

Supporting Information

Healable luminescent self-assembly supramolecular metallogels possessing lanthanide (Eu/Tb) depended rheological and morphological properties

Miguel Martínez-Calvo^{1‡†}, Oxana Kotova^{1‡}, Matthias E. Möbius², Alan P. Bell³, Thomas McCabe¹, John J. Boland³, Thorfinnur Gunnlaugsson^{1}*

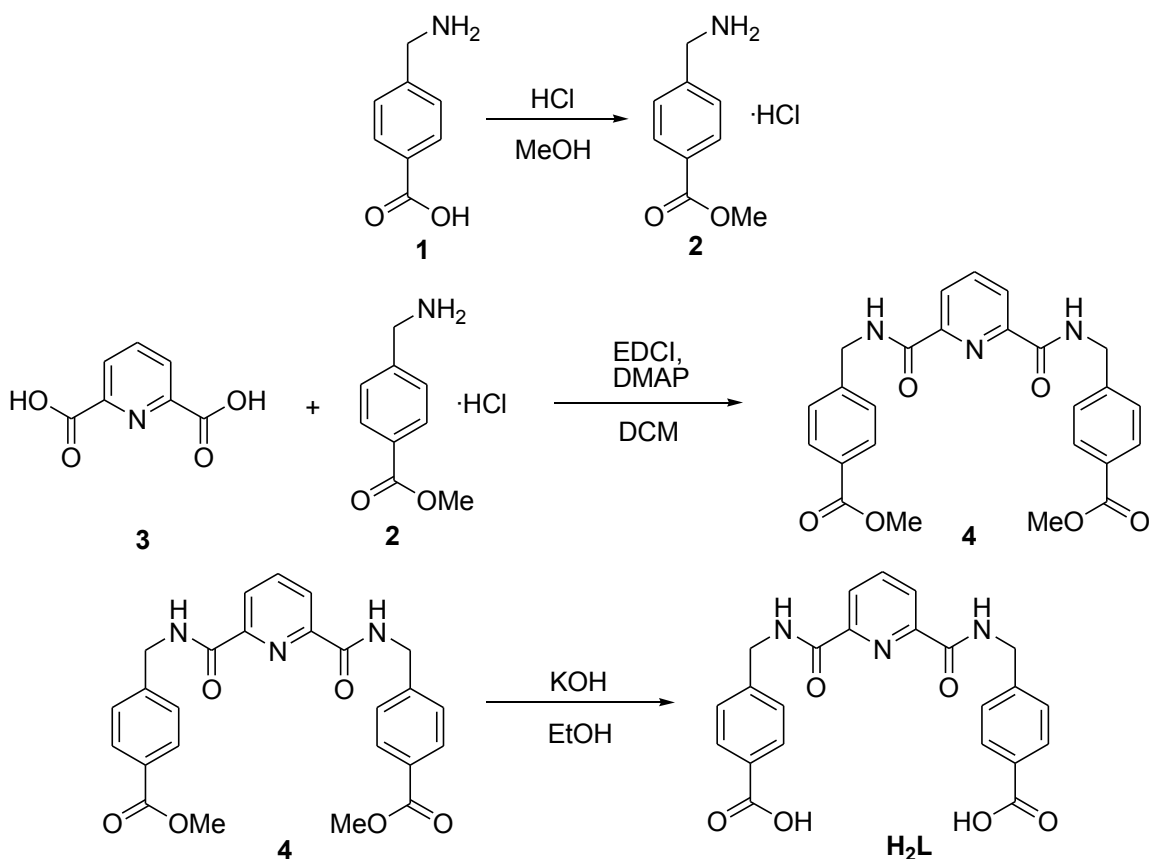
¹ School of Chemistry and Trinity Biomedical Sciences Institute, University of Dublin, Trinity College Dublin, Dublin 2 (Ireland)

² Sami Nasr Institute of Advanced Materials (SNIAM), School of Physics, University of Dublin, Trinity College Dublin, Dublin 2 (Ireland)

³ Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) and School of Chemistry, University of Dublin, Trinity College Dublin, Dublin 2 (Ireland)

Content:	Page
General synthetic procedure	S2-S5
Figures S1-S21	S7-S23
Tables S1-S7	S24-S28

General synthetic procedure



Scheme S1. Synthesis of the dipicolinic based dicarboxylic ligand **H₂L**.

Methyl 4-(aminomethyl)benzoate hydrochloride (**2**)

4-(aminomethyl)benzoic acid (6.05g, 0.040mmol) was dissolved in methanol (200mL). To this solution 6 mL of HCl (36%) were added in one portion, and the mixture was left refluxing overnight. After cooling to room temperature, the solvent was removed under reduced pressure and a white precipitate was formed, which was filtered and further washed with diethyleter. The solvent was fully removed under reduced pressure to yield a white solid (6.30g, 95%). m.p. 236 °C; ¹H-NMR (400MHz, (CD₃)₂SO): 8.68 (bs, 2H, NH₂), 7.96 (d, 2H, CH, *J* = 8.0 Hz), 7.65 (d, 2H, CH, *J* = 8.1 Hz), 4.09 (m, CH₂, *J*=5.6), 3.84 (s, 3H, CH₃); ¹³C-NMR (100 MHz, (CD₃)₂SO): 166.32, 139.86, 129.86, 129.64, 52.67, 42.11; IR(neat): 2961, 2880, 1719, 1596, 1478, 1465, 1435, 1282, 1190, 1112, 963, 863, 762, 702; HR-ESI-MS: *m/z* 166.10 [M + H]⁺;

Calculated for $C_9H_{13}NO_2$ $[M+H]^+$ 166.0868, Found 166.0909; Elemental analysis (calcd., found for $C_9H_{12}ClNO_2$): C (53.61, 53.55), H (6.00, 5.72), N (6.95, 6.88).

Dimethyl 4,4'-(((pyridine-2,6-dicarbonyl)bis(azanediyl))bis(methylene))dibenzoate (4)

A solution of 2,6-pyridyne dicarboxylic acid (**3**) (0.906g, 5.42mmol) in 150 mL of freshly distilled dichloromethane was allowed to cool in an acetone/ice bath for 15 minutes before adding **2** (1.791g, 10.84mmol), EDCI (5.196g, 27.11mmol) and DMAP (2.649g, 21.68mmol). The reaction mixture was left to slowly warm up to room temperature and left stirring overnight. The colour of the reaction mixture was changed from colourless to orange. The solvent was removed under reduced pressure before adding 80 mL of water. This gave rise to an orange solid, that after recrystallization from methanol gave rise to a crystalline white powder (2.16g, 86.8%). m.p. 178 °C; 1H -NMR (400 MHz, $(CD_3)_2SO$): 9.98 (t, 2H, NH, $J = 6.3$ Hz), 8.31-8.19 (m, 3H, CH_{py}), 7.94 (d, 4H, CH, $J = 8.2$ Hz), 7.47 (d, 4H, CH, $J = 8.2$ Hz), 4.69 (d, 2H, CH_2 , $J = 6.2$ Hz), 3.83 (s, 3H, CH_3); ^{13}C -NMR (100 MHz, $(CD_3)_2SO$): 166.50, 163.95, 148.89, 145.33, 140.13, 129.78, 128.66, 127.53, 125.09, 52.49, 42.48; IR(neat): 3281, 2949, 1716, 1671, 1644, 1528, 1432, 1276, 1178, 1107, 1021, 760, 673; HR-ESI-MS: m/z 462.17 $[M+H]^+$, 484.15 $[M+Na]^+$; Calculated for $C_{25}H_{23}N_3O_6Na$ 484.1485, Found 484.1487; Elemental analysis (calcd., found for $C_{25.5}H_{25}N_3O_{6.5}$): C (64.14, 64.20), H (5.28, 4.81), N (8.80, 8.71).

4,4'-(((pyridine-2,6-dicarbonyl)bis(azanediyl))bis(methylene))dibenzoic acid (H_2L)

A solution of **4** (0.590g, 1.27mmol) and KOH (0.160g, 2.81mmol) in 100 mL of absolute ethanol was refluxed overnight giving rise to a white solid. The solvent was removed under reduced pressure before adding 20mL of water in order to dissolve the white precipitate. The solution of H_2SO_4 (6M) was added to this water solution until pH 2 resulting in protonation of the carboxylic groups with the following precipitation of a white solid that was isolated by filtration. The recrystallization of the compound from methanol gave rise to a crystalline white powder (0.458g, 82%). m.p. 271 °C; 1H -NMR (600MHz, $(CD_3)_2SO$) 12.86 (s, 2H, OH), 9.95 (t, 2H, NH, $J = 6.3$ Hz), 8.27 (d, 3H, CH_{py} , $J = 7.2$ Hz), 8.22 (m, 1H, CH_{py} , $J = 7.2$ Hz), 7.92 (d, 4H, CH, $J = 8.2$ Hz), 7.44 (d, 4H, CH, $J = 8.2$ Hz), 4.68 (d, 2H, CH_2 , $J = 6.2$ Hz), 3.83 (s, 3H, CH_3); ^{13}C -NMR (150.9 MHz, $(CD_3)_2SO$) 167.10, 163.46, 148.50, 144.40, 139.65, 129.47, 129.39, 129.28, 127.06, 126.91, 124.61, 60.60, 42.04, 14.13; IR(neat): 3379, 3336, 2939, 1719, 1682, 1641, 1612, 1419,

1390, 1233, 1175, 1107, 1000, 846, 743; HR-ESI-MS: m/z 456.12 $[M+Na]^+$; Calculated for $C_{23}H_{19}N_3O_6Na$ 456.1172, Found 456.1191; Elemental analysis (calcd., found for $C_{23}H_{20}N_3O_{6.5}$): C (62.44, 62.47), H (4.56, 4.43), N (9.50, 9.39).

Synthesis of Eu(III) and Tb(III) complexes with H_2L

General procedure

$Ln(CF_3SO_3)_3$ (1 equivalent) was added to a solution of H_2L (3 equivalents) in methanol. The resulting mixture was irradiated in the microwave for 20 minutes at 75 °C giving rise to a clear colourless solution. The solution of the complex was concentrated under reduced pressure before the addition of diethyl ether, which gave rise to the formation of a white precipitate. The mixture was centrifuged, the supernatant solution was removed and the white solid was dried under vacuum.

Eu(H_2L)_{2.4}(CF_3SO_3)₃: (0.016g, 21%). m.p. 196 °C; 1H -NMR (400MHz, CD_3OD) δ 8.32, 8.19, 7.92, 7.64, 7.53, 7.40, 7.23, 7.00, 6.29, 6.01, 5.70, 5.27, 5.06, 4.68; IR(neat): 3273, 3098, 1698, 1633, 1613, 1560, 1460, 1422, 1225, 1168, 1110, 1022, 1000, 839, 749, 630; HR-ESI-MS: m/z 883.9498 $[Eu(H_2L)(CF_3SO_3)_2]^+$ Calculated for $C_{25}H_{19}N_3F_6O_{12}S_2Eu$ 883.9521, Found 883.9498 and 1317.0822 $[Eu(H_2L)_2(CF_3SO_3)_2]^+$ Calculated for $C_{46}H_{36}N_6F_6O_{18}S_2Eu$ 1317.0795, Found 1317.0822; Elemental analysis (calcd., found for $C_{58.2}H_{45.6}F_9S_3N_{7.2}O_{23.4}Eu$): C (42.30, 42.32), H (2.77, 2.85), N (5.96, 5.79).

Tb(H_2L)_{2.05}(CF_3SO_3)₃: (0.020g, 29%). m.p. 183 °C; 1H -NMR (400MHz, CD_3OD) δ 29.55, 28.15, 25.74, 23.55, 8.77, 8.35, 8.00, 7.49, 0.41, -2.24, -10.60, -28.85.; IR(neat): 3275, 3100, 1697, 1634, 1613, 1562, 1224, 1169, 1109, 1023, 839, 751, 631; HR-ESI-MS: m/z 740.0164 $[Tb(H_2L)(CF_3SO_3)]^+$ Calculated for $C_{24}H_{18}N_3F_3O_9STb$ 739.9964, Found 740.0164. and 1323.1147 $[Tb(H_2L)_2(CF_3SO_3)_2]^+$ Calculated for $C_{48}H_{38}N_6F_6O_{18}S_2Eu$ 1323.0836, Found 1323.1147; Elemental analysis (calcd., found for $C_{50.15}H_{38.95}F_9S_3N_{6.15}O_{21.3}Tb$): C (40.23, 40.35), H (2.62, 2.75), N (5.75, 5.22).

