Supporting Information

Self-assembly formation of healable lanthanide luminescent supramolecular metallogels from 2,6-bis(1,2,3-triazol-4-yl)pyridine (btp) ligands

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Experimental Section

1. Materials and Methods

All solvents and chemicals were purchased from commercial sources and used without further purification. Citrazinic acid, 4-(bromomethyl) benzoic acid, methyl 4-(bromomethyl) benzoate, benzyl bromide, ethynyltrimethylsilane, $Eu(C_2H_3O_2)_3 \cdot 6H_2O$ and $Eu(CF_3SO_3)_3 \cdot 6H_2O$ were purchased from Aldrich. Deuterated solvents used for NMR analysis ($CDCl_3$, CD_3OD, $(CD_3)_2SO$) were purchased from Apollo Scientific.

The ^1H NMR spectra were recorded at 400 MHz using a Bruker Spectrospin DPX-400 instrument. The ^{13}C NMR spectra were recorded at 100 MHz using a Bruker Spectrospin DPX-400 instrument. NMR spectra were also recorded using a Bruker AV-600 instrument operating at 600.1

MHz for ^{1}H NMR and 150.9 MHz for ^{13}C NMR. Chemical shifts are reported in ppm with the deuterated solvent as the internal reference. All NMR spectra were carried out at 293 K.

Mass-spectrometry was carried out using HPLC grade solvents. Electrospray mass spectra were determined on a Micromass LCT spectrometer and high resolution mass spectra were determined relative to a standard of leucine enkephaline. Maldi-Q-TOF mass spectra were carried out on a MALDI-Q-TOF-Premier (Waters Corporation, Micromass MS technologies, Manchester, UK) and high resolution mass spectrometry was performed using Glu-Fib with an internal reference peak of *m/z* 1570.6774.

Melting points were determined using an Electrothermal IA9000 digital melting point apparatus. Infrared spectra were recorded on a Perkin Elmer Spectrun One FT-IE spectrometer equipped with universal ATR sampling accessory.

Thermal gravimetric analysis was performed on Perkin Elmer Pyrus 1 TGA equipped with an ultra-micro balance with a sensitivity of 0.1 microgram. The temperature range is from 30-800 ^{o}C with a scan rate 20 ^{o}C/min.

Elemental analysis was carried out on Exter Analytical CE440 elemental analyser at the microanalysis laboratory, School of Chemistry and Chemical Biology, University College Dublin.

X-ray data as collected on Rigaku Saturn 724 CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). A suitable crystal was selected and mounted on a 0.3mm quartz fiber tip and placed on the goniometer head in a 150K N_2 gas stream. The data sets were collected using Crystalclear-SM 1.4.0 software. Space group determination was obtained using Crystalstructure ver.3.8 software. The structure was solved by direct methods (SHELXS-97) and refined against all F2 data (SHELXL- 97). (G.M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **A64**, 112). All H-atoms were positioned geometrically and refined using a riding model with $d(CH_{aro})$ = 0.95 Å, *U*iso = 1.2*U*eq (C) for aromatic and 0.98 Å, *U*iso = 1.2*U*eq (C) for CH_3. N-H protons were found from the difference map and either freely refined or fixed to the attached atoms with $U_H = 1.2U_N$.

2. Photophysical measurements

Unless otherwise stated, all measurements were performed at 298 K in methanol (HPLC grade) and acetonitrile (spectroscopic grade, Aldrich) solutions. UV-visible absorption spectra were measured in 1 cm quartz cuvettes (Hellma) on a Varian Cary 50 spectrophotometer. Baseline correction was applied for all spectra. Emission (fluorescence, phosphorescence and excitation) spectra and lifetimes were recorded on a Varian Cary Eclipse Fluorimeter. The temperature was kept constant throughout the measurements at 298 K by using a thermostated unit block. Phosphorescence lifetimes of the $Eu(^{5}D_0)$ excited states was measured in methanol, water and deuterated water in time-resolved mode at 298 K. They are averages of four independent measurements, which were made by

monitoring the emission decay at 618 nm, which corresponds to the maxima of the Eu(III) $^5D_0 \rightarrow {}^7F_2$ transition, enforcing a 0.1 ms delay. The data obtained was analysed using Origin 8.1®.

3. Spectrophotometric titrations and binding constants

The formation of the luminescent (**M:L**, where **M** = metal and **L** = **btp** based ligand) species was ascertained by both UV-visible and luminescence titrations of a solution of **L** (≈1 x 10^{-5} M) with **$M(CF_3SO_3)_3 \cdot 6H_2O$** (M= Eu(III)) (0-4 equivalents). The data was fitted using the non-linear regression analysis program, ReactLab™ Equilibria.[1]

4. Microscopy and Rheological studies of the gels

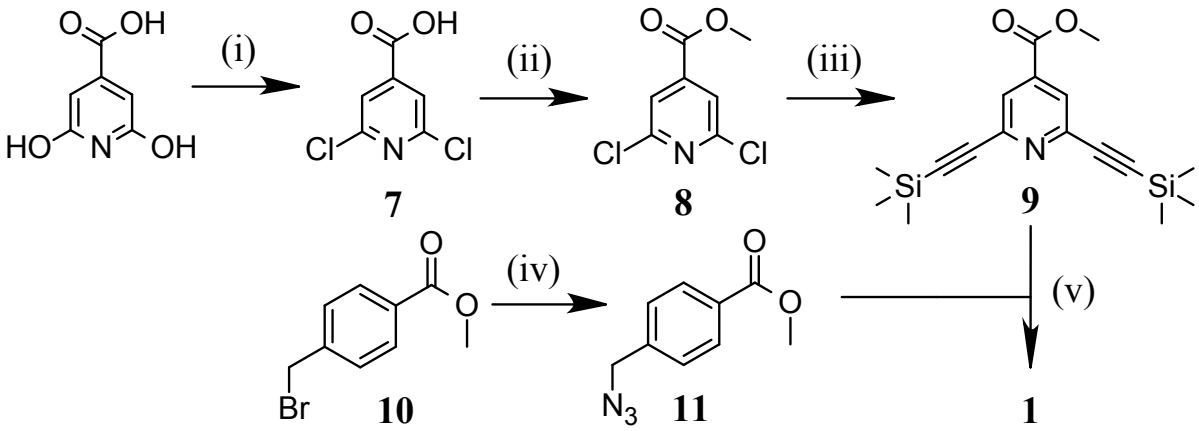
To image the gel samples by scanning electron microscopy (SEM), they were deposited manually onto clean silicon samples with a thick silicon dioxide layer. The spatula and glass pipettes used for dosing and silicon pieces used as substrates were all cleaned thoroughly by sonication in HPLC grade acetone followed by HPLC grade propan-2-ol. All components were dried in two steps using a high pressure nitrogen gun and further dried under ambient conditions. The gels were manually drop cast on to the silicon at room temperature and dried during 5 days at ambient conditions. SEM was carried out using the Zeiss ULTRA Plus using either an SE2 or in-lens detector in the Advanced Microscopy Laboratory, CRANN, Trinity College Dublin. The samples prepared for the imaging using SEM did not have any additional conductive layer cover.

A rheometer with a 50 mm parallel plate geometry was used to measure the rheology of the gels. After placing the sample, the upper plate was lowered slowly giving a final gap of 0.5 mm in size. Measurements commenced once the normal force equilibrated after the data for several initial oscillatory strain sweeps were collected reproducibly. The samples were kept at a constant temperature of 20 °C. To avoid the evaporation of water or methanol during the measurements of the hydrogel and metallogel respectively a solvent trap was used refilling with solvent if required. A frequency of 1 Hz was used for the oscillatory strain sweep measurements while a constant strain amplitude of 0.1% was used in the frequency sweeps.

5. General Synthetic Procedures

General procedure A for the synthesis of 1, 3 and 4.[2]

To a solution of methyl 4-(bromomethyl)benzoate or 4-(bromomethyl)benzoic acid (2 eq.) in 10 mL 4:1 DMF/water was added sodium azide (2 eq.) and the reaction mixture stirred for 1 hour, yielding the relevant azide compound which was not isolated due to the potential explosiveness of such compounds, and therefore used without further purification. After formation of the relevant azide, $CuSO_4 \cdot 5H_2O$ (0.4 eq.) and sodium ascorbate (0.8 eq.) were added to the reaction mixture, followed by anhydrous K_2CO_3 (2 eq.). The solution was degassed, flushed with Argon and stirred until the solution had turned yellow indicating formation of the desired Cu(I) catalytic species. To this solution was added the relevant bis-ethynylpyridine (1 eq.) and stirred under inert conditions at room temperature for 60 hours. 1M EDTA/NH_4OH solution was added to the reaction mixture and stirred for 1 hour before isolating the product.



Scheme S1. Synthesis of **1.** (i) TBACl, $POCl_3$, 140°C (ii) MeOH, H^+, 80°C (iii) CuI, $(PPh_3)_2PdCl_2$, Et_3N:THF 1:1, ethynyltrimethylsilane 0°C → 70°C, (iv) NaN_3, DMF:H_2O (4:1) rt (v) $Cu.SO_4.5H_2O$, K_2CO_3, Sodium Ascorbate, DMF:H_2O (4:1), rt.

Synthesis of dimethyl 4,4'-(4,4'-(4-methoxycarbonyl)pyridine-2,6-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene)dibenzoate (1)

Ligand **1** was synthesised according to General Procedure A[2] from methyl 4-(bromomethyl) benzoate and methyl-2,6-(bis(TMS)ethynyl)isonicotinate, see **9**, (51 mg, 0.155 mmol). The EDTA/NH_4OH aqueous solution was extracted with EtOAc (25 mL *x* 3). The blue/green aqueous layer was separated, and the organic layer was washed with water (20 mL *x* 3) and brine (20 mL *x* 3), then dried over $MgSO_4$ and concentrated under reduced pressure. This was triturated with cold methanol to yield a beige flaky powder (75 mg, 0.132 mmol, 85 %) The product decomposed over 186.2 °C. ^{1}H NMR (600MHz, $CDCl_3$): δ = 8.58 (2H, s, $CH_{triazolyl}$) 8.10 (2H, s, $CH_{pyridyl}$) 8.00 (4H, d, J=7.6Hz, $CH_{2,6\text{-}phenyl}$) 7.31 (4H, d, J=7.6Hz, $CH_{3,5\text{-}phenyl}$) 5.62 (4H, s, $CH_{methylene}$) 3.97 (3H, s, CH_{methyl}) 3.90 (6H, s, CH_{methyl}). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.3 (2C, methyl carbonyl), 165.1 (1C,

methyl carbonyl), 150.6 (2C, 2,6-pyridyl), 147.8 (2C, 4-triazolyl), 139.7 (1C, 4-pyridyl), 139.2(2C, 4-phenyl), 130.7 (2C, 1-phenyl), 130.4 (4C, 2,6-phenyl), 127.9 (4C, 3,5-phenyl), 122.9 (2C, 5-triazolyl), 119.0, (2C, 3,5-pyridyl), 53.9 (2C, methylene), 52.8 (1C, methyl), 52.3 (2C, methyl). HRMS (*m/z*) (LD^+): Calculated for $C_{29}H_{26}O_6N_7$ *m/z* = 568.1945. Found for $[M+H]^+$ $C_{29}H_{26}O_6N_7$ *m/z* = 568.1968. Elemental Analysis; calculated for $C_{29}H_{25}O_6N_7 \cdot 0.7CH_3OH$, %C = 60.5, %H = 4.7, %N=16.7. Found %C = 60.8, %H=4.5 %N=16.4. UV-Vis (MeCN) λ_{max} / nm (ε_{max} /dm^3 mol^{-1} cm^{-1}): 236 (52,000) 327 (8,000). IR ν_{max} (cm^{-1}): 1716, 1572, 1435, 1277, 1108, 1043, 1016, 963, 844, 805, 770, 749, 731, 563, 538, 529.

Synthesis of dimethyl 4,4'-(4,4'-(4-carboxypyridine-2,6-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene)dibenzoic acid (2)

Ligand **1** (70 mg, 0.154 mmol) was hydrolysed to **2** in aqueous MeOH and NaOH (3 eq.) mixture (10 mL) at 110 °C for 24 hours. The MeOH was removed under reduced pressure and the remaining aqueous fraction was acidified to pH=4. This was then extracted with EtOAc (10mL *x* 2), washed with brine (5 mL *x* 2) and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield a yellowish flaky powder (57 mg, 0.109 mmol, 71 %). The product decomposed over 301 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.11 (s, 3H, carboxylic), 8.82 (s, 2H, $CH_{pyridyl}$), 8.37 (s, 2H, $CH_{triazolyl}$), 7.96 (d, *J* = 8.2 Hz, 4H, CH_{phenyl}), 7.45 (d, *J* = 8.2 Hz, 4H, CH_{phenyl}), 5.82 (s, 4H, $CH_{methylene}$). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 167.4 (2C, carboxyl), 166.2 (1C, carboxyl), 151.4 (2C, 2,6-pyridyl), 147.3 (2C, 4-triazolyl), 141.1 (4C, 4-phenyl), 140.8 (1C, 4-pyridyl), 131.1 (2C, 1-phenyl), 130.3 (4C, 2,6-phenyl), 128.4 (4C, 3,5-phenyl), 124.8 (2C, 5-triazolyl), 117.8 (2C, 3,5-pyridyl), 53.2 (2C, methylene). HRMS (*m/z*) (ESI^+): Calculated for $C_{26}H_{19}O_6N_7Na$ *m/z* = 548.1289. Found for $[M+Na]^+$ $C_{26}H_{19}O_6N_7Na$ *m/z* = 548.1289. IR υ_{max} (cm^{-1}) 3278, 2980, 2117, 1727, 1704, 1681, 1612, 1568, 1404, 1329, 1251, 1231, 1214, 1122, 1111, 1095, 1054, 1015, 947, 905, 845, 808, 773, 751, 729, 683.

Synthesis of dimethyl 4,4'-(4,4'-(4-(benzyloxycarbonyl)pyridine-2,6-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene)dibenzoate (3)

Ligand **3** was synthesised according to General Procedure A[2] from methyl 4-(bromomethyl) benzoate and benzyl 2,6-bis((trimethylsilyl)ethynyl)isonicotinate, see **12**, (126 mg, 0.303 mmol). The EDTA/NH_4OH aqueous solution was extracted with EtOAc (20 mL *x* 3). The blue/green aqueous layer was separated, and the organic layer was washed with water (10 mL *x* 3) and brine (10 mL *x* 3), then dried over $MgSO_4$ and concentrated under reduced pressure. This was triturated with cold methanol to yield a white flaky powder (173 mg, 0.261 mmol, 84%). m.p. 210.4 – 210.5°C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.65 (s, 2H, $CH_{pyridyl}$), 8.17 (s, 2H, $CH_{triazolyl}$), 8.03 (d, *J* = 8.2 Hz, 4H, CH_{phenyl}), 7.49 – 7.36 (m, 5H, CH_{benzyl}), 7.35 (d, *J* = 8.2 Hz, 4H, CH_{phenyl}), 5.64 (s, 4H, $CH_{methylene}$),

5.43 (s, 2H, $CH_{methylene}$), 3.91 (s, 6H, CH_{methyl}). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.3 (2C, methyl carbonyl), 164.6 (1C, benzyl carbonyl), 150.6 (2C, 2,6-pyridyl), 147.8 (2C, 4-triazolyl), 139.9 (1C, 4-pyridyl), 139.2 (2C, 4-phenyl), 135.2 (1C, 1-benzyl), 130.7 (2C, 1-phenyl), 130.4 (4C, 2,6-phenyl), 128.7 (1C, 4-benzyl), 128.6 (2C, 3,5-benzyl), 128.6 (2C, 2,6-benzyl), 127.9 (4C, 3,5-phenyl), 122.8 (2C, 5-triazolyl), 119.1 (2C, 3,5-pyridyl), 67.7 (1C, methylene), 53.9 (2C, methylene), 52.3, (2C, methyl). HRMS (*m/z*) (ESI^+): Calculated for $C_{35}H_{29}O_6N_7Na$ *m/z* = 666.2062. Found for $[M+Na]^+$ $C_{35}H_{29}O_6N_7Na$ *m/z* = 666.2072. Elemental Analysis calculated for $C_{35}H_{29}O_6N_7 \cdot 0.5H_2O$, %C = 64.4, %H = 4.6, %N=15.0. Found %C = 64.6, %H = 4.5, %N = 15.0. UV-Vis (MeCN) λ_{max} / *nm* (ε_{max} /dm^3 mol^{-1} cm^{-1}) 236 (68,000) 327 (10,500). IR ν_{max} (cm^{-1}): 3094, 2951, 1720, 1615, 1574, 1511, 1456, 1429, 1401, 1385, 1361, 1317, 1277, 1259, 1216, 1187, 1180, 1145, 1109, 1082, 1040, 1020, 966, 940, 901, 871, 830, 806, 78, 768, 745, 733, 726, 698, 685, 677, 665.

