

## Electronic Supplementary Material (ESI)

# Tunable emissions in lanthanide-based supramolecular metallogels

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## Methods

**General characterization.** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken on a Bruker DRX 300. Mass spectroscopy samples were analyzed on a JEOL JMS-700 mass spectrometer. The high resolution mass spectra (HR-MS) were measured by electrospray ionization (ESI) with a micro TOF Focus spectrometer from SYNAPT G2 (Waters, U.K.). A UV-visible spectrophotometer (Jasco V-750) was used to obtain the absorption spectra. IR spectra were observed over the range  $500\text{-}4000\text{ cm}^{-1}$ , with a Thermo Scientific Nicolet iS 10 instrument.

**UV-vis studies:** The UV-vis spectra were determined over the range of  $200\text{-}700\text{ nm}$  using a quartz cell with 1, 2, and 10 mm path lengths. Scans were taken at the rate of  $500\text{ nm/min}$  with a sampling interval of  $0.5\text{ nm}$  and a response time of  $0.5\text{ s}$ .

**Rheological Properties:** The gels were loaded onto the rheometer plate according to the standard. Rheological properties were carried out by using AR-2000ex (TA Instruments Ltd., New Castle, DE, USA). A parallel plate with a diameter of  $20\text{ mm}$  was used. The gap between the gel and the plate was set to  $0.5\text{ mm}$ , and the experiments were carried out at  $25\text{ }^\circ\text{C}$ . Strain sweep tests were carried out with increasing amplitude oscillation from  $0.1\%$  to  $100\%$  apparent strain on the shear. Frequency sweep tests were carried out between  $0.1$  and  $100\text{ rad s}^{-1}$ .

**SEM observation.** FE-SEM images were observed using a JEOL (JSM-7900F). The images of samples using an accelerating voltage  $10\text{ kV}$  and an emission current of  $8\mu\text{A}$ . Samples were prepared by dropping dilute solution of supramolecular metallogels formed in a mixture of MeOH and  $\text{H}_2\text{O}$  ( $1:1\text{ v/v}$ ) on glasses following by spinning, drying, and coating them with a thin layer of Pt to increase the contrast.

**Temperature-dependent Isodesmic model.** The isodesmic model assumes a single equilibrium constant  $K_e$  during all aggregation steps. It is also known as the equal- $K$  model.<sup>1</sup> For an isodesmic aggregation pathway, the experimental  $\alpha_{\text{agg}}$  values can be related to temperature by a sigmoidal relation. The sigmoidal function for  $\alpha$  ( $0 \leq \alpha \leq 1$ ) can generally be expressed as Eq. (1):

$$\alpha(T) \cong \frac{1}{1 + \exp\left[-0.908\Delta H \frac{T - T_m}{RT_m^2}\right]} \quad (\text{eq. 1})$$

where  $T_m$  is melting temperature when  $\alpha = 0.5$ ,  $\Delta H$  is the molar enthalpy release related to the formation of non-covalent intermolecular interactions, and R is the universal gas constant.

**Preparation of gel. 1** (5 mg, 0.78 mmol) and  $\text{Ln}(\text{NO}_3)_3$  (3.0 equivalent) with different Eu/Tb molar ratios, and the mixture of MeOH/water (v/v, 1:1) 500  $\mu\text{L}$  of solvent was added. The mixture was sonicated to form the metallogel, followed by heating at 60 °C for 5 minutes in an oil bath, which was then allowed to cool gradually in the same oil bath to room temperature. Gels were left to stabilize overnight before measurements were performed. The vial inverting method was employed for determining the CGC of the samples. Following the above procedure, the gels were prepared with the provided concentrations in vials. The CGCs were determined as the samples did not flow for 60 s after the vials were inverted at room temperature.

## Material synthesis

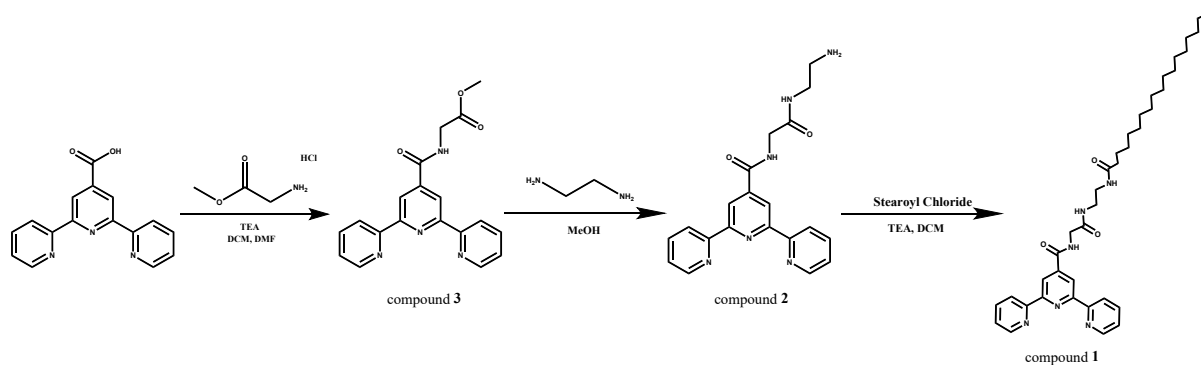
All chemical reagents were purchased commercially without further purification unless otherwise noted.

**Synthesis of compound 3.** terpyridine-4'-carboxylic acid(0.1 g, 0.36 mmol),glycine-methyl ester(0.054 g, 0.43 mmol), HOBt(0.0487 g, 0.36 mmol), EDC·HCl(0.104 g, 0.54 mmol) was added to a 100 mL round bottom flask. Anhydrous DCM(10 mL), DMF(2.5 mL) was then injected, and the reaction mixture was stirred at room temperature. Triethylamine (TEA, 0.15 mL, 1.08 mmol) was added slowly at 0 °C. The reaction mixture was stirred for 1h and was heated up to room temperature. After stirring for 2days at room temperature, the mixture was extracted with EA. The combined organics were washed with brine, dried Magnesium sulfate(MgSO<sub>4</sub>) and concentrated. The resulting crude product was purified by recrystallization from EA and Hexane to give Compound **3** (90 %) white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ= 8.88(s, 2H, Ar), 8.76(m, 2H, Ar), 8.65(d, 2H, Ar), 7.93(td, 2H,Ar), 7.41(ddd, 2H, Ar), 7.19(s, 1H, NH), 4.35(d, 2H,CH<sub>2</sub>), 3.85(s,3H, CH<sub>3</sub>). <sup>13</sup>C-NMR(125 MHz, CDCl<sub>3</sub>) δ; 170.10, 165.90, 156.54, 155.36, 149.26, 143.07, 136.96, 124.21, 121.33, 118.40, 52.57, 41.82 ESI-MS (m/z): Calculated for C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub> [M+H]<sup>+</sup> 349.37, Found [M+H]<sup>+</sup> 349 .33, [2M+Na<sup>+</sup>] 718.75.

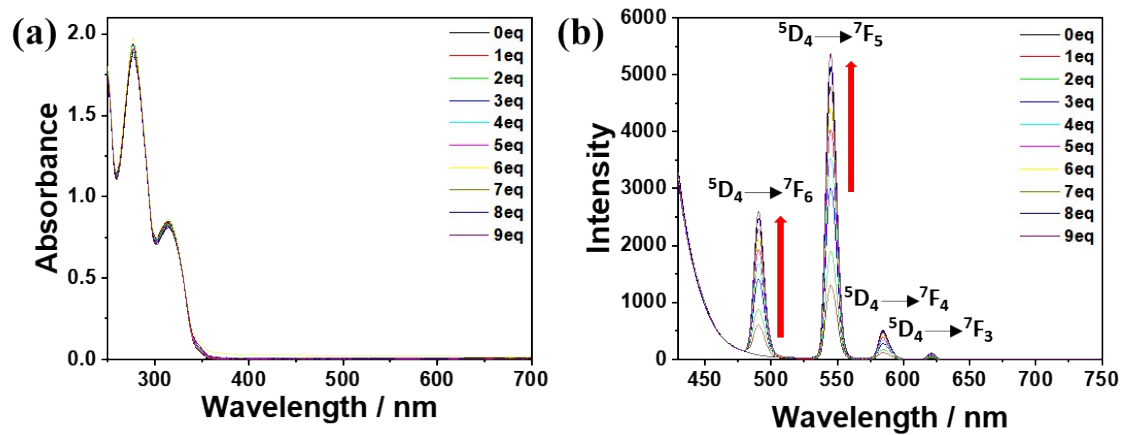
**Synthesis of compound 2.** Compound **3** (0.5 g, 1.43 mmol) was dissolved in MeOH(50 mL) and ethylenediamine(2.3 mL, 3.44 mmol) was added to a flask at 0 °C. The reaction mixture was stirred for 30 minutes and was heated up to room temperature and stirred for 1days. The resulting crude product was purified by recrystallization from toluene, washed with ether. Yield was (95 %). <sup>1</sup>H NMR(300 MHz, DMSO-*d*<sub>6</sub>) δ9.35(s, 1H,NH), 8.88(s, 2H, Ar), 8.78(m, 2H, Ar), 8.67(d, 2H, Ar), 8.06(td, 2H, Ar), 7.99(s, 1H,NH), 7.55(m, 2H, Ar), 3.93(d, 2H, CH<sub>2</sub>), 3.10(q, 3H, CH<sub>2</sub>), 2.59(t, 2H, NH<sub>2</sub>). <sup>13</sup>C-NMR(125 MHz, CDCl<sub>3</sub>) δ; 169.01, 165.46, 156.15, 155.05, 149.87, 144.23, 138.05, 125.22, 121.44, 118.94, 43.35, 42.64, 41.70 ESI-MS (m/z): Calculated for C<sub>20</sub>H<sub>21</sub>N<sub>6</sub>O<sub>2</sub> [M+H]<sup>+</sup> 377.43, [2M+H]<sup>+</sup> 753.85, Found [M+H]<sup>+</sup> 377.25, [2M+Na]<sup>+</sup> 752.83.