Synthesis of Eu(III)- and Tb(III)- luminescent gels

The synthesis of Eu(III)- and Tb(III)- luminescent gels was performed in two steps one pot reaction. Firstly, 1 equivalent of $\text{Ln}(\text{CF}_3\text{SO}_3)_3$ (1 equivalent) was added to a $\sim 10\text{mM}$ solution of H_2L (3 equivalents) in methanol. The solution of $\text{Ln}(\text{H}_2\text{L})_3(\text{CF}_3\text{SO}_3)_3$ (1 equivalent) was irradiated in the microwave for 20 minutes at 75°C giving rise to a clear colourless solution where 0.5 equivalents of $\text{Ln}(\text{CH}_3\text{COO})_3$ salt was added. Instantaneously a white soft precipitate could be observed as the acetate salt was dissolved. Similarly to the previous step, this mixture was irradiated again in the microwave for another 20 minutes at 75°C giving rise to the formation of a homogenous cottony white soft precipitate, which was centrifuged during 5 minutes at 3500 rpm. Then the solvent was decanted from the top of the gel and it was thus isolated. It has to be noted that the gel could be also formed by leaving the reaction mixture to slow evaporation during 48 hours to get the gels. However, in this case the content of CH_3OH is too high giving rise to a softer material very difficult to manipulate. With the aim of getting systematic reproducibility centrifugation is highly recommended, and was employed to all the gels presented in this manuscript.

Eu(III) gel: H_2L (0.0433 g, 9.99×10^{-5} mol) was dissolved in 10 mL of CH_3OH . $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ (0.0199 g, 3.33×10^{-5} mol) was added into this solution and resulting mixture was irradiated in the microwave for 20 minutes at 75°C . $\text{Eu}(\text{CH}_3\text{COO})_3$ (0.0055 g, 1.665×10^{-5} mol) was added into the resulting mixture and it was then again microwaved for another 20 minutes at 75°C .

Tb(III) gel: H_2L (0.0433 g, 9.99×10^{-5} mol) was dissolved in 10 mL of CH_3OH . $\text{Tb}(\text{CF}_3\text{SO}_3)_3$ (0.020 g, 3.33×10^{-5} mol) was added into this solution and resulting mixture was irradiated in the microwave for 20 minutes at 75°C . $\text{Tb}(\text{CH}_3\text{COO})_3$ (0.0055 g, 1.665×10^{-5} mol) was added into the resulting mixture and it was then again microwaved for another 20 minutes at 75°C .

It has to be noted that the synthesis can be scaled up to three times. The synthesis of the gels was reproduced for more than 6 times.

Self-healing experiments

Self-healing experiments were carried out by placing about 1 mL of the gel in the closed Petri dish at 22°C . The addition of methanol solution around the gel was required in order to create

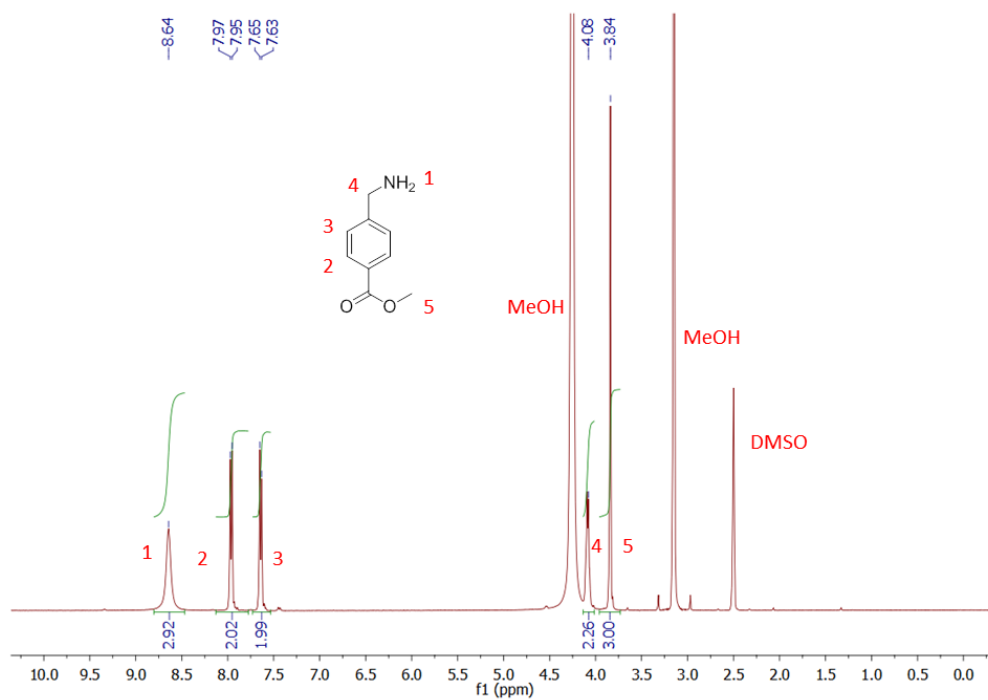
persistent methanol atmosphere surrounding the gel and protect the material from drying. The gel was cut into two pieces using standard scalpel and parts of the gel were separated on a distance of about 1 cm. Afterwards these two fractions were brought together again. Instantaneously it was possible to observe the self-healing process occurring by observing the cut line disappearing within seconds. This can be further confirmed by rheological studies (Figure S21; see the details on rheological experiments in the experimental part of the main text).

Spectrophotometric titrations:

In a typical experiment the formation of the luminescent (**M:H₂L**, where M = metal and **H₂L** = dipicolinic based dicarboxylic ligand) species was ascertained by both UV-visible and luminescence titrations of a solution of **H₂L** ($c = 1.43 \times 10^{-5}$ M; $V = 2.7$ mL) upon gradual addition of **M(CF₃SO₃)₃·6H₂O** solution ($c = 6.36 \times 10^{-4}$ M) in a range of 0→6 equivalents at 298 K. The time between each addition was 10 minutes. The dilution factor of 10% was taken into account.

Figure S1: (A) ^1H NMR of **2** (400 MHz, $(\text{CD}_3)_2\text{SO}$), (B) ^{13}C NMR of **2** (100 MHz, $(\text{CD}_3)_2\text{SO}$).

(A)



(B)

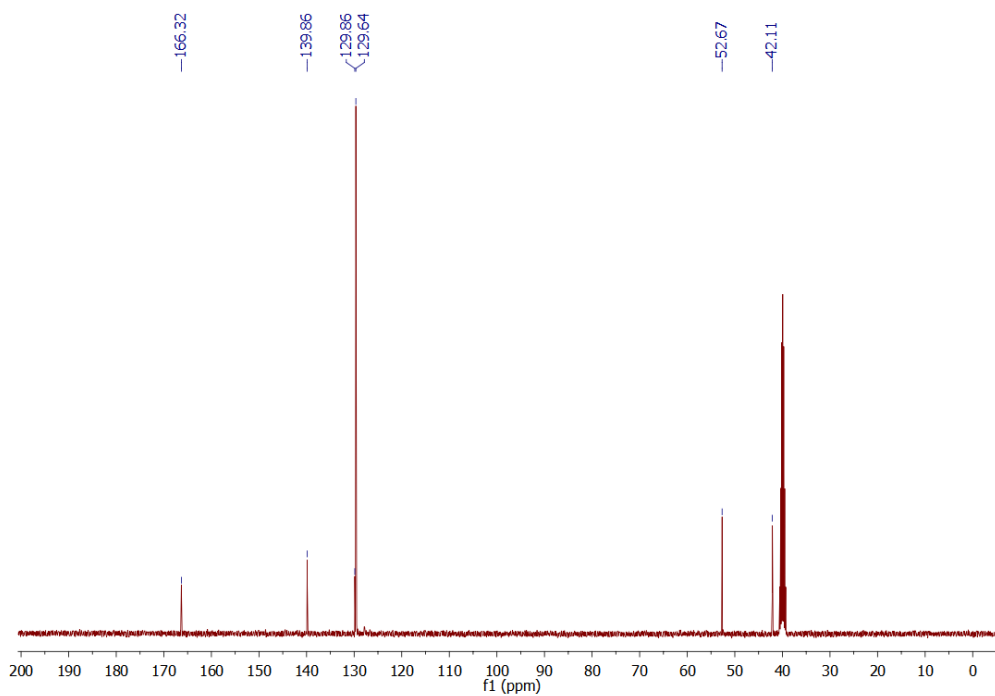
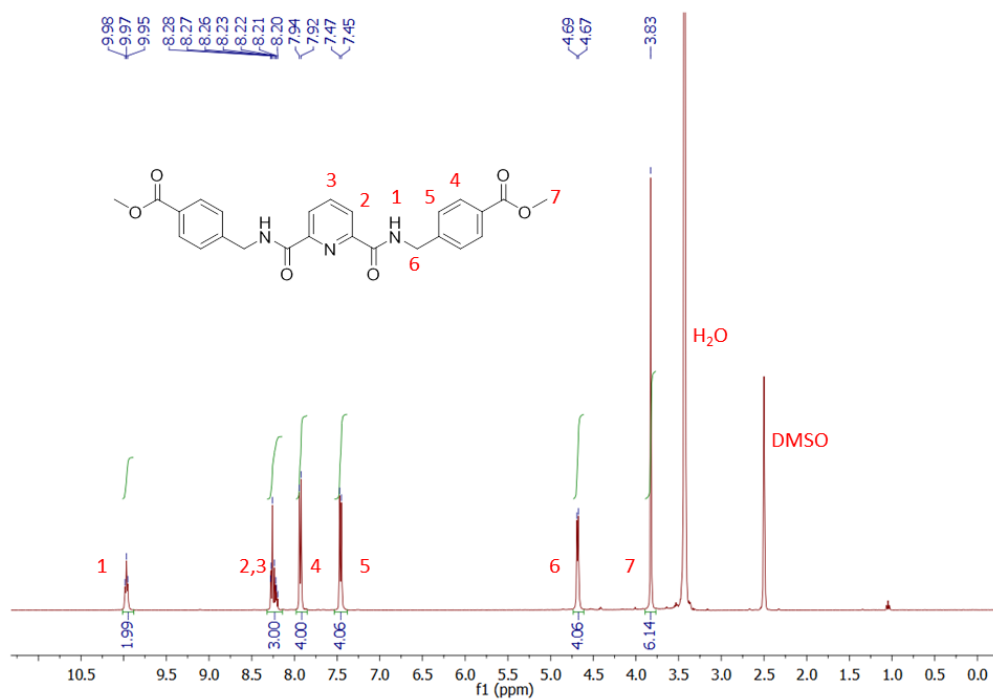


Figure S2: (A) ^1H NMR of **4** (400 MHz, $(\text{CD}_3)_2\text{SO}$), **(B)** ^{13}C NMR of **4** (100 MHz, $(\text{CD}_3)_2\text{SO}$).

