Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Metallopolymers Cross-Linked with Self-Assembled Ln_4L_4 Cages

Qian-Qian Yan,[a, ‡] Li-Peng Zhou,[a, ‡] Hai-Yue Zhou,[a, c] Zhuo Wang,[a, b] Li-Xuan Cai,[a] Xiao-Qing Guo,[a, b] Xiao-Qi Sun,[a, c] Qing-Fu Sun*[,a, b]

[a]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China.

[b]University of Chinese Academy of Sciences, Beijing 100049, PR China.

[c]Xiamen Institute of Rare Earth Materials, Haixi Institute, Chinese Academy of Sciences, Xiamen 361021, P. R. China
‡Equal contribution

Cooresponding to: qfsun@fjirsm.ac.cn

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1. General

Unless otherwise specified, all reagents and solvents were purchased from commercial sources and used without further purification. Commercial DVB-55 contains 55% effective crosslinker molecules of *para*- and *meta*-divinylbenzene isomers and 45% of the *para*- and *meta*-ethylvinyl isomers. Deuterated solvents were purchased from Admas, J&K scientific and Sigma-Aldrich. Dichloromethane (DCM) was dried by CaH_2. 1D and 2D-NMR spectra were measured on a Bruker Biospin Avance III (400 MHz) spectrometer. ^1H-NMR chemical shifts were determined with respect to residual signals of the deuterated solvents used. ESI-TOF-MS were recorded on an Impact II UHR-TOF mass spectrometry from Bruker, with tuning mix as the internal standard. Data analysis was conducted with the Bruker Data Analysis software (Version 4.3) and simulations were performed with the Bruker Isotope Pattern software. Excitation and emission spectra were recorded on the FS5 spectrofluorometer from Edinburg Photonics. Spectra were corrected for the experimental functions. The solid powder sample is sandwiched between two quartz plates one of which has a concave.The absolute luminescence quantum (Φ) was measured at room temperature by using the FS5 spectrofluorometer from Edinburg Photonics (SC-30 Integrating Sphere):

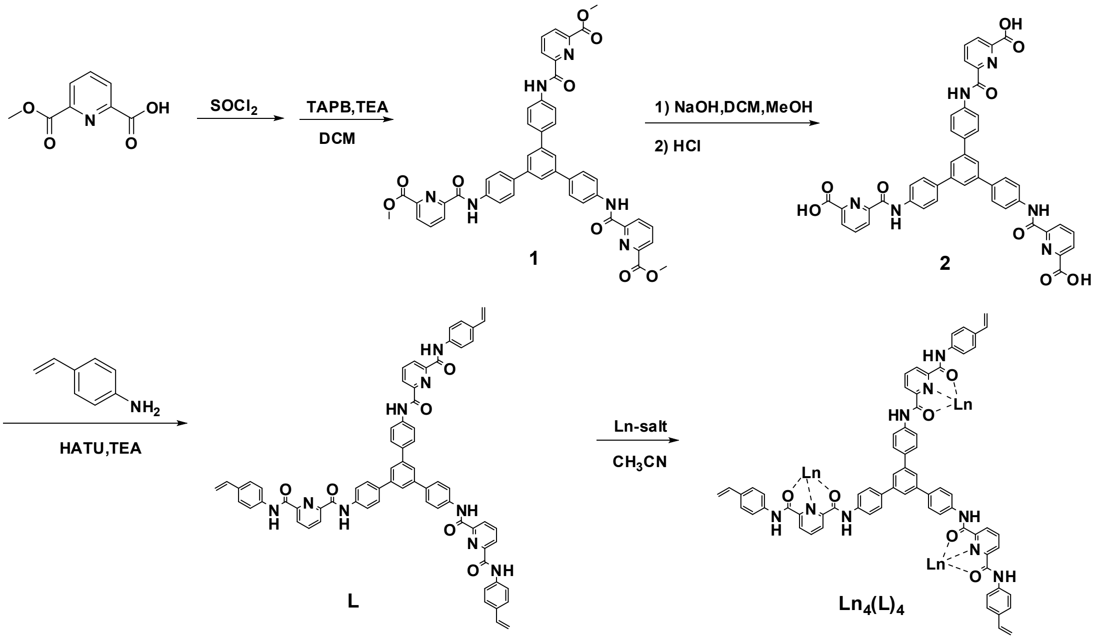
$$\Phi = \text{emissive photon number} / \text{absorbent photon number}$$

Thermogravimetric analyses (TGA) were carried out on STA449F3 analyzer (Netzsch) under N_2 atmosphere at a heating rate of 10 k • min^{-1} within a temperature range of 35-800 °C. Fourier transform infrared (FT-IR) spectra were taken on VERTEX70 from Bruker. Low-pressure volumetric N_2 gas adsorption measurements by Brunauer-Emmett-Teller (BET) method were performed on Intelligent Gravimetric Sorption Analyser (IGA 100B). FE-SEM images and energy-dispersive spectroscope (EDS) were obtained on a Field Emission Scanning Microscope (SU-8010).

Caution! Perchlorate salts are potentially explosive and should be handled carefully in small quantities.

2. Synthetic Procedures

Scheme S1. Synthesis procedure of the ligand **L** and lanthanide complexes Ln_4**L_4**.



Synthesis of 1,3,5-tris-(4-aminophenyl)benzene (TAPB). TAPB was synthesized according to previous procedures.[S1] ^{1}H NMR (400 MHz, d_6-DMSO, 298 K): δ 7.49 (s, 3H), 7.47 (d, *J* = 8.6 Hz, 6H), 6.67 (d, *J* = 8.5 Hz, 6H), 5.21 (s, 6H).