Synthesis of 4,4'-(4,4'-(4-(benzyloxycarbonyl)pyridine-2,6-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene)dibenzoic acid (4)

Ligand **4** was synthesised according to modified General Procedure A[2] from benzyl 2,6-diethynylisonicotinate, **12**, (72 mg, 0.278 mmol) and 4-(bromomethyl) benzoic acid (2 eq.) in the absence of K_2CO_3. (72mg, 0.278mmol) and 4-(bromomethyl) benzoic acid (2eq.) in the absence of K_2CO_3. The reaction mixture was diluted with 100 mL of distilled water and extracted with EtOAc (15 mL *x* 3). 1M HCl solution was added to aid phase separation due to partial solubility of **4** in water at pH ≥ 7. The organic layer was washed with brine (10 mL *x* 2), dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude brown powder was triturated with cold MeOH and filtered off and isolated as a white powder. (78 mg, 0.210 mmol, 75 %). The product decomposed over 247°C. ^1H NMR (600 MHz, DMSO-d_6): δ = 8.81 (s, 2H, $CH_{triazolyl}$), 8.38 (s, 2H, $CH_{pyridyl}$), 7.95 (d, *J* = 8.1 Hz, 4H, CH_{phenyl}), 7.53 (d, *J* = 7.3 Hz, 2H, CH_{benzyl}), 7.44 (m, 6H, $CH_{benzyl/\ phenyl}$), 7.39 (t, *J* = 7.3 Hz, 1H, CH_{benzyl}), 5.81 (s, 4H, $CH_{methylene}$), 5.46 (s, 2H, $CH_{methylene}$). ^{13}C NMR (151 MHz, DMSO-d_6): δ = 166.9 (2C, carboxylic), 164.2 (1C, methoxy carbonyl), 151.1 (2C, 2,6-pyridyl), 146.7 (2C, 4-triazolyl), 140.5 (2C, 1-phenyl), 139.1 (1C, 4-pyridyl), 135.5 (2C, 4-phenyl), 130.7 (1C, 1-benzyl), 129.9 (4C, 2,6-phenyl), 128.7 (2C, 3,5-benzyl), 128.5 (1C, 4-benzyl), 128.4 (2C, 2,6-benzyl), 127.9 (4C, 3,5-phenyl), 124.5 (2C, 5-triazolyl), 117.1 (2C, 3,5-pyridyl), 67.3 (2C, methylene), 52.8 (1C, methylene). HRMS (*m/z*) (ESI^-) Calculated for $C_{33}H_{24}N_7O_6$ *m/z* = 614.1793. Found for $C_{33}H_{24}N_7O_6$ *m/z* = 614.1803. IR υ_{max} (cm^{-1}) 3131, 2879, 2570, 21511957, 1702, 1682, 1611, 1571, 1497, 1455, 1421, 1403, 1386, 1328, 1298, 1268, 1257, 1185, 1109, 1090, 1055, 1041, 1018, 945, 924, 870, 856, 843, 807, 770, 751, 734, 694

Synthesis of 2,6-bis(1-(4-(methoxycarbonyl)benzyl)-1H-1,2,3-triazol-4-yl)isonicotinic acid (5)

Ligand **3** (50 mg, 0.078 mmol) was suspended in EtOH (50 mL), sonicated and 10 wt % Pd/C (16.5 mg) was added. The reaction flask was put in a Parr Hydrogenator, evacuated and filled with H_2 gas (repeated *x* 2) and allowed to shake at 3 bar for 24 hours. The solution was filtered through celite which was washed with EtOH (50 mL *x* 2) and the solvent was removed under reduced pressure to yield a white powder (40mg, 0.076 mmol, 97%). The product decomposed after exceeding 221°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.81 (s, 2H, $CH_{triazolyl}$), 8.36 (s, 2H $CH_{pyridyl}$), 7.97 (d, *J* = 8.1 Hz, 4H, CH_{phenyl}), 7.46 (d, *J* = 8.1 Hz, 4H, CH_{phenyl}), 5.82 (s, 4H, $CH_{methylene}$), 3.84 (s, 6H, CH_{methyl}). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 165.9 (2C, methoxy carbonyl), 165.9 (1C, carboxylic), 150.9 (2C, 2,6-pyridyl), 147.0 (2C, 5-triazolyl), 141.1 (2C, 4-phenyl), 129.8 (4C, 2,6-phenyl), 129.5 (2C, 1-phenyl), 128.2 (4C, 3,5-phenyl), 124.4 (2C, triazolyl), 118.1 (1C, 4-pyridyl), 117.5 (2C, pyridyl), 52.7 (2C, methylene), 52.3 (2C, methyl). HRMS (*m/z*) (ESI$^-$): Calculated for $C_{28}H_{22}O_6N_7$ *m/z* = 552.1637. Found for [M-H]$^-$ $C_{28}H_{22}O_6N_7$ *m/z* = 552.1641. IR υ_{max} (cm^{-1}) 3415. 3073, 2952, 2551, 2368, 2355, 2027, 1943, 1713, 1614, 1574, 1433, 1417, 1313, 1277, 1182, 1108, 1044, 1020, 961, 906, 839, 805, 775, 731, 680.

Synthesis of dimethyl 4,4'-(4,4'-(pyridine-2,6-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene)dibenzoate (6)

6 wasn't synthesised in this project but its preparation can be found in the literature.[2]

Synthesis of 2,6-dichloroisonicotinic acid (7)

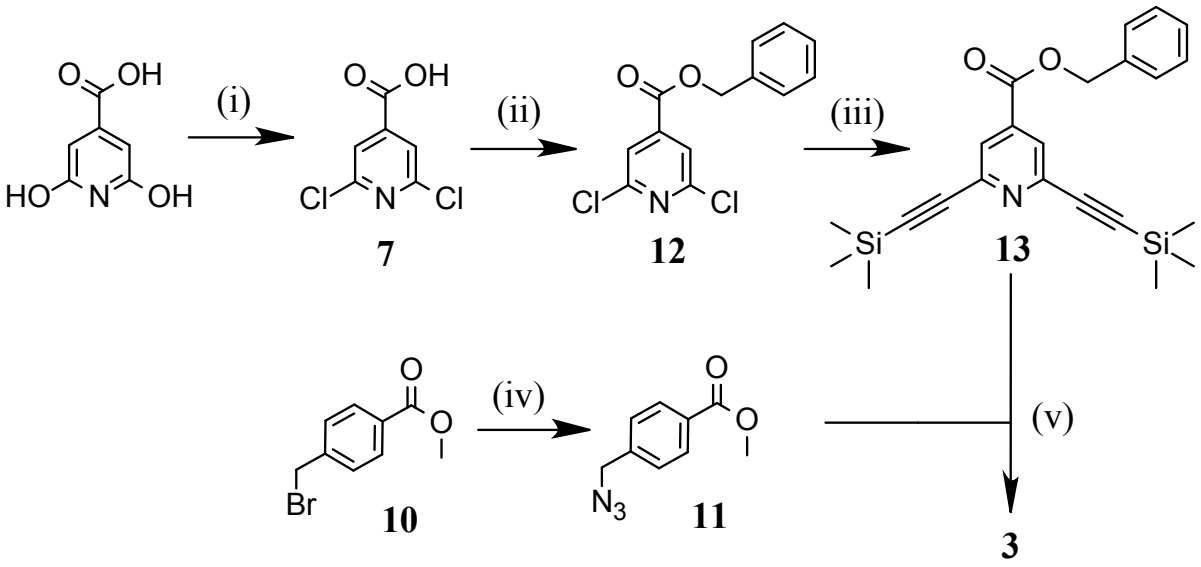
Compound **7** was synthesised according to modified literature procedure.[3] In this way, citrazinic acid (10 g, 64.5 mmol) was converted to **7** (11.59 g, 58.3 mmol, 90%). ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.83 (2H, s, $CH_{pyridyl}$). HRMS (*m/z*) (ESI$^-$) Calculated for $C_6H_2NO_2Cl_2$ *m/z* = 198.9463. Found for [M-H]$^-$ $C_5H_2NO_2Cl_2$ *m/z* = 198.9457. IR ν_{max} (cm^{-1}): 3078, 2848, 2580, 1719, 1595, 1544, 1418, 1363, 1252, 1229, 1162, 1000, 925, 894, 814, 767, 714, 677, 559.

Synthesis of methyl 2,6-dichloroisonicotinate (8)

Compound **8** was synthesised according to a modified literature procedure.[3] In this way, 2,6-dichloroisonicotinic acid (500mg, 2.6mmol) was converted to **8**. This was recrystallised from MeOH to afford clear needle-like crystals (200mg, 0.97mmol, 40%). ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.79 (2H, s, CH_{pyr}) 3.96 (3H, s, OCH_3). HRMS (*m/z*) (EI$^+$): Calculated for $C_7H_5NO_2Cl_2$ *m/z* = 204.9697. Found for [M]$^+$ $C_7H_5NO_2Cl_2$ *m/z* = 204.9700. IR ν_{max} (cm^{-1}): 3441, 3090, 2959, 1728, 1584, 1543, 1438, 1409, 1359, 1289, 1237, 1202, 1159, 1093, 974, 915, 895, 870, 813, 763, 736, 711, 624, 579.

Synthesis of methyl-2,6-(bis(TMS)ethynyl)isonicotinate (9)

Compound **9** was synthesised according to modified literature procedure[4] with the only modification being: heating the reaction mixture at 70°C instead of rt as in the case of bromo derivatives. In this way, methyl-2,6-(bis(TMS)ethynyl)isonicotinate (180 mg, 0.874 mmol) was converted to **9**, a brownish/yellowish oil (205 mg, 0.622 mmol, 72%) which was used without further purification. ^{1}H NMR (400MHz, $CDCl_3$) δ = 7.89 (2H, s, $CH_{pyridyl}$), 3.94 (3H, s, CH_{methyl}), 0.24 (18H, s, CH_{TMS}). HRMS (*m/z*) (ESI^+): Calculated for $C_{17}H_{24}NO_2Si_2$ *m/z* = 330.1346. Found for $[M+H]^+$ $C_{17}H_{24}NO_2Si_2$ *m/z* = 330.1337. TLC (Hex/EtOAc 92/8) R_f = 0.6. IR ν_{max} (cm^{-1}): 2956, 1725, 1558, 1436, 1395, 1329, 1245, 1185, 1119, 1106, 1071, 995, 975, 838, 757, 722, 695, 660, 636, 573.



Scheme S2. Synthesis of **3.** (i) TBACl, $POCl_3$, 140°C (ii) BnBr, $NaHCO_3$, DMF, 60°C (iii) CuI, $(PPh_3)_2PdCl_2$, ethynyltrimethylsilane, Et_3N:THF 1:1, 0°C - 70°C, (iv) NaN_3, DMF:H_2O (4:1) rt (v) $Cu.SO_4.5H_2O$, K_2CO_3, Sodium Ascorbate, DMF:H_2O (4:1), rt.

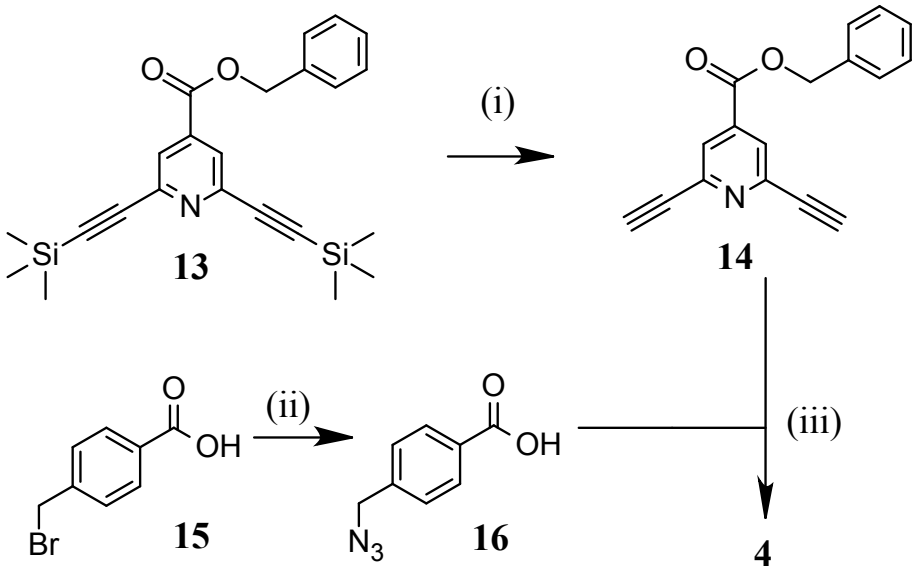
Synthesis of benzyl 2,6-dichloroisonicotinate (12)

Compound **12** was synthesised according to literature procedure.[5] In this way, 2,6-dichloroisonicotinic acid (200mg, 1.042mmol) was converted to **12**. The reaction mixture was diluted with water, and the resulting mixture was extracted with ethyl acetate, washed with aqueous NaHCO3 (20 mL *x* 3), water (20 mL *x* 1) and brine (20 mL *x* 1), dried with $MgSO_4$ and the solvent was evaporated under reduced pressure to afford a yellowish crystalline semi-solid (252 mg, 0.896 mmol, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 2H, $CH_{pyridyl}$), 7.42 – 7.37 (m, 5H, CH_{benzyl}), 5.37 (s, 2H, $CH_{methylene}$). HRMS (*m/z*) (ESI^+): Calculated for $C_{13}H_{10}NO_2Cl_2$ *m/z* = 282.0083. Found for $[M+H]^+$ $C_{13}H_{10}NO_2Cl_2$ *m/z* = 282.0080. IR ν_{max} (cm^{-1}): 3036, 2626, 1726, 1652, 1597, 1566, 1550,

1498, 1457, 1443, 1395, 1381, 1356, 1337, 1317, 1280, 1243, 1214, 1157, 1102, 1092, 1081, 1030, 1003, 976, 943, 913, 896, 880, 857, 829, 815, 766, 748, 740, 723, 695, 681, 667, 664, 661.

Synthesis of benzyl 2,6-bis((trimethylsilyl)ethynyl)isonicotinate (13)

Compound **13** was synthesized according to the same literature procedure as **9**. In this way, benzyl 2,6-dichloroisonicotinate (478mg, 1.695mmol) was converted to **13**. The reaction mixture was concentrated under reduced pressure. This was then dissloved in hexane and filtered through celite. This yellow solution was purified by column chromatography in hexane increasing to 98:2 hexane:ethyl acetate mixture to yield a yellow oil (343mg, 0.848mmol, 50%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (s, 2H, $CH_{pyridyl}$), 7.45-7.43 (m, 5H, CH_{benzyl}), 5.40 (s, 2H, $CH_{methylene}$), 0.28 (s, 18H, CH_{TMS}). HRMS (*m/z*) (ESI^+): Calculated for $C_{23}H_{28}NO_2Si_2$ *m/z* = 406.1653. Compound Found for $[M+H]^+$ $C_{23}H_{28}NO_2Si_2$ *m/z* = 406.1701. IR ν_{max} (cm^{-1}): 3094, 2951, 1720, 1615, 1574, 1511, 1456, 1429, 1401, 1385, 1361, 1317, 1277, 1259, 1216, 1187, 1180, 1145, 1109, 1082, 1040, 1020, 966, 940, 901, 871, 830, 806, 78, 768, 745, 733, 726, 698, 685, 677, 665.



Scheme S3. Synthesis of **4.** (i) TBAF, THF 0°C - rt (ii) NaN_3, DMF:H_2O (4:1) rt (iii) $Cu.SO_4{\cdot}5H_2O$, Sodium Ascorbate, DMF:H_2O (4:1), rt.