(A)



(B)

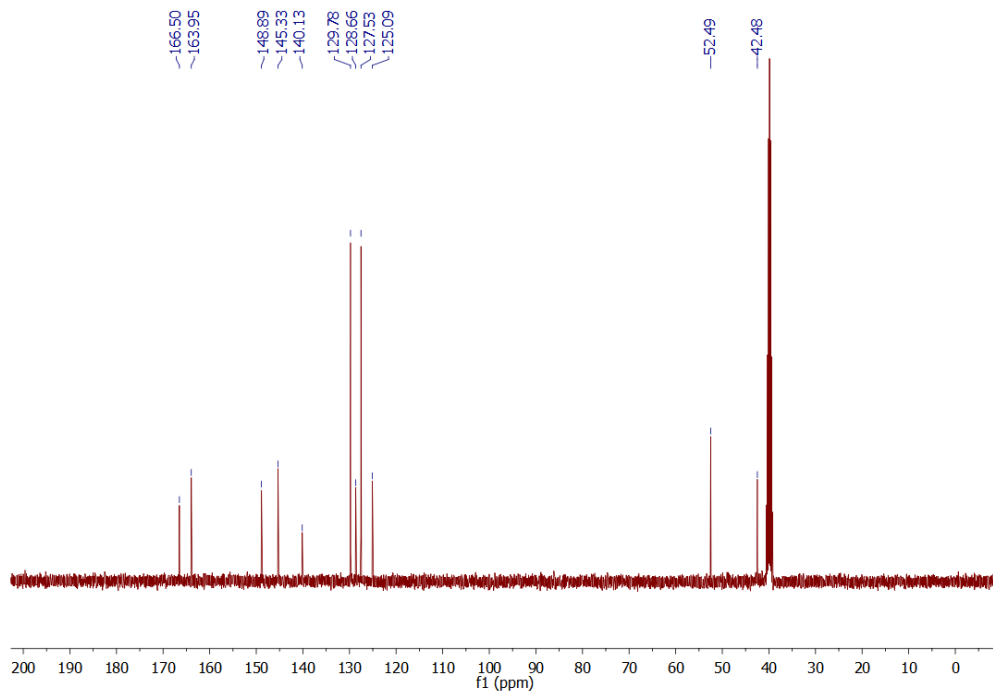
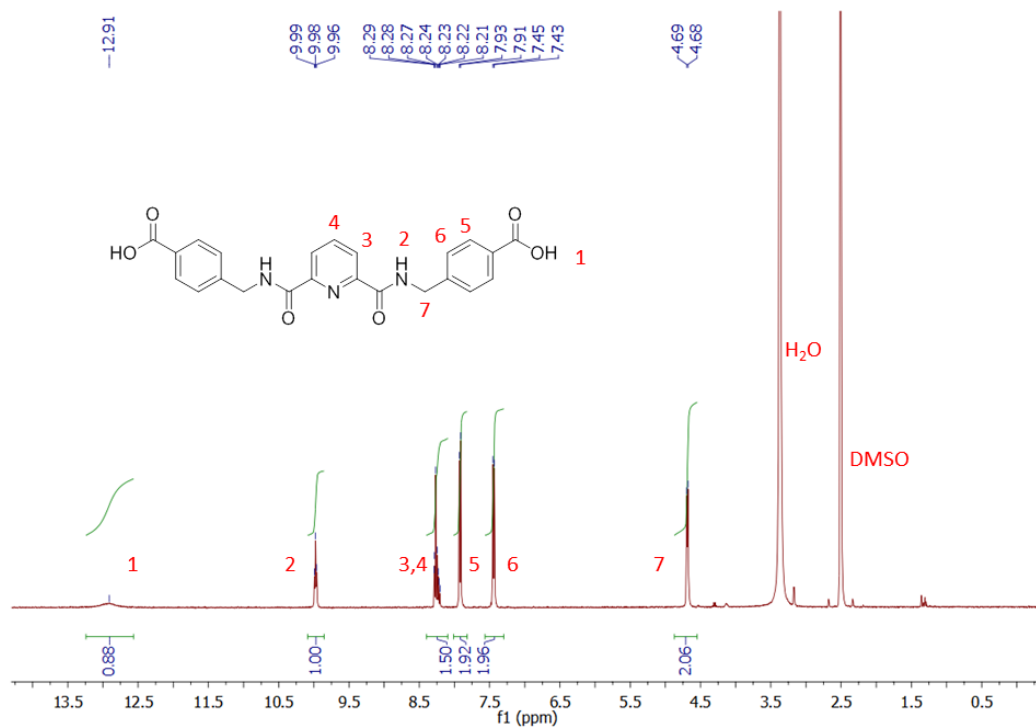
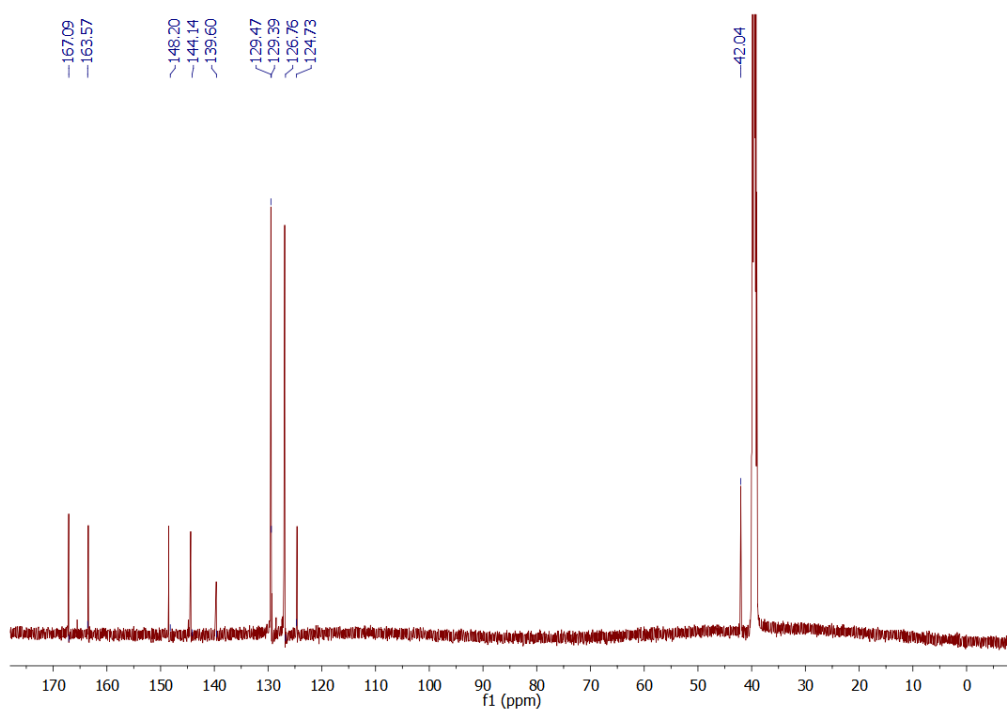


Figure S3: (A) ^1H NMR of **H₂L** (600 MHz, $(\text{CD}_3)_2\text{SO}$), (B) ^{13}C NMR of **H₂L** (150.9 MHz, $(\text{CD}_3)_2\text{SO}$), (C) DEPT NMR of **H₂L** (150.9 MHz, $(\text{CD}_3)_2\text{SO}$).

(A)



(B)



(C)

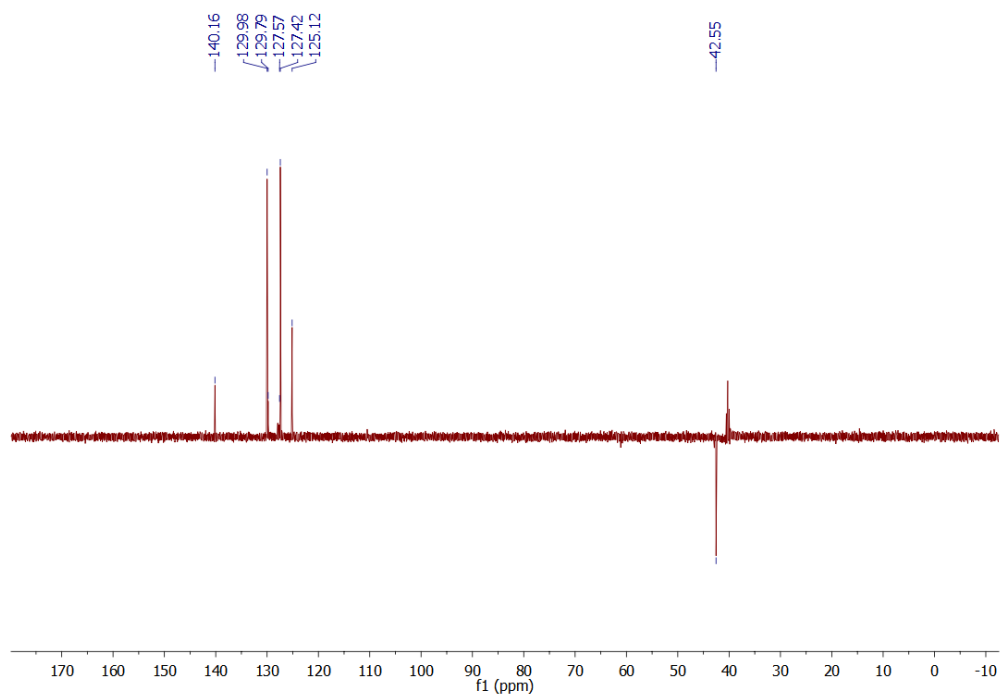


Figure S4: (A) ORTEP scheme of the ligand H_2L ; (B) H-Bonds and π - π stacking interactions of H_2L and (C) crystal lattice of H_2L .

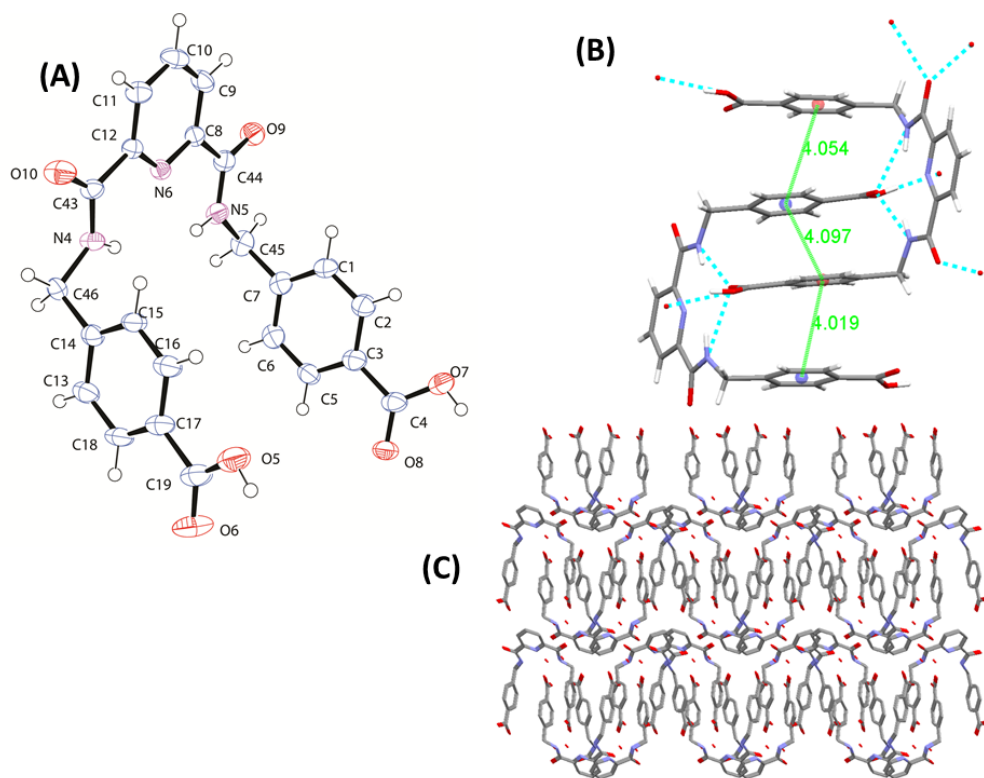


Figure S5: ^1H NMR of the complex $\text{Eu}(\text{H}_2\text{L})_{2.4}(\text{CF}_3\text{SO}_3)_3$ (400 MHz, CD_3OD).

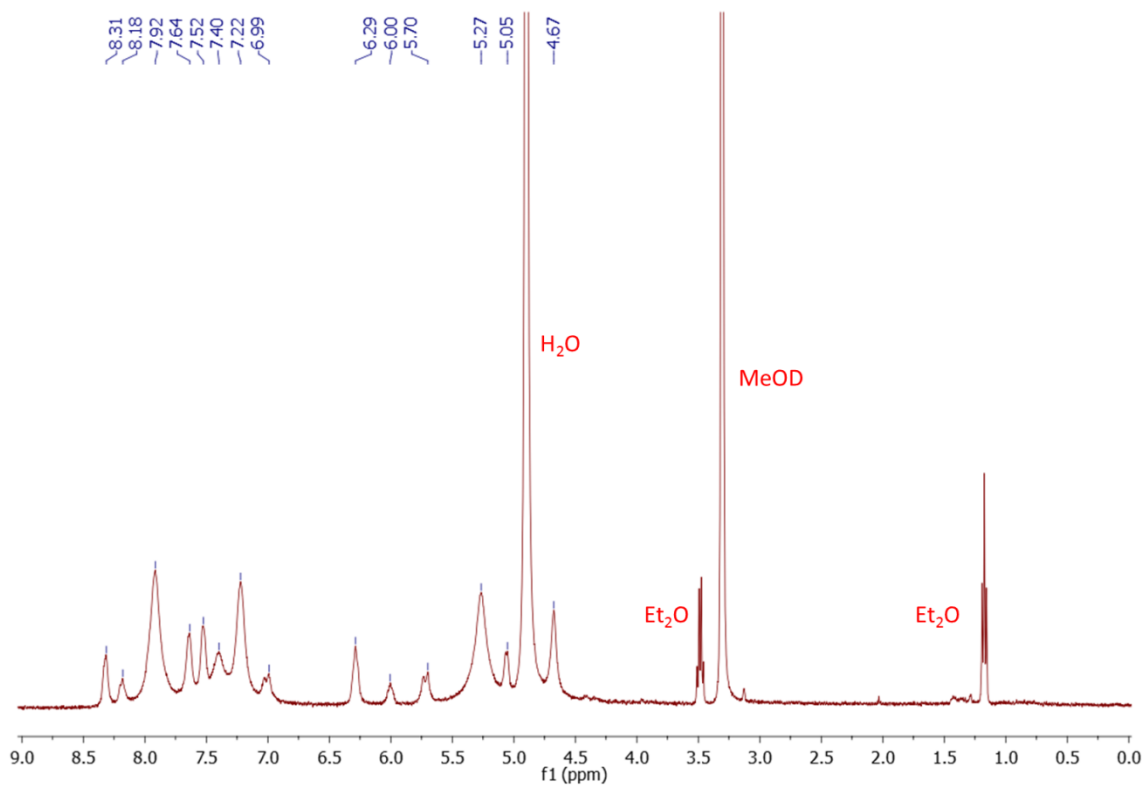


Figure S6: ^1H NMR of the complex $\text{Tb}(\text{H}_2\text{L})_{2.05}(\text{CF}_3\text{SO}_3)_3$ (400 MHz, CD_3OD).

