CH_2Cl_2). Product containing fractions were combined and concentrated *in vacuo* to give **127(*S,S*)** as a white solid. Yield: 65%; HRMS (*m/z*) (ES^+) Calculated for $C_{38}H_{38}N_5O_3$ *m/z* = 612.2975 $[M - H]^-$. Found *m/*z = 612.2964. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.5 Hz, 2H, aryl-CH), 7.85 (dd, *J* = 22.1, 17.2 Hz, 6H, aryl-CH), 7.58 – 7.33 (m, 8H, aryl-CH), 6.04 – 5.78 (m, 2H, aliphatic-CH), 5.66 (s, 1H, alkene-CH), 5.30 (s, 1H, alkene-CH), 3.25 (m, 4H, CH_2), 1.72 (m, 2H, CH_2) 1.61 (m, 6H, CH_3), 1.24 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.03, 156.55, 144.09, 135.33, 133.98, 133.38, 130.95, 128.91, 128.34, 127.28, 126.55, 125.84, 125.38, 123.30, 77.22, 77.01, 76.80, 45.52, 29.70, 21.05, 18.69, 18.58, 14.77. IR ν_{max} (cm^{-1}): 3290, 3051, 2961, 2935, 2870, 1763, 1651, 1607, 1519, 1451, 1376, 1172, 990, 868, 800, 776.

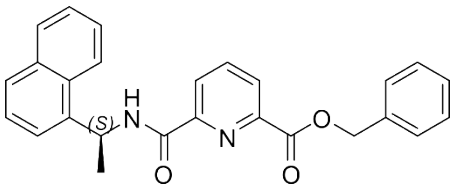
6-((benzyloxy)carbonyl)pyridine-2-carboxylic acid – **6**[a]



2,6-pyridinedicarboxylic acid (**5**, 2.043 g, 12.23 mmol, 1 equiv.) and $NaHCO_3$ (1.233 g, 14.66 mmol, 1.2 equiv.) were stirred in anhydrous *N,N*-dimethylformamide (DMF) (100 mL) at 60 °C under argon for 30 minutes. Benzyl bromide (1.7 mL, 15 mmol, 1.2 equiv.) was added dropwise and the reaction stirred under argon at 60 °C for 24 hours**.** The resulting yellow solution was diluted with water (100 ml), basified to pH 8 with $NaHCO_3$ (sat. aq.) and

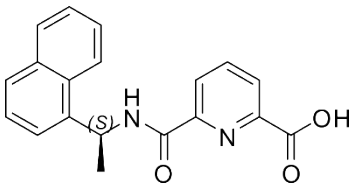
extracted with EtOAc (2 x 100 ml). The aqueous layer was then acidified to pH 3 with conc. HCl and extracted with EtOAc (2 x 100 ml). The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The resulting solid was dissolved in CH_2Cl_2 (100 ml). This solution was washed with water (100 ml) and NaCl (sat. aq., 3 x 100 mL) after which the organic layer was dried over $MgSO_4$, filtered and dried *in vacuo* to afford **6** as a white solid. Yield: 1.0205 g, 33 %; m.p. 133 - 134 ^oC; HRMS (*m/z*) (ES^-) Calculated for $[C_{14}H_{10}NO_4]^-$ *m/z* = 256.0610 $[M - H]^-$. Found *m/z* = 256.0615*;* ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.34 (m, 2H, pyridine-CH), 8.12 (t, *J* = 7.8 Hz, 1H, pyridine-CH), 7.53 – 7.34 (m, 5H, phenyl-CH), 5.46 (s, 2H, CH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 146.7, 146.4, 139.7, 135.0, 128.9, 128.8, 128.6, 126.8, 68.1. IR ν_{max} (cm^{-1}): 2575, 1736, 1692, 1576, 1499, 1466, 1418, 1376, 1289, 1243, 1151, 1083, 994, 956, 941, 856, 797, 754, 729, 710, 691.

(R)-6-((1-(naphthalen-1-yl)ethyl)carbamoyl)-2-((benzyloxy)carbonyl)-pyridine – **6a(S)**[a]



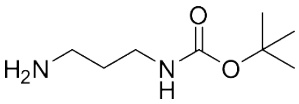
Compound **6** (1.021 g, 3.97 mmol, 1 equiv.), (*R*)-1-(1-naphthyl)-ethylamine (0.64 mL, 3.97 mmol, 1 equiv.), HOBt (0.536 g,3.97 mmol, 1 equiv.) and triethylamine (0.55 mL, 3.97 mmol, 1 equiv.) were stirred in anhydrous THF at 0 °C (50 ml) under argon 0.5 hours. To this solution, EDCI·HCl (0.760 g, 3.97 mmol, 1. equivalent) was then added and the reaction mixture left stirring at 0 °C for a further 0.5 hours. The mixture was allowed to warm to RT and stirred for an additional 24 hours. All insoluble residues were filtered and the filtrate concentrated *in vacuo* and dissolved in CH_2Cl_2 (100 ml) which was washed with 1 M HCl (2 x 100 ml), $NaHCO_3$ (sat. aq., 100 ml), water (100 ml) and NaCl (sat. aq., 100 ml). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford **6a(*S*)** as a pale yellow oil. Yield: 1.3792 g, 85 %; HRMS (*m/z*) (ES^+) Calculated for $[C_{26}H_{22}N_2O_3Na]^+$ *m/z* = 433.1528 $[M - Na]^+$. Found *m/z* = 433.1354. ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.6 Hz, 1H, aryl-CH), 8.42 (d, *J* = 7.8 Hz, 1H, aryl-CH), 8.26 – 8.14 (m, 2H, aryl-CH), 7.98 (t, *J* = 7.8 Hz, 1H, aryl-CH), 7.87 (d, *J* = 7.9 Hz, 1H, aryl-CH), 7.81 (d, *J* = 8.6 Hz, 1H aryl-CH), 7.62 (d, *J* = 7.1 Hz, 1H, aryl-CH), 7.57 – 7.32 (m, 8H, aryl-CH), 6.29 – 6.02 (m, 1H, aliphatic CH), 5.40 (s, 2H, CH_2), 1.80 (d, *J* = 6.8 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 162.3, 150.1, 146.5, 138.5, 138.4, 135.4, 133.9, 131.0, 128.8, 128.6, 128.4, 128.2, 128.1, 127.3, 126.4, 125.7, 125.5, 125.3, 123.3, 122.6, 67.4, 44.9, 21.4. IR ν_{max} (cm^{-1}): 3385, 3301, 3049, 2979, 2875, 2319,, 1725, 1671, 1598, 1588, 1571, 1511, 1446, 1397, 1376, 1306, 1285, 1232, 1163, 1132, 1078, 998, 959, 908, 862, 843, 800, 778, 750, 733, 696.