Synthesis of compound 1 The 2, 6-pyridinedicarboxylic acid monomethyl ester (2.71 g, 15.0 mmol) was dissolved in thionyl chloride (12mL), followed by the addition of 2 drops of DMF at room temperature. The reaction mixture was then stirred at room temperature for 12 h until the solution came to clear. The excess $SOCl_2$ was removed in vacuo. The resulting residue was used without further purification. The acid chloride was dissolved in DCM (50 mL) and treated with TAPB (1.50 g, 4.27 mmol). Triethylamine (TEA, 3 mL, 21.6 mmol) was added dropwise to the suspension at 0 °C and stirred for overnight. The solid was collected by filtration and washed with CH_2Cl_2, then dried under vacuum to give the product as an off white powder (3.43 g, 4.08 mmol, yield 95.5%). ^{1}H NMR (400 MHz, MeOD:$CDCl_3$=1:2, 298 K): δ 10.97 (s, 3H), 8.53 (d, *J* = 7.8Hz, 3H), 8.33 (d, *J* = 7.8Hz, 3H), 8.17 (t, *J* = 7.8 Hz, 3H), 8.07 - 8.02 (m, 6H), 7.87 - 7.80 (m, 9H), 4.12 (s, 9H).^{13}C NMR (100 MHz, MeOD:$CDCl_3$ = 1:2, 298 K): δ 165.91, 162.38, 150.98, 146.25, 142.07, 139.51, 137.83, 137.66, 128.06, 127.92, 126.52, 124.68, 121.24, 53.58.

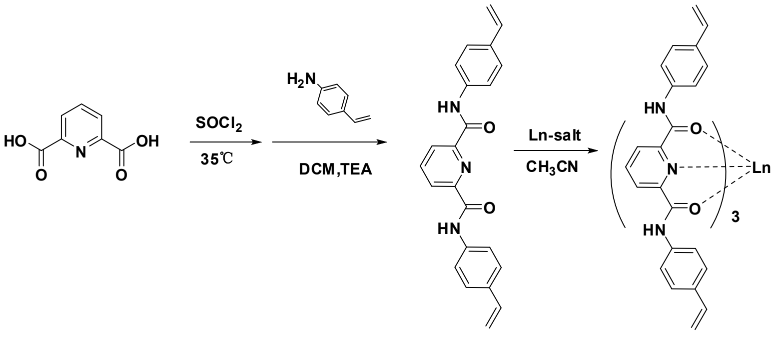
Synthesis of compound 2 Compound **1** (1.983 g, 2.36 mmol), NaOH (1.12 g, 28 mmol) were placed in a 2:3 mixture of MeOH and CH_2Cl_2 (250 mL total) with 1 mL of water. The reaction mixture was then refluxed for overnight. The solvent was removed in vacuo by rotary evaporation and then redissolved in 200 mL of water. After removing the insoluble by filtration, the filtrate was acidified to a pH value of ~2 with a 1.0 M HCl solution. The precipitation was collected by filtration and dried under vacuum to give the product as greyish-green solid (1.73 g, 2.17 mmol, yield 91.84%). ^{1}H NMR (400 MHz, d_6-DMSO, 298 K): δ 11.07 (s, 3H), 8.41 (d, *J* = 7.3 Hz, 3H), 8.34 - 8.23 (m, 6H), 8.12 - 7.84 (m, 15H).

Synthesis of Ligand L To a 60 mL DMF solution of Compound **2** (1.4 g, 1.88 mmol), 4-aminostyrene (0.783 g, 6.57 mmol) and TEA (TEA, 3 mL, 21.6 mmol), HATU(4.21 g, 11.3 mmol) was added in ice bath and stirred for overnight at room temperature to get a pale yellow solution. After DMF was removed in vacuo by rotary evaporation, 150 mL water was added into the residues. The emerging precipitate was filtered and washed with water, CH_2Cl_2, CH_3CN, CH_3OH, respectively. Finally, the precipitate was dried at room temperature in vacuo to obtain off white solids (1.81 g, 1.64 mmol, yield 88.2%). ^{1}H NMR (400 MHz, *d*$_6$-DMSO, 298 K): δ 11.15 (d, *J* = 22.0 Hz, 6H), 8.45 (t, *J* = 7.1 Hz, 6H), 8.34 (t, *J* = 7.7 Hz, 3H), 8.14 (d, *J* = 8.7 Hz, 6H), 8.07 - 8.00 (m, 9H), 7.97 (d, *J* = 8.6 Hz, 6H), 7.58 (d, *J* = 8.6 Hz, 6H), 6.76 (dd, *J* = 17.6, 11.0 Hz, 3H), 5.83 (d, *J* = 17.7 Hz, 3H), 5.25 (d, *J* = 11.3 Hz, 3H).^{13}C NMR (100 MHz, *d*$_6$-DMSO, 298 K) δ 161.80, 161.68, 148.89, 148.88, 141.13, 140.10, 137.89, 137.81, 136.18, 136.02, 133.32, 127.56, 126.68, 125.47, 123.60, 121.35, 121.03, 120.59, 113.50.

Synthesis of $Eu_4L_4(OTf)_{12}$ To a suspension of **L** (12 mg, 0.011 mmol) in 0.6 mL CD_3CN, a solution of $Eu(OTf)_3$ (6.6 mg, 0.011 mmol) in CD_3CN was added, and then stirred at 40°C for 1 h. The yellow suspension turned into homogeneous yellow solution. This solution was characterized without further treatment (yield 96 %). ^{1}H NMR (400 MHz,CD_3CN, 298 K) δ 8.03 (s, 6H), 7.65 (d, *J* = 3.9 Hz, 6H), 7.60 - 7.53 (m,3H), 7.47 (s, 3H), 7.31 (d, *J* = 5.8 Hz, 6H), 7.27 (s, 3H), 7.09 (s, 6H), 6.98 (d, *J* = 5.3 Hz, 3H), 6.86 (d, *J* = 5.9 Hz, 3H), 6.77 (s, 3H), 6.69 (dd, *J* = 16.9, 11.2 Hz, 3H), 5.74 (d, *J* = 17.5 Hz, 3H), 5.26 (d, *J* = 10.6 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ 162.18, 161.59, 157.16, 145.71, 144.81, 140.75, 139.76, 137.94, 136.28, 136.02, 135.29, 128.05, 127.33, 125.17, 124.91, 124.10, 121.92, 115.98, 93.88. ESI-TOF-MS (CH_3CN) calcd for $[Eu_4L_4(OTf)_4\text{-}5H]^{3+}$ 1869.3502， found 1869.3485.