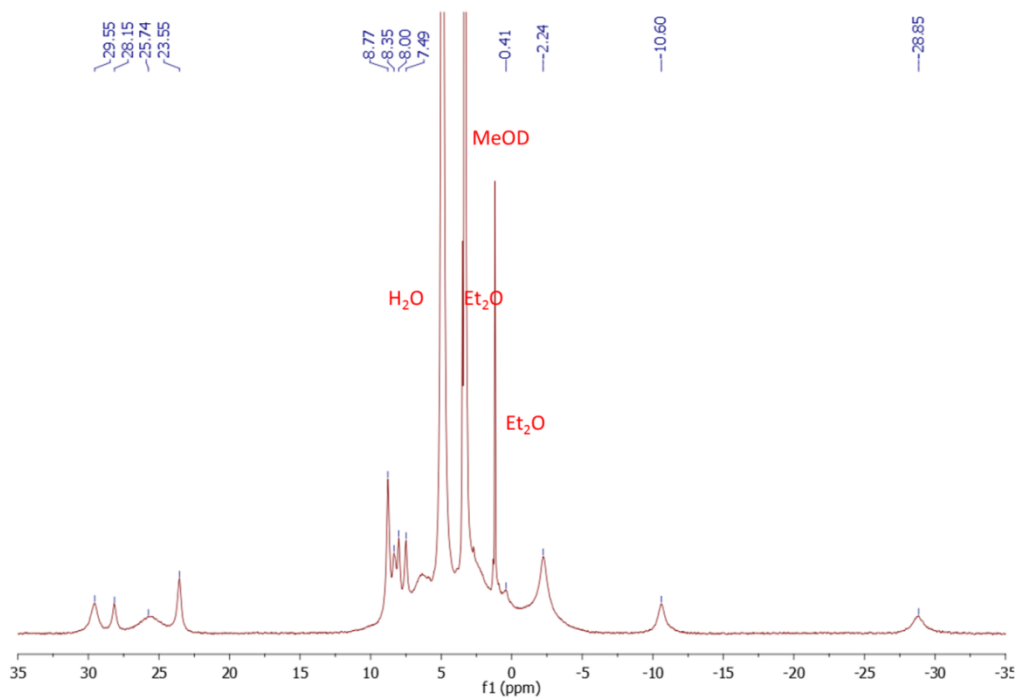


Figure S7: Experimental and calculated HR-MALDI-MS spectra of **(A)** Eu(III) and **(B)** Tb(III) complexes.

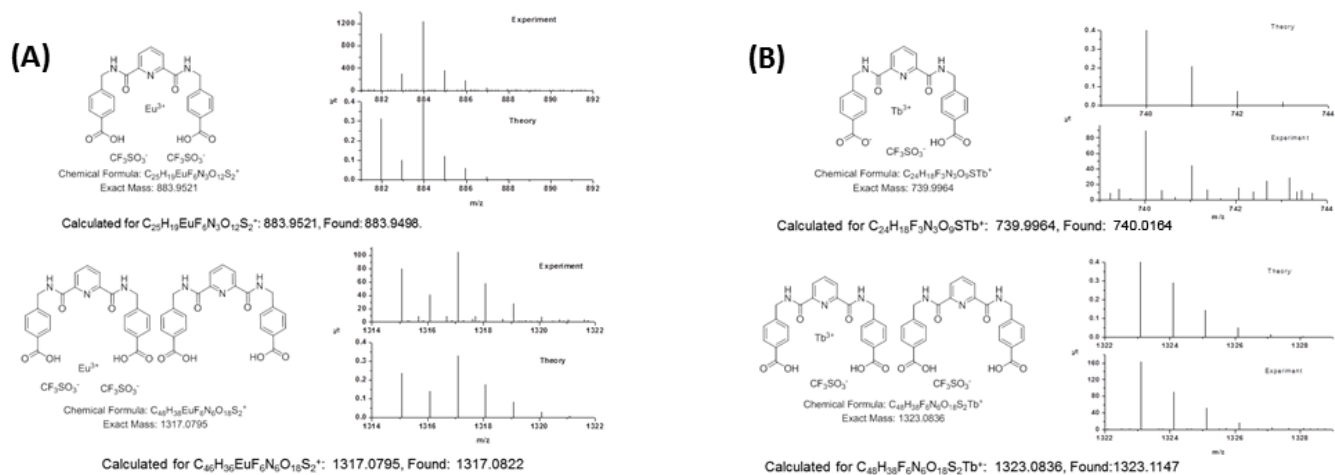


Figure S8: The weight loss of **H₂L** versus temperature under air atmosphere.

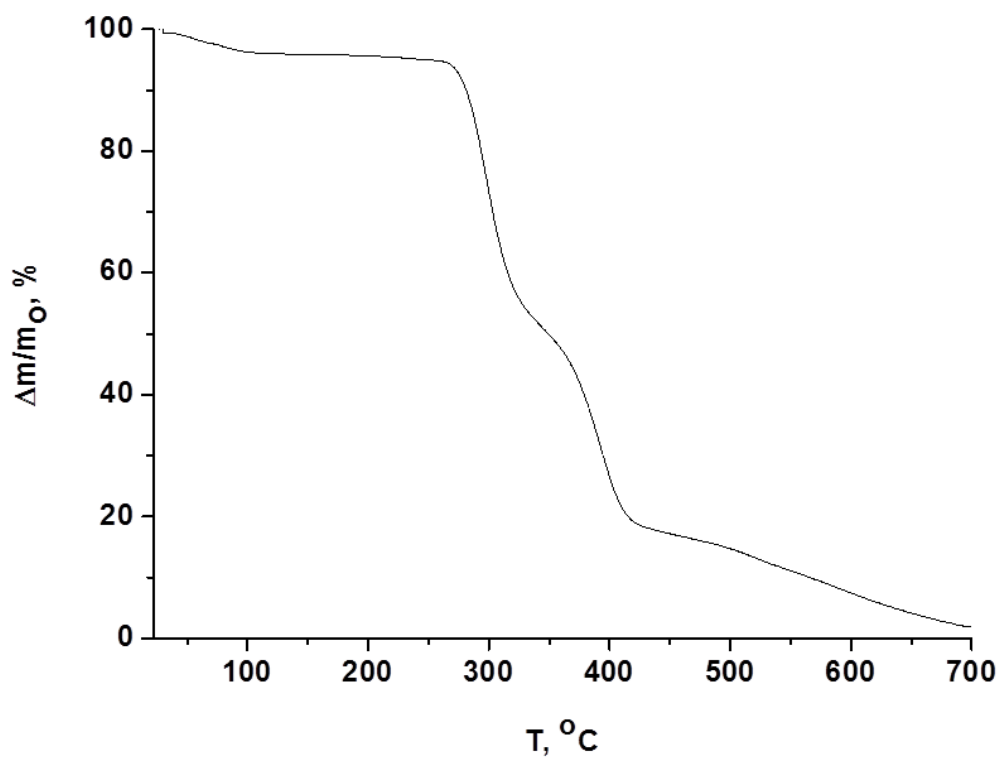


Figure S9: The weight loss of (A) Eu(III)-gel and (B) Tb(III)-gel versus temperature under air.

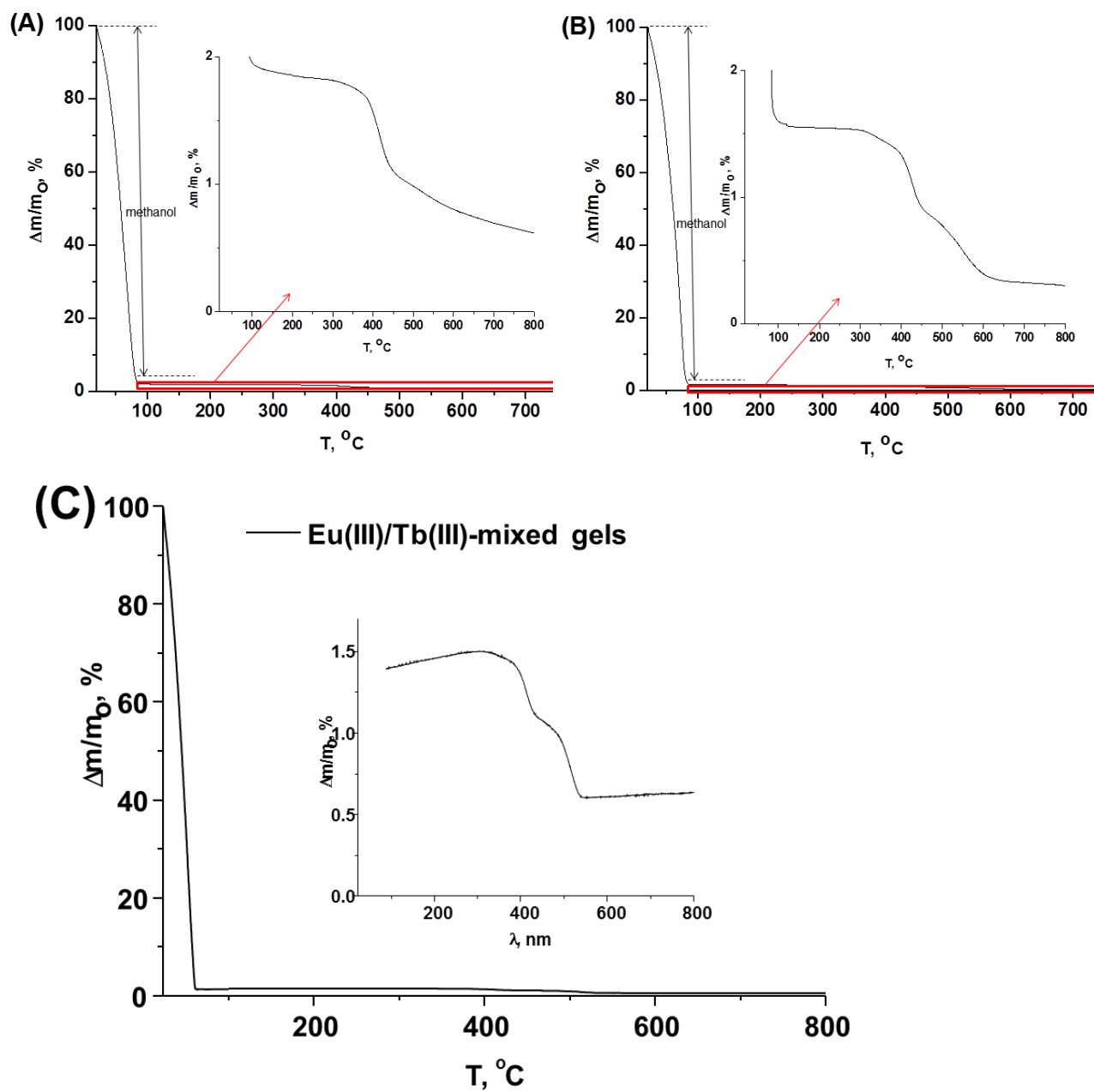


Figure S10: (A) Changes in the absorption spectrum of H_2L ($7.80 \times 10^{-6} \text{ M}$), (B) binding isotherms and their corresponding fits upon titration with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ ($0 \rightarrow 6$ equivalents) in methanol at 298 K; (C) changes in the absorption spectrum of H_2L ($7.70 \times 10^{-6} \text{ M}$), (D) binding isotherms and their corresponding fits upon titrating with $\text{Tb}(\text{CF}_3\text{SO}_3)_3$ ($0 \rightarrow 6$ equivalents) in methanol at 298 K.