(R)-6-((1-(naphthalen-1-yl)ethyl)carbamoyl)pyridine-2-(carboxylic acid) – **7(*S*)**



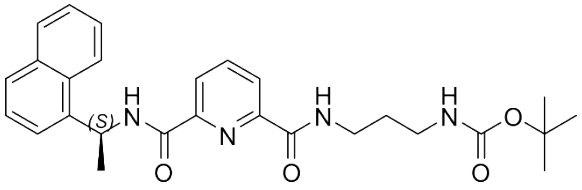
Compound **6a(*S*)** (1.34g, 3.36 mmol, 1 equiv.) was dissolved in CH_3OH (60 mL) treated with 10 wt % Pd/C (0.054 g, 0.05 mmol, 0.15 equivalent). The reaction mixture was placed in a Parr hydrogen shaker under H_2 (3 atm.) and shaken for 24 hours. After the reaction had gone to completion, the mixture was filtered through Celite® and the filtrate concentrated *in vacuo* to afford **7(*S*)** as off white crystals. Yield: 0.95 g, 88 %; m.p. 102 – 104 °C; HRMS (*m/z*) (ES^-) Calculated for $[C_{19}H_{15}N_2O_3]^-$ *m/z* = 319.1088 $[M-H]^-$. Found *m/z* = 319.1085; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.8 Hz, 1H, aryl-CH), 8.27 (d, *J* = 7.7 Hz, 1H, aryl-CH), 8.15 (d, *J* = 8.2 Hz, 1H, aryl-CH), 8.09 (d, *J* = 8.4 Hz, 1H, aryl-CH), 8.03 (t, *J* = 7.8 Hz, 1H, aryl-CH), 7.82 (d, *J* = 8.2 Hz, 1H aryl-CH), 7.75 (d, *J* = 8.1 Hz, 1H, naphthyl-CH), 7.57 – 7.43 (m, 3H, aryl-CH), 7.43 – 7.37 (m, 1H, aryl-CH), 6.16 – 5.88 (m, 1H, aliphatic CH_2), 1.73 (d, *J* = 6.8 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 162.0, 149.2, 145.0, 139.5, 137.7, 133.8, 131.0, 128.8, 128.4, 126.7, 126.6, 125.8, 125.2, 123.1, 122.8, 50.8, 45.1, 20.8. IR ν_{max} (cm^{-1}): 3259, 2981, 1735, 1647, 1598, 1523, 1453, 1346, 1285, 1238, 1173, 1141, 1077, 1000, 920, 846, 800, 777, 745, 719.

^{t}Butyl (3-aminopropyl)carbamate – **8**



To a stirred solution of 1,3-diaminopropane (6 mL, 71.88 mmol, 1 equiv.) in $CHCl_3$ (50 mL) at 0 °C, a solution di-*tert*-butyldicarbonate (1.57 g, 7.19 mmol, 1 equiv.) in $CHCl_3$ (20 mL) was added dropwise and stirred at RT for 24 hours. The reaction mixture was subsequently washed with NaCl (sat. aq., 3 × 100 ml) and water (1 × 100 ml), dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford **8** as a colourless oil. Yield: 1.05 g, 84 %; HRMS (*m/z*) (ES^-) Calculated for $[C_8H_{17}N_2O_2]^-$ *m/z* = 173.1290 $[M-H]^-$. Found *m/z* = 173.1283; ^1H NMR (400 MHz, $CDCl_3$) δ 3.21 (m, 2H, CH_2), 2.76 (t, *J* = 7 Hz, 2H, CH_2), 1.61 (t, *J* = 7 Hz, 2H, CH_2), 1.44 (s, 9H, CH_3), 1.37 (br. S., 2H, NH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 78.9, 39.5, 38.2, 33.3, 28.3.

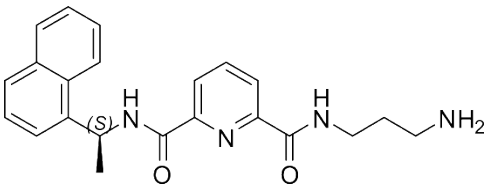
(R)-(3-(6-((1-(naphthalen-1-yl) ethyl)carbamoyl)pyridine-2-amido)propyl)carbamate349 – **9(*S*)**



Compound **7(*S*)** (0.843 g, 2.63 mmol, 1 equiv.) was dissolved in anhydrous THF (50 mL) at 0 °C and HOBt (0.356 g, 2.63 mmol, 1 equiv.), NEt_3 (0.37 mL, 2.63 mmol, 1 equiv.) and **8** (0.4615 g, 2.63 mmol, 1 equiv.) were added to the solution. EDCI·HCl (0.50 g, 2.63 mmol, 1 equiv.) was then added and the mixture allowed to warm to RT after 0.5 hours. After 24

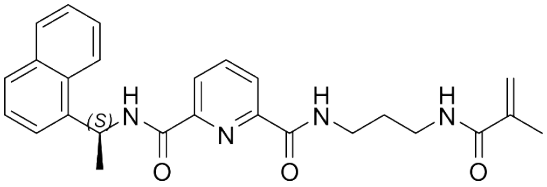
hours stirring at RT all insoluble materials were filtered, the filtrate concentrated *in vacuo* and the recovered residue dissolved in CH_2Cl_2. The organic phase was washed with 1M HCl (2 x 100 mL), $NaHCO_3$ (sat. aq., 100 mL), H_2O (100 mL) and NaCl (sat. aq., 100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford **9(*S*)** as a pale yellow solid. Yield: 0.99g, 79%; m.p. 80 – 83 °C; HRMS (*m/z*) (ES^+) Calculated for $[C_{27}H_{32}N_4O_4Na]^+$ *m/z* = 499.2321 $[M + Na]^+$. Found *m/z* = 499.2328. ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.63 (s, 1H), 8.35 (d, *J* = 7.7 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.97 (t, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.56 – 7.42 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.22 – 6.01 (m, 1H, aliphatic CH), 4.84 (s, 1H, amide-NH), 3.53 – 3.36 (m, 2H, CH_2), 3.19 – 3.08 (m, 2H, CH_2), 1.76 (d, *J* = 6.9 Hz, 3H, CH_3), 1.66 – 1.53 (m, 2H, CH_2), 1.40 (s, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 162.7, 148.9, 148.8, 138.7, 133.9, 130.9, 128.8, 128.0, 126.4, 125.6, 125.2, 124.9, 124.7, 123.3, 122.9, 79.5, 67.9, 45.3, 36.4, 34.8, 30.9, 30.5, 28.4, 28.4, 25.6, 21.2. IR ν_{max} (cm^{-1}): 3305, 2978, 2933, 2324, 1655, 1599, 1513, 1443, 1391, 1365, 1311, 1274, 1243, 1164, 1143, 1072, 999, 955, 935, 918, 845, 800, 777, 727, 675, 663.

(R)-6-((1-(naphthalen-1-yl)ethyl)carbamoyl)-2-((3-aminopropyl)carbamoyl)- pyridine – **9a(*S*)**



To a solution of **9(*S*)** in anhydrous CH_2Cl_2 (0.78, 2.08 mmol, 1 equiv.) TFA was added (5 mL, 65.3 mmol) and the reaction stirred under an argon atmosphere. The reaction was monitored until completion then diluted with CH_2Cl_2 (50 mL) and basified to pH 10 with 1M NaOH. The organic phase was isolated and washed with H_2O (100 mL) and NaCl (sat. aq., 100 mL) before being dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford **9a(*S*)** as an off-white solid. Yield: 0.46g, 75%; m.p. 85 – 88 °C; HRMS (*m/z*) (ES^+) Calculated for $[C_{22}H_{25}N_4O_2Na]^+$ *m/z* = 377.1732 $[M + H]^+$. Found *m/z* = 377.1978; ^1H NMR (400 MHz, $CDCl_3$) δ 9.35 (br. s, 1H), 8.37 (d, *J* = 7.1 Hz, 1H), 8.28 (d, *J* = 7.7 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 8.00 (t, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.56 – 7.45 (m, 3H), 6.21 – 6.06 (m, 1H), 3.47 (t, *J* = 13.3 Hz, 2H), 2.77 – 2.62 (m, 2H), 1.81 (d, *J* = 6.7 Hz, 3H), 1.62 – 1.47 (m, 2H), 1.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 162.6, 149.0, 148.3, 138.8, 137.9, 133.9, 131.3, 128.7, 128.7, 126.9, 126.1, 125.0, 124.6, 124.5, 123.5, 122.7, 44.8, 41.6, 39.9, 30.0, 20.2. IR ν_{max} (cm^{-1}): 3283, 2981, 2932, 1648, 1598, 1522, 1442, 1376, 1340, 1311, 1239, 1173, 1119, 1074, 999, 966, 910, 845, 800, 777, 746, 719, 677.