**Synthesis of compound 1.** Compound **2** (0.1 g, 0.27 mol), Stearoyl chloride(0.12 mL, 0.35 mmol) was dissolved in DCM(10 mL) and triethylamine (TEA, 0.2 mL, 1.35 mmol) was added to a 100 mL round bottom flask at 0 °C. The reaction mixture was stirred for 30 minutes and was heated up to room temperature. After stirring for 1days at room temperature, the mixture was extracted with DCM. The combined organics were washed with water, dried Magnesium sulfate(MgSO<sub>4</sub>) and concentrated. The resulting crude product was purified by recrystallization from DCM and ether to give white solid, compound **1** (84 %). <sup>1</sup>H NMR(300MHz, CDCl<sub>3</sub>) δ8.79(s, 1H, Ar), 8.70(s, 2H, Ar), 8.55(d, 2H, Ar), 7.87(td, 2H, Ar), 7.73(s, 1H, NH), 7.38(ddd, 2H, Ar), 7.25(s, 1H,NH), 6.40(s, 1H, NH), 4.22(d,

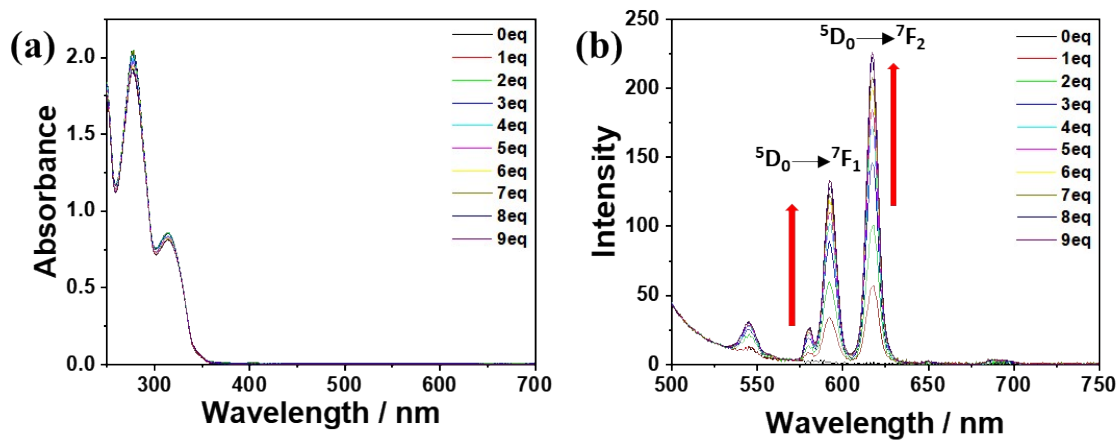
2H,CH<sub>2</sub>), 3.47(s,4H, 2CH<sub>2</sub>), 1.24(m, 32H,16CH<sub>2</sub>),0.89(m, 2H, CH<sub>3</sub>) ;<sup>13</sup>C-NMR(125 MHz, CDCl<sub>3</sub>) δ; 174.74, 169.53, 166.46, 158.28, 155.20, 149.13, 142.68, 136.90, 124.20, 121.28, 118.38, 45.84, 43.92, 40.30, 39.45, 36.64, 31.93, 29.71, 29.67, 29.62, 29.51, 29.37, 29.34, 29.30, 25.65, 22.70, 41.13, 8.68  
ESI-MS (m/z): Calculated for C<sub>38</sub>H<sub>55</sub>N<sub>6</sub>O<sub>3</sub> [M+H]<sup>+</sup> 643.90, [2M+Na]<sup>+</sup> 1308.77, Found [M+H]<sup>+</sup> 643.42, [2M+Na]<sup>+</sup> 1307.08.



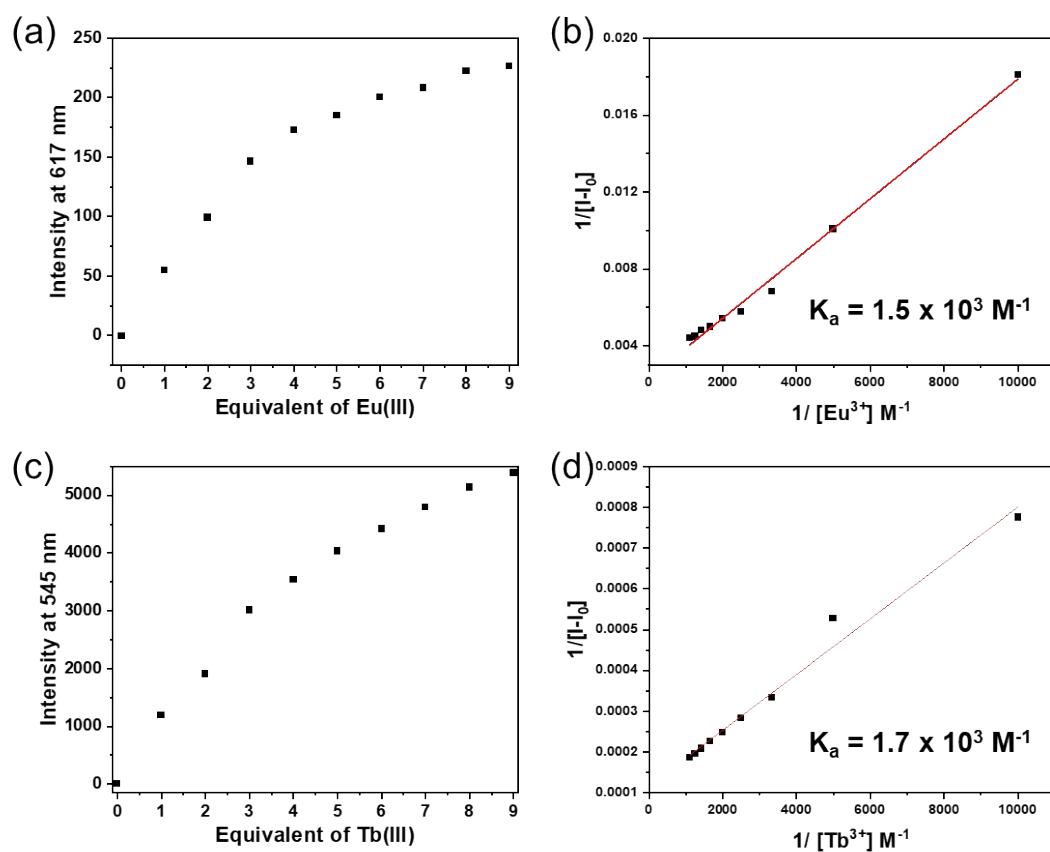
**Scheme S1.** Synthesis route to compound 1.



**Fig. S1** (a) UV-vis absorption and (b) emission spectra of **1** ( $1 \times 10^{-6}$  M) upon titrating with  $\text{Tb}(\text{NO}_3)_3$  (0-9.0 equiv.) in methanol at 298 K ( $\lambda_{\text{ex}} = 322$  nm).

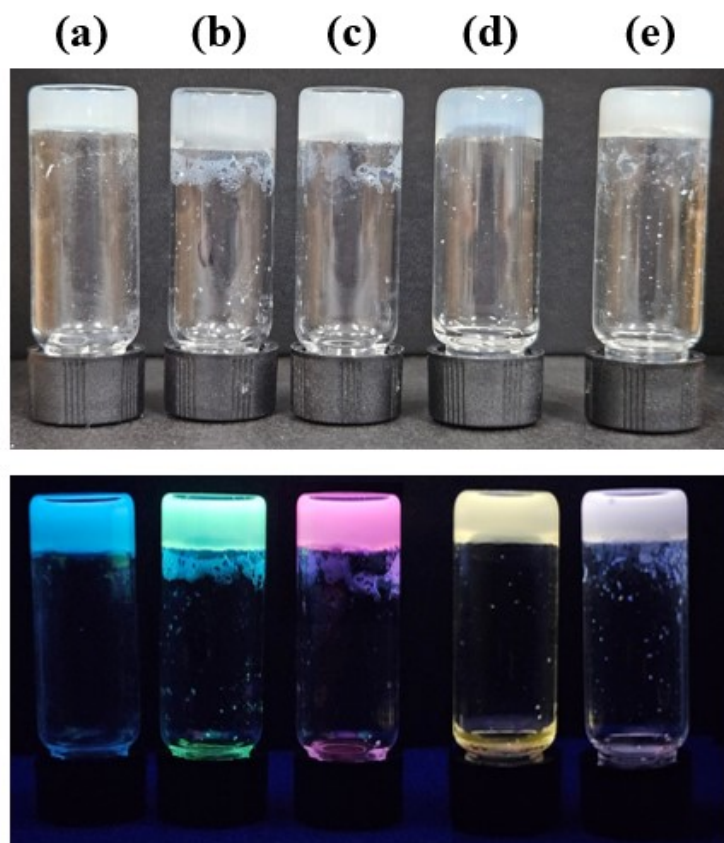


**Fig. S2** (a) UV-vis absorption and (b) emission spectra of **1** (1 × 10<sup>-6</sup> M) upon titrating with Eu(NO<sub>3</sub>)<sub>3</sub> (0-9.0 equiv.) in methanol at 298 K ( $\lambda_{\text{ex}} = 322$  nm).

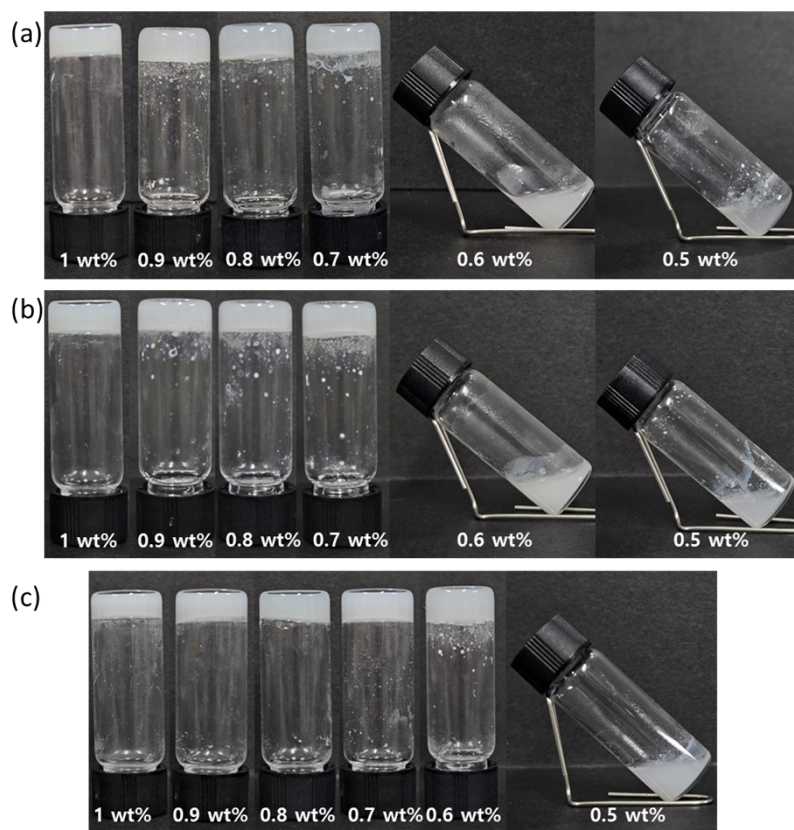


**Fig.S3** Plot of emission intensity of **1** ( $1 \times 10^{-6}$  M) upon titrating with (a)  $Eu(NO_3)_3$  and (c)  $Tb(NO_3)_3$  (0-9.0 equiv.) in methanol at 298 K. Benesi-Hildebrand plot to calibrate association constant of **1** to (b)  $Eu(III)$  and (d)  $Tb(III)$  ions.