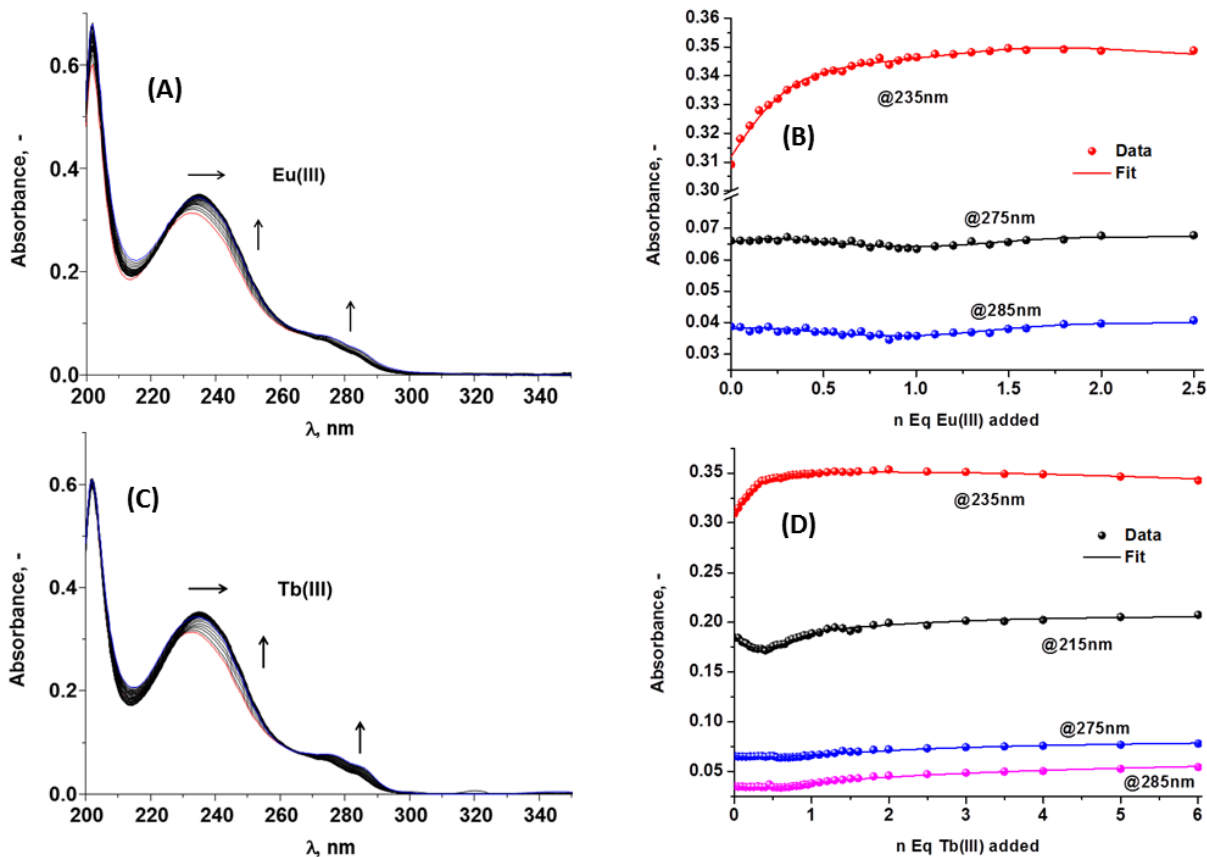


Figure S11: (A) Changes in absorption spectrum of H_2L ($7.80 \times 10^{-6} \text{ M}$), (B) binding isotherms and their corresponding fits upon titration with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ ($0 \rightarrow 6$ equivalents) in methanol at 298 K; (C) changes in the absorption spectrum of H_2L ($7.70 \times 10^{-6} \text{ M}$), (D) binding isotherms and their corresponding fits upon titration with $\text{Tb}(\text{CF}_3\text{SO}_3)_3$ ($0 \rightarrow 6$ equivalents) in acetonitrile at 298 K.

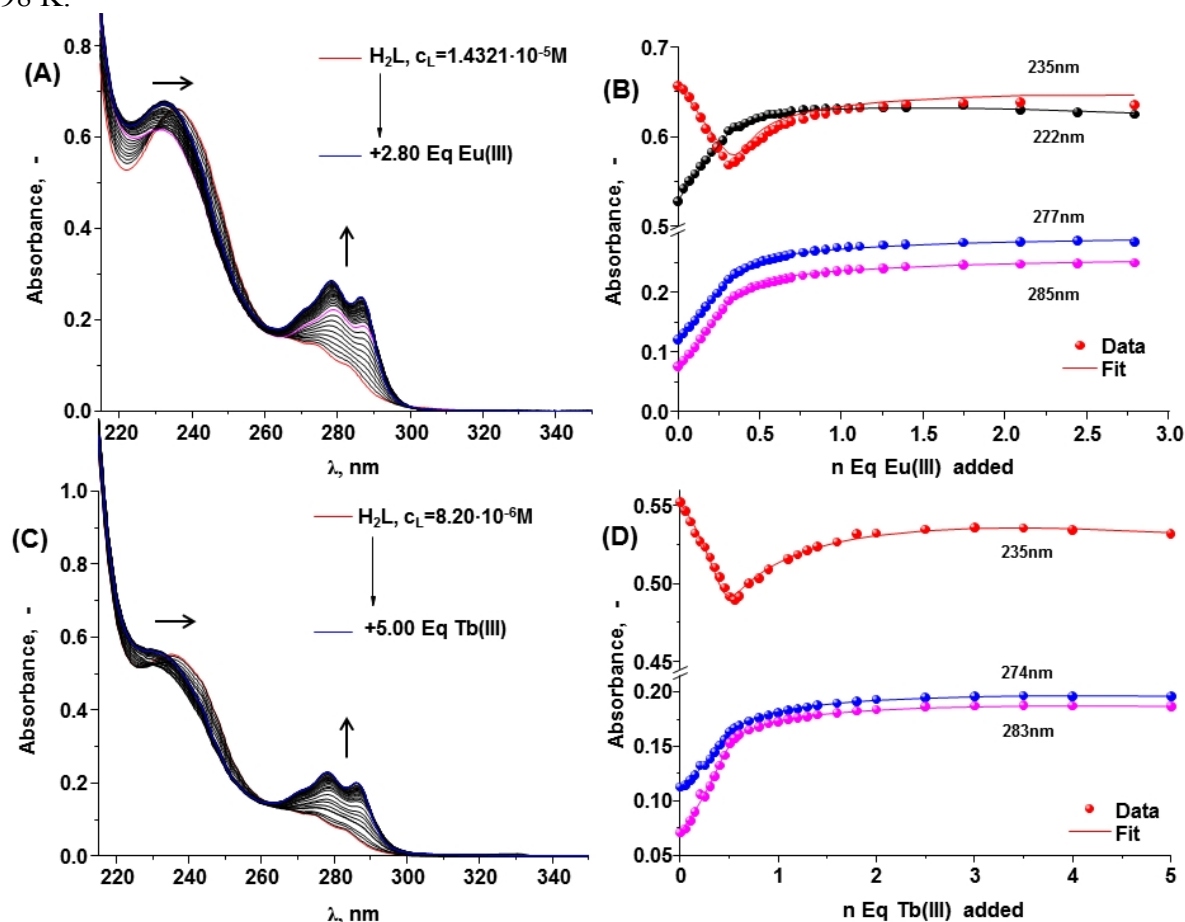


Figure S12: Changes in (A) the Eu(III) centred emission spectra upon titrating H_2L ($1.43 \cdot 10^{-5}$ M) with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ (0→6 equivalents), (B) experimental binding isotherms (•••) and their corresponding fits (–) for the titration with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$; (C) changes in the Tb(III) centred emission spectra upon titrating H_2L ($8.20 \cdot 10^{-6}$ M) with $\text{Tb}(\text{CF}_3\text{SO}_3)_3$ (0→6 equivalents), (D) experimental binding isotherms (•••) and their corresponding fits (–) for the titration with $\text{Tb}(\text{CF}_3\text{SO}_3)_3$ in acetonitrile at 298 K.

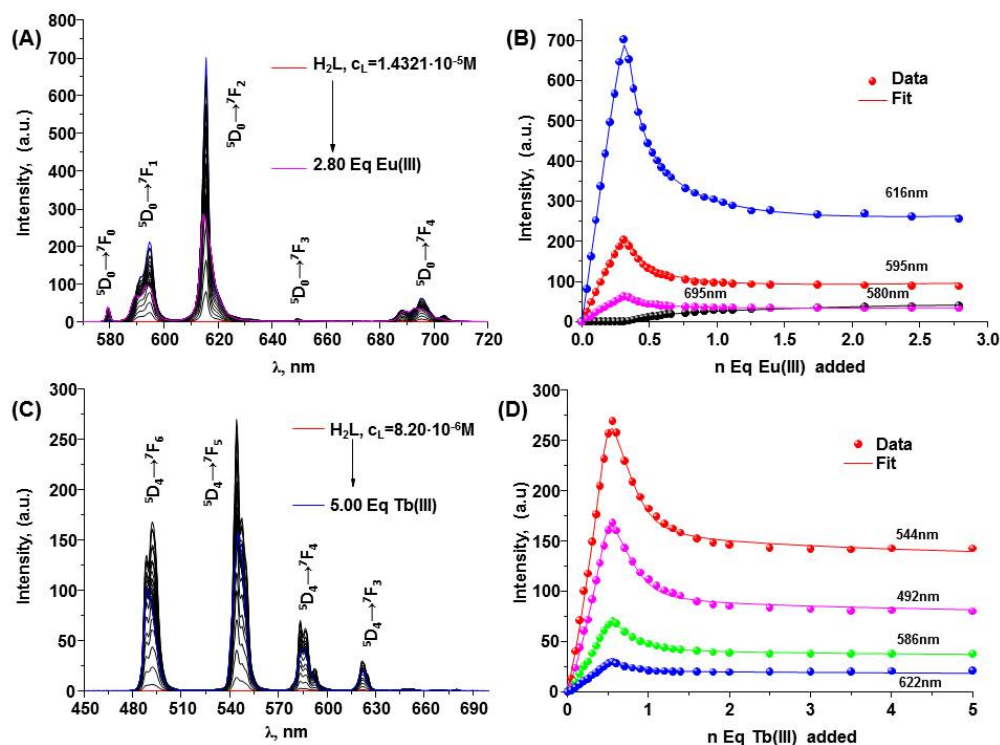


Figure S13: ^1H NMR titration of H_2L (1.10×10^{-3} M, CD_3OD) by $\text{La}(\text{CF}_3\text{SO}_3)_3$ from 0 to 2 equivalents.