(R)-6-((1-(naphthalen-1-yl)ethyl)carbamoyl)-2-((3-methacrylamidopropyl)-carbamoyl)-pyridine – **2(*S*)**



To a solution of **9a(*S*)** (0.165g, 0.44 mmol, 1 equiv.) in CH_2CL_2 (20 mL) at 0 °C methacrylic anhydride (0.27 mL, 1.76 mmol, 4 equiv.) was added and the reaction stirred at RT for 24 hours. The reaction mixture was subsequently diluted with CH_2Cl_2 (50 mL) and washed with H_2O (100 mL) and NaCl (sat. aq., 100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford a crude oily liquid which was eluted in silica (RediSep®, 5% CH_3OH in CH_2Cl_2). Product containing fractions were combined and concentrated *in vacuo*, the recovered residue dissolved in EtOAc and eluted on silica (RediSep®, 100% EtOAc). Again, product containing fractions were combined and concentrated *in vacuo* to afford **2(*S*)** as a glassy oil. Yield: 0.095g, 48%; m.p. 90 – 92 °C; HRMS (*m/z*) (ES^-) Calculated for $[C_{26}H_{27}N_4O_3]^-$ *m/z* = 443.2089 $[M - H]^-$. Found *m/z* = 443.2093; ^1H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 9.18 – 9.12 (m, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 8.28 (d, *J*= 7.7 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J*= 8.1 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.43 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 6.22 – 6.11 (m, 2H), 5.73 (s, 1H), 5.33 (s, 1H), 3.55 – 3.34 (m, 4H), 1.94 (s, 3H), 1.75 (d, *J* = 6.9 Hz, 3H), 1.69 – 1.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 163.7, 162.8, 148.9, 139.5, 139.3, 138.7, 133.8, 131.0, 128.6, 127.7, 126.2, 125.5, 125.1, 124.8, 124.4, 123.5, 122.9, 120.5, 45.1, 35.4, 34.2, 29.9, 21.2, 18.9, 14.2. IR ν_{max} (cm^{-1}): 3295, 2980, 1654, 1613, 1517, 1443, 1397, 1374, 1311, 1226, 1174, 1119, 1088, 1073, 1000, 979, 924, 845, 800, 777, 744, 726, 676, 663.

Preparation of complexes under microwave irradiation

Ligand was dissolved in CH_3OH (5 mL) and treated with 0.33 equivalents of the appropriate Ln(III) salt for 30 minutes at 70 °C. The resulting solutions were concentrated *in vacuo* then re-dissolved into minimal CH_3OH. The concentrated solution was subsequently precipitated in rapidly stirred diethyl ether (100 ml) to give white solids. Precipitates were collected by centrifuging and filtering the recovered solids; products were washed with Et_2O and dried under high vacuum.

[Eu.(1(*S*,*S*))$_3$](CF$_3$SO$_3$)$_3$: HRMS (*m/z*) (MALDI) Calculated for **[Eu.(1(*S*,*S*)(*S*,*S*))$_2$](CF$_3$SO$_3$)$_2$** m/z = 1677.4359. Found = 1667.4328. IR ν_{max} (cm^{-1}): 3328, 3067, 2981, 1598, 1558, 1524, 1380, 1245, 1158, 1245, 1028, 859, 776.

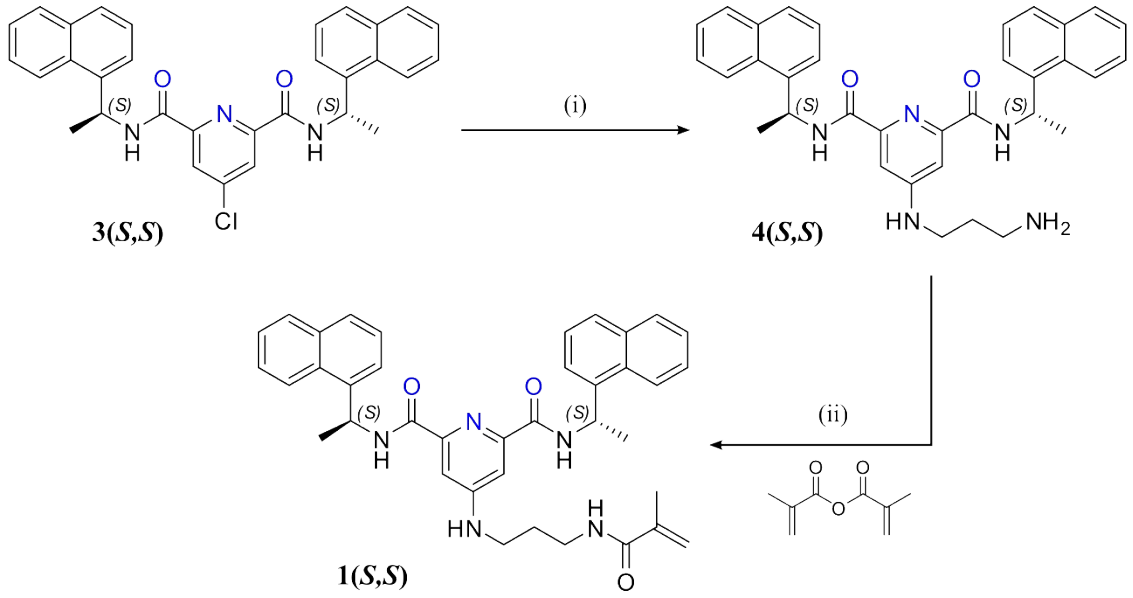
[Eu.(2(*S*))$_3$](CF$_3$SO$_3$)$_3$: HRMS (*m/z*) (MALDI) Calculated for **[Eu.(2(*S*))$_2$](CF$_3$SO$_3$)$_2$** *m/z* = 1339.2576. Found = *m/z* 1339.2639. IR ν_{max} (cm^{-1}): 3296, 3096, 2982, 1632, 1596, 1560, 1458, 1380, 1349, 1277, 1240,1224, 1161, 1028, 936, 862, 840, 802, 779, 753, 727, 660, 634, 572

poly(HEMA-*co*-EGDMA-*co*-1(*S*,*S*))