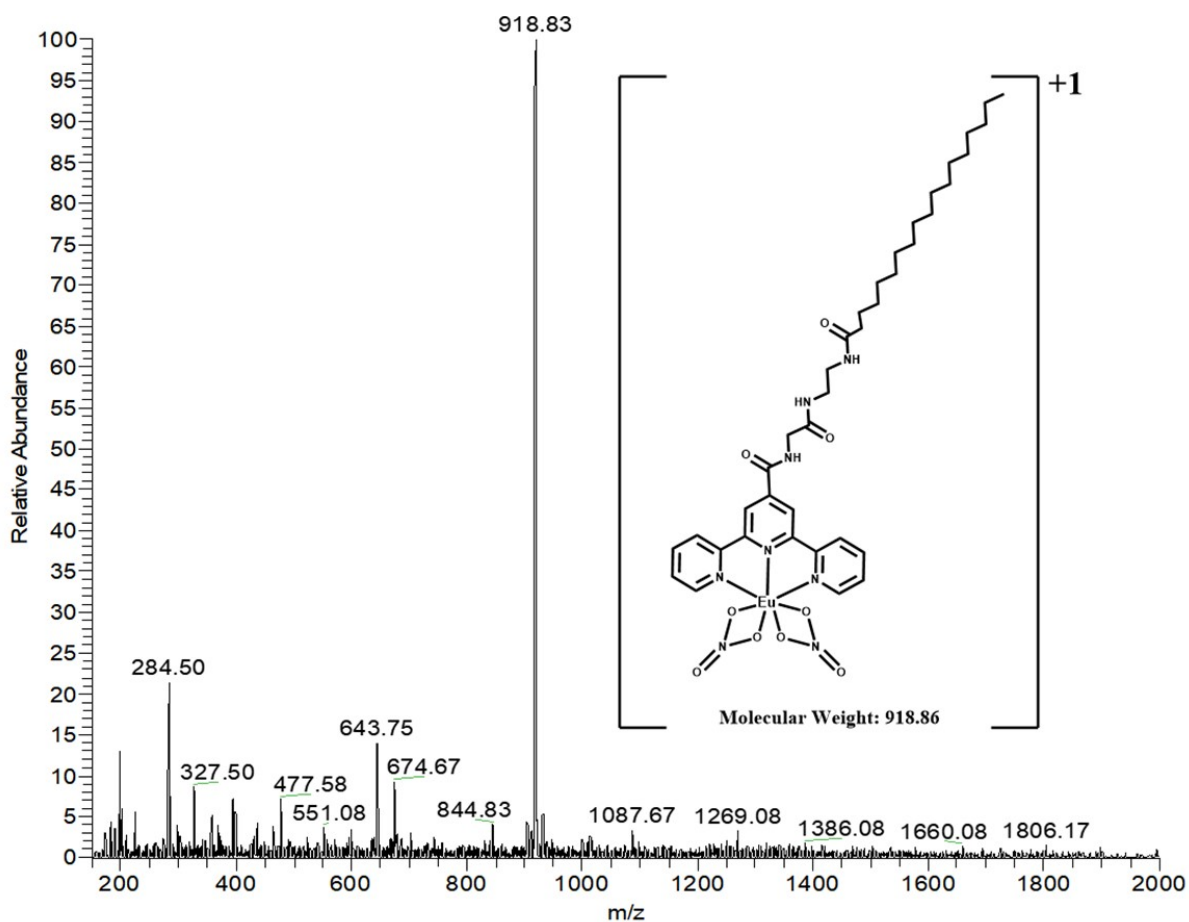




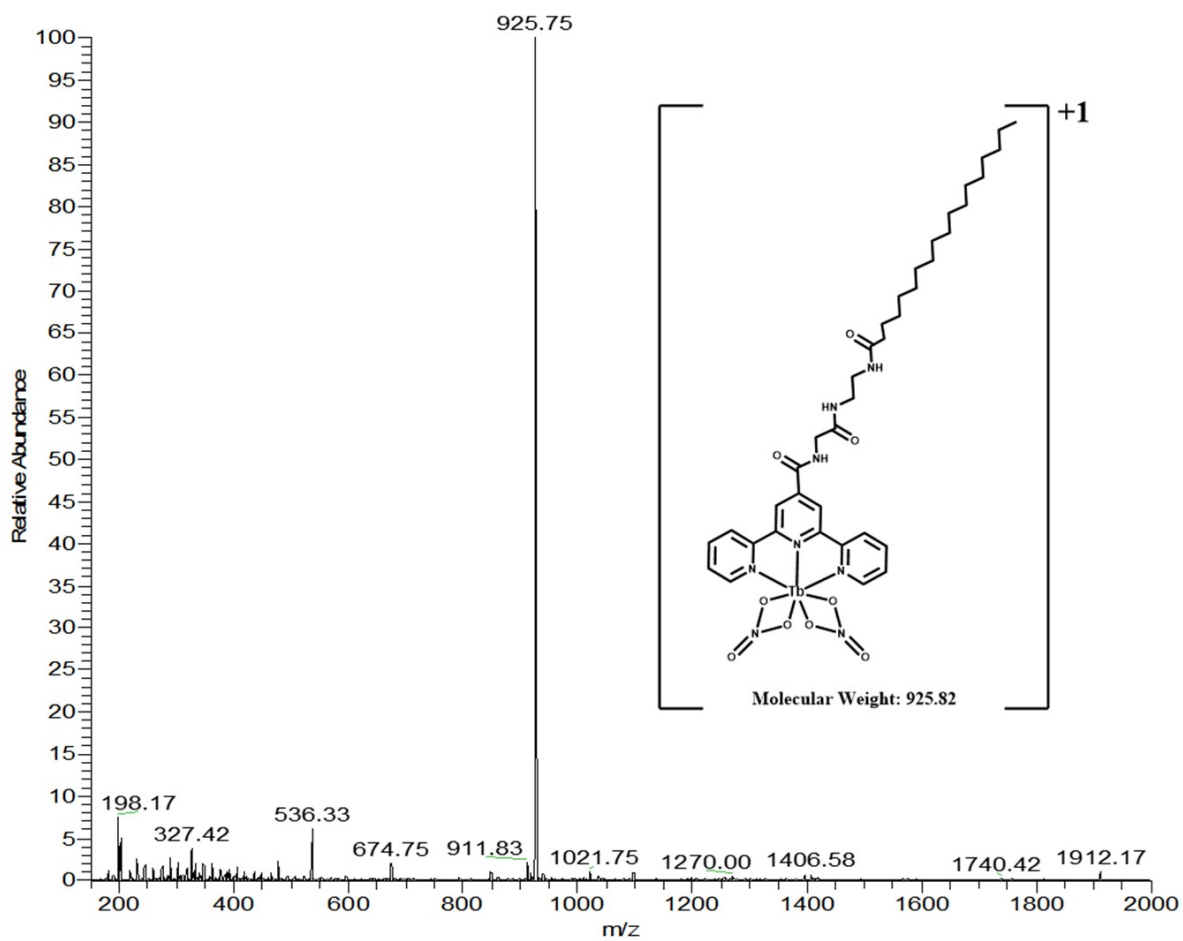
**Fig. S4** Photograph of supramolecular metallogels (1 wt%) at various molar ratios of Eu:Tb in the mixture of MeOH/water (v/v, 1:1). (a) **1** only, (b) Eu:Tb=0:10, (c) Eu:Tb=10:0, (d) Eu:Tb=6:4, (e) Eu:Tb=12:13.



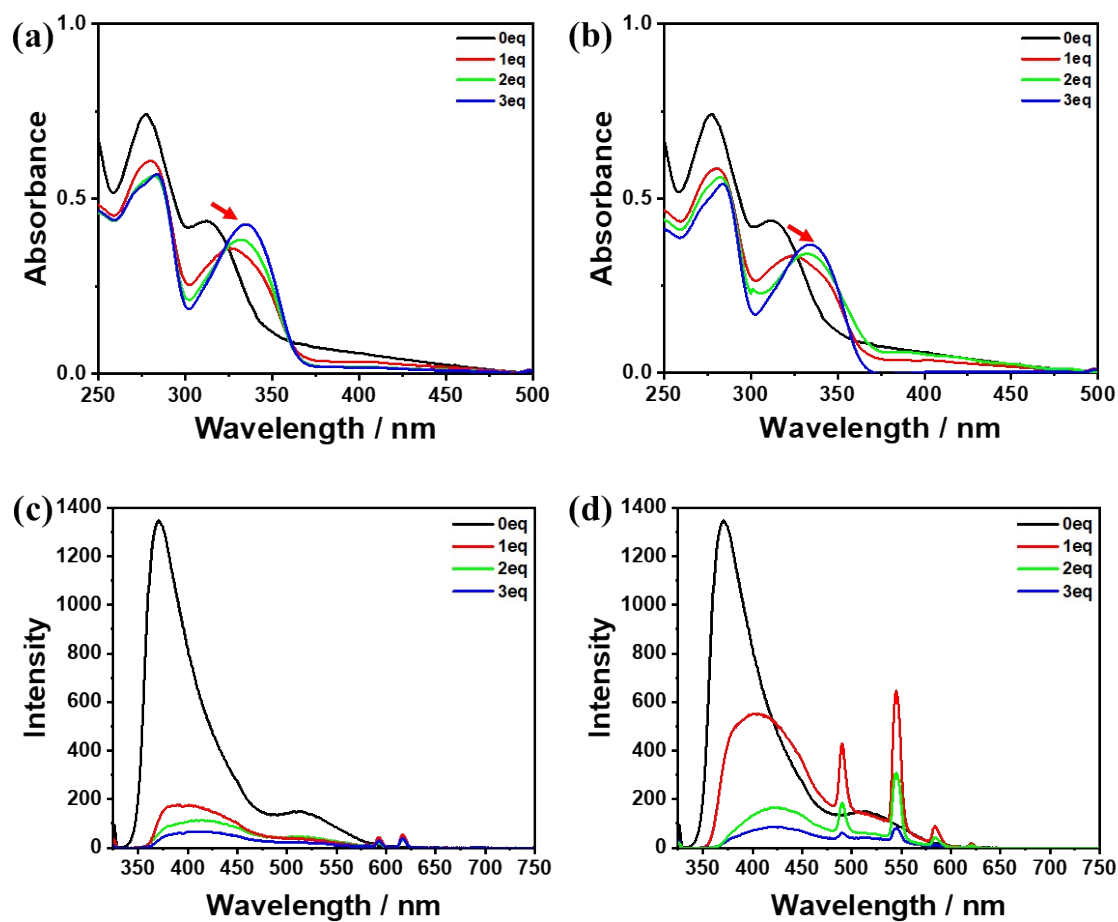
**Fig. S5** Photograph of supramolecular gels at different concentrations (0.5-1.0 wt%) of (a) **1** only, (b) **1-Eu**, and (c) **1-Tb** in the mixture of MeOH/water (v/v, 1:1).