The complex of $Eu_4L_4(ClO_4)_{12}$, $La_4L_4(OTf)_{12}$, $La_4L_4(ClO_4)_{12}$ were also prepared by a same procedure, only replaced with the corresponding rare earth sources.

Scheme S2. Synthesis procedure of the ligand **L′** and lanthanide complexes Ln**L′**$_3$.



L'

LnL'$_3$

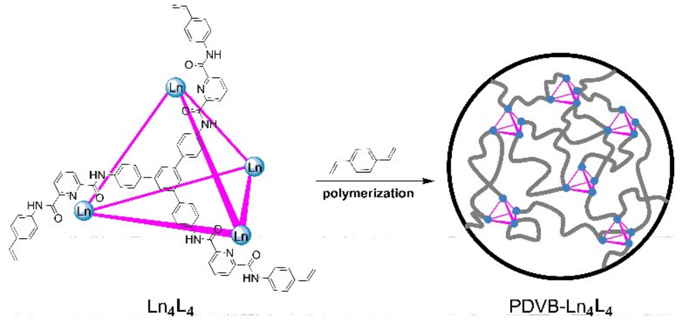
Synthesis of Ligand L′ 2,6-pyridinedicarboxylic acid (500 mg, 2.99 mmol) was dissolved in thionyl chloride (10mL), followed by the addition of 2 drops of DMF at room temperature. The reaction mixture was then stirred at room temperature for 12 h until the solution come to clear. The excess $SOCl_2$ was removed in vacuo. The resulting residue was used without further purification. The acid chloride was dissolved in DCM (50 mL) and treated with 4-aminostyrene (891 mg, 7.48 mmol).

Triethylamine (TEA, 2 mL) was added dropwise into the suspension at 0 °C and stirred for overnight. The resulting residue was purified with flash column chromatography (DCM) to give **L′** as a white solid (728 mg, 1.97 mmol, yield 66 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.53 (s, 2H), 8.48 (d, J = 7.8 Hz, 2H), 8.13 (t, J = 7.8 Hz, 2H), 7.74 (d, J = 8.5 Hz, 4H), 7.45 (d, J = 8.5 Hz, 4H), 6.71 (dd, J = 17.6, 10.9 Hz, 2H), 5.73 (d, J = 17.6 Hz, 2H), 5.25 (d, J = 10.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 161.15, 149.07, 139.80, 136.73, 136.15, 134.59, 127.18, 125.78, 120.28, 113.70.

Synthesis of $Eu(L')_3(OTf)_{12}$ $Eu\mathbf{L}'_3(OTf)_3$ was synthesized according to the same procedure as $La_4\mathbf{L}_4(OTf)_{12}$. To a suspension of **L′** (2.0 mg, 5.41 μmol) in 0.5 mL CD_3CN, a solution of $Eu(OTf)_3$ (1.1 mg, 1.83 μmol) in CD_3CN was added, and then stirred at 40°C for 1 h. The gained homogeneous yellow solution was characterized without further treatment (yield 98 %). ^{1}H NMR (400 MHz, CD_3CN，298 K): δ 7.39 (d, *J* = 7.6 Hz, 4H), 6.87 (s, 4H), 6.71 (dd, *J* = 17.7, 11.0 Hz, 2H), 5.88 (s, 1H), 5.72 (d, *J* = 17.7 Hz, 2H), 5.20 (d, *J* = 11.0 Hz, 2H), 4.61 (d, *J* = 79.9 Hz, 4H). ^{13}C NMR (100 MHz, CD_3CN, 298 K) ：δ 137.81, 136.77,135.17, 127.45, 124.16, 121.77, 118.61, 115.97, 115.44, 112.27.

Synthesis of polymer

Scheme S3. Synthesis procedure of the copolymer PDVB-$Ln_4\mathbf{L}_4$.



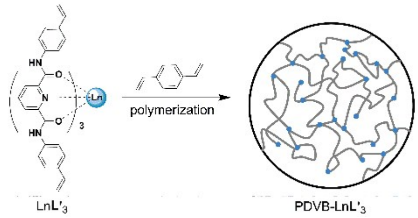
PDVB-Eu_4L_4 **L** (73.84 mg, 0.067 mmol, 10 wt % relative to DVB-55), $Eu(OTf)_3$ (40 mg, 0.067mmol) and 11.4 mL of CH_3CN were added into a 25 mL reaction tube. The reaction mixture was then stirred at 40°C for 1 h and the solid progressively dissolved to give a homogeneous yellow solution. Then, DVB-55 (800 μL, 734 mg, 5 vol % relative to total solvent), AIBN (14.6 mg, 2.0 wt % relative to DVB-55) and 3.8 mL of toluene were added. The solution was elevated to 75℃ within 30 min and stirred for 24 h under the N_2 atmosphere. Solvent was removed from the gained yellow collosol by rotary evaporation to give yellow solid. To remove the unreacted monomer, free $\mathbf{Eu_4L_4}$ complex, soluble oligomer and trace initiator residue, the solid was washed with CH_3CN, CH_3OH, CH_2Cl_2, respectively. Finally, the solid was dried at room temperature in vacuo to obtain yellow powder (661 mg, yield 78.0 %). The content of Eu in the copolymers PDVB-$Eu_4\mathbf{L}_4$ was determined to be 11.787 mg/g by ICP-AES, close to the theoretical value of 11.763 mg/g.