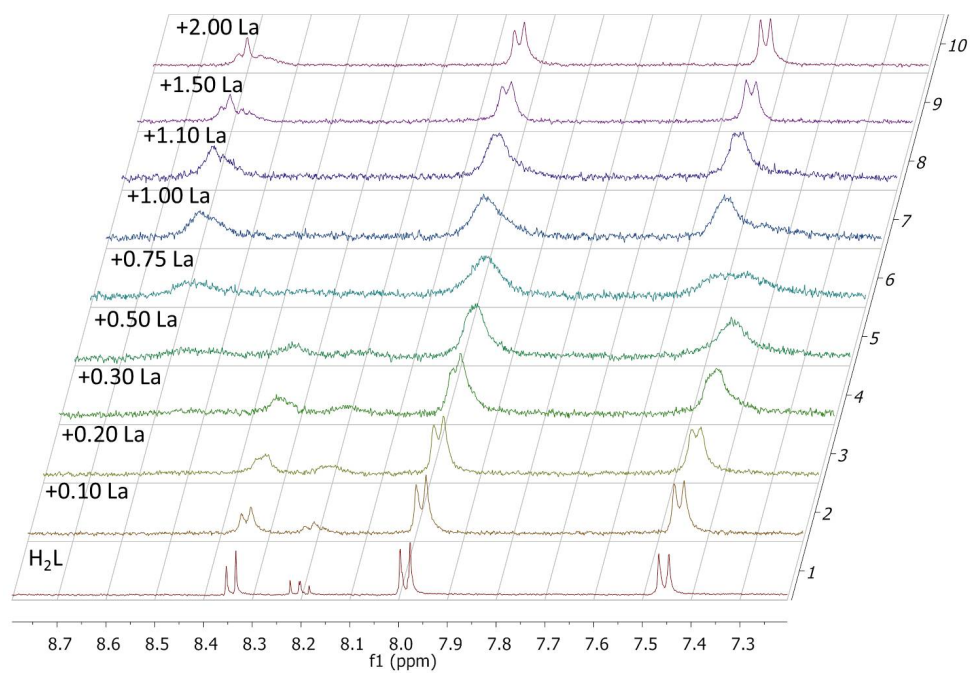


Figure S14: (A–D) Healing experiment of Tb(III) gel where (A) is Tb(III) gel in the day light, (B) same gel under UV light, (C) gel after being cut in half and (D) self-healing properties of the gel (scale bars, 1 cm).

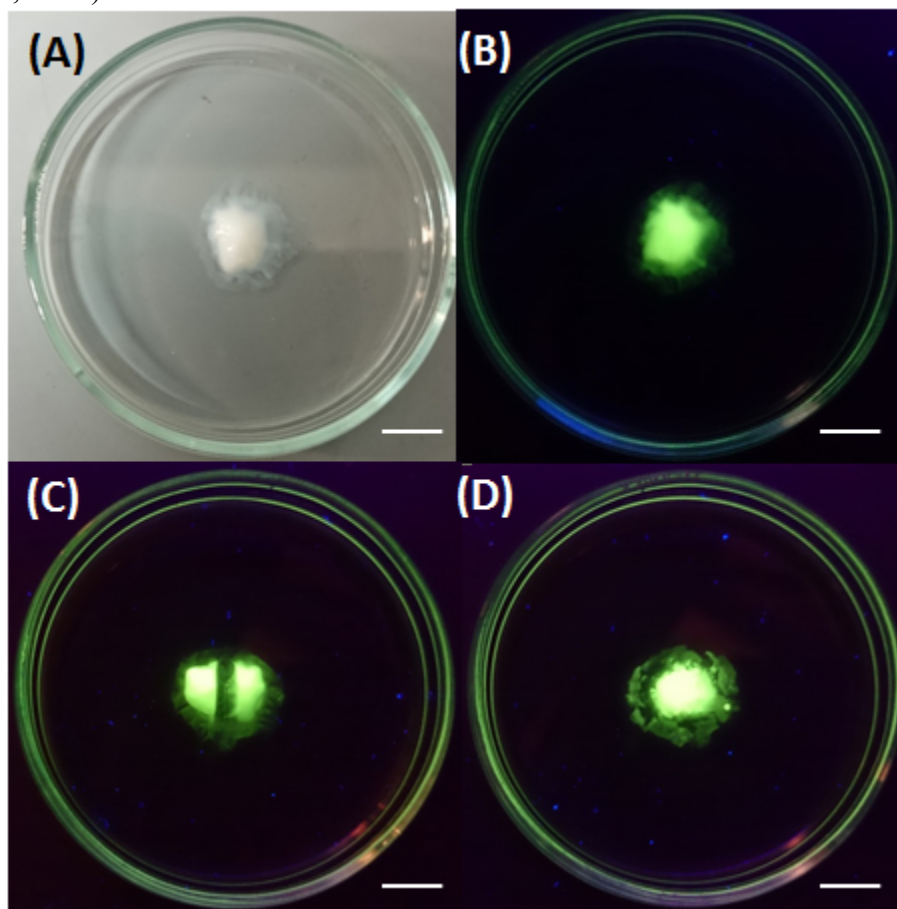


Figure S15: (A–D) Healing experiment of Tb(III) and Eu(III) gels where (A) is Tb(III) and Eu(III) gels in the day light, (B) same gel under UV light, (C) gel after being cut in half and (D) self-healing properties of the gel (scale bars, 1 cm).

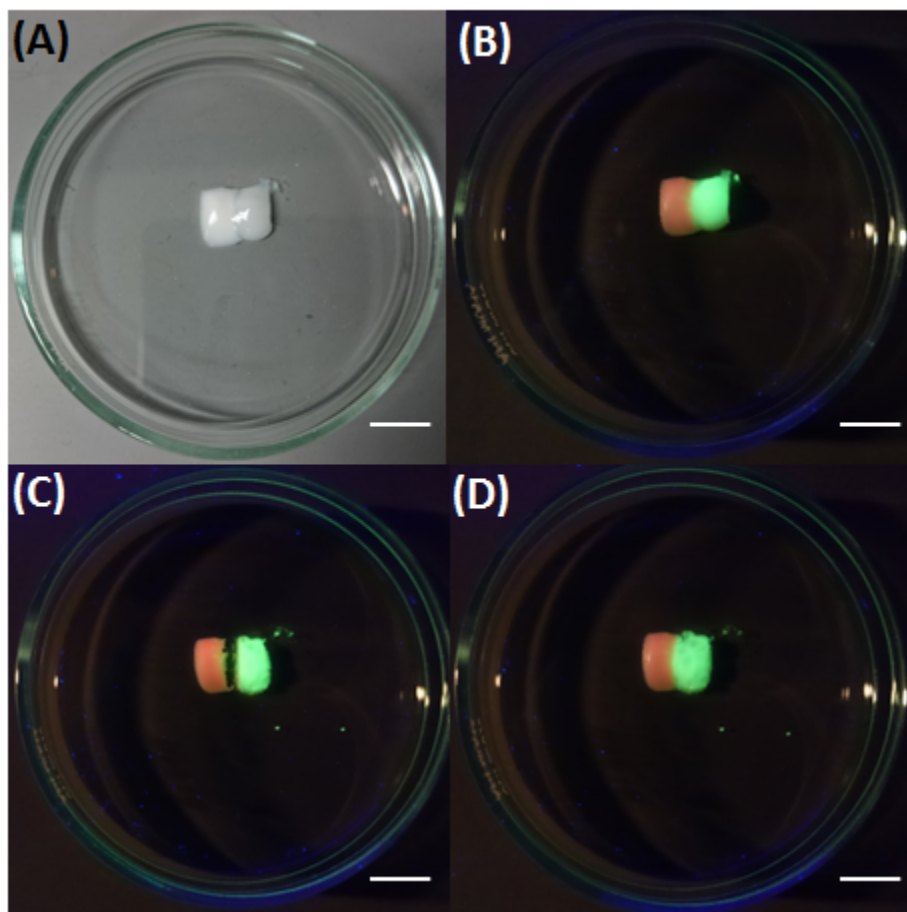


Figure S16: Chromaticity diagram (CIE) for Tb(III), Eu(III) and Eu(III)/Tb(III) gel.

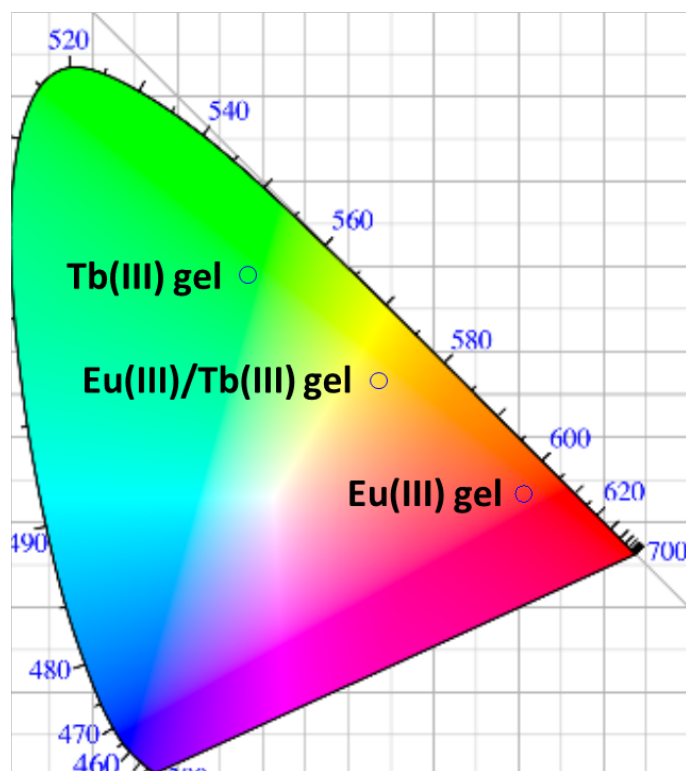


Figure S17: Luminescent spectrum of Eu(III) and Tb(III)-gels obtained on top of one another ($\lambda_{\text{ex}} = 275 \text{ nm}$).

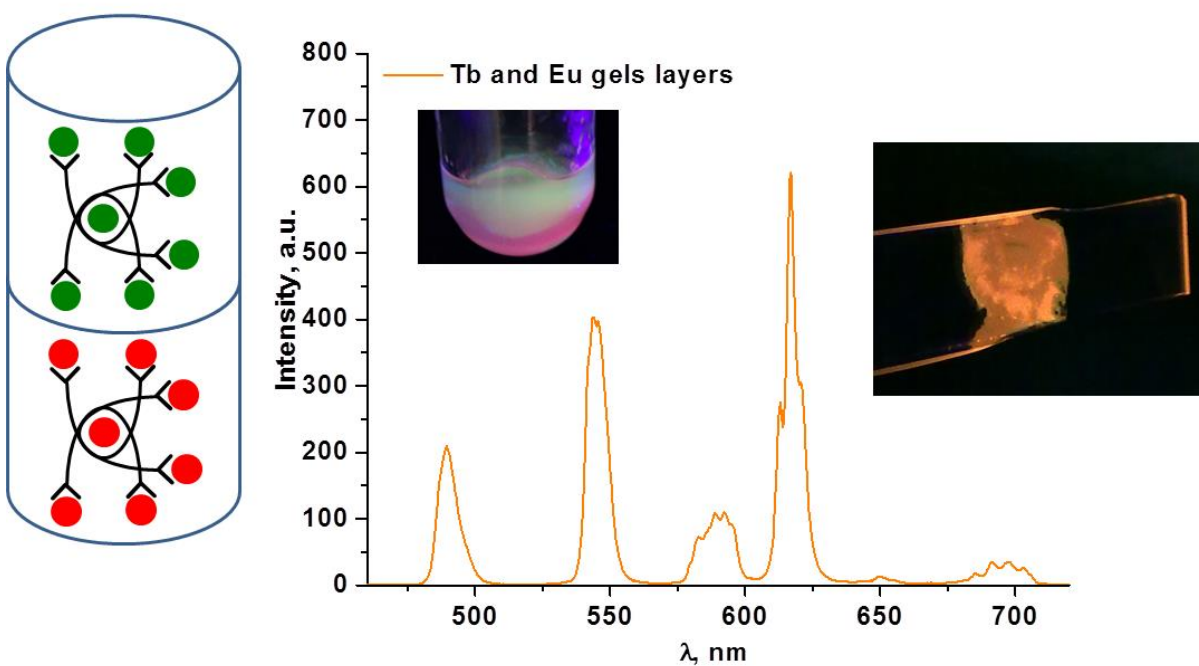


Figure S18: (A) Luminescent spectrum of the gel obtained by first forming **Eu:H₂L** complexes in solution and treading it with Tb(CH₃COO)₃ (λ_{ex} = 275 nm); (B) corresponding CIE diagram for this gel.