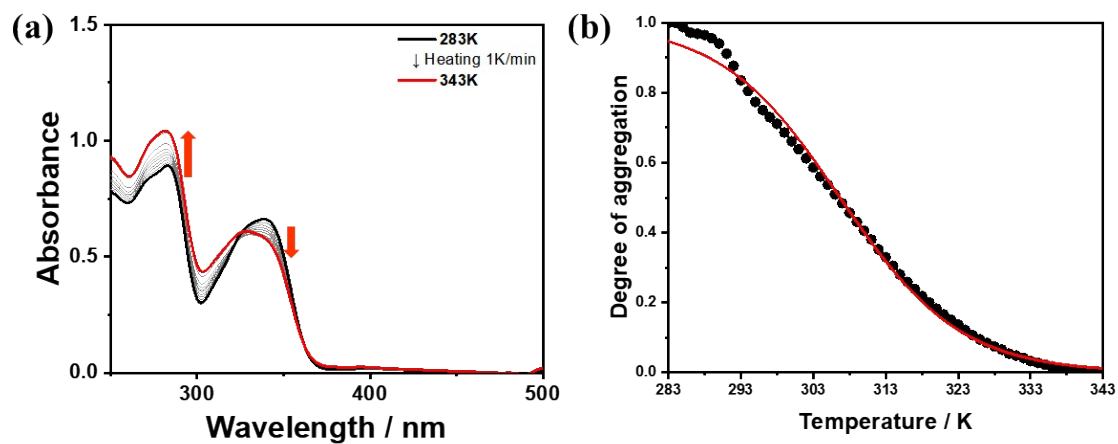
**Fig. S6** ESI-MS spectrum of **1** with Eu(III).



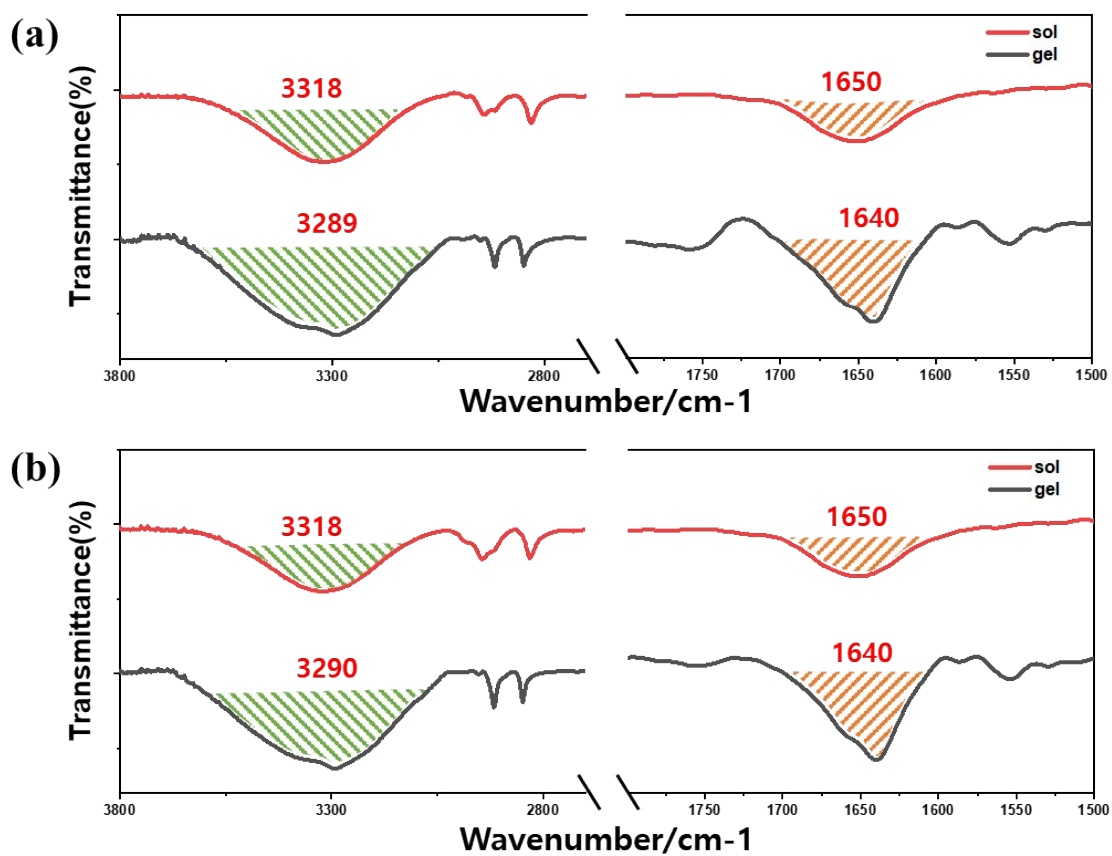
**Fig. S7** ESI-MS spectrum of **1** with Tb(III).



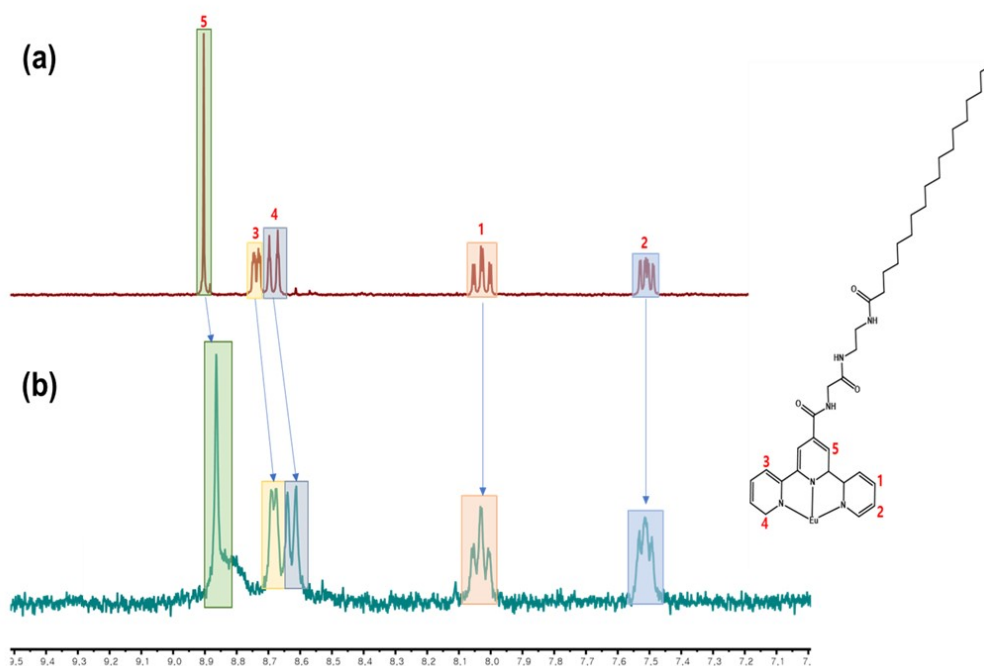
**Fig. S8** UV-vis absorption and emission spectra of **1** (0.1 mM) with (a and c) Eu(III) and (b and d) Tb(III) ions at different concentrations (0-3.0 equiv.) ( $\lambda_{\text{ex}} = 322$  nm).



**Fig. S9** (a) Temperature-dependent UV-vis spectra changes of **1-Tb** (0.1 mM) in the mixture of MeOH and water (v/v, 1:1). (b) Heating curve of **1-Tb**, monitoring the absorption at 340 nm. The red line denotes the isodesmic fitting.