PDVB, PDVB-**L**, PDVB-Eu$\mathbf{L}'_3$ were synthesized with the similar procedure, starting from DVB-55 without ligand and metal salt, DVB-55 with ligand, and DVB-55 with metal complex Eu$\mathbf{L}'_3$.

PDVB DVB-55 (800 µL, 734 mg, 5 vol % relative to total solvent), AIBN (14.6 mg, 2.0 wt % relative to DVB-55), 11.4 mL CH_3CN and 3.8 mL toluene were added into a 25 mL reaction tube. The solution was elevated to 75℃ within 30 min and stirred for 24 h under the N_2 atmosphere. Solvent was removed by rotary evaporation to give white powder. The unreacted monomer, soluble oligomer and trace initiator residue were removed by successively washing the power with CH_3CN, CH_2Cl_2, respectively. Finally, the powder was dried at room temperature in vacuo to obtain white solid (496 mg, yield 67.6 %).

PDVB-L For solubility reasons, PDVB-L was synthesized in the mixture solution (DMF: toluene =75:25). DVB-55 (800 µL, 734 mg, 5 vol % relative to total solvent), **L** (73.84 mg, 0.067 mmol, 10 wt % relative to DVB-55), AIBN (14.6 mg, 2.0 wt % relative to DVB-55), 11.4 mL DMF and 3.8 mL of toluene were added into a 25 mL reaction tube. The solution was elevated to 75℃ within 30 min and stirred for 24 h under the N_2 atmosphere. Solvent was removed by rotary evaporation to give yellow solid. The unreacted monomer, soluble oligomer and trace initiator residue were removed by successively washing with DMF, CH_3CN, CH_2Cl_2, respectively. Finally, the solid were dried at room temperature in vacuo to obtain yellow powder (582 mg, yield 72.0 %).

Scheme S4. Synthesis procedure of the copolymer PDVB-Ln $\mathbf{L}'_3$.



PDVB-EuL′$_3$ L′ (74.25 mg, 0.20 mmol), Eu(OTf)$_3$ (40 mg, 0.067mmol) and 11.4 mL of CH_3CN were added into a 25 mL reaction tube. The reaction mixture was then stirred at 40°C for 1 h and the solid progressively dissolved to give a homogeneous yellow solution. Then, DVB-55 (800 µL, 734 mg, 5 vol % relative to total solvent), AIBN (14.6 mg, 2.0 wt % relative to DVB-55) and 3.8 mL of toluene were added. The solution was elevated to 75℃ within 30 min and stirred for 24 h under the N_2 atmosphere. Solvent was removed by rotary evaporation to give yellow solid. To remove the unreacted monomer, free **EuL′**$_3$ complex, soluble oligomer and trace initiator residue, the solid was washed with CH_3CN, CH_3OH, CH_2Cl_2, respectively. Finally, the solid was dried at room temperature in vacuo to obtain yellow powder (640 mg, yield 75.4 %). The content of Eu in the copolymers PDVB-**EuL′**$_3$ was determined to be 13.852 mg/g by ICP-AES, higher than the theoretical value of 11.758 mg/g.

3. Single crystal X-ray diffraction study

Single crystals of Eu$_4$**L**$_4$ complex was obtained by slow diffusion of DCM vapor into the acetonitrile solution of the $Eu_4\mathbf{L}_4$ complex. The X-ray diffraction studies for the complex $Eu_4\mathbf{L}_4$ was carried out on the BL17U1 macromolecular crystallography beamline in Shanghai Synchrotron Facility.[S2] We thank the staff of BL17B/BL18U1/ BL19U1 beamlines at National Centre for Protein Sciences Shanghai and Shanghai Synchrotron Radiation Facility, Shanghai, People's Republic of China, for assistance during data collection. The collected diffraction data were processed with the HKL2000 software program.[S3] The structures were solved by direct methods and refined by full-matrixleast-squares on *F2* with anisotropic displacement using the SHELXTL software package.[S4]

Crystal data for $Eu_4\mathbf{L}_4(ClO_4)_{12}$ (CCDC-1883128): Space group *fddd*, a = 15.1924(19) Å, b = 62.679(10) Å, c = 95.062(13) Å, α = β= γ = 90°, V = 90523(22) $Å^3$, Z = 8, T = 293(2) K. Anisotropic least-squares refinement for the framework atoms and isotropic refinement for the other atoms on 4284 independent merged reflections (R_{int} = 0.1376) converged at residual $wR2$ = 0.4808 for all data; residual $R1$ = 0.1634 for 3382 observed data [$I > 2\sigma(I)$], and goodness of fit (GOF) = 2.478.

CCDC-1883128 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving. html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk)

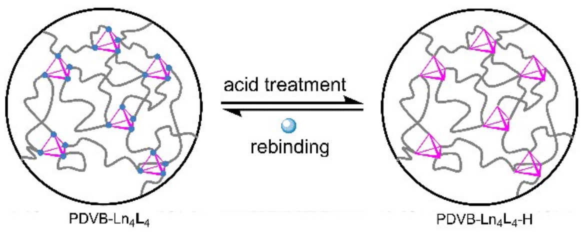
Note: The crystals of this giant supramolecular assembly diffract very weekly in nature. There was just no significant diffraction intensity at high angles (Theta > 15.3) even though we optimized the measurement based on synchrotron radiations. During the refinement, a lot of constrains and restraints have to to be applied due to the poor data/parameter ratio. The main purpose of providing such a poor crystal structure is to confirm the successful self-assembly of the tetrahedral complex.

4. Ion adsorption and separation

ICP test: 20 mg polymer sample was suspended in CH_3CN (0.8 mL) and $CHCl_3$ (0.2 mL), followed the addition of 1.0 M HNO_3 (1 mL). The suspension solution was sonicated and then stirred for 3 hours at room temperature. The supernatant liquor (1 mL) was condensed, dried, and redissolved in 1M HNO_3 (1mL) and H_2O (9 mL) for ICP test.