Synthesis of benzyl 2,6-diethynylisonicotinate (14)

Compound **14** was synthesised according to modified literature procedure.[6] In this way, **13** (1.13 g, 3.37 mmol) was dissolved in dry THF (25 mL), cooled to 0°C and a solution of TBAF (1 eq.) in the same solvent (5 mL) was added dropwise. The mixture was then allowed to stir at rt for 1 hour. The mixture was concentrated under reduced pressure, dissolved in EtOAc (75 mL *x* 3), washed with

water (25 mL *x* 4), brine and dried with $MgSO_4$.. The solvent was removed under reduced pressure to yield a reddish semi-solid (750 mg, 2.88 mmol, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 2H, $CH_{pyridyl}$), 7.54 – 7.31 (m, 5H, CH_{benzyl}), 5.39 (s, 2H, $CH_{methylene}$), 3.22 (s, 2H, CH_{alkyne}). HRMS (*m/z*) (EI^+) Calculated for $C_{17}H_{11}NO_2$ *m/z* = 261.0790. Found for *m/z* =261.0779. IR υ_{max} (cm^{-1}) 3269, 2111, 1714, 1551, 1499, 1453, 1388, 1320, 1225, 1186, 1106, 975, 893, 766, 727, 693.

6. Preparation of Ln(III) Complexes

Synthesis of $Eu1_3$ complex

Ligand **1** (40mg, 0.07mmol) and $Eu(CF_3SO_3)_3 \cdot 6H_2O$ (16.3mg, 0.023mmol) were dissolved in MeOH (5mL) in a microwave tube. This underwent microwave irradiation at 70°C for 20 minutes. The complex was precipitated out of MeOH *via* ether diffusion followed by centrifugation to yield the white powder, (55 mg, 0.023 mmol, 99 %). Single crystals crystals were obtained via ether diffusion into a MeCN solution of **$Eu1_3$** over a two day period. These showed red luminescence under UV lamp excitation at 365nm. The product decomposed over 145°C. ^{1}H NMR (400 MHz, CD_3OD): δ = 7.82 (d, *J* = 8.0 Hz, 4H, CH_{phenyl}), 7.69 (s, 2H, $CH_{pyridyl}$), 7.23 (d, *J* = 8.0 Hz, 4H, CH_{phenyl}), 6.30 (d, *J* = 14.6 Hz, 2H, $CH_{methylene}$), 5.52 (d, *J* = 14.6 Hz, 2H, $CH_{methylene}$), 5.35 (s, 2H, $CH_{triazolyl}$), 3.97 (s, 3H, CH_{methyl}), 3.92 (s, 6H, CH_{methyl}). ^{13}C NMR (101 MHz, CD_3OD): δ = 167.6 (2C, methyl carbonyl), 160.4 (2C, 5-triazolyl), 159.9 (1C, methyl carbonyl), 154.0 (1C, 4-pyridyl), 142.0 (2C, 1-phenyl), 135.8 (2C, 2,6-pyridyl), 131.8 (2C, 4-phenyl), 131.0 (4C, 2,6-phenyl), 129.4 (4C, 3,5-phenyl), 105.5 (2C, 3,5-pyridyl), 87.5 (2C, triazolyl), 54.0 (2C, methylene), 52.9 (2C, methyl), 49.9 (1C, methyl). HRMS (*m/z*) (LD^+): Calculated for $C_{89}H_{75}N_{21}O_{24}F_6S_2Eu$ *m/z* = 2152.3852. Found for [Eu**1**$_3$ $(CF_3SO_3^-)_2]^+$ *m/z* = 2152.3796 (see Fig. S9 for isotopic distribution pattern). Elemental Analysis; calculated for $C_{90}H_{75}N_{21}O_{27}F_9S_3Eu \cdot 3.5H_2O$, %C = 45.7, %H = 3.5, %N=12.4. Found %C = 45.1, %H = 2.9, %N = 12.1. IR ν_{max} (cm^{-1}): 3104, 2957, 1719, 1615, 1587, 1549, 1437, 1276, 1254, 1223, 1183, 1155, 110, 1071, 1029, 965, 817, 772, 730. Crystallographic data can be found below, see **Section 13**.

Synthesis of $Eu2_3$ complex

$Eu2_3$ was synthesised according to the same procedure as **$Eu1_3$** above. **2** (20 mg, 0.04 mmol) and $Eu(CF_3SO_3)_3 \cdot 6H_2O$ (9.4 mg, 0.013 mmol) were suspended in MeOH (5 mL) in a microwave tube. This underwent microwave irradiation at 80 °C for 60 minutes. The complex was precipitated out of MeOH *via* ether diffusion followed by centrifugation to yield the white powder (29 mg, 0.013 mmol, 99 %). The product decomposed over 260°C. ^{1}H NMR (400 MHz, CD_3OD): δ = 7.82 (br, 4H, CH_{phenyl}), 7.62 (br, 2H, $CH_{pyridyl}$), 7.21 (br, 4H, CH_{phenyl}), 6.08 (br, 2H, $CH_{methylene}$), 5.63 (br, 2H, $CH_{methylene}$), 5.23 (br, 2H, $CH_{triazolyl}$). HRMS (*m/z*) (ESI^+): Calculated for $C_{78}H_{57}N_{21}O_{18}Eu$ *m/z* =

1728.3403. Found for $[Eu\mathbf{2}_3]^{3+}$ *m/z* = 1728.3342. Also, calculated for $C_{79}H_{57}N_{21}O_{21}EuF_3S$ *m/z* = 1877.2912. Found for $[Eu\mathbf{2}_3\ (CF_3SO_3^-)]^{2+}$ *m/z* = 1877.2968 (see Fig. S10 for isotopic distribution patterns). IR υ_{max} (cm^{-1}) 3411, 1591, 1539, 1405, 1241, 1225, 1169, 1070, 1028, 907, 863, 817, 782, 737, 674.

7. Preparation of Hydrogel

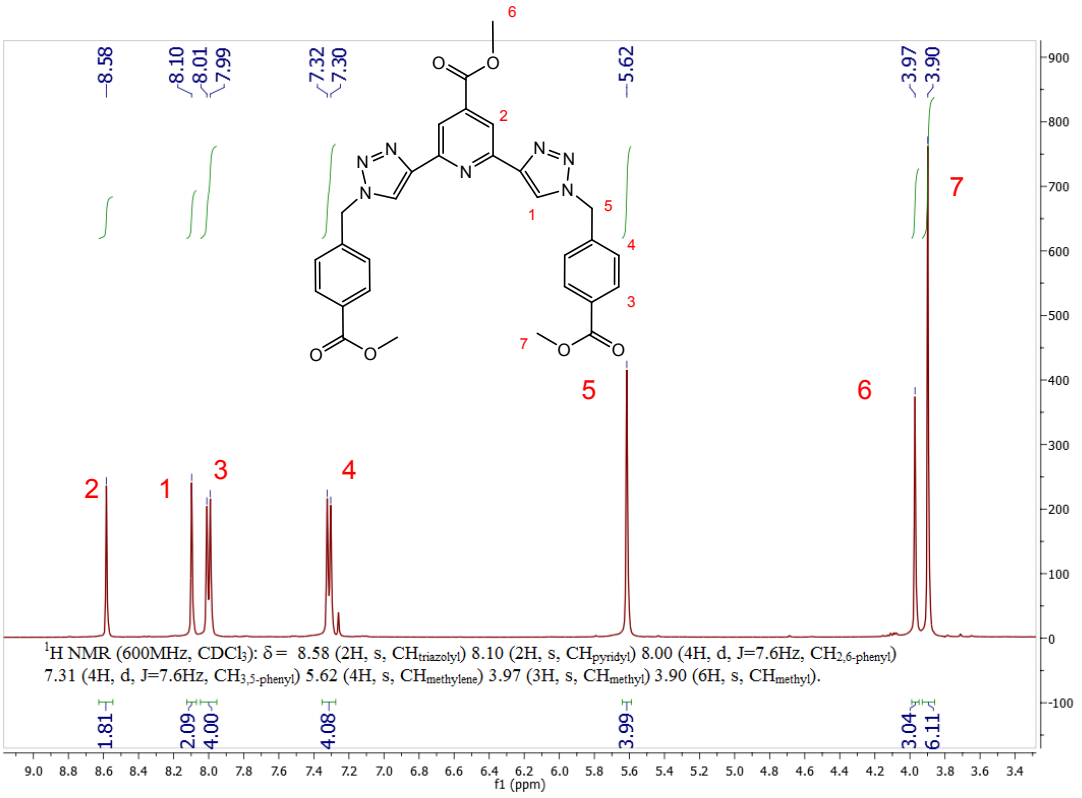
The hydrogel of **2** was prepared by dissolving the compound in a NaOH solution. This was slowly acidified with HCl solution to pH~6. At this point, a fluffy off-white soft precipitate was formed which was allowed to settle for 5 minutes before decanting off the excess solvent and isolating **2** in its gel form.

8. Preparation of Metallogel

The synthesis of the Eu(III) luminescent gel was performed in a two step one pot reaction. Firstly, $Eu(CF_3SO_3)_3$ (1 eq.) and **2** (3 eq.) were suspended in methanol to give a 1.55 mM solution relative to the Ln(III). The mixture was irradiated in the microwave for 60 minutes at 80 ^oC giving rise to a clear colourless solution. Then, $Eu(C_2H_3O_2)_3$ salt (3 eq.) was added. Instantaneously a white soft precipitate could be observed as the acetate salt was dissolved. This mixture was irradiated again in the microwave for 30 minutes at 80 ^oC giving rise to the formation of a fluffy off-white precipitate, the luminescence of which far exceeded that of the mixture prior to addition of the acetate salt. This was centrifuged for 5 minutes at 3500 rpm and isolated in its gel form.

9. NMR Spectra

(A)



(B)

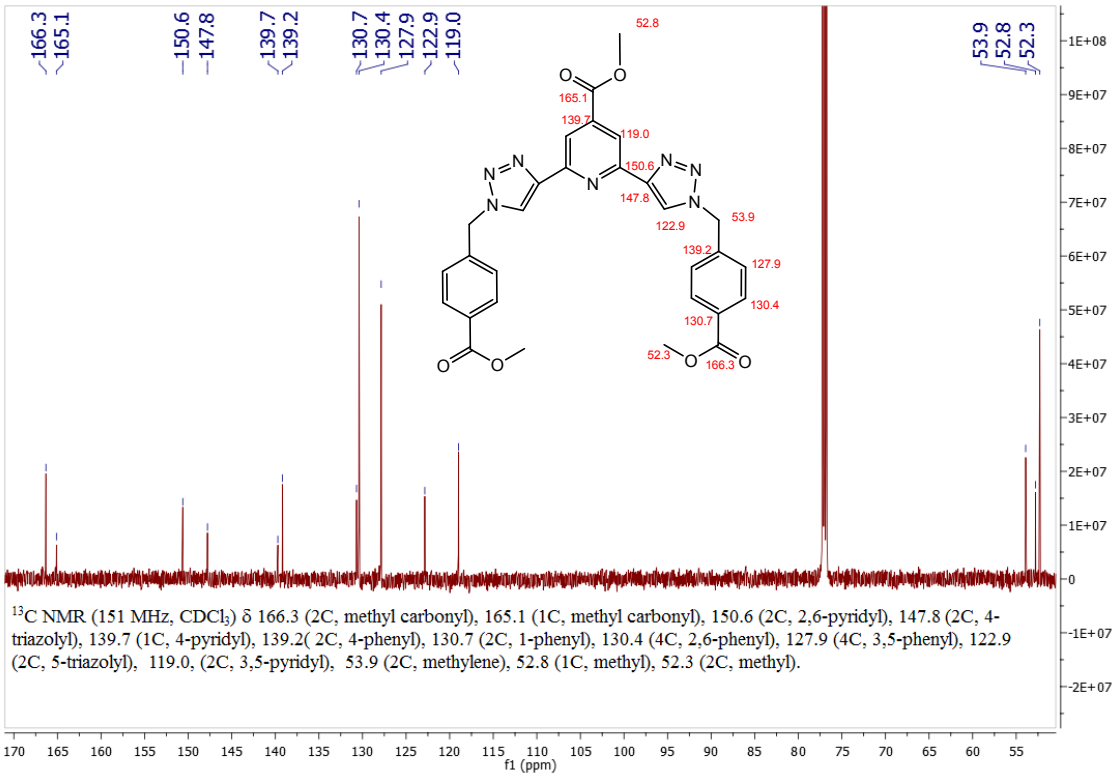
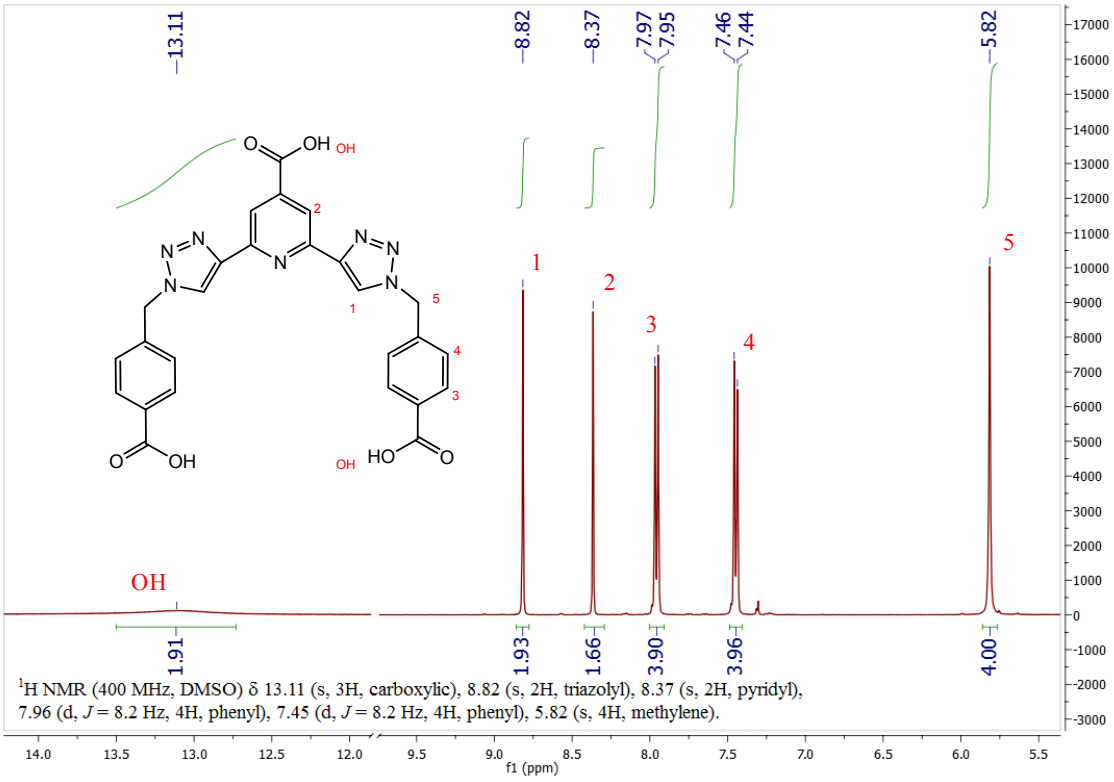


Figure S1: (A) ^{1}H NMR of **1** (600 MHz, $CDCl_3$), **(B)** ^{13}C NMR of **1** (151 MHz, $CDCl_3$).