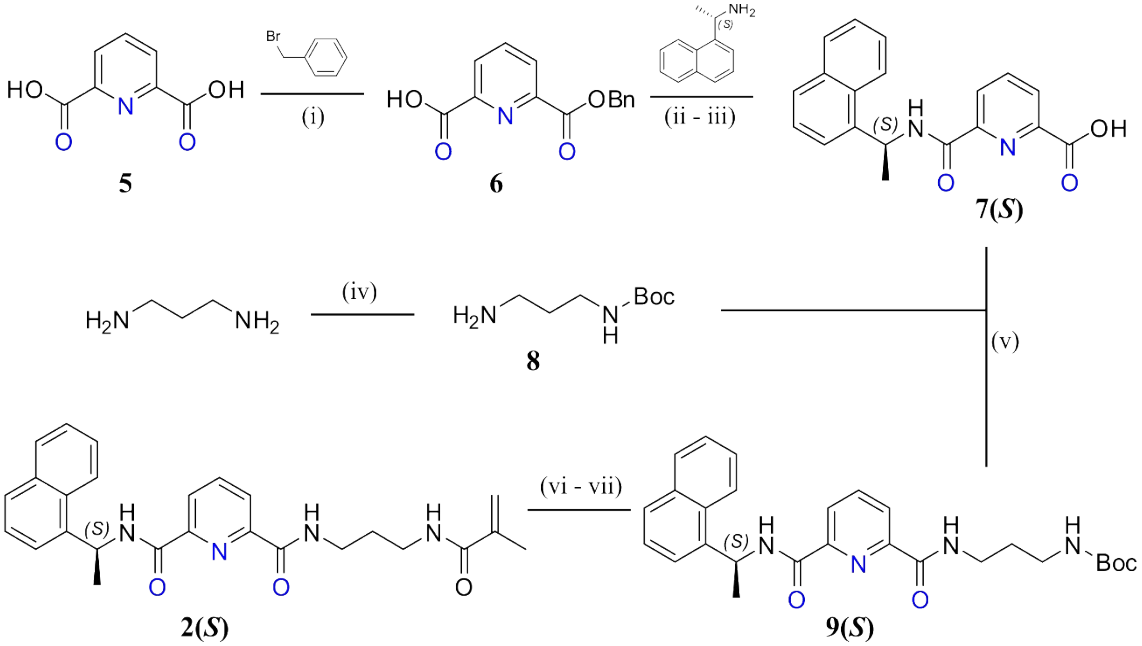
2-hydroxyethyl methacrylate (HEMA, 10 mL), ethylene glycol dimethacrylate (EGDMA, 0.1 mL) and **1(*S*,*S*)** (1, 5 or 10 mg, 0 were stirred at RT till complete dissolution had occurred. AIBN (100 mg) was added and the clear, homogenous solution injected into a non-stick mould and placed in a 90 °C oven for 6 hours. Then resulting acrylic materials were allowed to cool to RT, removed from the moulds and washed in excess H_2O to remove initiator side-products and unreacted monomer. IR ν_{max} (cm^{-1}): 3412, 2946, 2884, 1702, 1453, 1384, 1244, 1151, 1071, 1021, 940, 896, 842, 748.

poly(HEMA-*co*-EGDMA-*co*-2(*S*))

2-hydroxyethyl methacrylate (HEMA, 10 mL), ethylene glycol dimethacrylate (EGDMA, 0.1 mL) and **2(*S*)** (13.1 mg) were stirred at RT till complete dissolution had occurred. AIBN (100 mg) was added and the clear, homogenous solution injected into a non-stick mould and placed in a 90 °C oven for 6 hours. Then resulting acrylic materials were allowed to cool to RT, removed from the moulds and washed in excess H_2O to remove initiator side-products and unreacted monomer. IR ν_{max} (cm^{-1}): 3412, 2933, 2873, 1719, 1453, 1388, 1239, 1151, 1067, 1023, 943, 897, 851, 748.



Scheme S1 Synthesis of symmetrical naphthyl-**dpa** ligand monomer **1(*S,S*)** possessing a pendent methacrylate moiety **(i)** 1,3-diaminopropane, Δ 135 °C, 18 hours; **(ii)** NEt_3 (1.1 equiv.), CH_2Cl_2



Schem S2 Synthesis of asymmetrical naphthyl-**dpa** ligand **2(*S*)** possessing a methacrylate moiety. **(i)** $NaHCO_3$, DMF, 60 °C; **(ii)** EDCI, HOBt, NEt_3, THF, 0 °C → RT; **(iii)** H_2 (3 atm), 10 wt% Pd/C (0.15 equiv.), CH_3OH, RT; **(iv)** Boc_2O, $CHCl_3$, RT; **(v)** EDCI, HOBt, NEt_3, THF, 0°C → RT; **(vi)** TFA:CH_2Cl_2 (1:3 v/v); **(vii)** methacrylic anhydride, NEt_3, CH_2Cl_2.

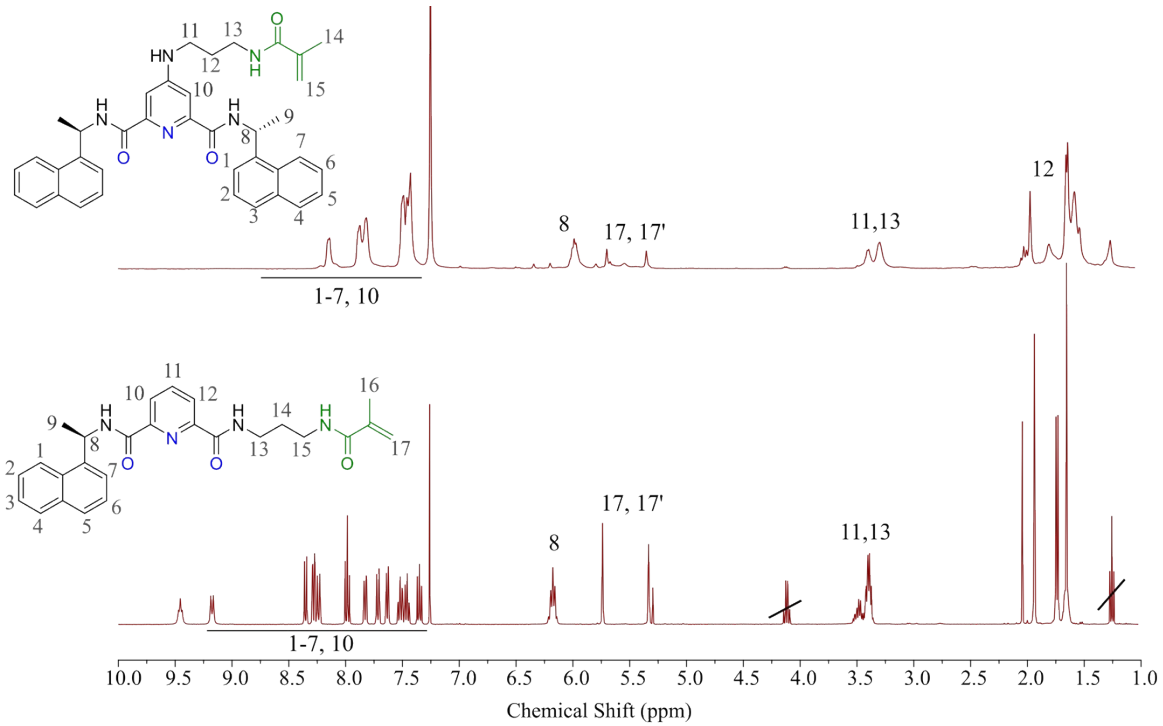


Figure S1 ^{1}H NMR spectra (400 MHz, $CDCl_3$) for ligands **a) 1(*S,S*)**; and **b) 2(*S*)**.