The lanthanide ions were leached from the above synthesized lanthanide-containing polymers by acid treatment (**Scheme S3**). PDVB-Eu_4L_4 (200 mg) was suspended in CH_3CN (2 mL) and $CHCl_3$ (2 mL), followed the addition of 0.5 M HCl (2 mL). The suspension solution was sonicated and then stirred at room temperature. After an hour, centrifuge and remove the supernatant liquor. Repeat preceding procedures for three times and the precipitation was finally dried under vacuum at 70 ℃ for 5 hours. The PDVB-Eu_4L_4-H polymer was obtained for the further adsorption studies (150 mg). In a similar method, other lanthanide-free polymers were prepared.

Scheme S5. The leach and rebinding of lanthanide ion from the PDVB-$Ln_4\mathbf{L}_4$ ploymer



The absorption of the lanthanide ions of the polymers was studied. To the four vials filled with 50 mg PDVB, PDVB-L, PDVB-EuL$_3$, PDVB-Eu$_4$L$_4$, respectively, Eu(OTf)$_3$(2.34mg，3.90μmol)、La(OTf)$_3$ (2.29 mg，3.90 μmol), CH$_3$CN (3.5 mL) and CHCl$_3$ (0.5 mL) were added and then stirred for 3 hours at room temperature. The supematant solution was collected after centrifugation and the content of the Eu^{3+} and La^{3+} in the solution were determined by ICP-MS. While PDVB-**L**, PDVB-Eu(**L′**)$_3$-H and PDVB-Eu$_4$**L**$_4$-H showed absorption for lanthanide ions, nearly no lanthanide ion was extracted into the PDVB due to the absence of the coordination site.

The extraction coefficients of PDVB-**L**, PDVB-Eu(**L′**)$_3$-H and PDVB-Eu$_4$**L**$_4$-H were evaluated by the extraction percentage of metal ions adsorbed on the sorbent (E), sorption capacity of the polymers relative to the metal ions (Q), distribution ratio of metal ions between the polymers and aqueous solutions (D) and selectivity coefficients for specific lanthanide ions relative to other lanthanide ions (S) which were determined using Eq(1)-(4):

$$E(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq(1)}$$

$$Q = \frac{C_i - C_f}{m} \times V \qquad \text{Eq(2)}$$

$$D = \frac{C_i - C_f}{C_f} \times \frac{V}{m} \qquad \text{Eq(3)}$$

$$S_{Ln^2/Ln^1} = \frac{D_{Ln^2}}{D_{Ln^1}} \qquad \text{Eq(4)}$$

where C_i and C_f (mg/L) are the initial and final concentrations of metal ions, V is the volume of the solution, m is the mass of polymer materials (mg).[S5]

5. Figures and tables.

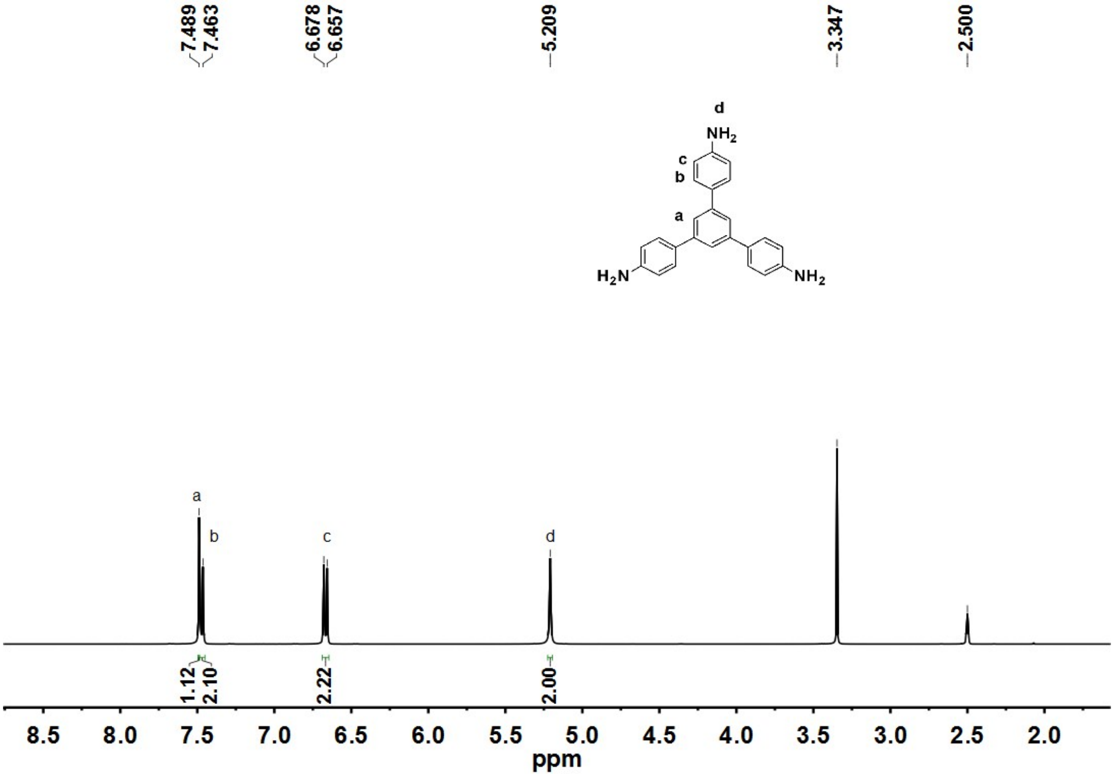


Figure S1. ^{1}H NMR spectrum of **TAPB** (400 MHz, d_6-DMSO, 298K).