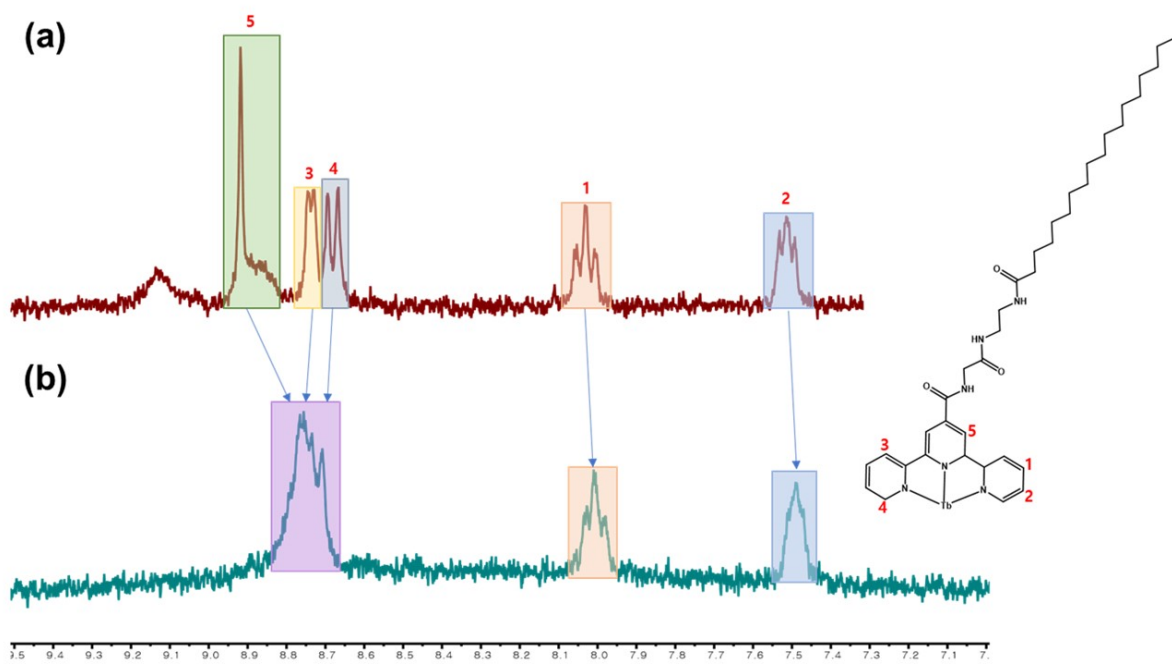


**Fig. S10** FT-IR spectra of (a) 1-Eu and (b) 1-Tb in sol (red line, MeOH) and gel (black line, MeOH/water) states.

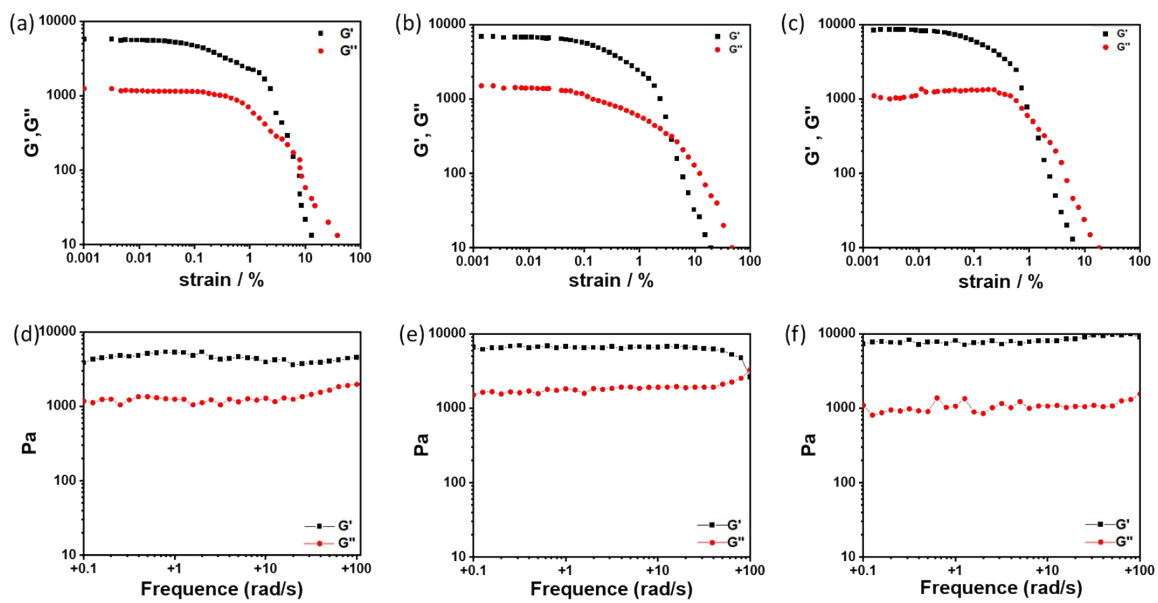


**Fig. S11**  $^1\text{H}$  NMR spectra of the (a) sol ( $\text{MeOH-d}_4$ ) and (b) gel ( $\text{MeOH-d}_4:\text{D}_2\text{O}$ ) states for **1-Eu** (6 mM) at 298 K.

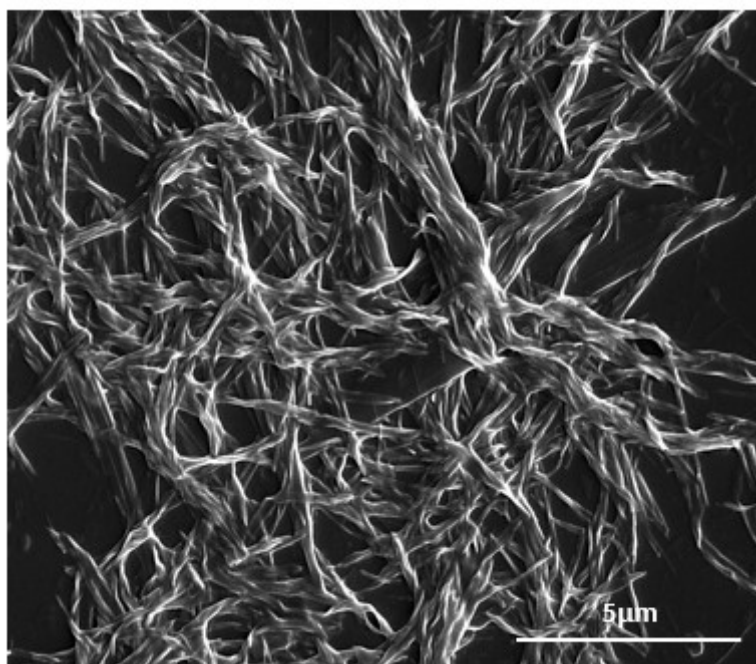




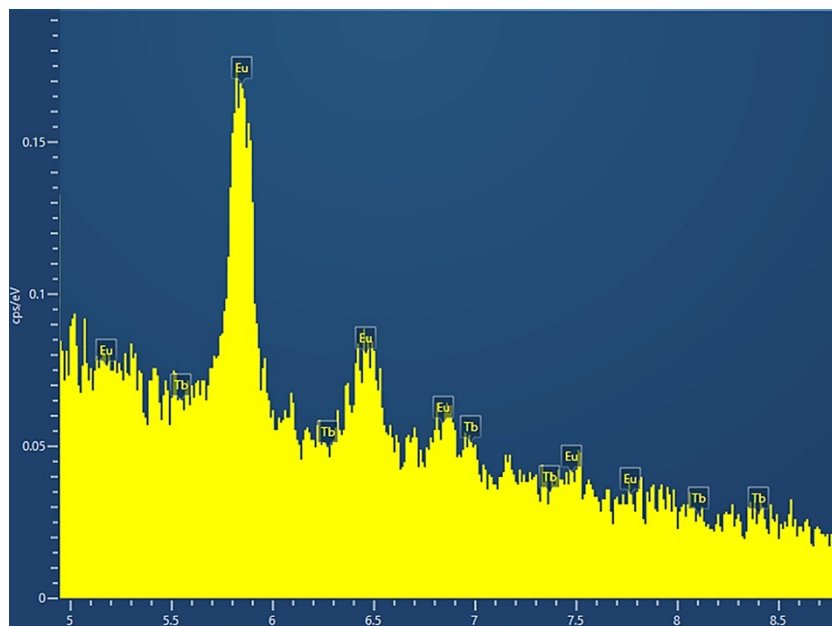
**Fig. S12** <sup>1</sup>H NMR spectra of the (a) sol (MeOH-d<sub>4</sub>) and (b) gel (MeOH-d<sub>4</sub>:D<sub>2</sub>O) states for 1-Tb (6 mM) at 298 K.



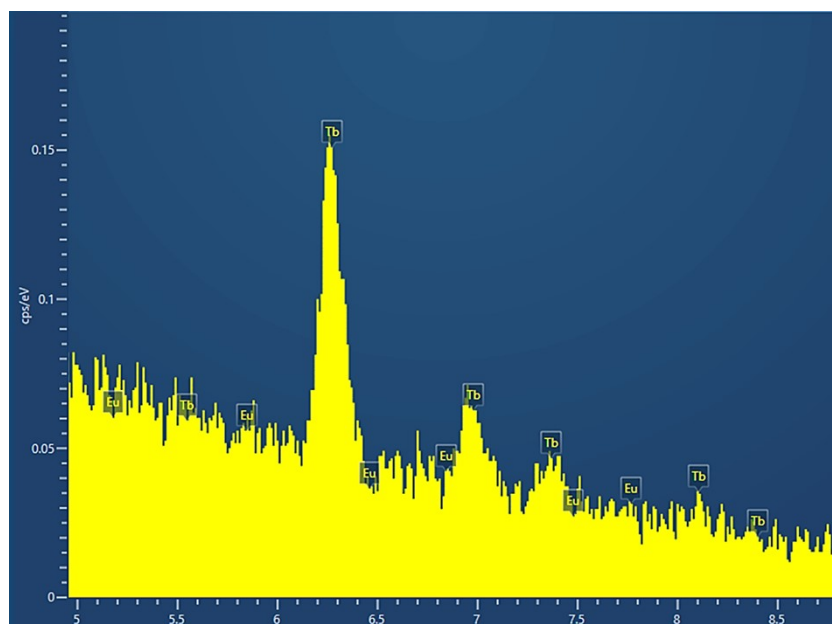
**Fig. S13** Rheological properties of supramolecular gels (1 wt%). Strain (frequency = 0.01 rad/s) and frequency (strain = 0.1 %) sweets of (a,d) **1**, (b,e) **1-Eu**, and (c,f) **1-Tb**.



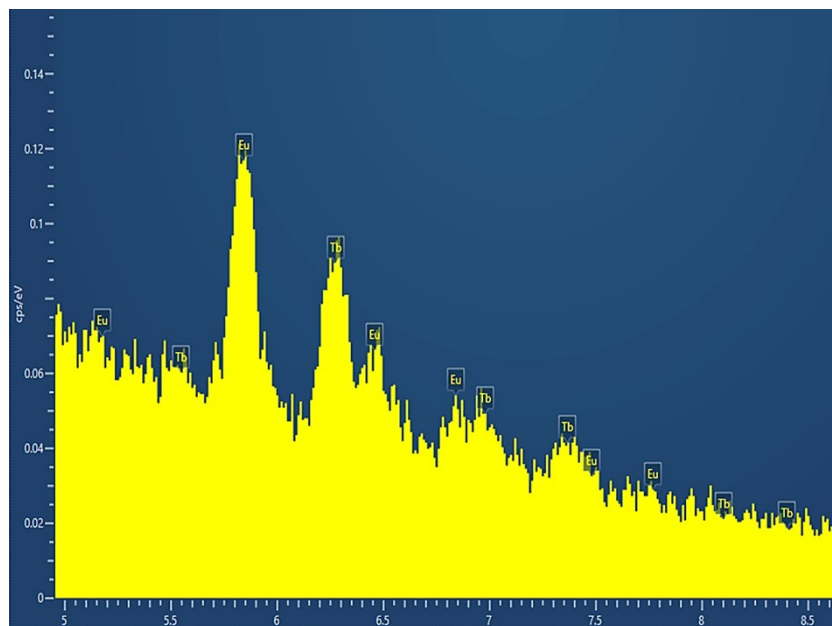
**Fig. S14** SEM image of yellow gel (1 wt%).



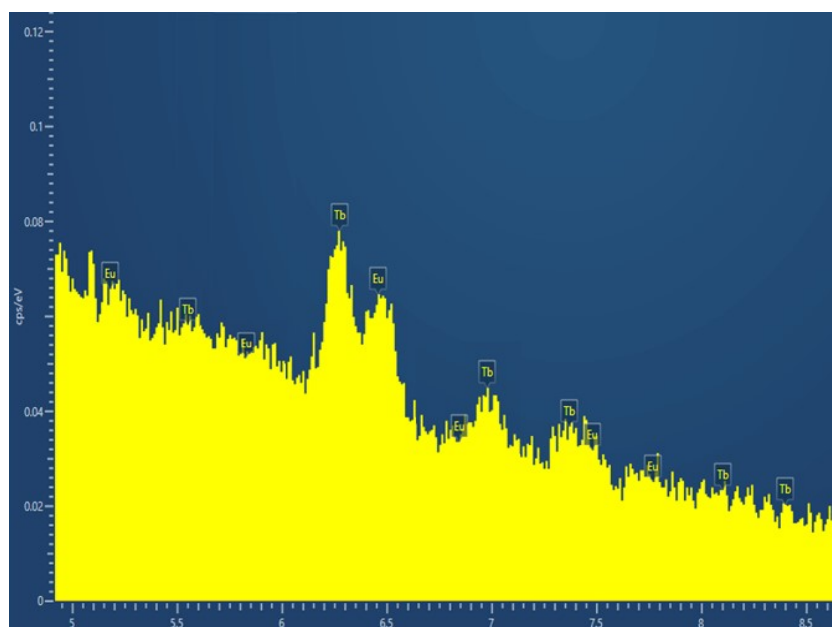
**Fig. S15** EDXS of 1-Eu gel showing the presence of Eu(III) in xerogel.