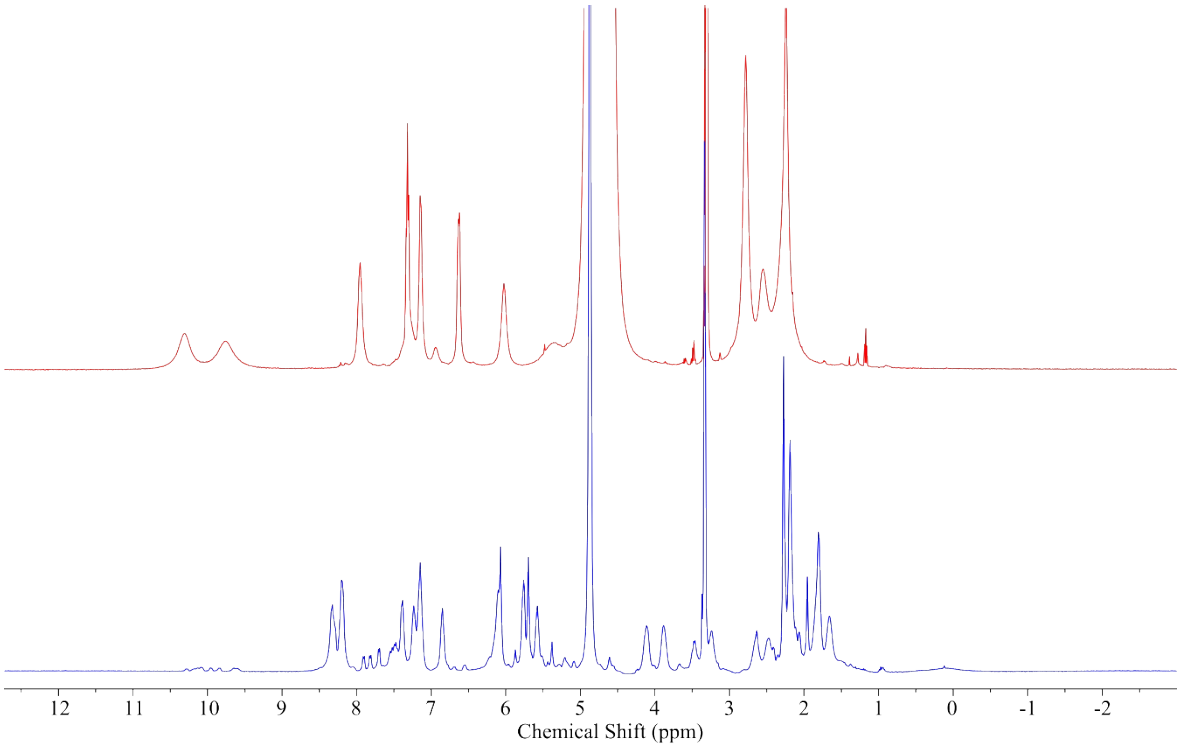


Figure S2 ^{1}H NMR (400 MHz, CD_3OD) for **[Eu.(1(*S,S*))$_3$](CF$_3$SO$_3$)$_3$** (red) and **[Eu.(2(*S*))$_2$](CF$_3$SO$_3$)$_3$** (blue), showing similar LIS consistent with similar geometry and crystal field splitting. Multiple species clearly visible for **[Eu.(2(*S*))$_2$](CF$_3$SO$_3$)$_3$** (blue) while **[Eu.(1(*S,S*))$_3$](CF$_3$SO$_3$)$_3$** (red) showed more broadening.

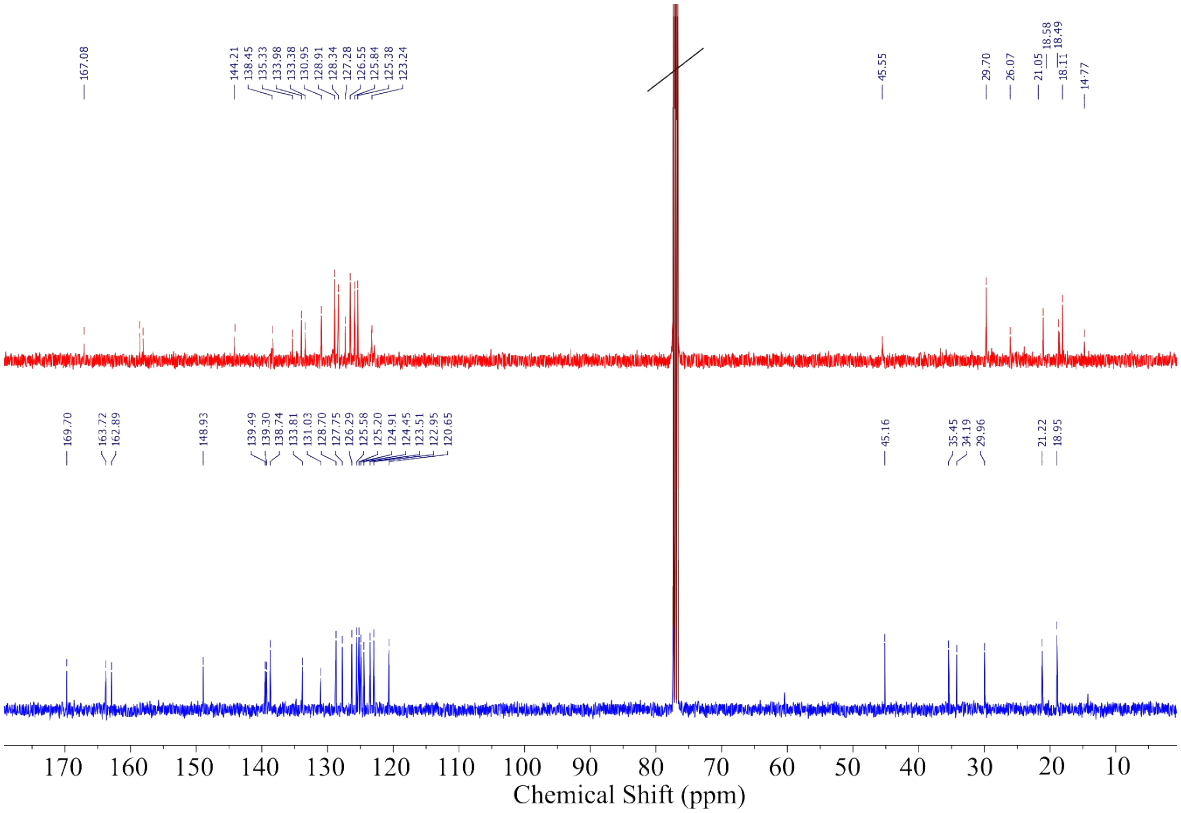


Figure S3 ^{13}C NMR (600 MHz, $CDCl_3$) for **1(*S,S*)** (red) and **2(*S*)** (blue).

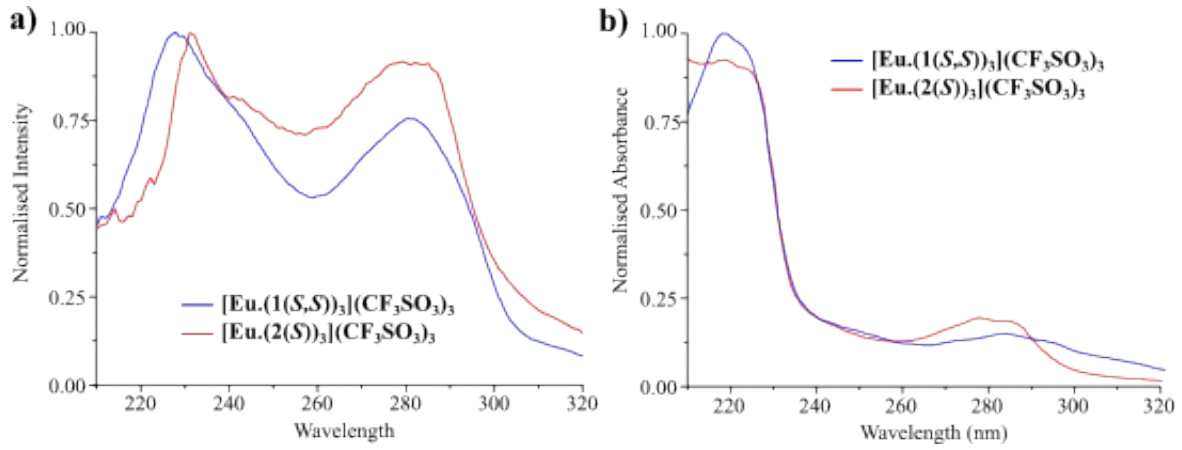


Figure S4 a) Normalised excitation spectra of **[Eu.(1(*S,S*))$_3$](CF$_3$SO$_3$)$_3$** (blue) and **[Eu.(2(*S*))$_2$](CF$_3$SO$_3$)$_3$** (red), showing key structural features of the ligand absorbance bands in CH_3CN; and **b)** normalised absorption spectra for **[Eu.(1(*S,S*))$_3$](CF$_3$SO$_3$)$_3$** and **[Eu.(2(*S*))$_3$](CF$_3$SO$_3$)$_3$** in CH_3CN.