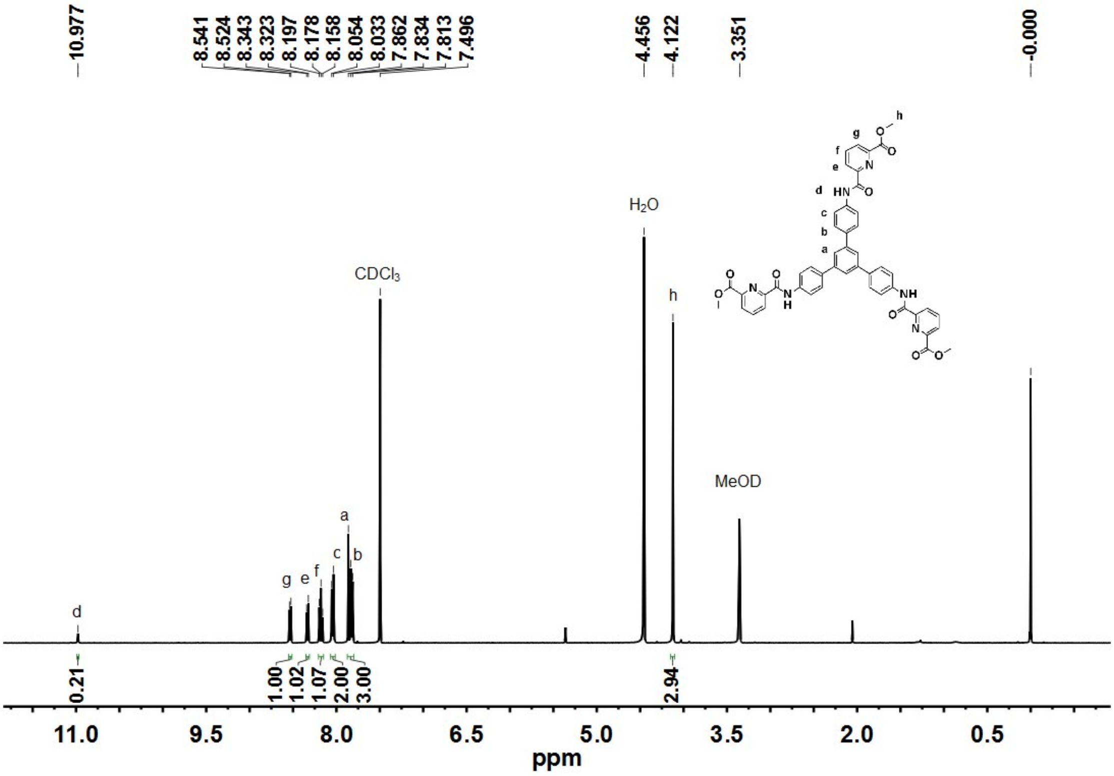


Figure S2. ^{1}H NMR spectrum of compound **1** (400 MHz, MeOD:CDCl$_3$=1:2, 298 K).

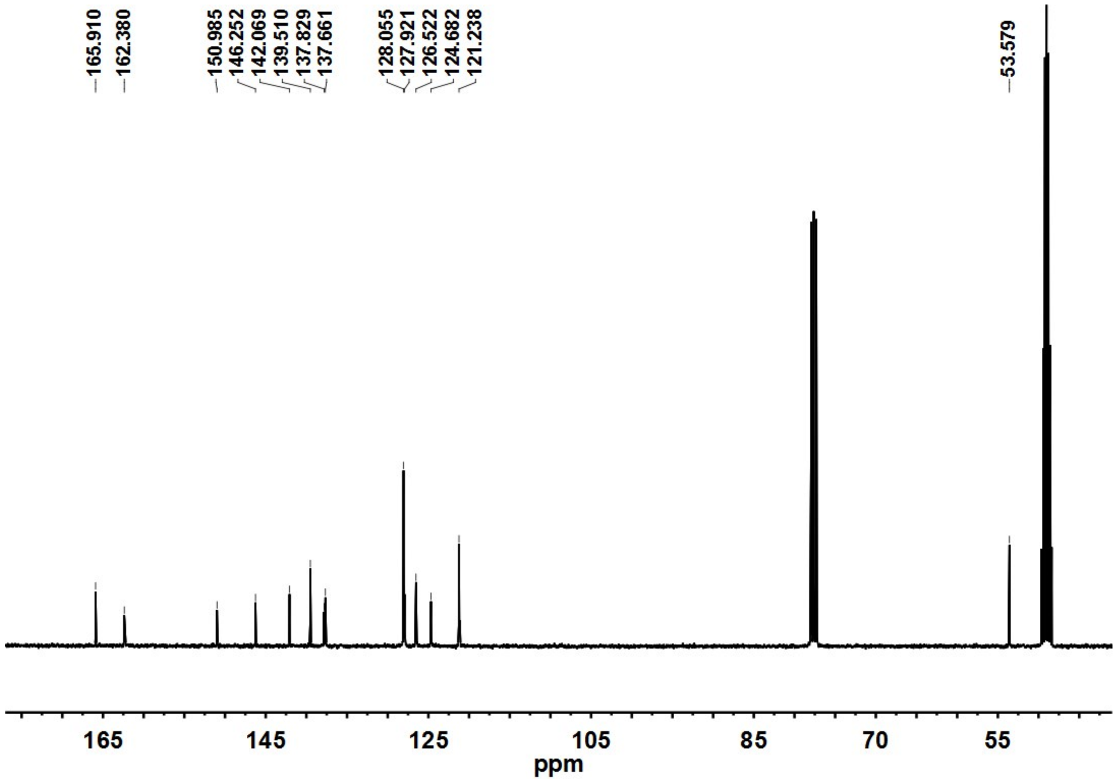


Figure S3. ^{13}C NMR spectrum of compound **1** (100 MHz, MeOD:$CDCl_3$=1:2, 298 K).