(A)



(B)

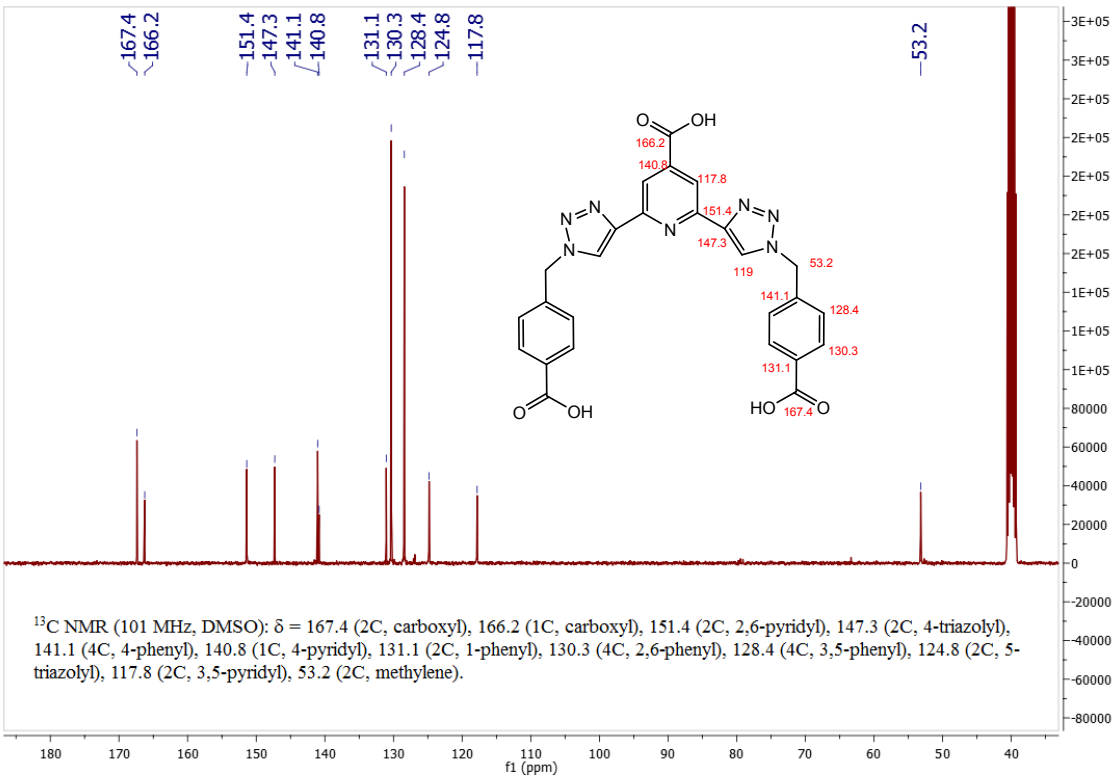
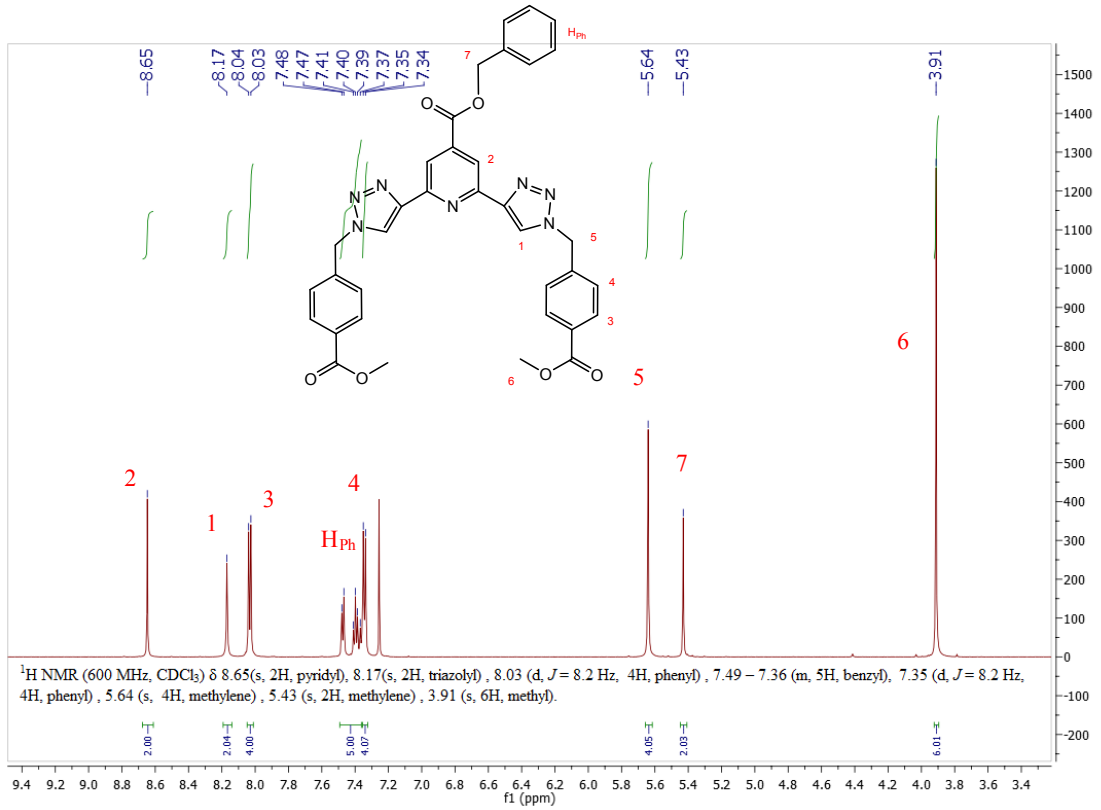


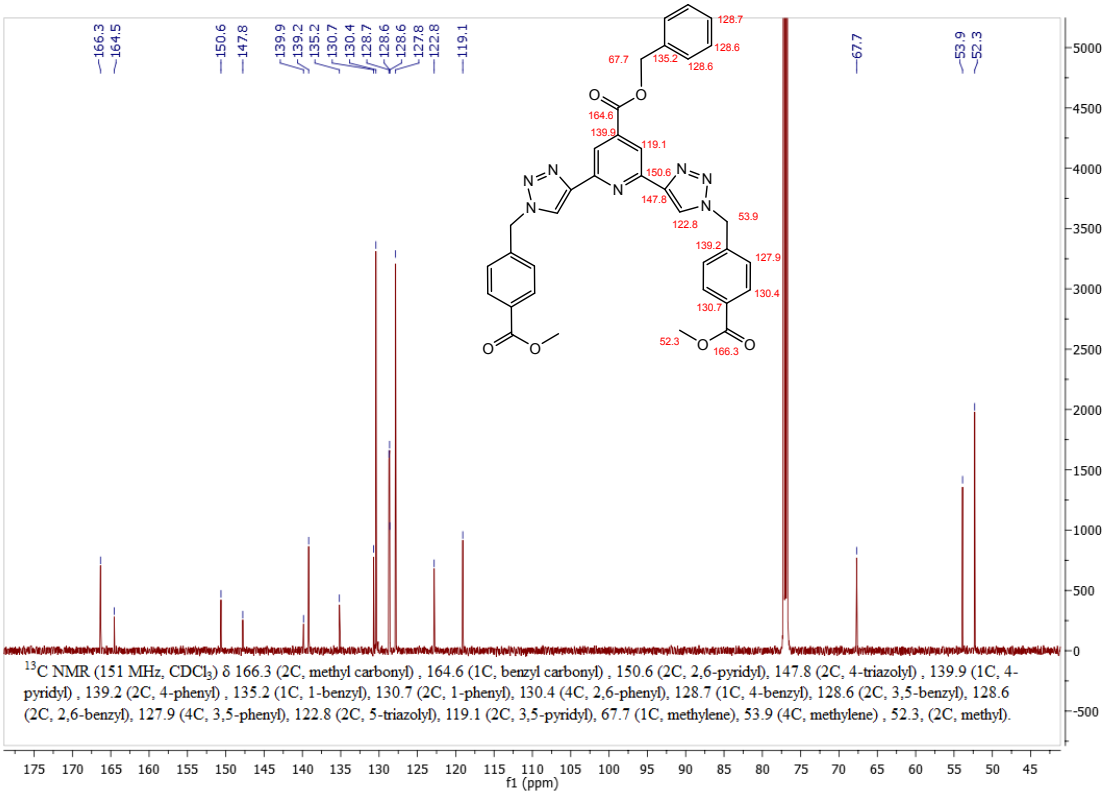
Figure S2: (A) ^{1}H NMR of **2** (400 MHz, DMSO), **(B)** ^{13}C NMR of **2** (101 MHz, DMSO).

(A)



^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65(s, 2H, pyridyl), 8.17(s, 2H, triazolyl) , 8.03 (d, J = 8.2 Hz, 4H, phenyl) , 7.49 – 7.36 (m, 5H, benzyl), 7.35 (d, J = 8.2 Hz, 4H, phenyl) , 5.64 (s, 4H, methylene) , 5.43 (s, 2H, methylene) , 3.91 (s, 6H, methyl).

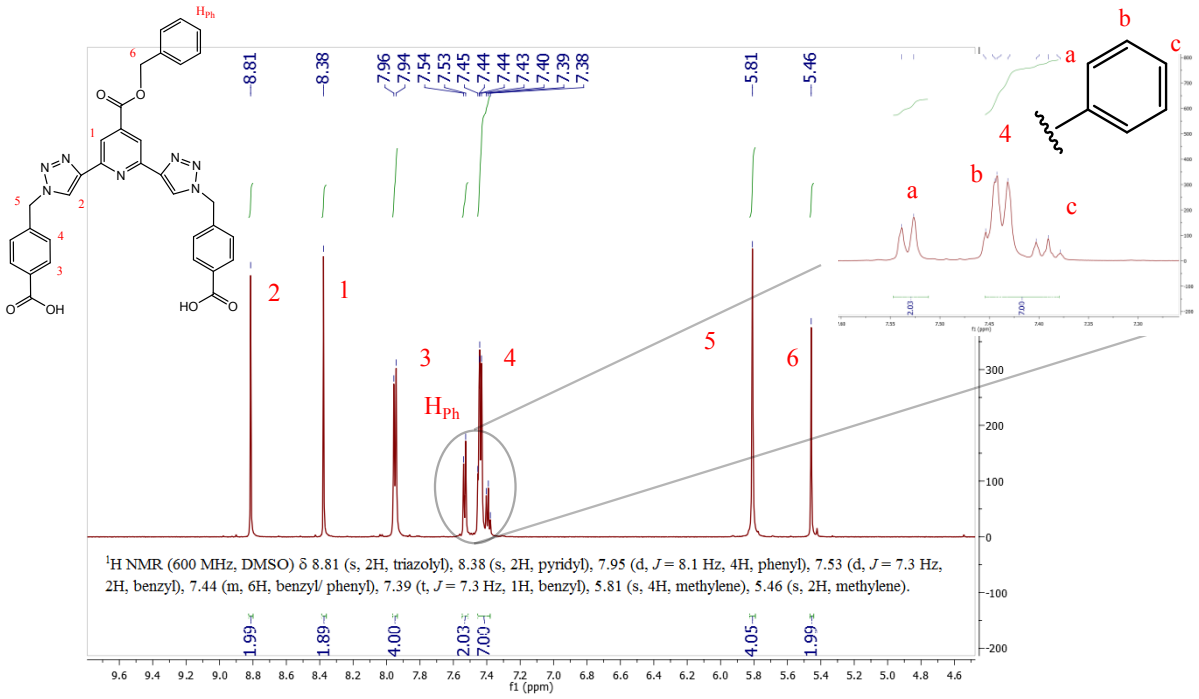
(B)



^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3 (2C, methyl carbonyl) , 164.6 (1C, benzyl carbonyl) , 150.6 (2C, 2,6-pyridyl), 147.8 (2C, 4-triazolyl) , 139.9 (1C, 4-pyridyl) , 139.2 (2C, 4-phenyl) , 135.2 (1C, 1-benzyl), 130.7 (2C, 1-phenyl), 130.4 (4C, 2,6-phenyl), 128.7 (1C, 4-benzyl), 128.6 (2C, 3,5-benzyl), 128.6 (2C, 2,6-benzyl), 127.9 (4C, 3,5-phenyl), 122.8 (2C, 5-triazolyl), 119.1 (2C, 3,5-pyridyl), 67.7 (1C, methylene), 53.9 (4C, methylene) , 52.3, (2C, methyl).

Figure S3: (A) ^{1}H NMR of **3** (600 MHz, $CDCl_3$), **(B)** ^{13}C NMR of **3** (151 MHz, $CDCl_3$).

(A)



(B)

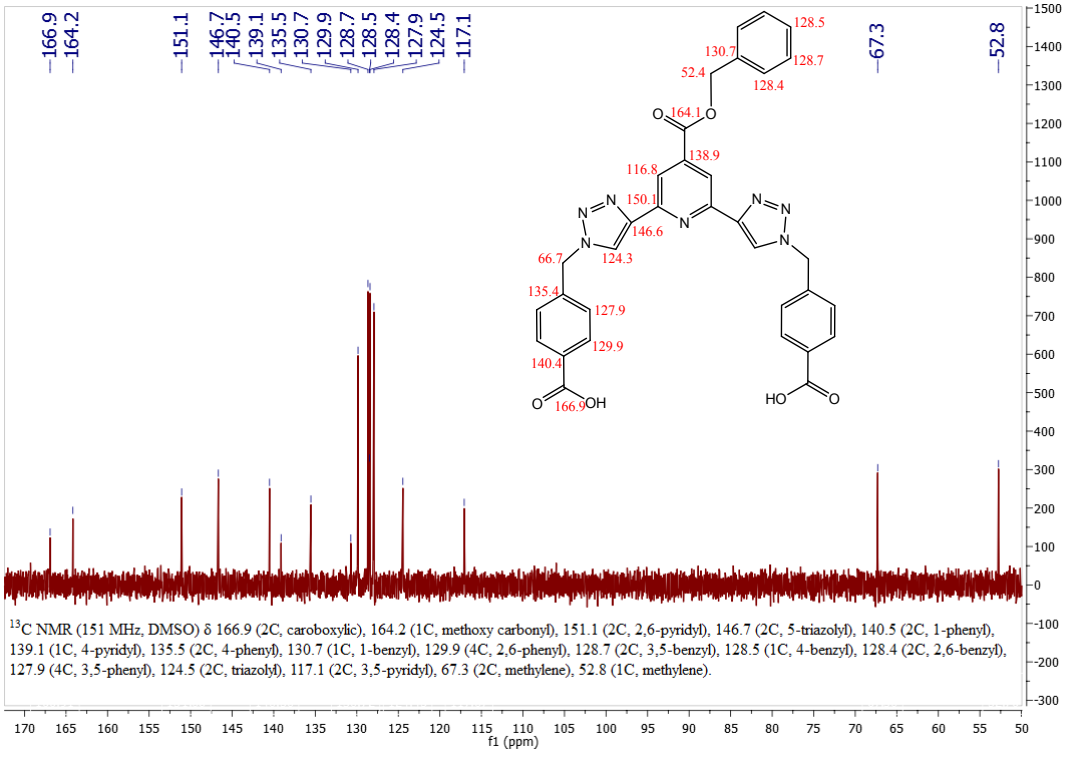
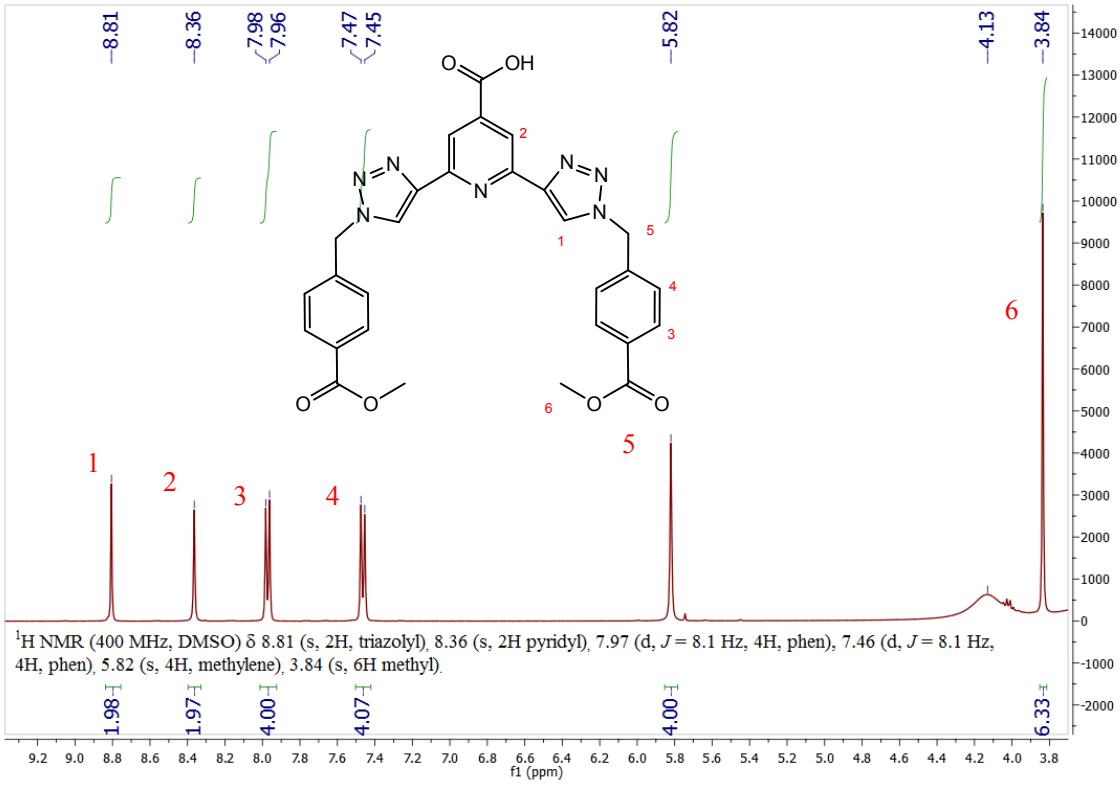


Figure S4: (A) ^{1}H NMR of **4** (600 MHz, DMSO), **(B)** ^{13}C NMR of **4** (151 MHz, DMSO).