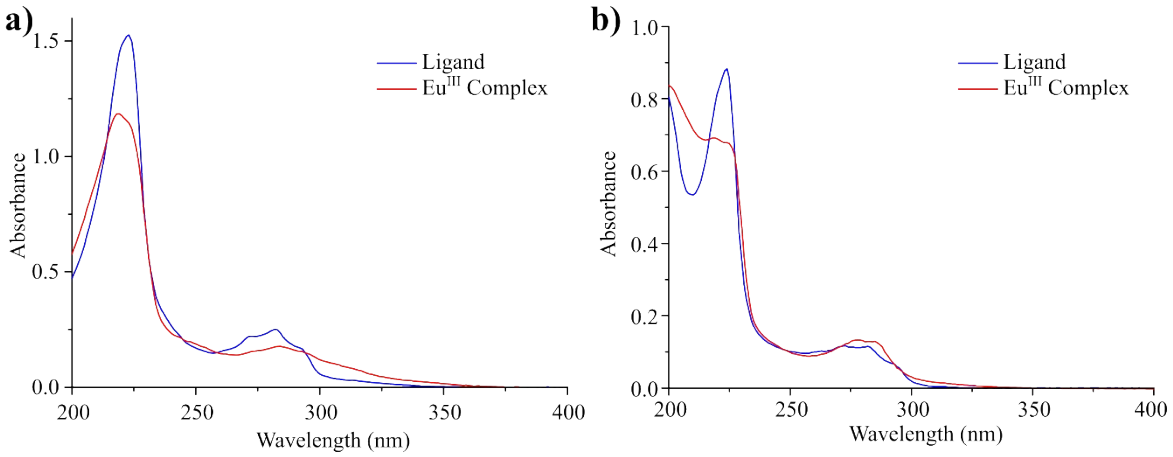


Figure S5 Overlaid UV-visible absorption spectra in CH_3CN for: **a) 1(*S,S*)** (blue) and **[Eu.(1(*S,S*))$_3$]$^{3+}$** (red); and **b) 2(*S*)** (blue) and **[Eu.(2(*S*))$_3$]$^{3+}$** (red). Spectra were recorded at effective ligand concentrations of $c = 1 \times 10^{-5}$ M at 24 °C.

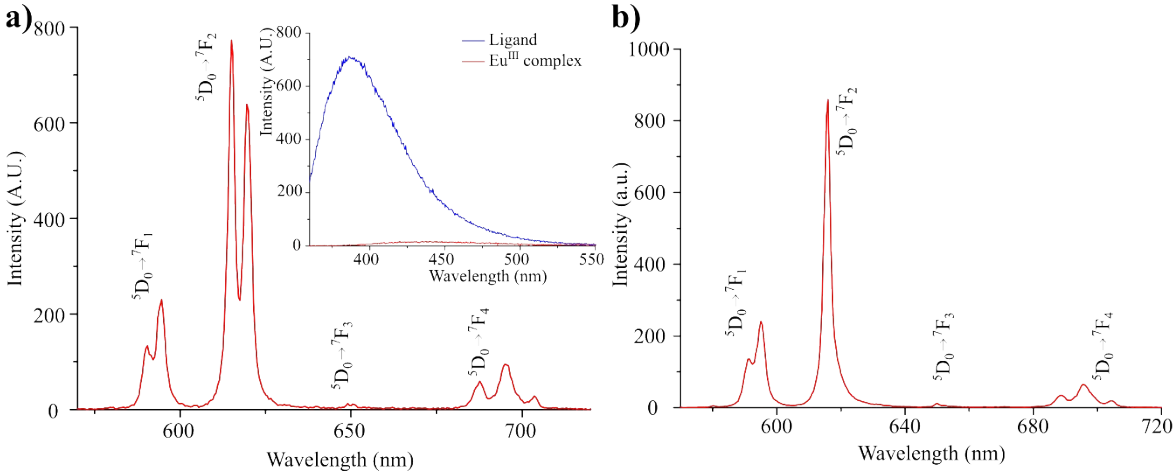


Figure S6 Time-gated emission spectra in CH_3CN for complexes: **a) [Eu.(1(*S,S*))$_3$]$^{3+}$** ***inset***: **1(*S,S*)**-centred fluorescence emission from **1(*S,S*)** and **[Eu.(1(*S,S*))$_3$]$^{3+}$** showing quenching upon coordination; and **b) [Eu.(2(*S*))$_3$]$^{3+}$**. Spectra recorded at effective ligand concentration $c = 1 \times 10^{-5}$ M at 24 °C.

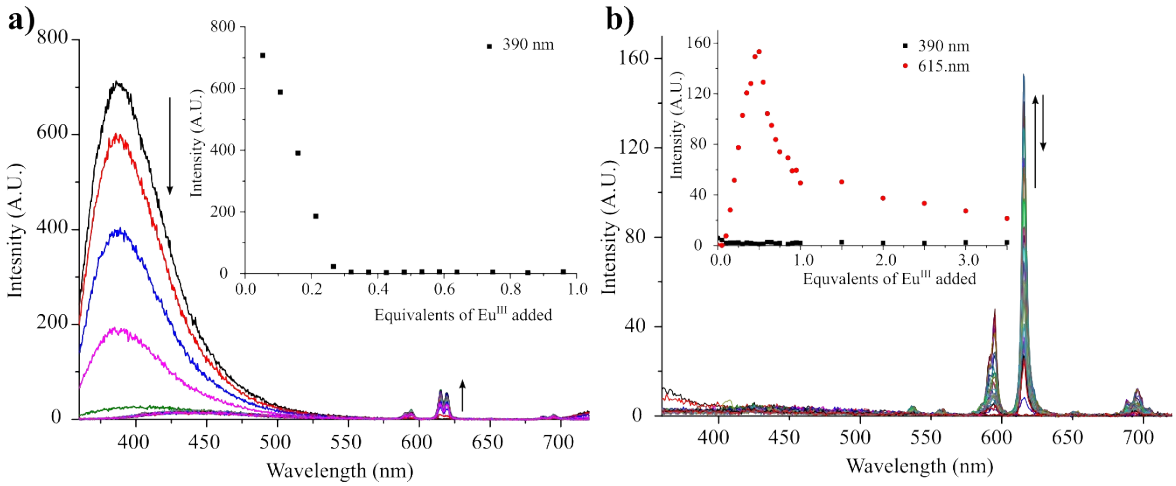


Figure S7 Overlaid fluorescence emission spectra from titrations with 0.00 → 4.00 equivalents of $Eu(CF_3SO_3)_3$ in CH_3CN for: **a)** ligand **1(*S,S*)** ***inset:*** single wavelength binding isotherms for ligand emission at λ_{em} = 390 nm as a function of added equivalents of Eu(III); and **b)** ligand **2(*S*)** ***inset***: single wavelength binding isotherms for ligand emission at λ_{em} = 390 nm and Eu(III)-emission at λ_{abs} = 615nm as a function of added equivalents of Eu(III). Spectra recorded from initial ligand concentrations of $c = 1 \times 10^{-5}$ M at 24 °C.