**Fig. S16** EDXS of 1-Tb gel showing the presence of Tb(III) in xerogel.



**Fig. S17** EDXS of yellow emissive gel showing the presence of Tb(III) and Eu(III) in xerogel.



**Fig. S18** EDXS of white emissive gel showing the presence of Tb(III) and Eu(III) in xerogel.

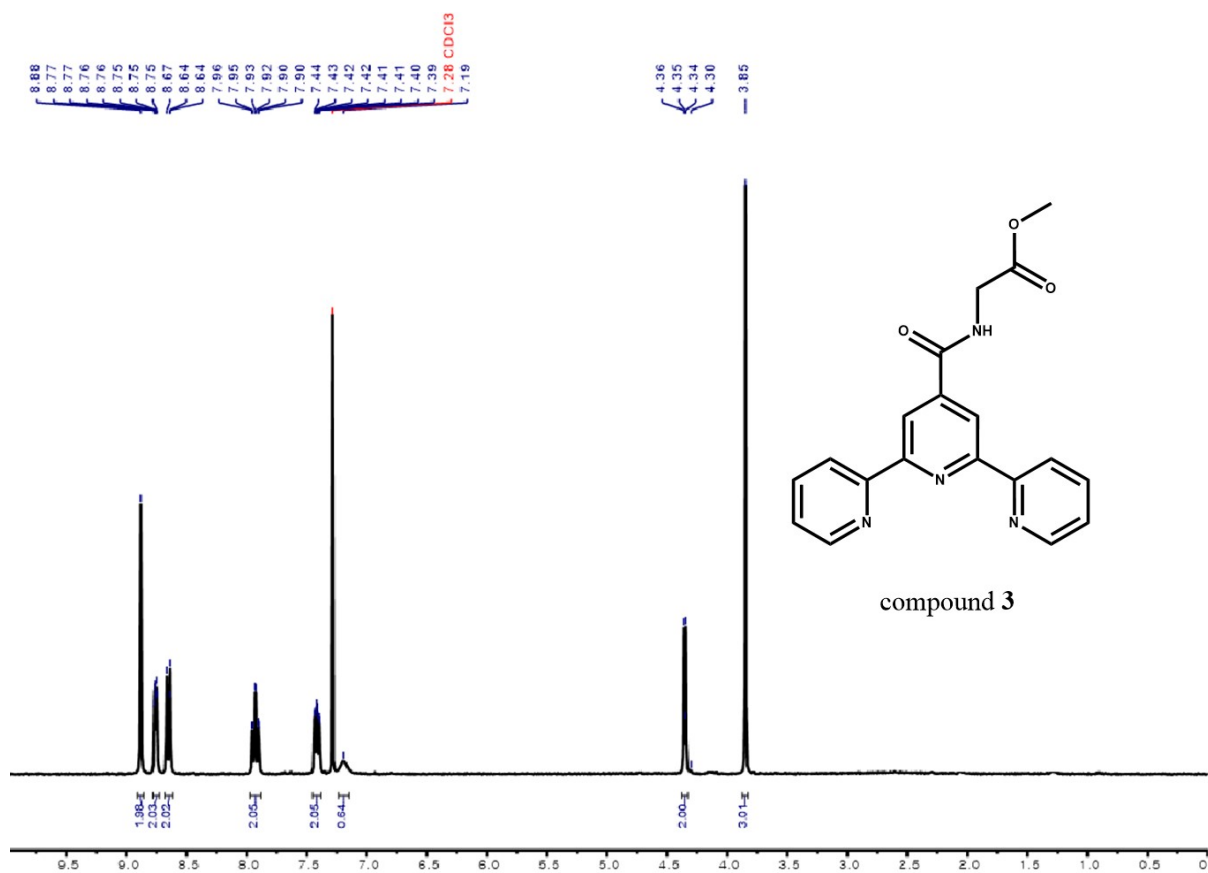
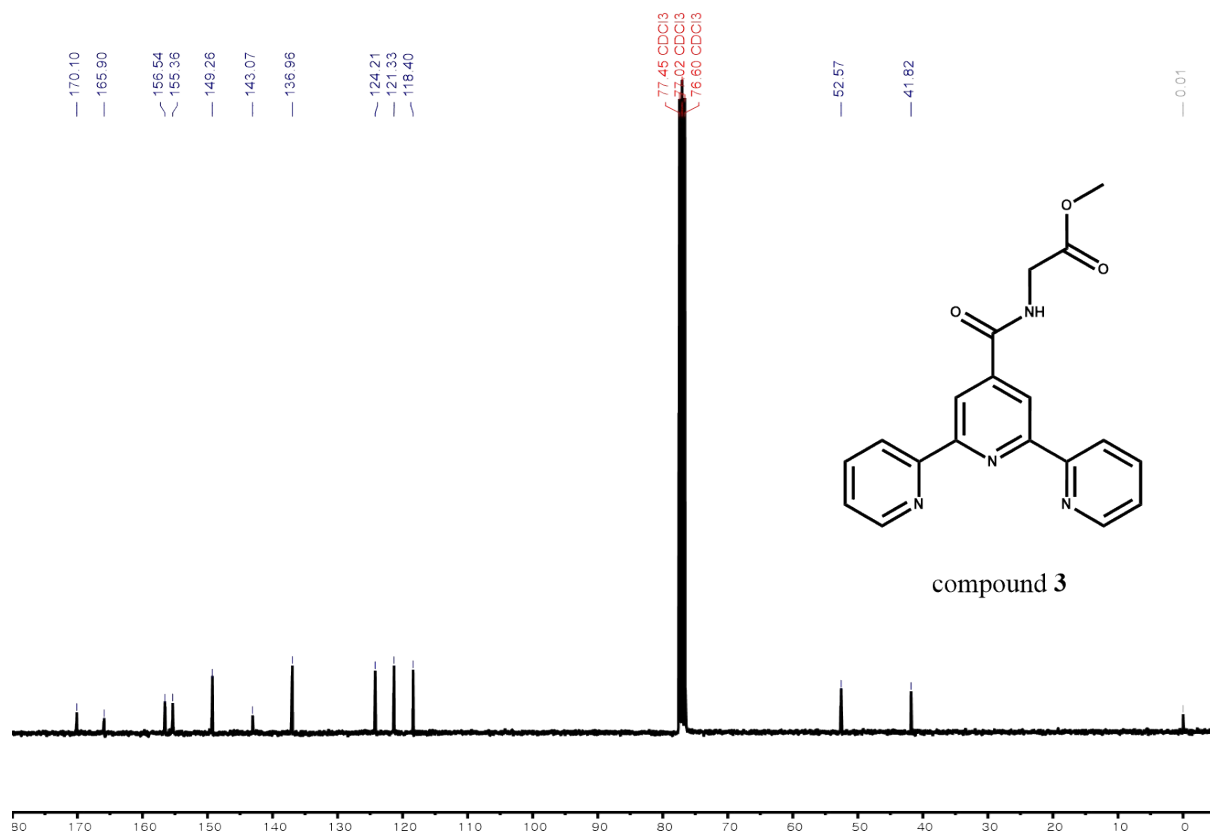


Fig. S19  $^1\text{H}$  NMR spectrum (300 MHz) of compound 3 in  $\text{CDCl}_3$  at 298 K.