(A)



(B)

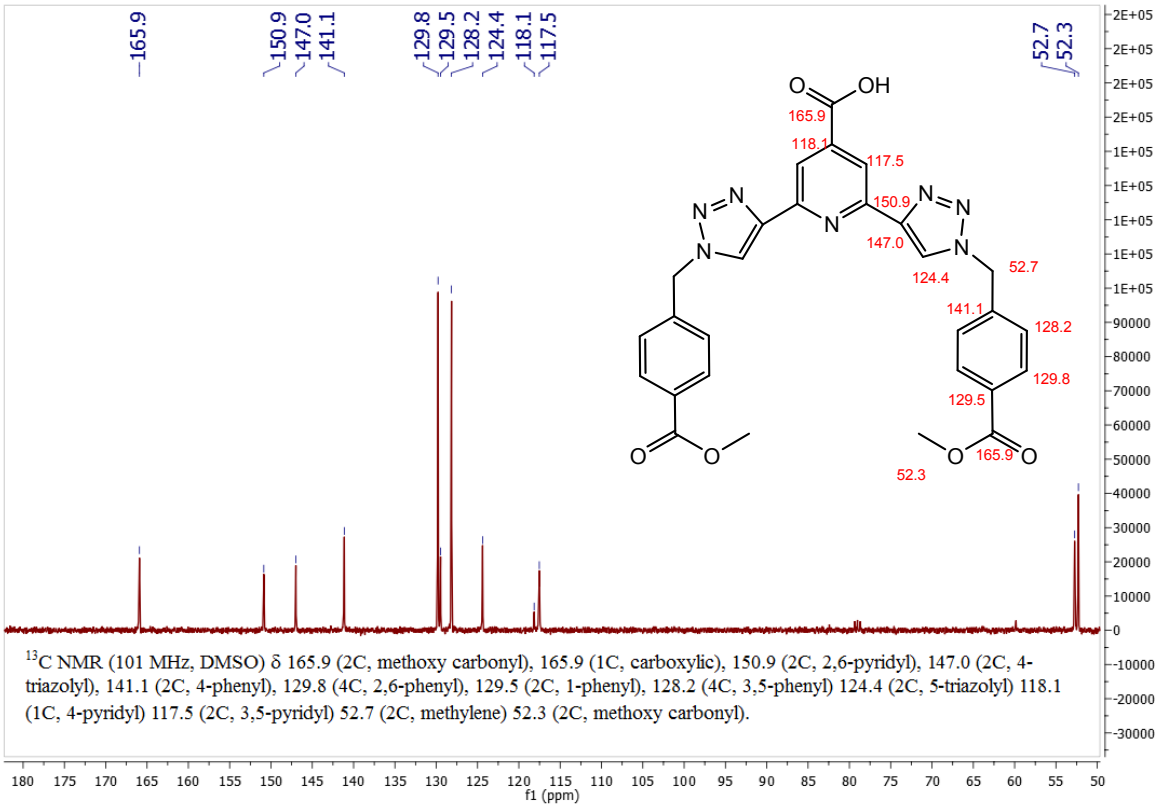
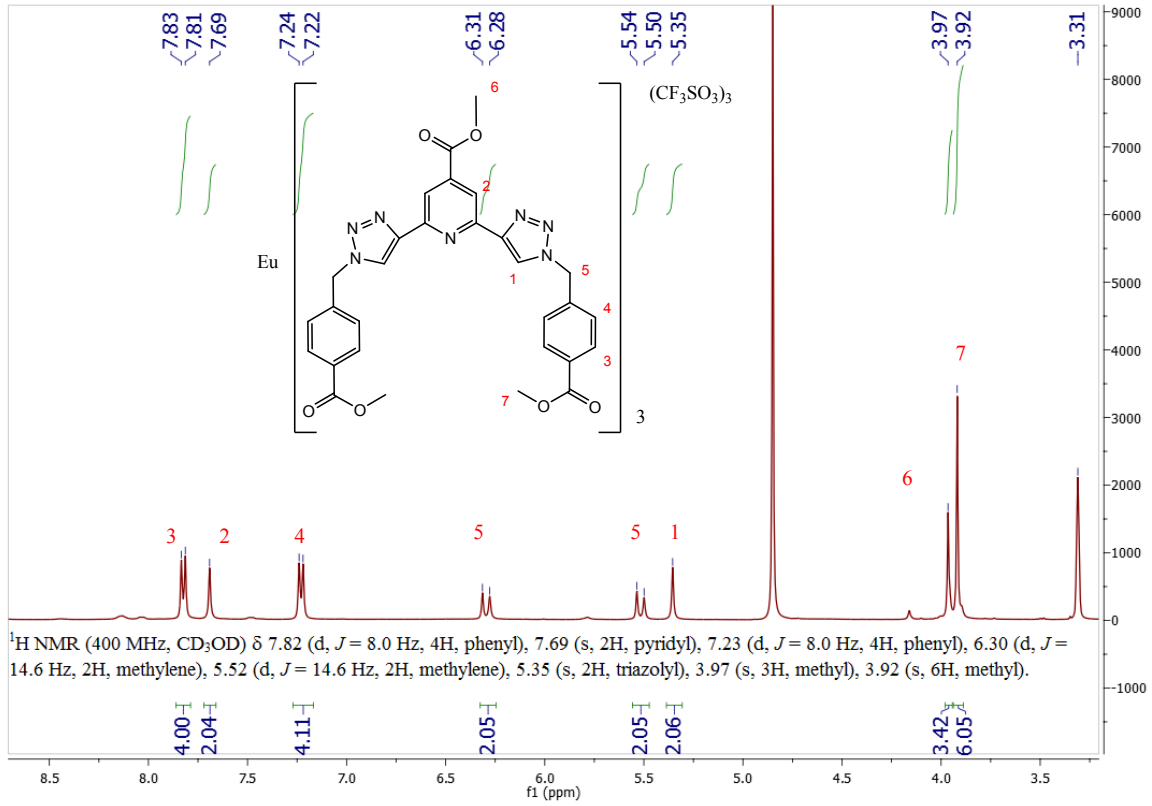


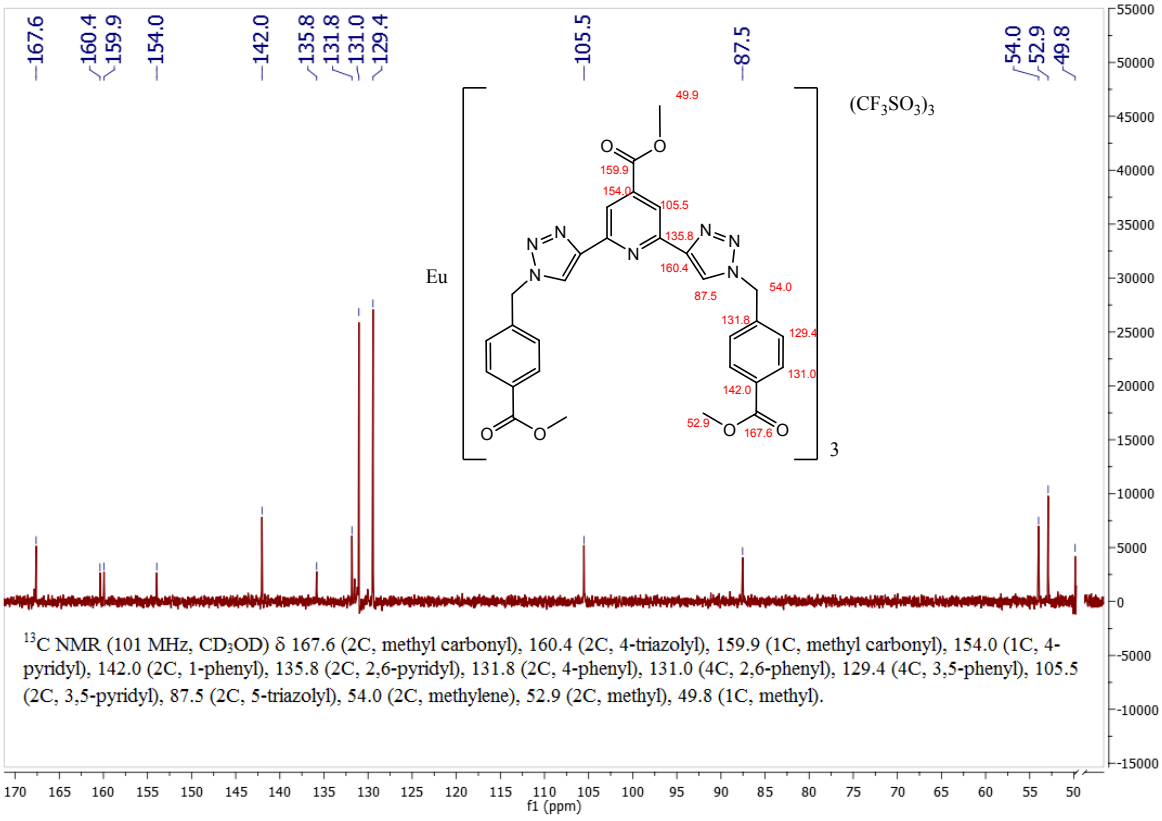
Figure S5: (A) ^{1}H NMR of **5** (400 MHz, DMSO), **(B)** ^{13}C NMR of **5** (101 MHz, DMSO).

(A)



^{1}H NMR (400 MHz, CD_3OD) δ 7.82 (d, J = 8.0 Hz, 4H, phenyl), 7.69 (s, 2H, pyridyl), 7.23 (d, J = 8.0 Hz, 4H, phenyl), 6.30 (d, J = 14.6 Hz, 2H, methylene), 5.52 (d, J = 14.6 Hz, 2H, methylene), 5.35 (s, 2H, triazolyl), 3.97 (s, 3H, methyl), 3.92 (s, 6H, methyl).

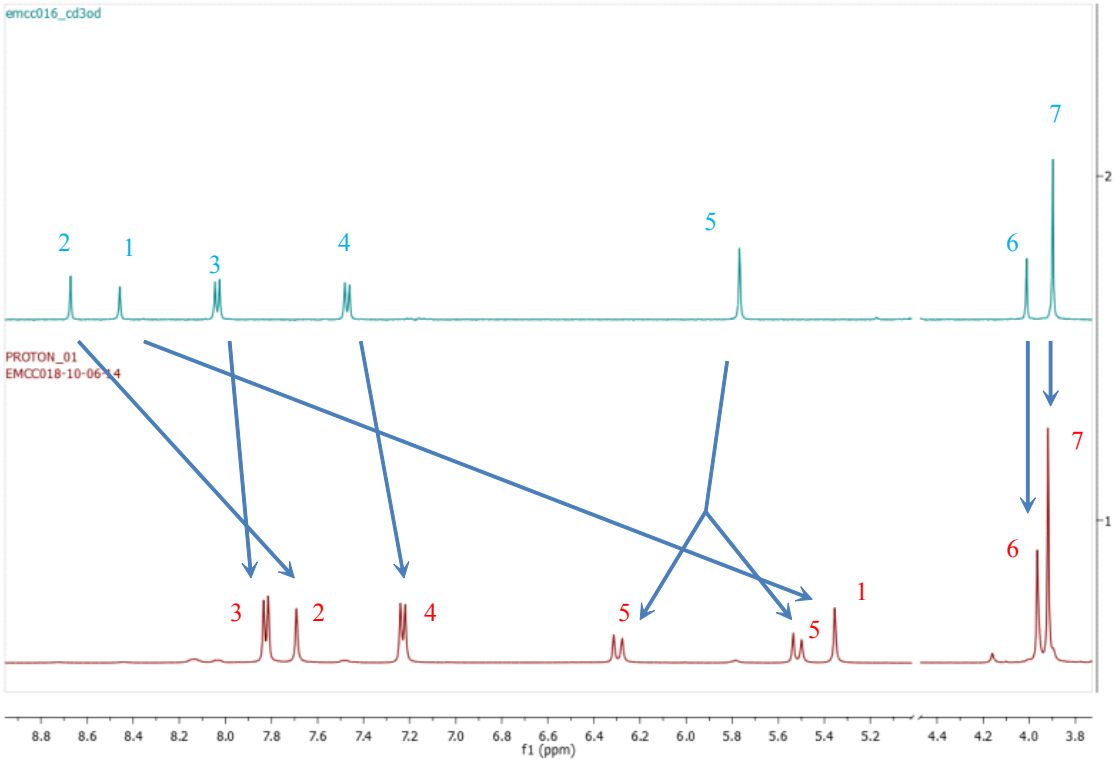
(B)



^{13}C NMR (101 MHz, CD_3OD) δ 167.6 (2C, methyl carbonyl), 160.4 (2C, 4-triazolyl), 159.9 (1C, methyl carbonyl), 154.0 (1C, 4-pyridyl), 142.0 (2C, 1-phenyl), 135.8 (2C, 2,6-pyridyl), 131.8 (2C, 4-phenyl), 131.0 (4C, 2,6-phenyl), 129.4 (4C, 3,5-phenyl), 105.5 (2C, 3,5-pyridyl), 87.5 (2C, 5-triazolyl), 54.0 (2C, methylene), 52.9 (2C, methyl), 49.8 (1C, methyl).

Figure S6: (A) ^{1}H NMR of Eu**1**$_3$ (400 MHz, CD_3OD), **(B)** ^{13}C NMR of Eu**1**$_3$ (101 MHz, CD_3OD).

(A)



(B)

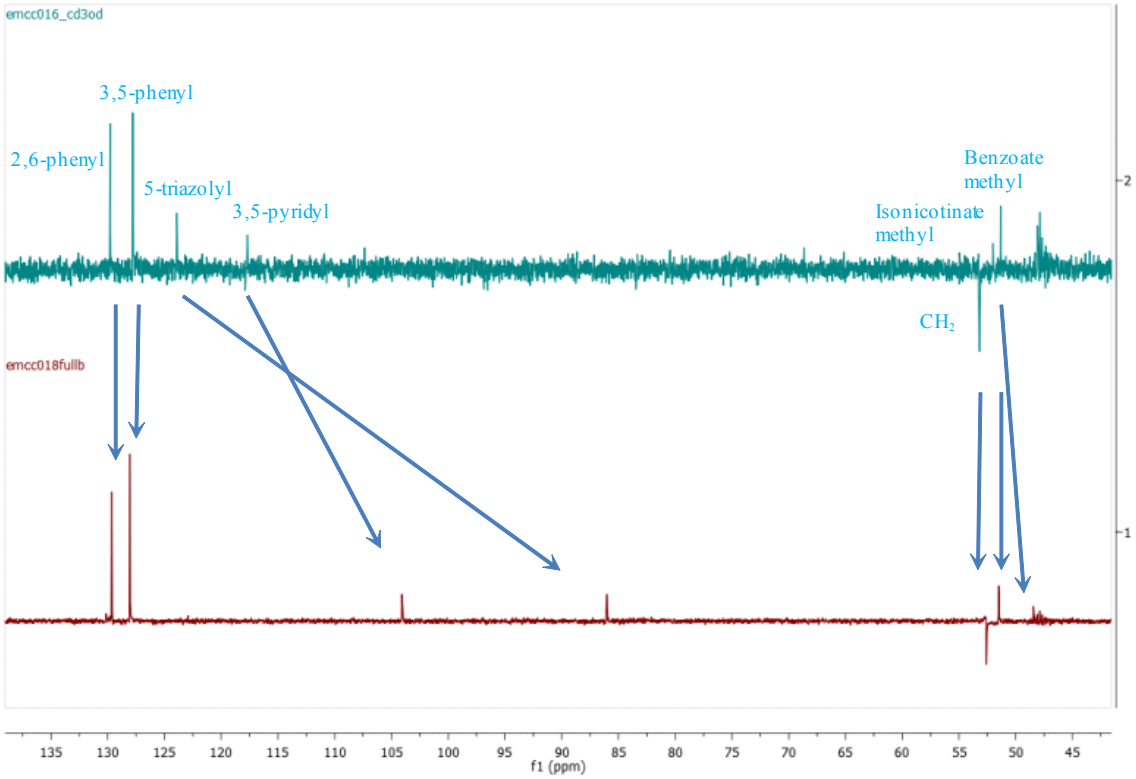
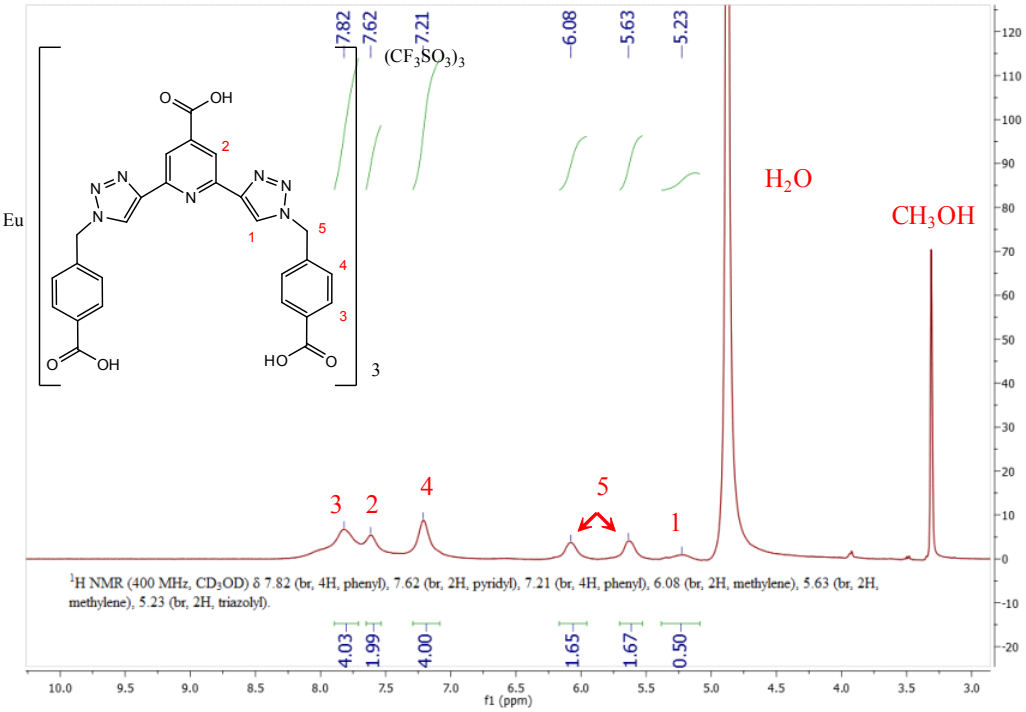