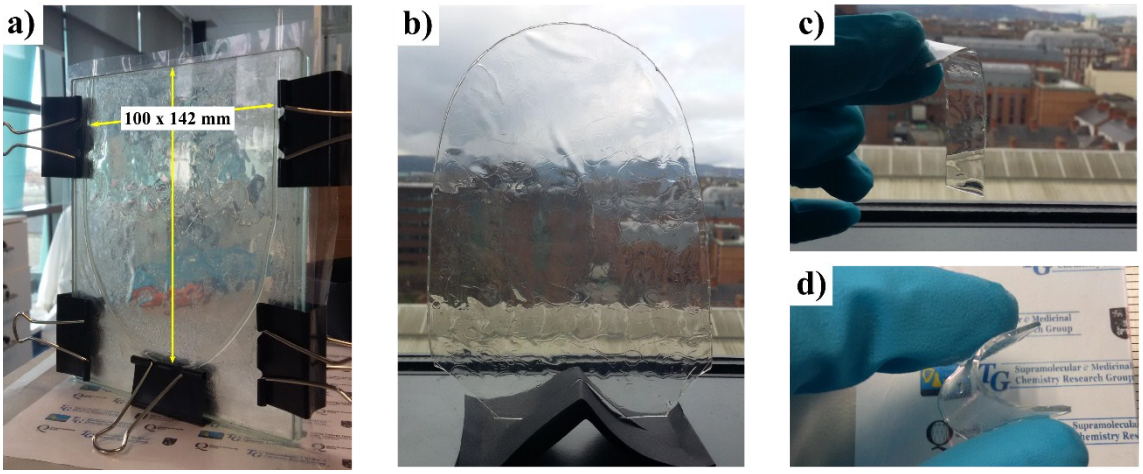


Figure S8 Photographs of: **a)** cast used to fabricate polymer monoliths made from glass and lined with a non-stick coating; **b)** polymer monolith of **1(*S,S*)** after 5 hours curing, transparent and hard; and **c)** and **d**) cut strips of hard polymer swelled in H_2O for 2 hours showing soft, flexible materials that remain transparent.

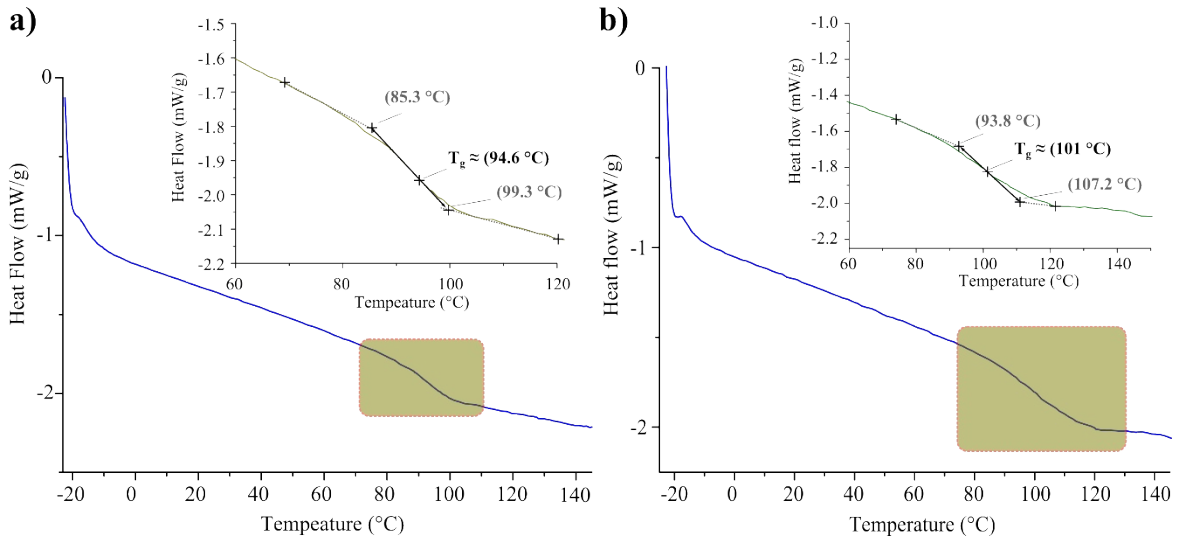


Figure S9 Dynamic scanning calorimetry (DSC) curves recorded from solids samples of: **a)** p(HEMA-*co*-EGDMA-*co*-**1**(***S,S***)) ***inset***: zoomed region and determination of T_g from extrapolation methods; and **b)** p(HEMA-*co*-EGDMA-*co*-**2**(***S***)) ***inset***: zoomed region and determination of T_g from extrapolation methods. Curves shown are second heating cycles and T_g was determined using therelevant instrument software.

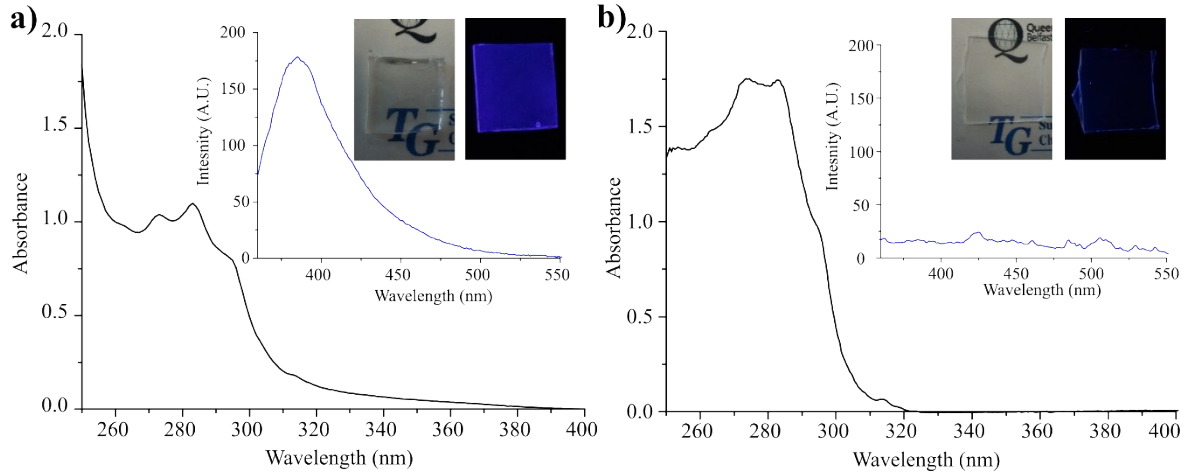


Figure S10 UV-visible absorption and fluorescence emission (***inset***) spectra of swelled samples of: **a)** p(HEMA-*co*-EGDMA-*co*-**1**(***S,S***)); and **b)** p(HEMA-*co*-EGDMA-*co*-**2**(***S***)). Materials were equilibrated in H_2O for 2 hours prior to measurement and fully swelled, the spectra were recorded of gels in supernatant H_2O at 24 °C.