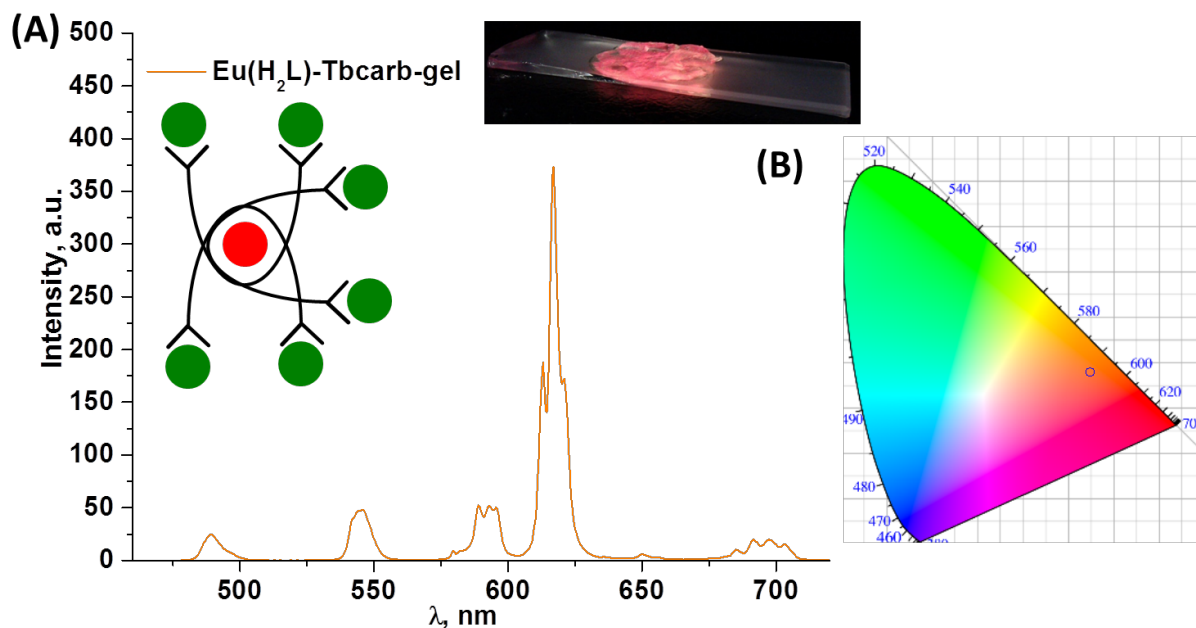


Figure S19: (A) Luminescent spectrum of the gel obtained by first forming **Tb:H₂L** complexes in solution and treading it with Eu(CH₃COO)₃ (λ_{ex} = 275 nm); (B) corresponding CIE diagram for this gel.

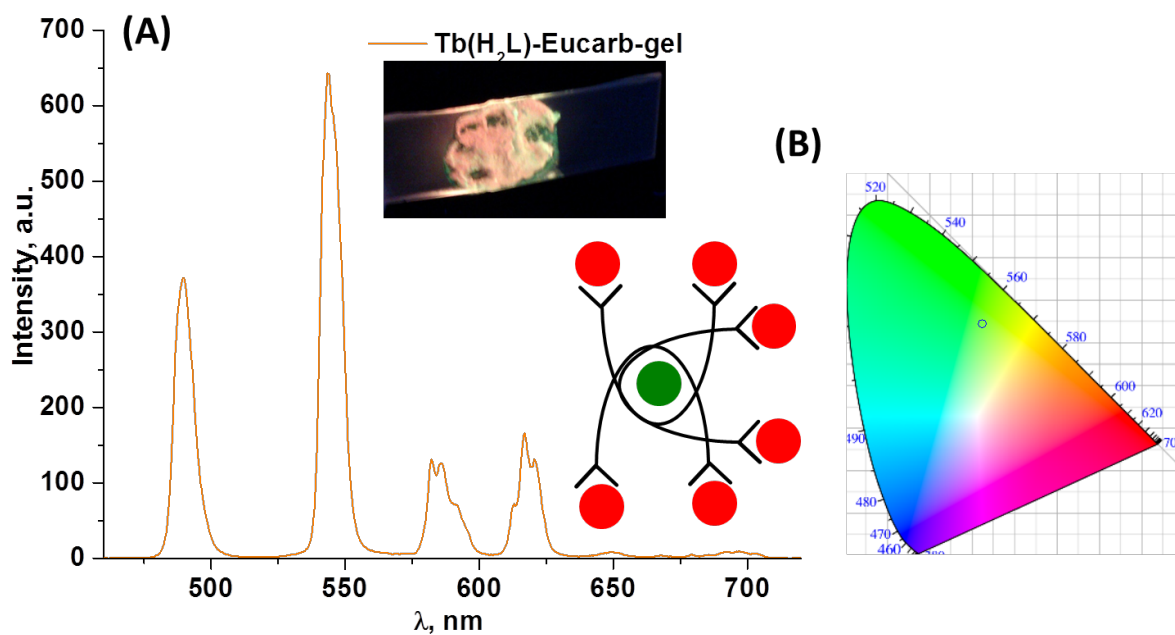


Figure S20: Additional SEM imaging of the (A, B) Eu(III)-gel, (C, D) Tb(III)-gel and (E, F) Eu(III)-Tb(III)-gel.

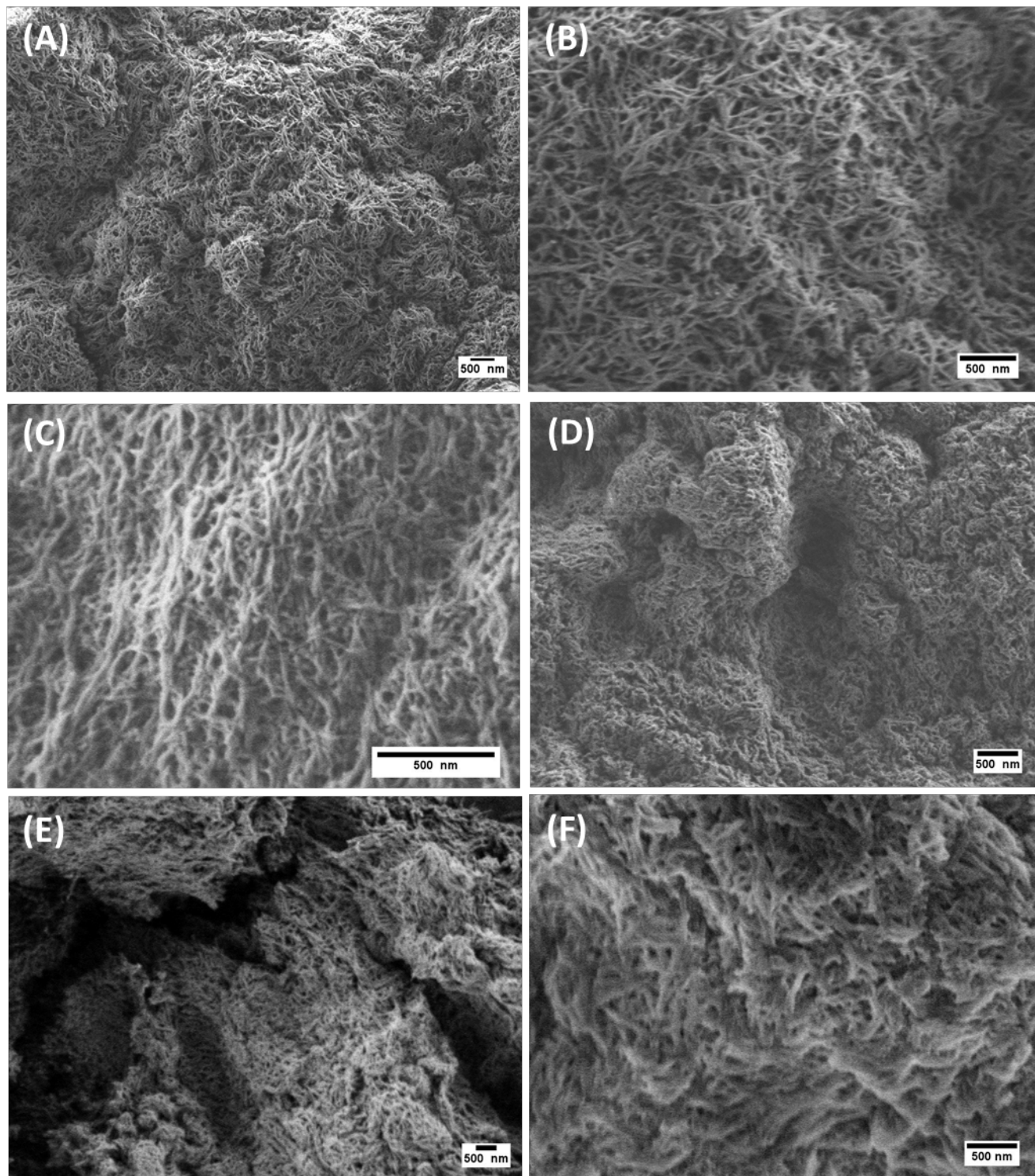


Figure S21. Consecutive strain sweeps performed over the **(A)** Eu(III) and **(B)** Tb(III) original gels. During one sweep, the strain amplitude goes from 0.01% to 100% at a frequency of 1 Hz. In the grey areas the strain amplitude is beyond the yield strain where the gel is fluidised and exhibits a liquid-like response. After fluidisation, when the strain amplitude reverts back to 0.01%, the G' plateau is recovered within 30 seconds which demonstrates that both gels are self-healing.

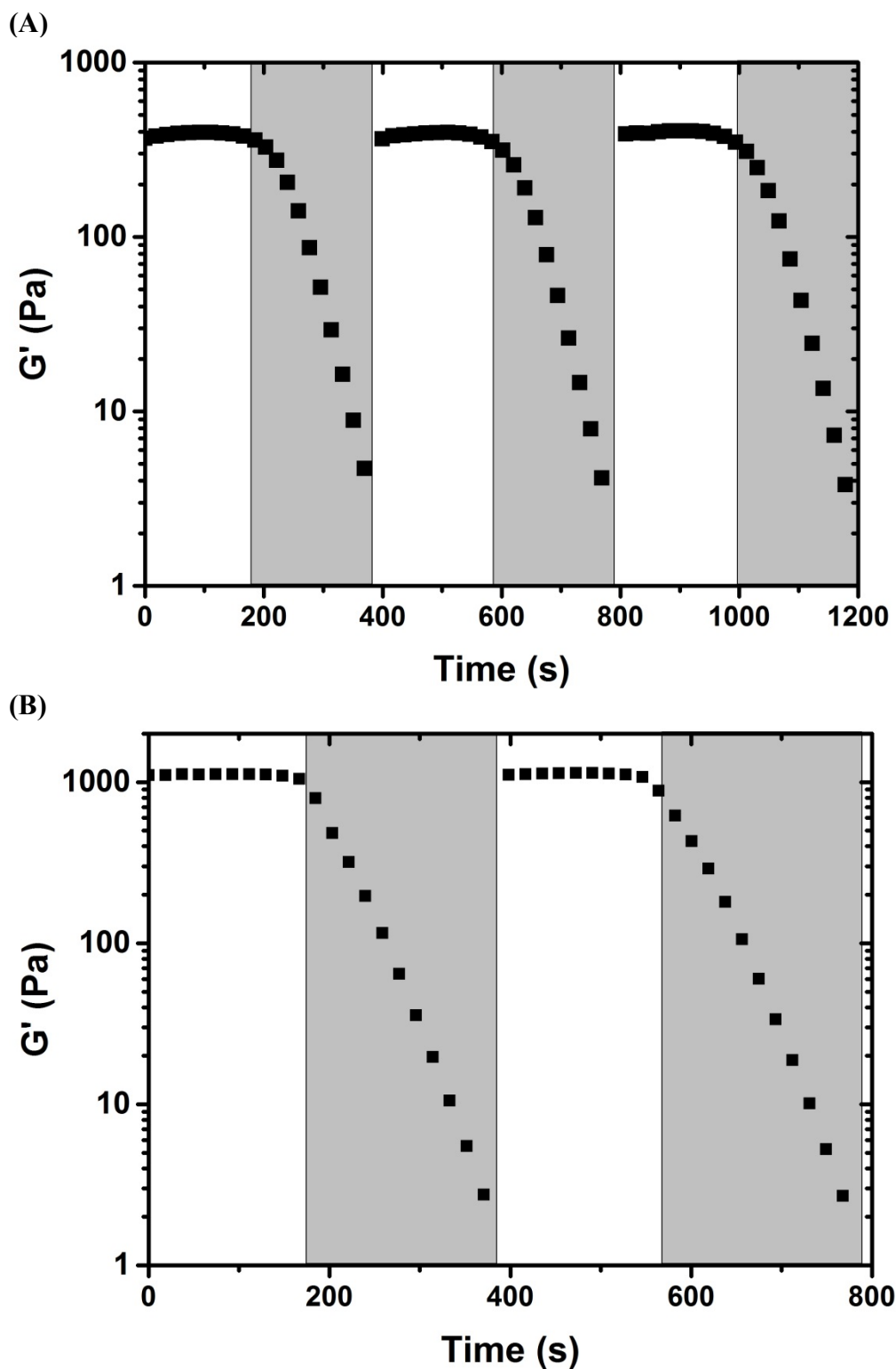


Table S1. Main crystallographic data for **H₂L**.