Figure S7: (A) ^{1}H NMR comparison of peak shift of **1** (blue) and Eu**1**$_3$ (red) (400 MHz, CD_3OD), **(B)** ^{13}C NMR comparison of peak shift of **1** (blue) and Eu**1**$_3$ (red) (101 MHz, CD_3OD).

(A)



(B)

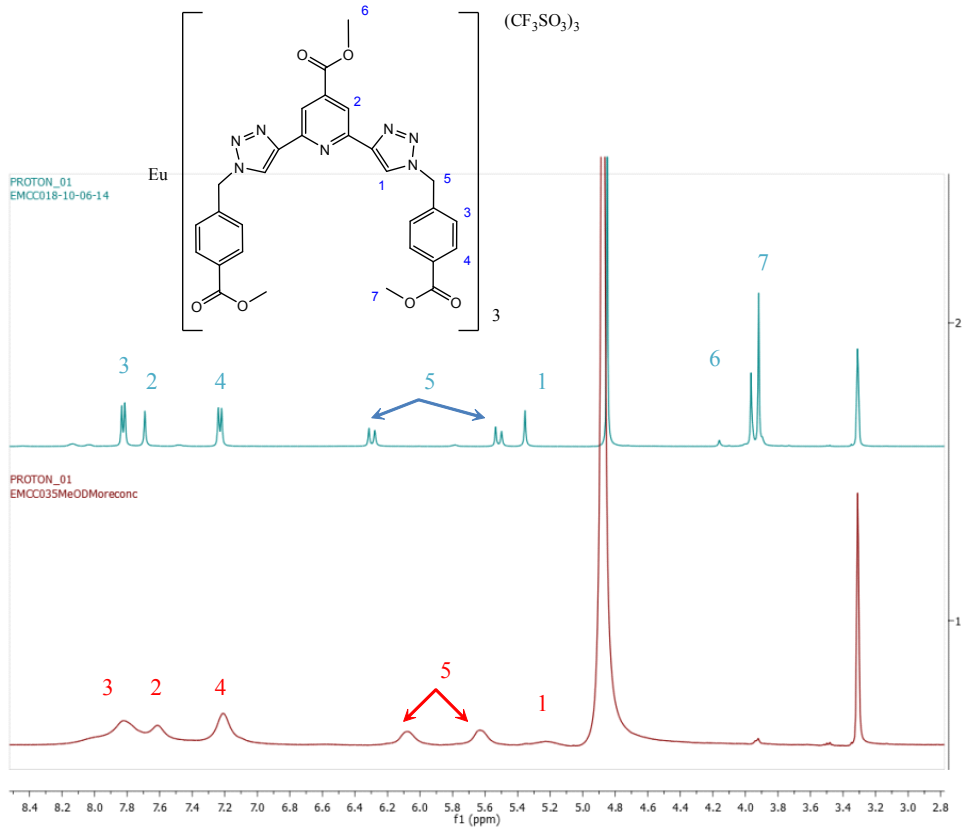


Figure S8: (A) ^{1}H NMR of Eu**2**$_3$ (400 MHz, CD_3OD), **(B)** ^{1}H NMR comparison of peak shift of Eu**1**$_3$ (blue) and Eu**2**$_3$ (red) (400 MHz, CD_3OD).

10. Mass Spectrometry of Complexes

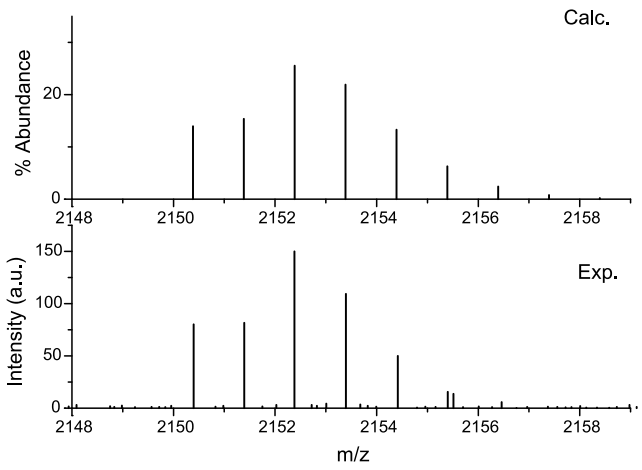


Figure S9: HRMS (*m/z*) (LD$^+$) of Eu**1**$_3$; Calculated for $C_{89}H_{75}N_{21}O_{24}F_6S_2Eu$ *m/z* = 2152.3852. Found for $[Eu\mathbf{1}_3\,(CF_3SO_3^-)_2]^+$ *m/z* = 2152.3796

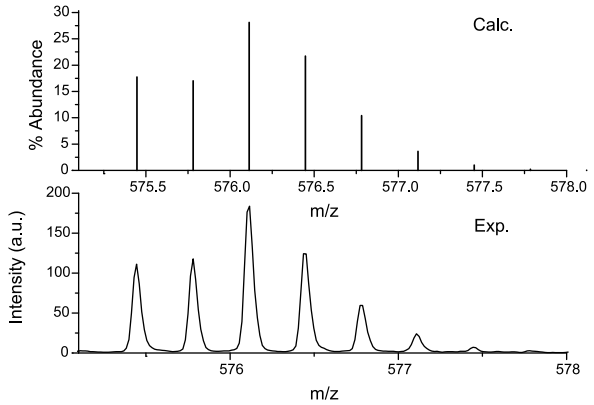


Figure S10: HRMS (*m/z*) (ESI$^+$) of Eu**2**$_3$: Calculated for $[Eu\mathbf{2}_3]^{3=}$; 576.1134 (above) *i.e. m/z* = 1728.3403. Found for $[Eu\mathbf{2}_3]^{3+}$; 576.1114 (above) *i.e. m/z* = 1728.3342.

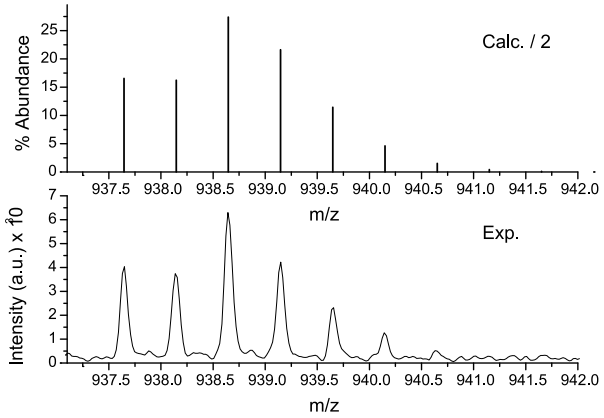


Figure S11: HRMS (*m/z*) (ESI$^+$) of Eu**2**$_3$: Also, calculated for $[Eu\mathbf{2}_3(CF_3SO_3^-)]^{2=}$; 938.6456 (above) *i.e. m/z* = 1877.2912. Found for $[Eu\mathbf{2}_3\,(CF_3SO_3^-)]^{2+}$; 938.6484 i.e. *m/z* = 1877.2968.

11. Photophysical Studies

The photophysical properties of these ligands were also analysed. The UV-Vis absorption spectrum of **1** in CH_3CN (c = 1x10^{-5} M) exhibited bands centred at λ_{max} = 236 nm (ε = 52,000 $M^{-1}cm^{-1}$) and 327 nm (ε = 8,000 $M^{-1}cm^{-1}$), tentatively assigned to π→π* transitions from the aromatic rings and to n→π* transitions from the **btp** core, respectively.[3c] Excitation at 327 nm gave rise to strong fluorescence emission centred at λ_{max} = 375 nm, being significantly red-shifted by 20 nm with respect to that of **6**.[7]

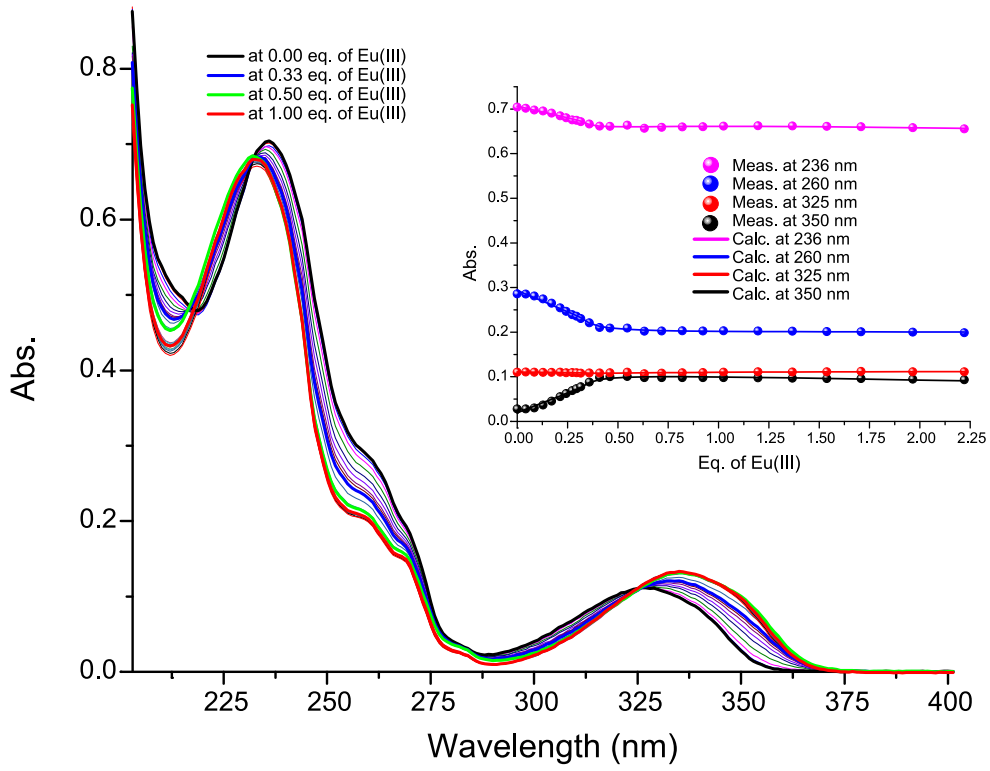


Figure S12: UV-*Vis* Titration of **1** (c=1x10^{-5}M) upon addition of $Eu(CF_3SO_3)_3$ 0 – 4 eq. in MeCN solution at 20.9°C

The UV-Vis absorption spectra of **Eu1$_3$** showed a hypsochromic shift in the π→π* transition by 2 nm and a bathochromic shift in the n→π* transition by 6 nm with respect to that of 1. This is also evident in the band shifts above. Similar observations were seen for **Eu2$_3$** (Figure S21).

Upon gradual addition of Eu(III) the n→π* band of **1** experienced a significant hyperchromic effect and red-shift with corresponding blue-shift of the π →π* transition, indicative of the self-assembly of **1** with Eu(III) and formation of an isosbestic point at 325 nm.

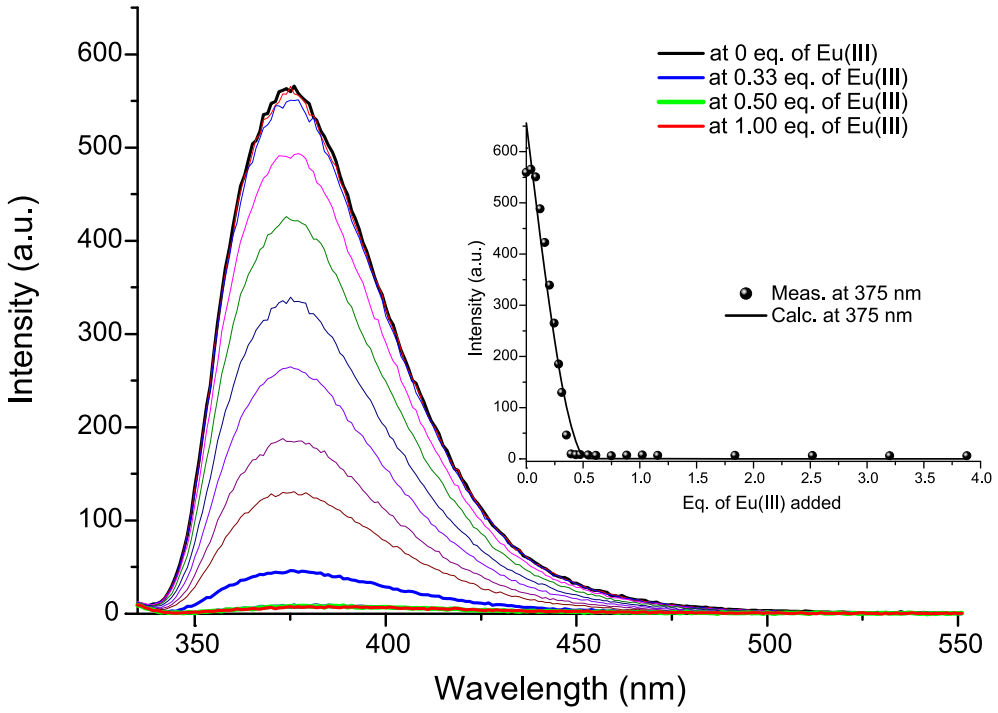


Figure S13: Fluorescence Titration of **1**(c=1x10^{-5}M) upon addition of Eu(CF_3SO_3)$_3$ 0– 4 eq. in MeCN solution at 25 ^{o}C

Moreover, the ligand fluorescence became quenched upon addition of Eu(III). This was characteristic of the population of the Eu(III) excited state by energy transfer from the **btp** antenna giving rise to Eu(III) emission due to the formation of the expected 1:3 M:L stoichiometry but also the formation of other stoichiometries at higher Eu(III) concentrations.