**Fig. S20**  $^{13}\text{C}$  NMR spectrum (125 MHz) of compound 3 in  $\text{CDCl}_3$  at 298 K.

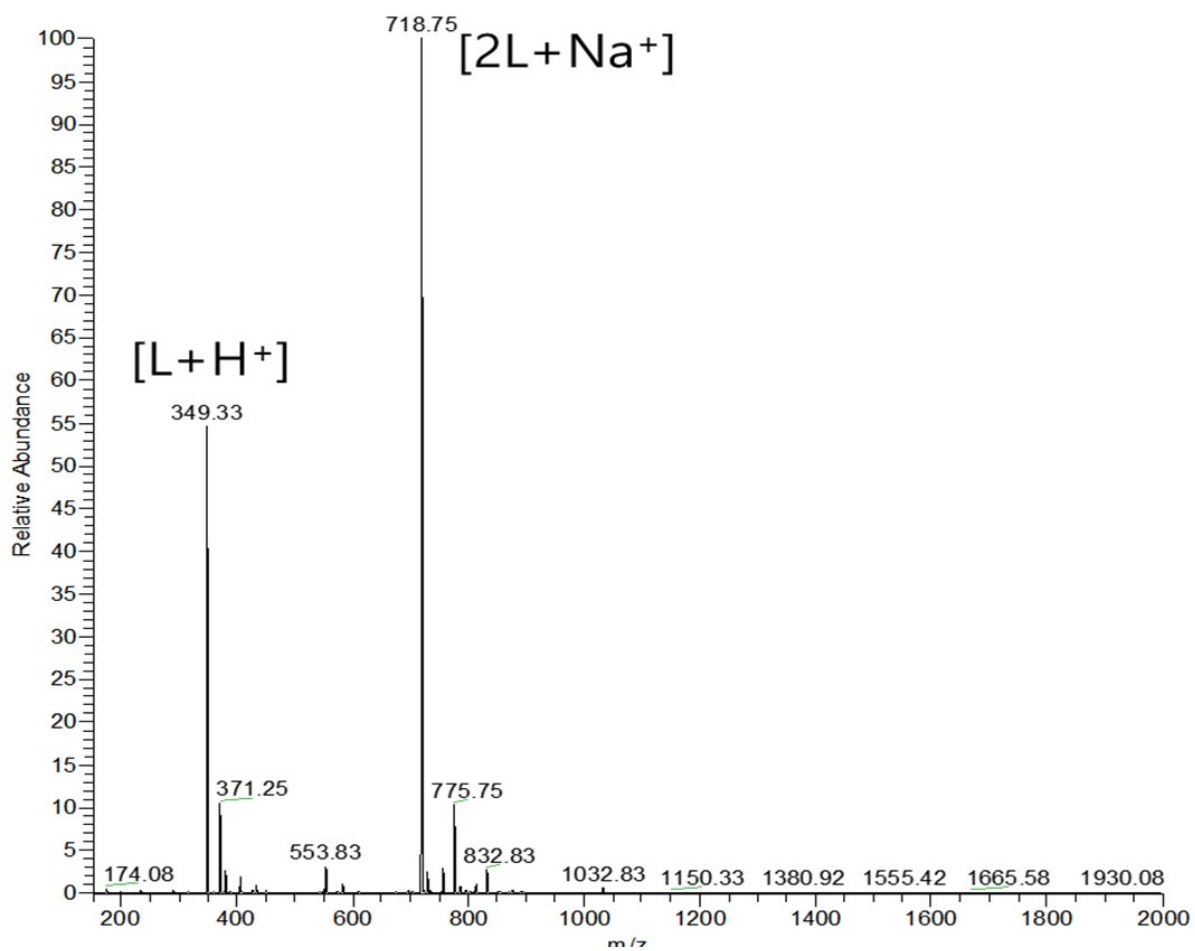
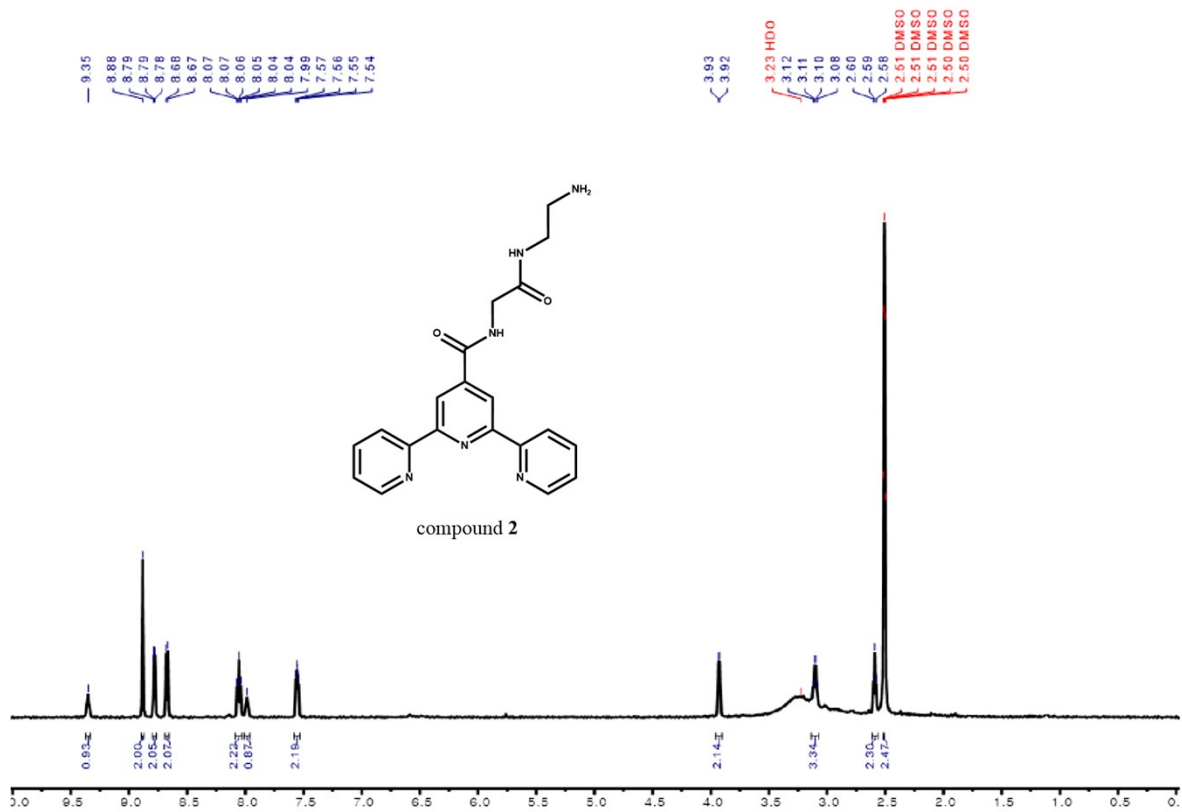
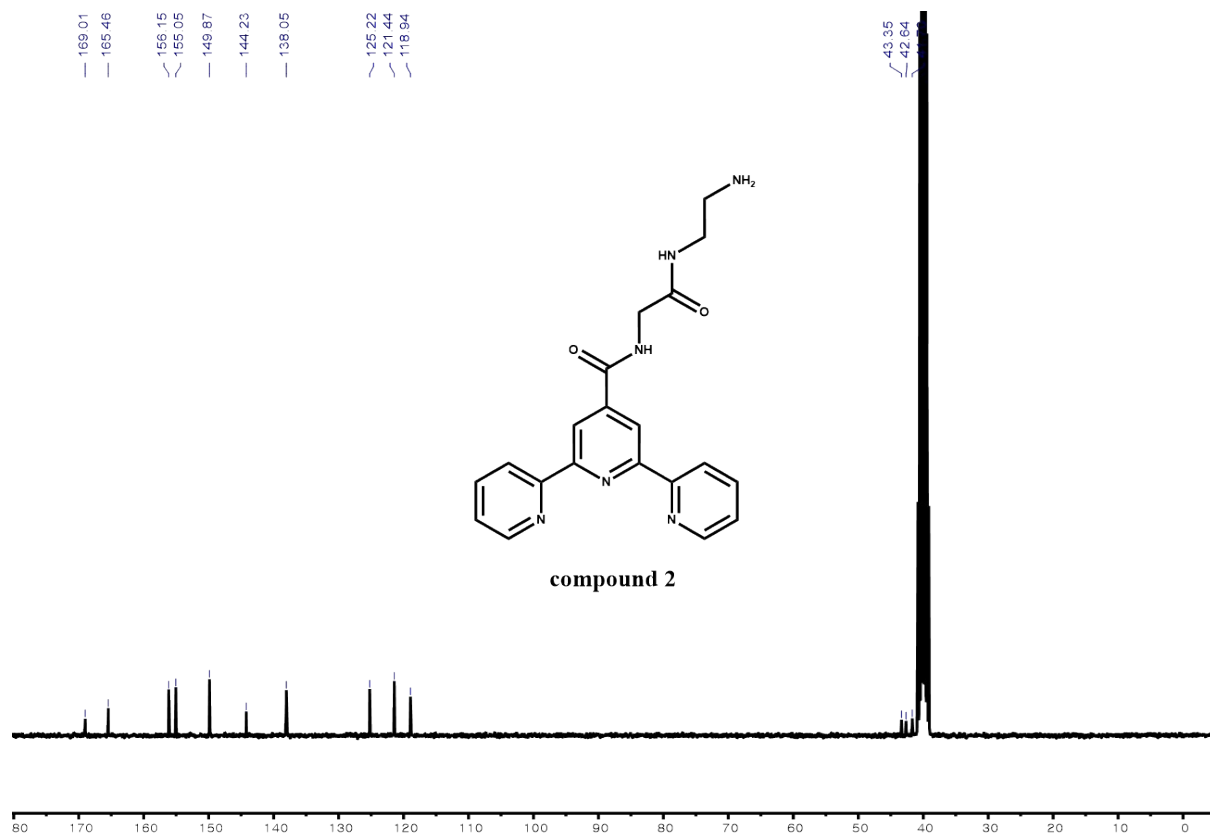


Fig. S21 ESI-Mass Spectrum of compound 3 in MeOH.