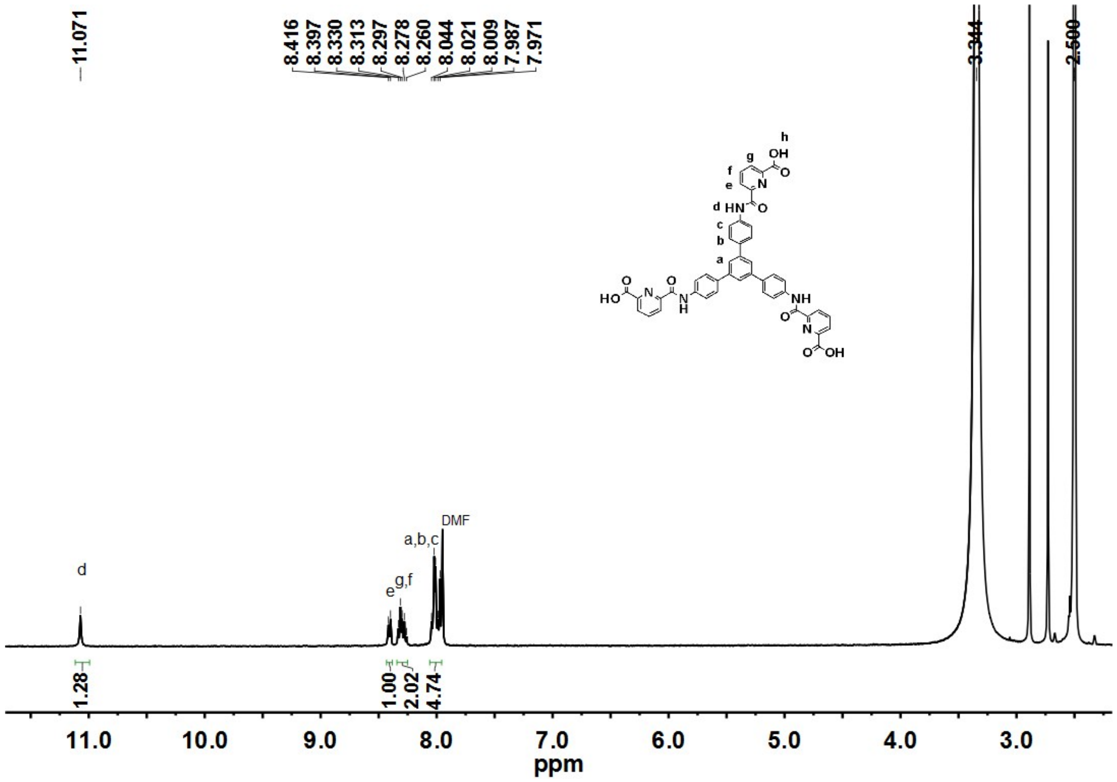


Figure S4. ^{1}H NMR spectrum of compound **2** (400 MHz, d_6-DMSO, 298 K).

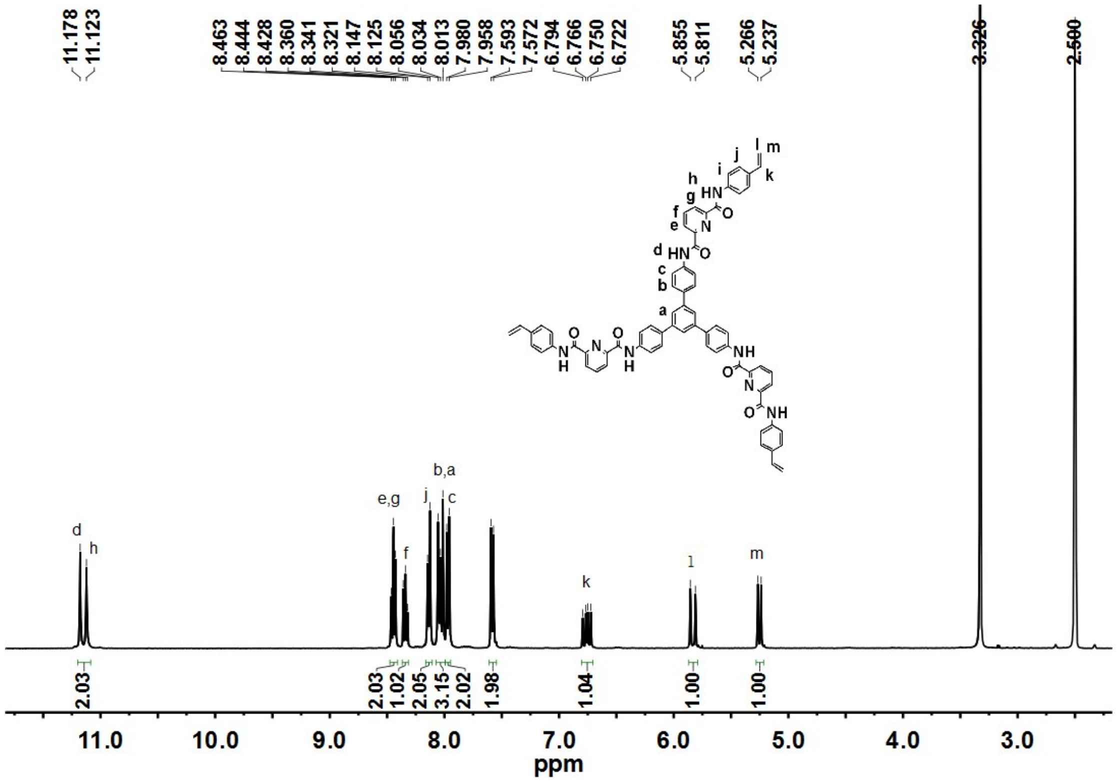


Figure S5. ^{1}H NMR spectrum of ligand **L** (400 MHz, d_6-DMSO, 298 K).