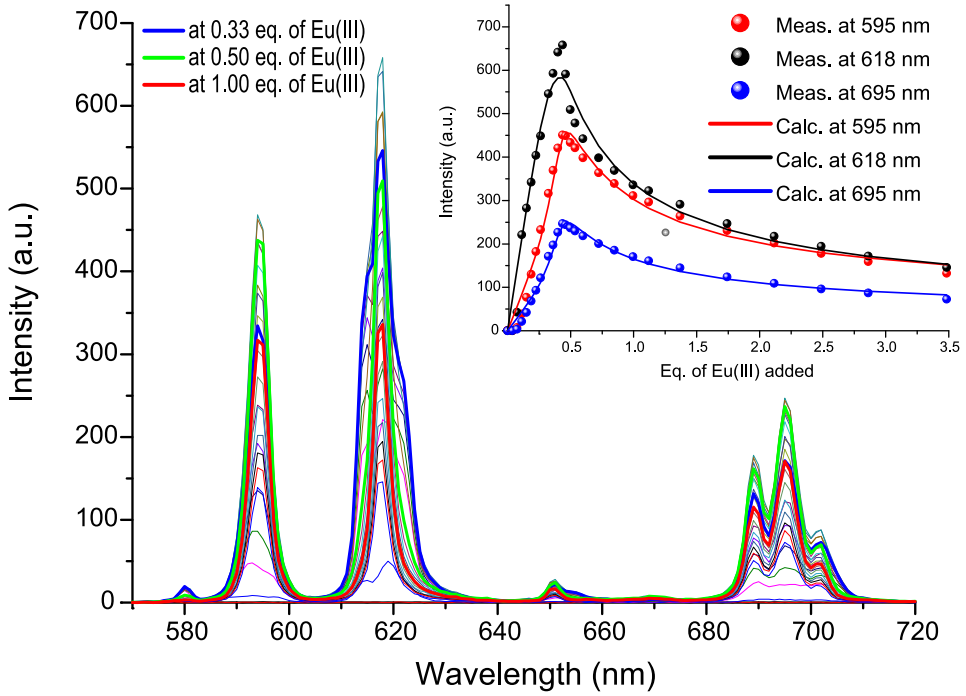


Figure S14: Changes in Eu(III) centred luminescence spectra upon titration of **1** in CH_3CN (c = 1x10^{-5} M) against 0→3.5 eq. of $Eu(OTf)_3$ recorded at 25 ^{o}C. (Inset) Experimental binding isotherms at band wavelengths. (λ_{ex} = 325 nm).

As the metal concentration increased, the equilibrium was shifted to a less emissive self-assembly and the emission intensity decreased. Hence, the change in intensity of the hypersensitive ΔJ = 2 transition, along with the change in splitting patterns, demonstrated a reorientation in the coordination environment of the Eu(III) metal centre. {J. -C. G. Bünzli, G. R. Eds. Choppin,, *Luminescent probes. In Lanthanide Probes in Life, Chemical and Earth Sciences. Theory and Practice*, Elsevier Science Publ. B.V., Amsterdam, 1989.}

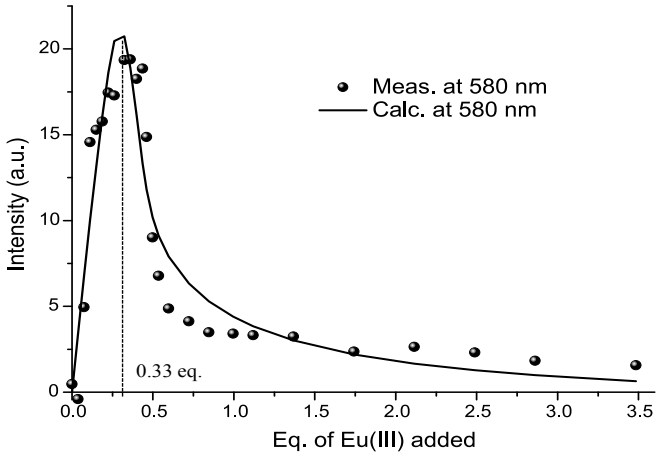


Figure S15: Experimental binding isotherm for the Eu(III) centred emission titration of **1** (*c*=1x10^{-5}M) upon addition of $Eu(CF_3SO_3)_3$ 0 – 4 eq. in MeCN solution at 25 ^{o}C at 580 nm ($^5D_0$ – $^7F_0$) and its corresponding fit.

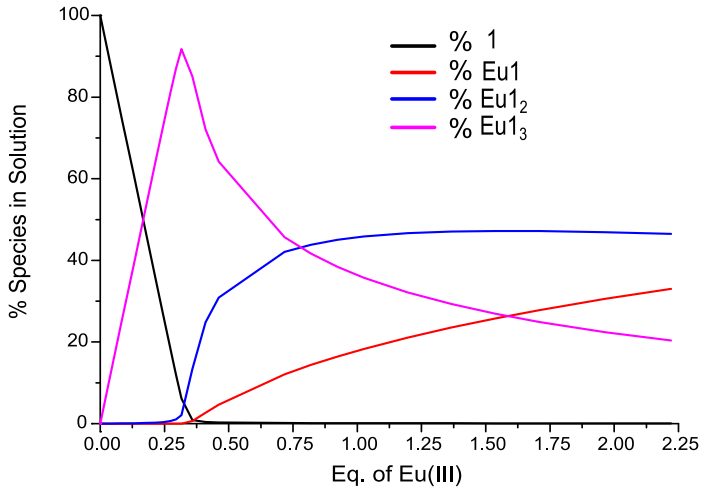


Figure S16a: Speciation Distribution Diagram calculated using ReactLab from UV-Vis absolution spectral changes of **1** in CH_3CN ($c = 1x10^{-5}$ M) upon addition of $Eu(CF_3SO_3)_3$ recorded at 25 °C.

Figure S16a shows that at 0.33 eq. of Eu(III) the 1:3 M:L species was present in 92.5% yield, with the ligand **1** becoming fully bound at slightly higher eq. of Eu(III). The formation of the 1:1 and 1:2 M:L species was also seen upon increasing the concentrations of Eu(III) with concomitant decrease in the abundance of the 1:3 M:L species and decrease in overall luminescence.

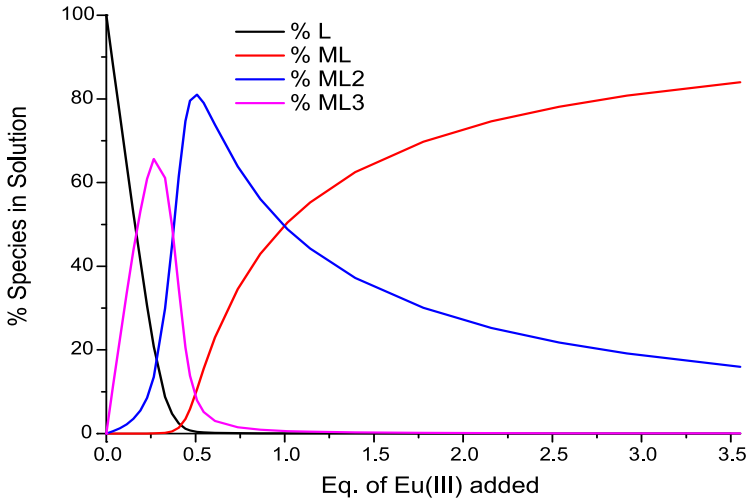


Figure S16b: Speciation Distribution of **1** from Phosphorescence Titration

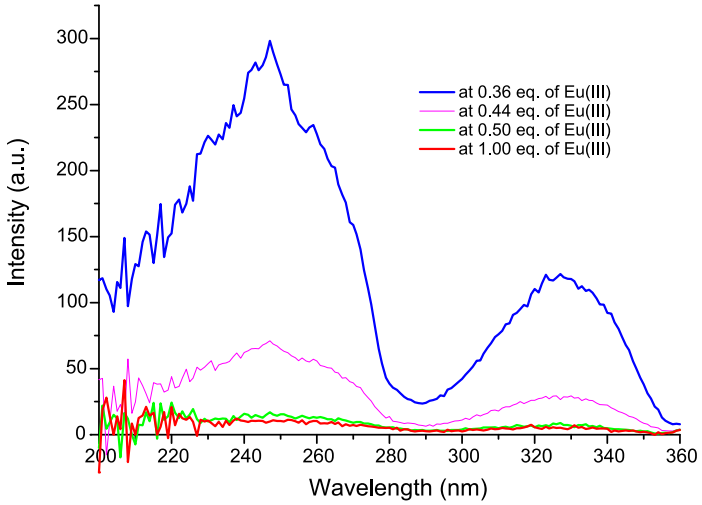


Figure S17: The changes in excitation spectra of Eu:$\mathbf{1}_n$ (n=1-3) assemblies during the spectroscopical titration (λ_{ex} at 375 nm)

Photophyscial characterisation of the Eu$\mathbf{1}_3$ and Eu$\mathbf{2}_3$.

Both **Eu$\mathbf{1}_3$** and **Eu$\mathbf{2}_3$** were found to be red emissive under a UV-lamp, demonstrating the sensitisation of the Eu(III) excited state by the antenna effect. Excitation at 327 nm gave rise to metal centred emission, typical of that seen for Eu(III) for the deactivation of the $^5D_0$ excited state. Quantum yields of luminescence for Eu1_3 and Eu2_3 (Φ_{tot} = 2.5 – 7.4 %) were also carried out (Table S1). Excited state lifetime measurements in H_2O and D_2O allowed for the hydration state (q) for **Eu$\mathbf{1}_3$** and **Eu$\mathbf{2}_3$** to be determined as zero,{R. M. Supkowski and W. D. Horrocks Jr, *Inorg. Chim. Acta*, 2002, **340**, 44.} indicating that the coordination sphere of the Eu(III) was fully saturated with no metal ion bound water molecules (Table S2).

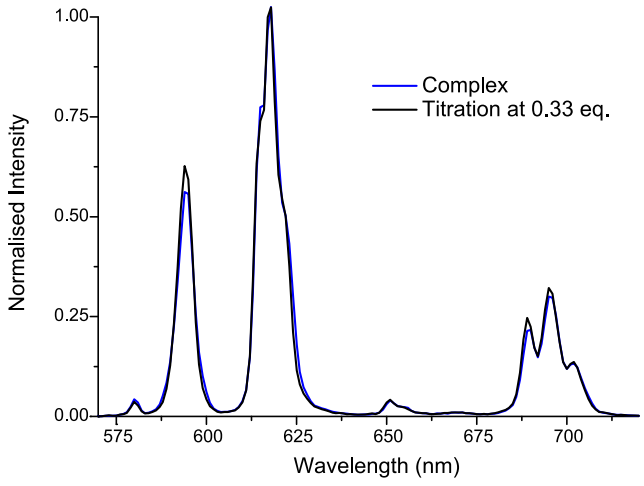


Figure S18: Luminescence Spectra of **1** and Eu$\mathbf{1}_3$ (c=1x10^{-5}M, acetonitrile, 25 ^{o}C))

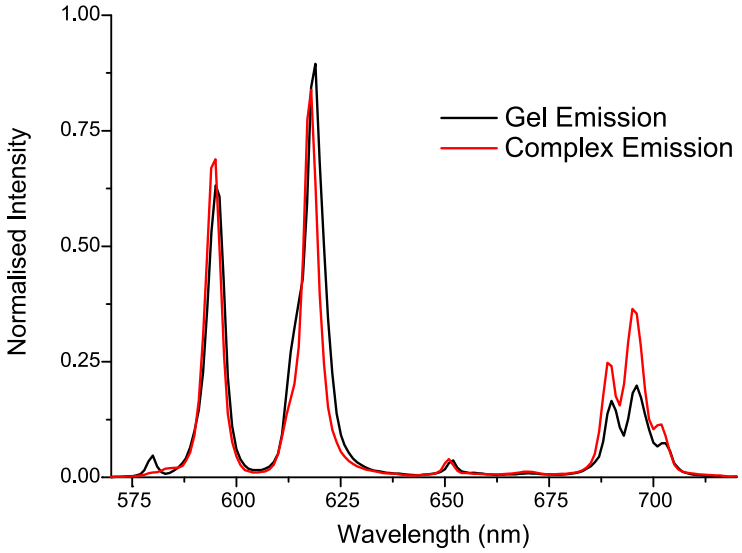


Figure S19: Luminescence Spectra of Eu**2**$_3$ (c=1x10^{-5}M, acetonitrile, 25 ^{o}C) and gel of Eu**2**$_3$:Eu(OAc)$_3$ applied to quartz slide, see Fig. S20

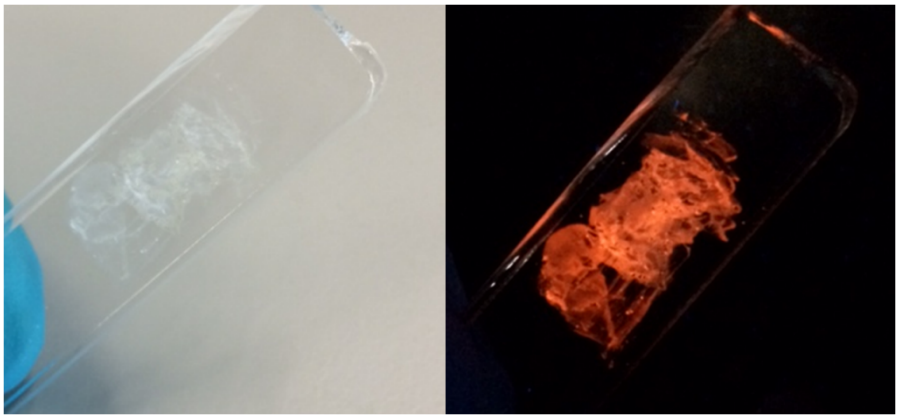


Figure S20: Gel of Eu**2**$_3$:Eu(OAc)$_3$ applied to quartz slide (in daylight and under UV lamp at 365 nm).

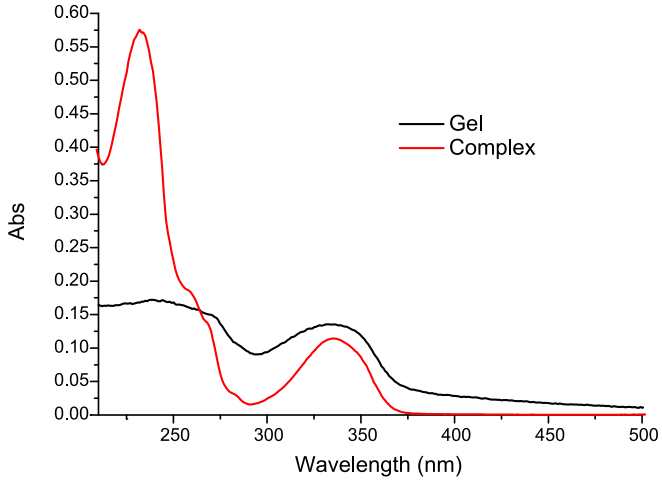


Figure S21: Absorption Spectra of Eu**2**$_3$ (c=1x10^{-5}M, CH_3CN, 25 ^{o}C) and gel of Eu**2**$_3$:Eu(OAc)$_3$.

Complex[a]	Φ_{tot}, %
Eu**1**$_3$[b]	4.8±0.8
Eu**1**$_3$[c]	2.5±0.4
Eu**2**$_3$[c]	7.4±1.3

Table S1: Experimental overall luminescence quantum yield (Φ_{tot}) upon excitation (λ_{ex} = 279 m). [a] All the complexes obtained with the formula $EuL_3(CF_3SO_3)_3$. [b] in MeCN. [c] in MeOH.[8]

Complex[a]	τ_{obs}[b], ms	τ_{obs}[c], ms	q_{value}
Eu**1**$_3$	1.6(1)	1.8(1)	-0.2(5)
Eu**2**$_3$	1.7(1)	2.5(1)	-0.1(5)

Table S2– Observed lifetimes, τ_{obs}, (λ_{ex} = 326 nm), and calculated q values. [a] All the complexes obtained with the formula Eu**L**$_n(CF_3SO_3)_3$. [b] in H_2O. [c] in D_2O

Species	τ_{obs}, ms	τ_{obs}, ms
Eu**2**$_3$ [a]	1.4(1)	-
Eu**2**$_3$ [b]	1.4(1)	-
Gel [c]	1.3(1)	0.50(5)

Table S3– Observed lifetimes, τ_{obs}, (λ_{ex} = 326 nm). [a] Monoexponential in MeOH reaction solution after first microwave irradiation. [b] Monoexponential in MeOH supernatant after 2 eq. of $Eu(OAc)_3$ added, microwave irradiated and decanted from metallogel. [c] Biexponential after application of metallogel to quartz slide.