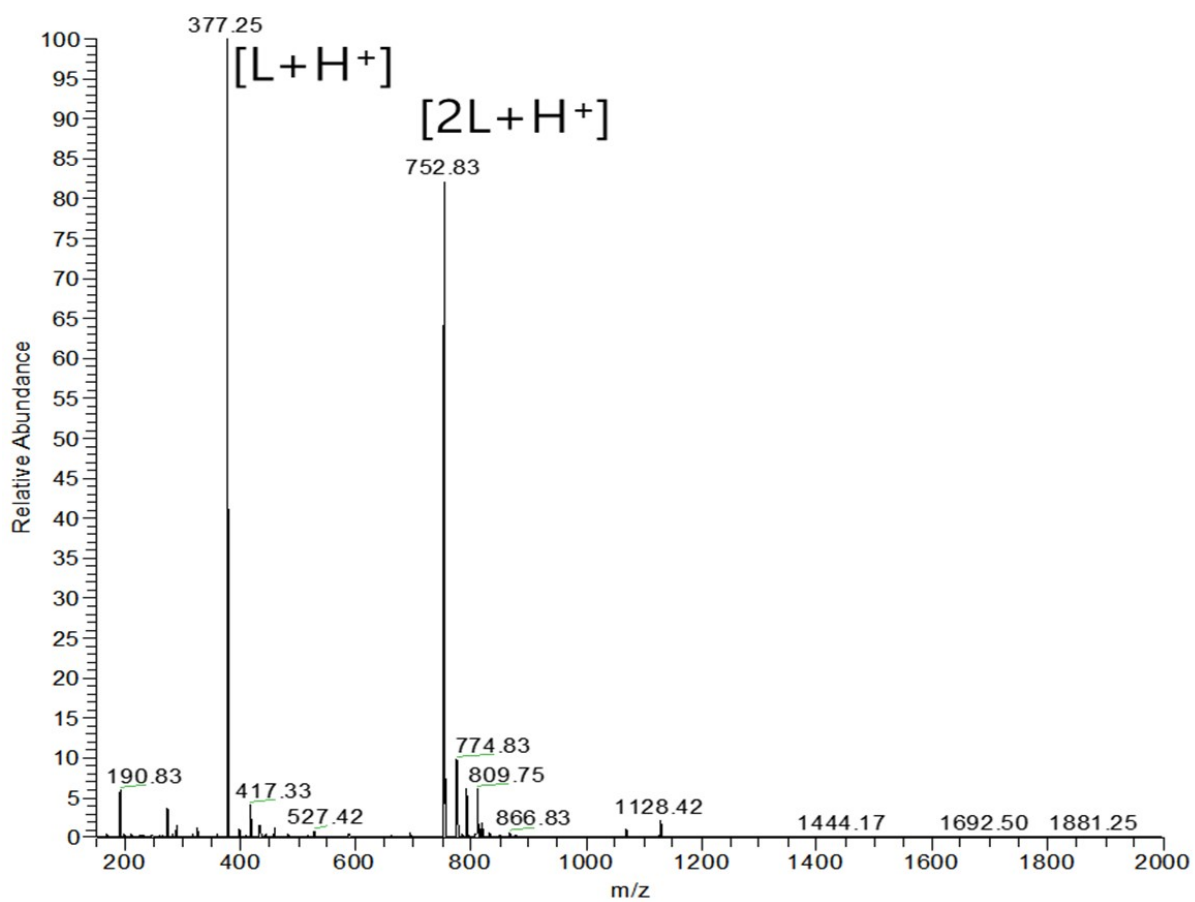




**Fig. S22**  $^1\text{H}$  NMR spectrum (300 MHz) of compound **2** in  $\text{DMSO-}d_6$  at 298 K.



**Fig. S23**  $^{13}\text{C}$  NMR spectrum (125 MHz) of compound 2 in DMSO- $d_6$  at 298 K.



**Fig. S24** ESI-Mass Spectrum of compound **2** in MeOH.

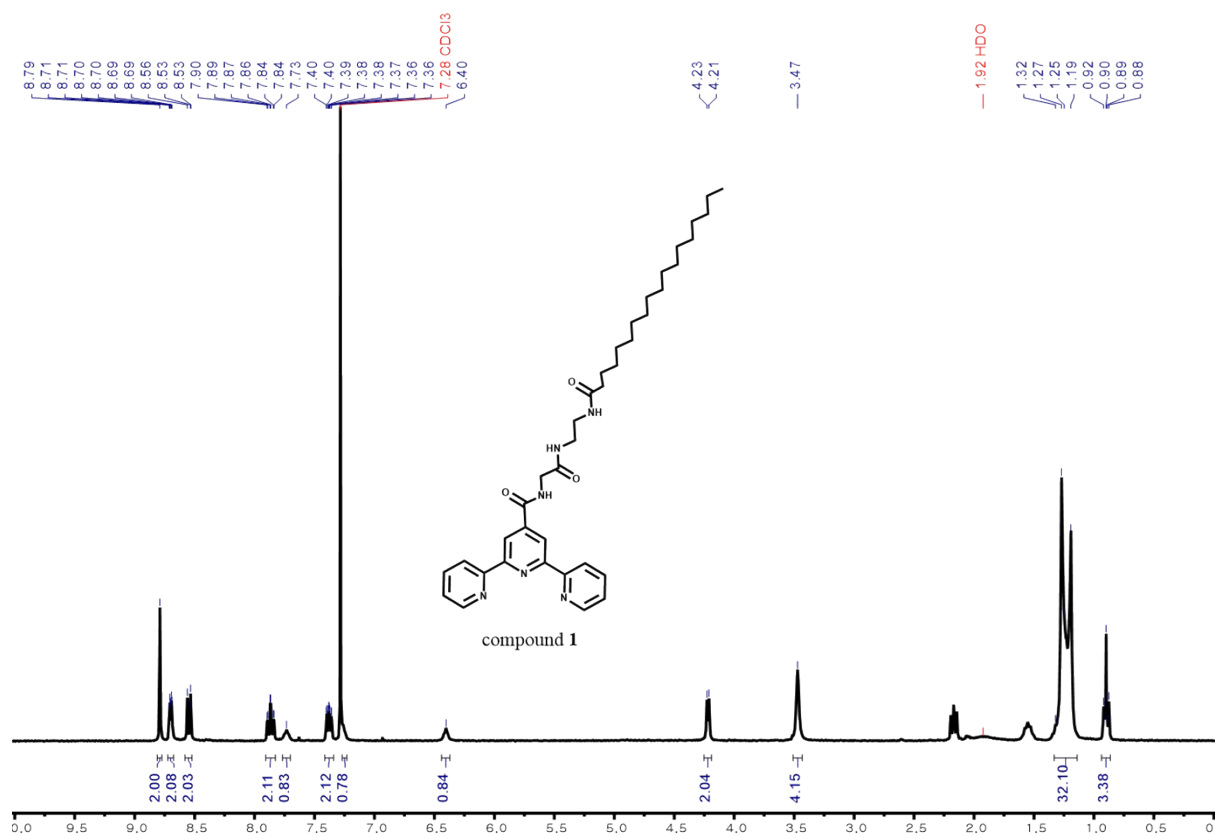
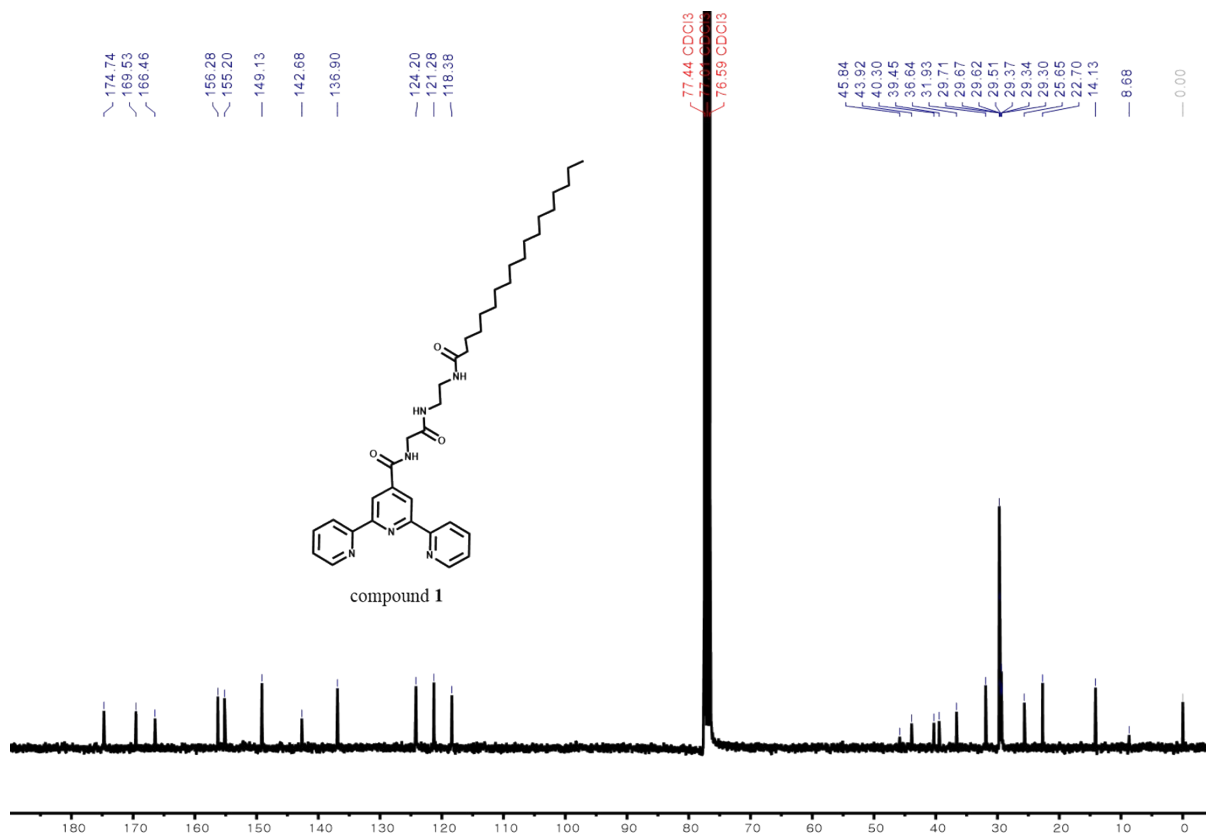


Fig. S25 <sup>1</sup>H NMR spectrum (300 MHz) of compound 1 in CDCl<sub>3</sub> at 298 K.



**Fig. S26**  $^{13}\text{C}$  NMR spectrum (125 MHz) of compound **1** in  $\text{CDCl}_3$  at 298 K.

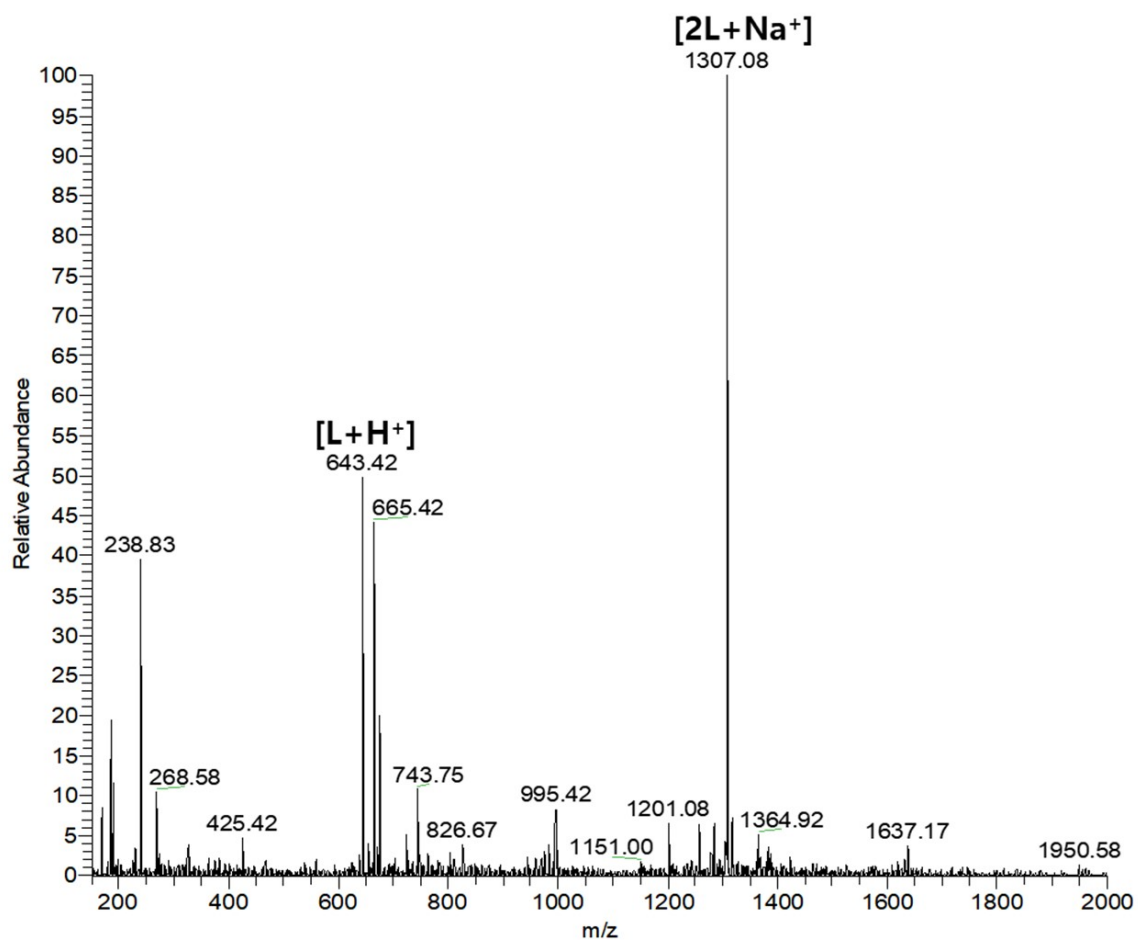


Fig. S27 ESI-Mass Spectrum of compound 1.

## References

1. M. M. Smulders, M. M. Nieuwenhuizen, T. F. de Greef, P. van der Schoot, A. P. Schenning, E. W. Meijer, *Chem.Eur.J.*, 2010, **16**, 362-367.