Formula	C ₉₂ H ₈₂ N ₁₂ O ₃₂	μ / mm⁻¹	0.107
Molecular weight	1867.70	F(000)	974
Temperature (K)	150(2)	Crystal size mm	0.60 x 0.60 x 0.60
Crystal system,	Monoclinic,	θ range [°]	1.63 to 25.00
Space group	P2(1)	Reflections collected / unique	16235 / 7148
a/Å	11.998(2)	[R(int) = 0.0200]	
b/Å	14.851(3)	Data / restraints / parameters	7148 / 1 / 625
c/Å	12.524(3)	Goodness-of-fit on F²	1.120
β/°	93.80(3)	Final R indices [I>2sigma(I)],	0.0513 [0.1563]
Volume (Å³)	2226.6(8)	R indices (all data),	0.0593 [0.1873]
Z, Calculated	1,	Residuals (e.Å⁻³)	0.730 and -0.709
density (Mg/m³)	1.393		

Table S2. Bond lengths [Å] and angles [°].

Bond distances (Å)					
O(1)-C(40)	1.242(5)	C(28)-C(29)	1.412(7)	N(6)-C(8)	1.344(4)
O(2)-C(39)	1.252(5)	C(29)-C(30)	1.383(7)	C(1)-C(7)	1.384(6)
O(3)-C(26)	1.309(5)	C(30)-C(31)	1.379(6)	C(1)-C(2)	1.398(5)
O(4)-C(26)	1.222(4)	C(31)-C(39)	1.513(6)	C(2)-C(3)	1.404(5)
O(11)-C(38)	1.328(5)	C(32)-C(37)	1.380(6)	C(3)-C(5)	1.384(6)
O(12)-C(38)	1.201(5)	C(32)-C(33)	1.403(6)	C(3)-C(4)	1.481(5)
N(1)-C(40)	1.333(5)	C(32)-C(42)	1.515(6)	C(5)-C(6)	1.376(5)
N(1)-C(41)	1.456(4)	C(33)-C(34)	1.386(5)	C(6)-C(7)	1.391(5)
N(2)-C(31)	1.332(5)	C(34)-C(35)	1.398(5)	C(7)-C(45)	1.509(5)
N(2)-C(27)	1.339(5)	C(35)-C(36)	1.401(6)	C(8)-C(9)	1.381(5)
N(3)-C(39)	1.317(6)	C(35)-C(38)	1.490(5)	C(8)-C(44)	1.499(5)
N(3)-C(42)	1.455(6)	C(36)-C(37)	1.364(6)	C(9)-C(10)	1.382(6)
C(20)-C(21)	1.386(5)	O(5)-C(19)	1.330(5)	C(10)-C(11)	1.381(5)
C(20)-C(25)	1.387(5)	O(6)-C(19)	1.208(5)	C(11)-C(12)	1.390(5)
C(21)-C(22)	1.383(5)	O(7)-C(4)	1.313(5)	C(12)-C(43)	1.507(4)
C(22)-C(23)	1.388(5)	O(8)-C(4)	1.221(5)	C(13)-C(18)	1.395(5)
C(22)-C(26)	1.484(4)	O(9)-C(44)	1.247(4)	C(13)-C(14)	1.393(5)
C(23)-C(24)	1.374(5)	O(10)-C(43)	1.316(4)	C(14)-C(15)	1.395(6)
C(24)-C(25)	1.398(5)	N(4)-C(43)	1.473(4)	C(14)-C(46)	1.512(5)
C(25)-C(41)	1.508(5)	N(4)-C(46)	1.330(5)	C(15)-C(16)	1.377(5)
C(27)-C(28)	1.394(5)	N(5)-C(44)	1.458(5)	C(16)-C(17)	1.401(5)
C(27)-C(40)	1.502(5)	N(5)-C(45)	1.341(4)	C(17)-C(18)	1.380(6)
		N(6)-C(12)	1.248(4)	C(17)-C(19)	1.492(5)
Bond Angles (°)					
C(40)-N(1)-C(41)	124.2(3)	C(36)-C(35)-C(38)	118.4(3)	N(6)-C(8)-C(9)	122.7(3)
C(31)-N(2)-C(27)	118.5(3)	C(34)-C(35)-C(38)	122.4(4)	N(6)-C(8)-C(44)	116.1(3)
C(39)-N(3)-C(42)	124.2(4)	C(37)-C(36)-C(35)	119.7(4)	C(9)-C(8)-C(44)	121.2(3)
C(21)-C(20)-C(25)	120.7(3)	C(36)-C(37)-C(32)	122.2(4)	C(8)-C(9)-C(10)	118.9(3)
C(22)-C(21)-C(20)	120.0(3)	O(12)-C(38)-O(11)	122.1(4)	C(11)-C(10)-C(9)	119.1(3)
C(21)-C(22)-C(23)	119.6(3)	O(12)-C(38)-C(35)	124.8(4)	C(10)-C(11)-C(12)	118.5(3)
C(21)-C(22)-C(26)	119.6(3)	O(11)-C(38)-C(35)	113.1(3)	N(6)-C(12)-C(11)	122.8(3)
C(23)-C(22)-C(26)	120.8(3)	O(2)-C(39)-N(3)	123.1(4)	N(6)-C(12)-C(43)	115.7(3)
C(24)-C(23)-C(22)	120.5(3)	O(2)-C(39)-C(31)	120.9(4)	C(11)-C(12)-C(43)	121.4(3)
C(23)-C(24)-C(25)	120.5(3)	N(3)-C(39)-C(31)	115.9(3)	C(18)-C(13)-C(14)	120.8(4)
C(20)-C(25)-C(24)	118.7(3)	O(1)-C(40)-N(1)	122.7(4)	C(15)-C(14)-C(13)	118.0(3)
C(20)-C(25)-C(41)	120.6(3)	O(1)-C(40)-C(27)	122.4(3)	C(15)-C(14)-C(46)	121.4(3)
C(24)-C(25)-C(41)	120.7(3)	N(1)-C(40)-C(27)	114.9(3)	C(13)-C(14)-C(46)	120.6(3)
O(4)-C(26)-O(3)	123.0(3)	N(1)-C(41)-C(25)	112.4(3)	C(16)-C(15)-C(14)	121.7(3)

O(4)-C(26)-C(22)	122.2(3)	N(3)-C(42)-C(32)	111.2(3)	C(15)-C(16)-C(17)	119.6(4)
O(3)-C(26)-C(22)	114.7(3)	C(43)-N(4)-C(46)	124.5(3)	C(18)-C(17)-C(16)	119.5(3)
N(2)-C(27)-C(28)	122.8(4)	C(44)-N(5)-C(45)	123.4(3)	C(18)-C(17)-C(19)	119.4(3)
N(2)-C(27)-C(40)	116.6(3)	C(12)-N(6)-C(8)	117.8(3)	C(16)-C(17)-C(19)	121.0(4)
C(28)-C(27)-C(40)	120.6(4)	C(7)-C(1)-C(2)	121.2(3)	C(17)-C(18)-C(13)	120.3(3)
C(27)-C(28)-C(29)	116.8(4)	C(1)-C(2)-C(3)	119.0(4)	O(6)-C(19)-O(5)	122.3(4)
C(30)-C(29)-C(28)	120.5(4)	C(5)-C(3)-C(2)	119.3(3)	O(6)-C(19)-C(17)	123.8(4)
C(31)-C(30)-C(29)	117.2(4)	C(5)-C(3)-C(4)	119.7(3)	O(5)-C(19)-C(17)	113.9(3)
N(2)-C(31)-C(30)	124.0(4)	C(2)-C(3)-C(4)	121.0(4)	O(10)-C(43)-N(4)	124.5(3)
N(2)-C(31)-C(39)	116.8(3)	O(8)-C(4)-O(7)	122.9(4)	O(10)-C(43)-C(12)	120.1(3)
C(30)-C(31)-C(39)	119.3(3)	O(8)-C(4)-C(3)	122.7(4)	N(4)-C(43)-C(12)	115.4(3)
C(37)-C(32)-C(33)	118.4(4)	O(7)-C(4)-C(3)	114.4(3)	O(9)-C(44)-N(5)	123.6(3)
C(37)-C(32)-C(42)	120.6(4)	C(6)-C(5)-C(3)	121.1(3)	O(9)-C(44)-C(8)	121.6(3)
C(33)-C(32)-C(42)	121.0(4)	C(5)-C(6)-C(7)	120.4(4)	N(5)-C(44)-C(8)	114.8(3)
C(34)-C(33)-C(32)	120.3(4)	C(1)-C(7)-C(6)	119.0(3)	N(5)-C(45)-C(7)	112.1(3)
C(33)-C(34)-C(35)	120.1(4)	C(1)-C(7)-C(45)	120.3(3)	N(4)-C(46)-C(14)	111.7(3)
C(36)-C(35)-C(34)	119.2(4)	C(6)-C(7)-C(45)	120.6(4)		

Table S3. Hydrogen bonds with $H..A < r(A) + 2.000$ Angstroms and $\angle DHA > 110$ deg.

D-H	d(D-H)	d(H..A)	$\angle DHA$	d(D..A)	A	Symmetry operation
O3-H3	0.820	1.742	176.05	2.560	O21	[-x+1, y-1/2, -z]
O11-H11	0.820	1.934	160.99	2.723	O2	[-x+1, y+1/2, -z]
N1-H1	0.860	2.116	150.87	2.897	O8	[x, y, z-1]
N3-H3A	0.860	2.155	148.35	2.922	O8	[x, y, z-1]
O5-H5	0.820	1.899	170.60	2.712	O22	[x, y-1, z+1]
O7-H7	0.820	1.819	162.14	2.612	O25	[x-1, y, z+1]
N4-H4	0.860	2.100	148.77	2.871	O4	[x, y, z+1]
N5-H5A	0.860	2.134	153.70	2.930	O4	[x, y, z+1]
O22-H61	0.631	2.110	171.92	2.736	O10	[x, y+1, z]
O25-H63	0.640	2.090	173.97	2.728	O9	[x+1, y, z]
O21-H64	0.761	2.000	170.06	2.752	O1	[-x+1, y+1/2, -z+1]

Table S4. Binding constants obtained by fitting various spectroscopic data from the titration of **H₂L** with Eu(CF₃SO₃)₃ in acetonitrile.

Species	Absorbance	Eu(III)-centered emission
	$\log\beta_{M/L}$	$\log\beta_{M/L}$
$\log\beta_{1:1}$	6.6 (6)	7.5 (5)
$\log\beta_{1:2}$	14.15 (6)	15.8 (7)
$\log\beta_{1:3}$	21.03 (8)	22.5 (8)

Table S5. Binding constants obtained by fitting various spectroscopic data from the titration of **H₂L** with Tb(CF₃SO₃)₃ in acetonitrile.

Species	Absorbance	Tb(III)-centered emission
	$\log\beta_{M/L}$	$\log\beta_{M/L}$
$\log\beta_{1:1}$	6.9 (1)	9.1 (3)
$\log\beta_{1:2}$	13.8 (2)	16.5 (4)
$\log\beta_{1:3}$	18.7 (5)	21.6 (7)

Table S6. Binding constants obtained by fitting various spectroscopic data from the titration of **H₂L** with Eu(CF₃SO₃)₃ in methanol.

Species	Absorbance	Eu(III)-centered emission
	$\log\beta_{\text{M/L}}$	$\log\beta_{\text{M/L}}$
$\log\beta_{1:1}$	-	6.70 (7)
$\log\beta_{1:2}$	12.2 (2)	12.56 (7)
$\log\beta_{2:2}$	18.9 (4)	18.5 (1)
$\log\beta_{3:2}$	25.2 (4)	23.3 (1)

Table S7. Binding constants obtained by fitting various spectroscopic data from the titration of **H₂L** with Tb(CF₃SO₃)₃ in methanol.

Species	Absorbance	Tb(III)-centered emission
	$\log\beta_{\text{M/L}}$	$\log\beta_{\text{M/L}}$
$\log\beta_{1:1}$	-	6.6 (1)
$\log\beta_{1:2}$	12.4 (4)	11.63 (10)
$\log\beta_{2:2}$	19.7 (6)	18.7 (2)
$\log\beta_{3:2}$	24.0 (6)	22.7 (2)