12. SEM Images of Gels

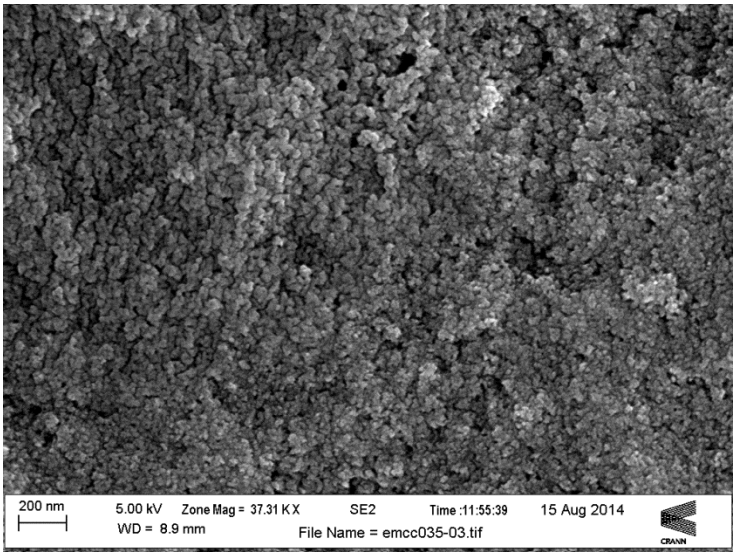


Figure S22: SEM images of gel of Eu**2**$_3$:Eu(OAc)$_3$

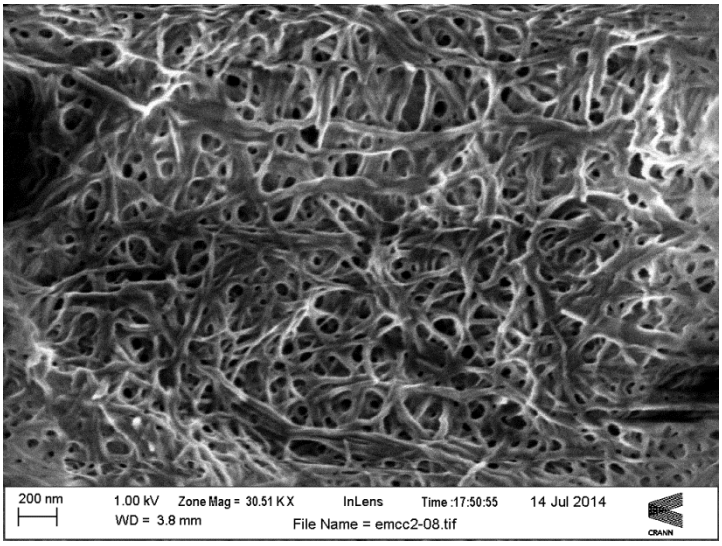


Figure S23: SEM image of hydrogel of **2**.

13. Thermogravimetric Analaysis

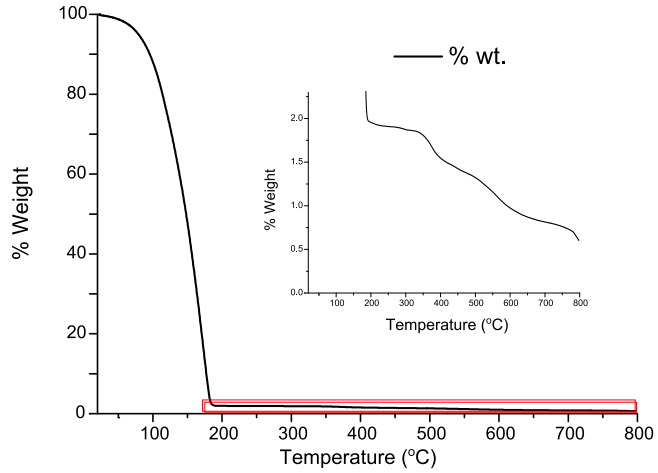


Figure S24: Thermogravimetric Analysis of hydrogel of **2** with 1.93±0.04 wt. %. NaCl content from gelation procedure is the cause of high wt. % even at 800°C.

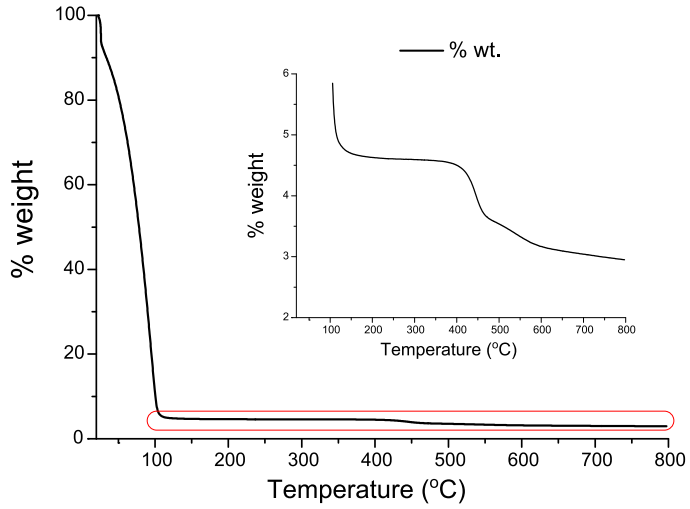


Figure S25: Thermogravimetric Analysis of metallogel of Eu**2**$_3$:Eu(OAc)$_3$ with 4.85±0.08 wt. %. Heavy metal salt content is the cause of high wt. % even at 800°C.

14. Rheological Studies

The data shown for the strain amplitude and frequency sweep experiments were reproduced three times before performing a larger time series experimental run for the samples.

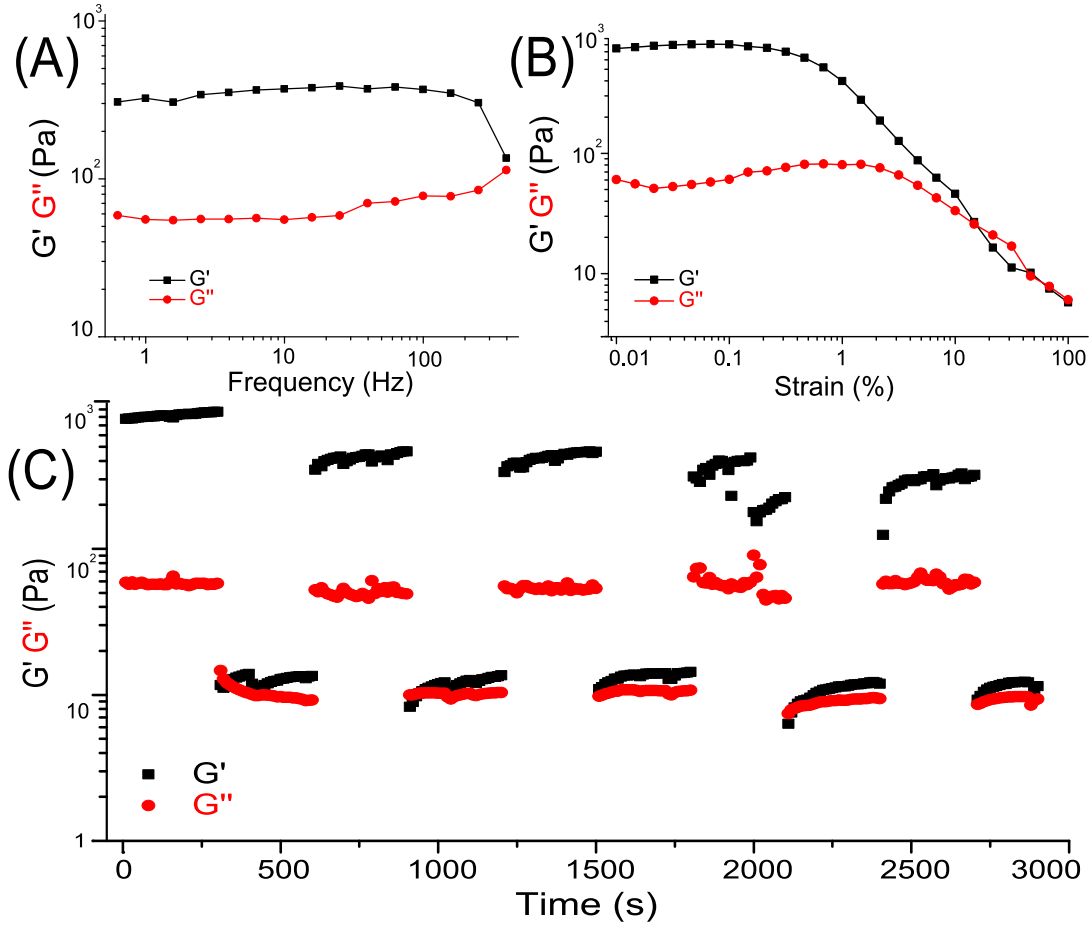


Figure S26: Oscillatory rheology measurements of the hydrogel of **2**. (A) Frequency sweeps at 0.1% strain amplitude of the storage modulus G′(■) and loss modulus G″(●) are shown. (B) The corresponding strain dependence at a $f = 1$ Hz. (C) Recovery test for hydrogel with alternating strain amplitudes of 20 % and 0.1 % at $f = 1$ Hz.

After a certain period of time (1,800 s), it was evident that the ligand gel was not recovering because as the strain sweeps alternated between high and low strain the values for G' and G'' were not being reproduced in the same smooth manner as for the Eu(III) gel. As the bonds are being broken they are not being reformed quickly enough. Each carboxylic group can bind to a maximum of one other carboxylic group limiting, once this interaction has been broken, the rate of reformation.

However, in the case of the Eu(III) metallogel the bridging Eu(III) ions are not fully saturated as evident from the lifetimes. When a carboxlate - Ln(III) bond is broken there is an increased possibility of the carboxylate finding a vacant Eu(III) coordination site and re-establishing a supramolecular interaction. As a result, the Eu(III) metallogels show more pronounced healing ability as the G', G" values are consistent over consecutive runs as shown from the recovery test.

15. Crystal Structure Report for Eu**1**$_3$

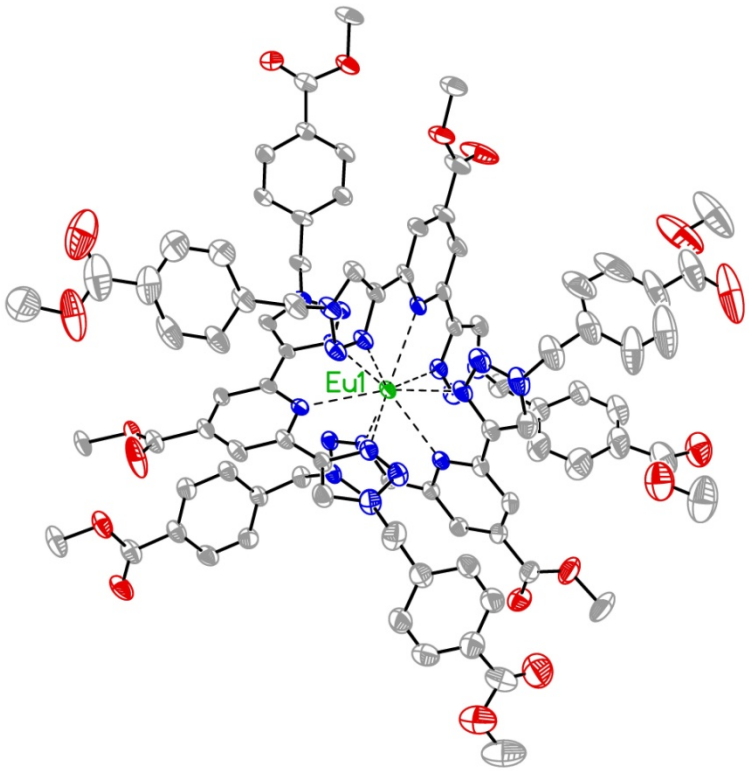


Figure S27: Structure of Eu**1**$_3$ complex (thermal displacement 50%). Hydrogen atoms omitted for clarity.

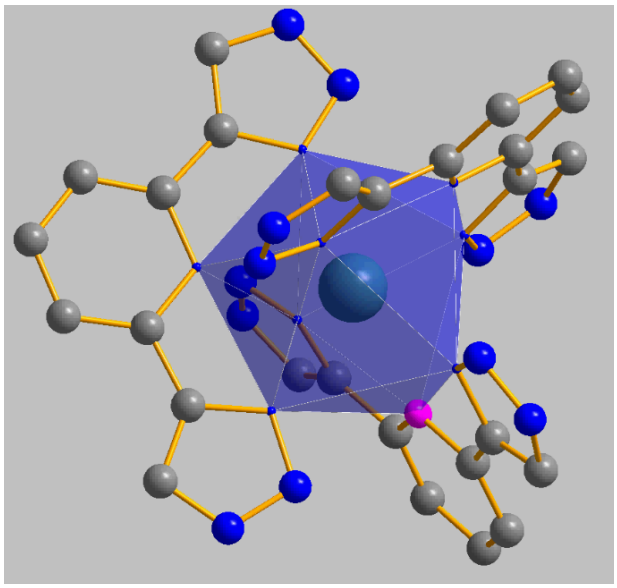


Figure S28 – Coordination polyhedron of Eu**1**$_3$ inner sphere showing distorted triaugmented trigonal prism geometry

A specimen of $C_{94.50}H_{81.75}EuF_9N_{23.25}O_{27}S_3$, approximate dimensions 0.100 mm x 0.100 mm x 0.130 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 150(2)K using an Oxford Cryosystems Cobra low temperature device using a MiTeGen

micromount. See Table S4 for collection parameters and exposure time. Bruker APEX software was used to correct for Lorentz and polarization effects.

The integration of the data using a triclinic unit cell yielded a total of 118699 reflections to a maximum θ angle of 26.02° (0.81 Å resolution), of which 21057 were independent (average redundancy 5.637, completeness = 99.6%, R_{int} = 5.19%, R_{sig} = 3.93%) and 17108 (81.25%) were greater than 2σ(F^2). The final cell constants of a = 15.6080(9) Å, b = 15.7058(9) Å, c = 22.7440(13) Å, α = 88.9700(10)°, β = 80.5030(10)°, γ =77.2110(10)°, volume = 5361.5(5) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6989 and 0.7454.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{94.50}H_{81.75}EuF_9N_{23.25}O_{27}S_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 1517 variables converged at R1 = 6.26%, for the observed data and wR2 = 18.16% for all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was2.680 $e^-/Å^3$ and the largest hole was -1.141 $e^-/Å^3$ with an RMS deviation of 0.125 $e^-/Å^3$. On the basis of the final model, the calculated density was1.483 g/cm^3 and F(000), 2439 e^-.

Refinement Note: Two triflate anions were disordered in two positions. These were modelled as rigid groups with refined occupancies of ca. 60% for the major component. The highest residual is located among the disordered triflates anions. Further modelling of the triflate did not produce a realistic model. One terminal methoxy group was disordered in two positions with an occupancy of 50%. Restraints were applied to thermal parameters to allow the refinement to converge. Only one acetonitrile solvent molecule was fully occupied. Two were modelled with 50% occupancy and one with 25% occupancy.

References:

Bruker APEX v2012.12-0, Bruker AXS Inc., Madison, Wisconsin, USA.

SADABS (2014) Bruker AXS Inc., Madison, Wisconsin, USA; Sheldrick, G. M. University of Göttingen, Germany.

SHELXL-2013, Sheldrick, G. M. (2013). University of Göttingen, Germany.

Acknowledgement:

Facility funded by PRTLI and ERDF.

Table S4:. Crystal data and structure refinement for emc018table.

Empirical formula	C94.50 H81.75 Eu F9 N23.25 O27 S3	
Formula weight	2394.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.6080(9) Å	□= 88.9700(10)°.
	b = 15.7058(9) Å	□= 80.5030(10)°.
	c = 22.7440(13) Å	□ = 77.2110(10)°.
Volume	5361.5(5) $Å^3$	
Z	2	
Density (calculated)	1.483 Mg/m^3	
Absorption coefficient	0.743 mm^{-1}	
F(000)	2439	
Crystal size	0.130 x 0.100 x 0.100 mm^3	
Theta range for data collection	1.330 to 26.022°.	
Index ranges	-19≤h≤19, -19≤k≤19, -28≤l≤28	
Reflections collected	118699	
Independent reflections	21057 [R(int) = 0.0519]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6989	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21057 / 90 / 1517	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2σ(I)]	R1 = 0.0626, wR2 = 0.1660	
R indices (all data)	R1 = 0.0817, wR2 = 0.1816	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.680 and -1.141 $e.Å^{-3}$	

15. References

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