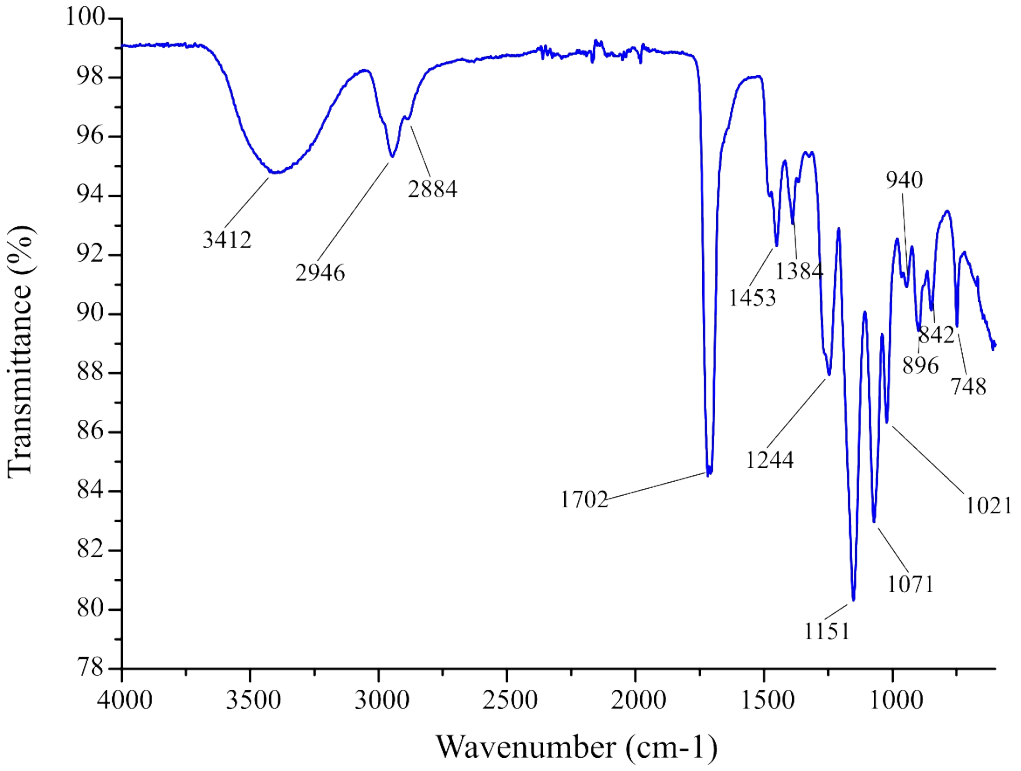


Figure S11 IR spectrum (ATR) of p(HEMA-co-EGDMA-co-**1(*S*,*S*)**).

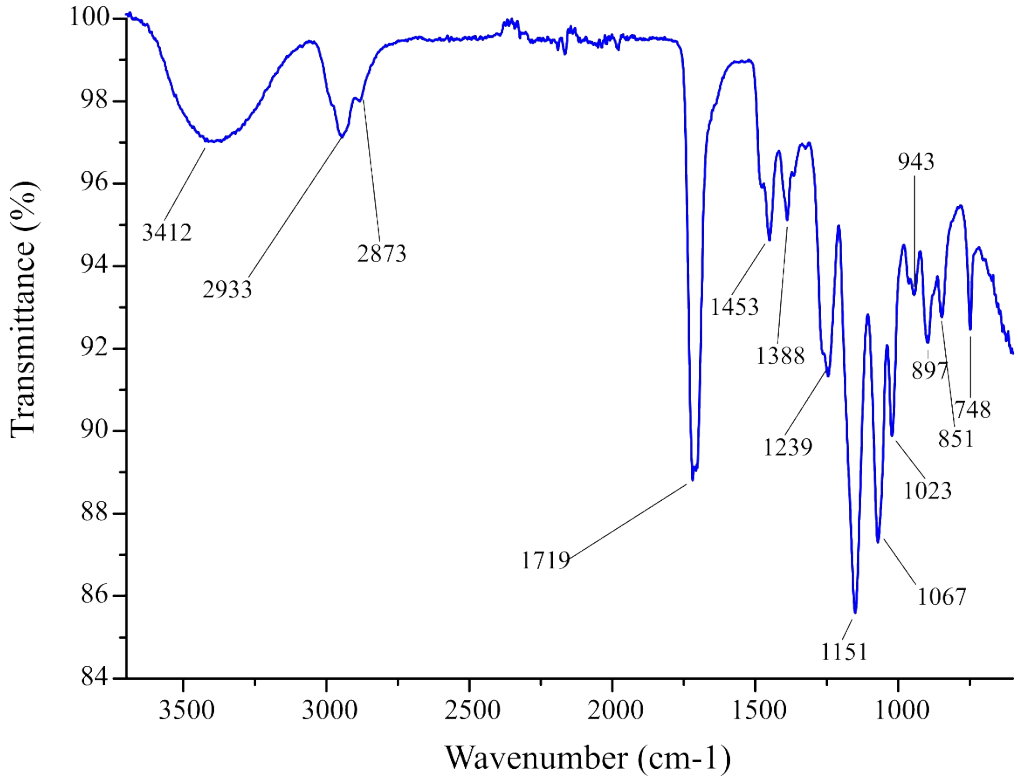


Figure S12 IR spectrum (ATR) of p(HEMA-co-EGDMA-co-**2(*S*)**).

Table S1 Eu(III)-centred luminescence lifetime measurements for **[Eu.(1(*S,S*))$_3$]$^{3+}$** and **[Eu.(2(*S*))$_3$]$^{3+}$** in H_2O, D_2O, CH_3CN and CH_3OH at λ_{em} = 615 nm. Uncertainty was determined as the standard deviation from independent replicates. [a]Only one emissive species was found in solution.

Complex	Solvent	τ_1 / ms	τ_2 / ms
[Eu.(1(*S,S*))$_n$]$^{3+}$	CH_3CN	1.43 ± 0.02 (91%)	0.44 ± 0.01 (9%)
	H_2O	1.33 ± 0.01 (100%)	-[a]
	D_2O	2.96 ± 0.02 (100%)	-[a]
	CH_3OH	1.29 ± 0.01	0.48 ± 0.01
	CD_3OD	2.54 ± 0.02	0.84 ± 0.01
[Eu.(2(*S*))$_n$]$^{3+}$	CH_3CN	1.43 ± 0.01 (100%)	-[a]
	H_2O	1.43 ± 0.01 (94%)	0.30 ± 0.01 (6%)
	D_2O	3.20 ± 0.05 (93%)	1.77 ± 0.30 (7%)
	CH_3OH	0.52 ± 0.01 (100%)	-[a]
	CD_3OD	2.49 ± 0.02 (100%)	-[a]

Table S2 Number of water molecules bound to Eu(III) in **[Eu.(1(*S,S*))$_3$]$^{3+}$** and **[Eu.(2(*S*))$_3$]$^{3+}$** as estimated from *q*-value models of lifetime values in H_2O and D_2O and CH_3OH and CD_3OD (Table S1) from Horrocks and Parker. The associated error with each *q*-value is ± 0.5. [a]Only one lifetime was identified in solution.

Complex	Solvents	*q*-value (Horrock's)		*q*-value (Parker)	
		τ_1	τ_2	τ_1	τ_2
[Eu.(1(*S,S*))$_n$]$^{3+}$	H_2O/D_2O	0.2	-[a]	-0.2	-[a]
[Eu.(2(*S*))$_n$]$^{3+}$	H_2O/D_2O	0.2	3.1	-0.1	2.7
[Eu.(1(*S,S*))$_n$]$^{3+}$	CD_3OD/CH_3OH	0.2	3	-0.3	2.8
[Eu.(2(*S*))$_n$]$^{3+}$	CD_3OD/CH_3OH	3.1	-[a]	2.9	-[a]

Table S3 Eu(III)-centred luminescence lifetime measurements for p(HEMA-*co*-EGDMA-*co*-**1(*S,S*)**) and p(HEMA-*co*-EGDMA-*co*-**2(*S*)**) polymer gels after fully equilibrating with 0.33 equivalents $Eu(CF_3SO_3)_3$ at λ_{em} = 615 nm. Uncertainty was determined as the standard deviation from independent replicates. [a]Only one emissive species was found in solution. [b]Samples were dehydrated from swelled gels. [c]Absolute *q*-values could not be determined.

Complex	Solvent	τ_1 / ms	τ_2 / ms	*q*-value
[Eu.(1(*S,S*))$_n$]$^{3+}$	Dry[b]	1.31 ± 0.01 (86%)	0.56 ± 0.01 (14%)	-[c]
	H_2O	1.32 ± 0.01 (100%)	-[a]	0
	D_2O	2.79 ± 0.01 (100%)	-[a]	
[Eu.(2(*S*))$_n$]$^{3+}$	Dry[b]	0.40 ± 0.02 (51%)	0.91 ± 0.01 (49%)	-[c]

H_2O	0.48 ± 0.03 (100%)	-[a]	3
D_2O	2.65 ± 0.02 (100%)		