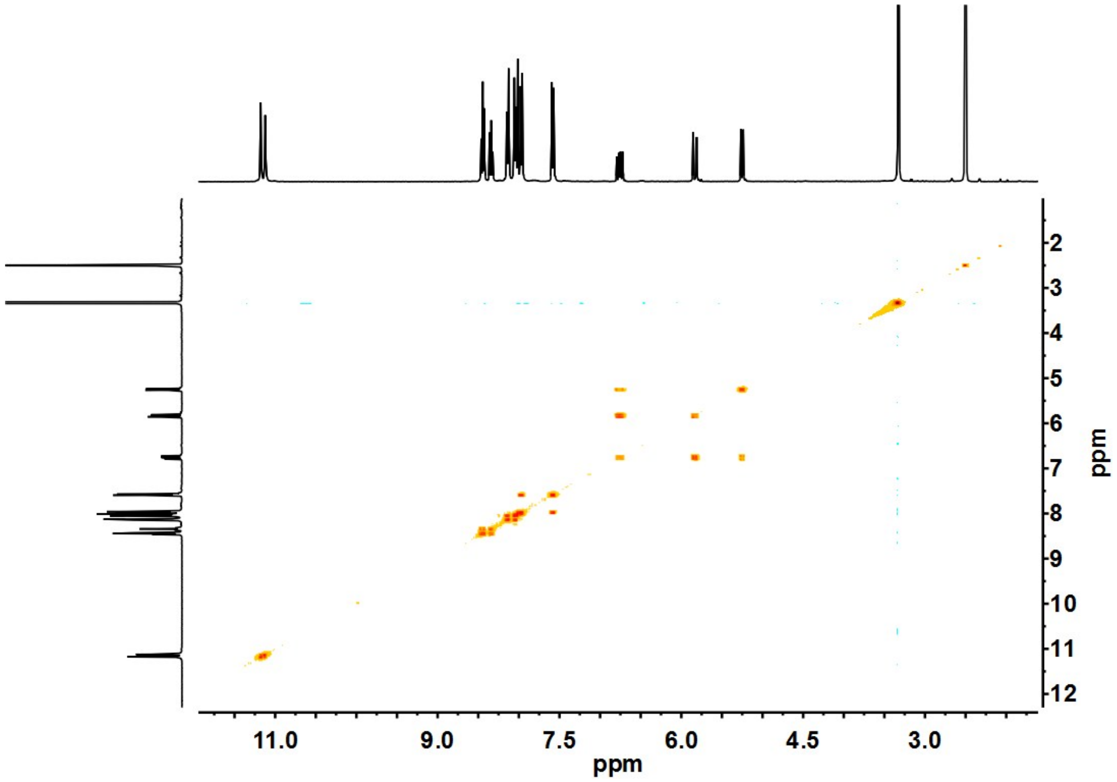


Figure S6. ^{1}H-^{1}H COSY spectrum of ligand **L** (400 MHz, d_6-DMSO, 298 K).

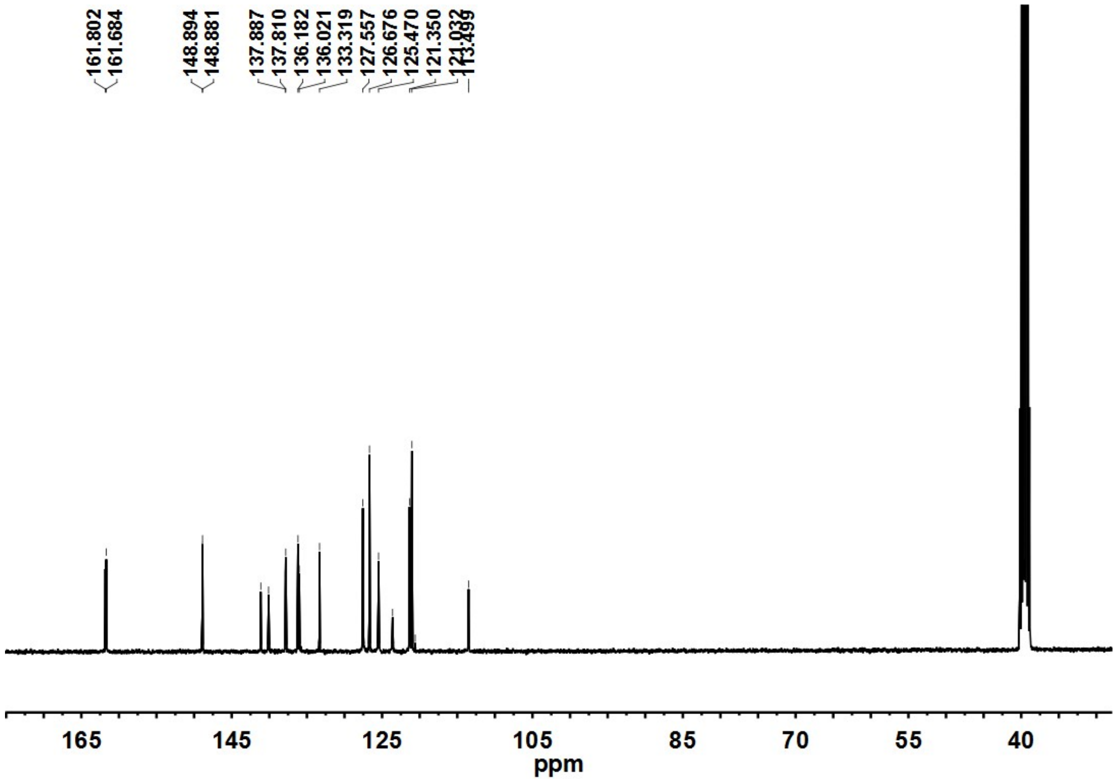


Figure S7. ^{13}C NMR spectrum of Ligand **L** (100 MHz, d_6-DMSO, 298 K).

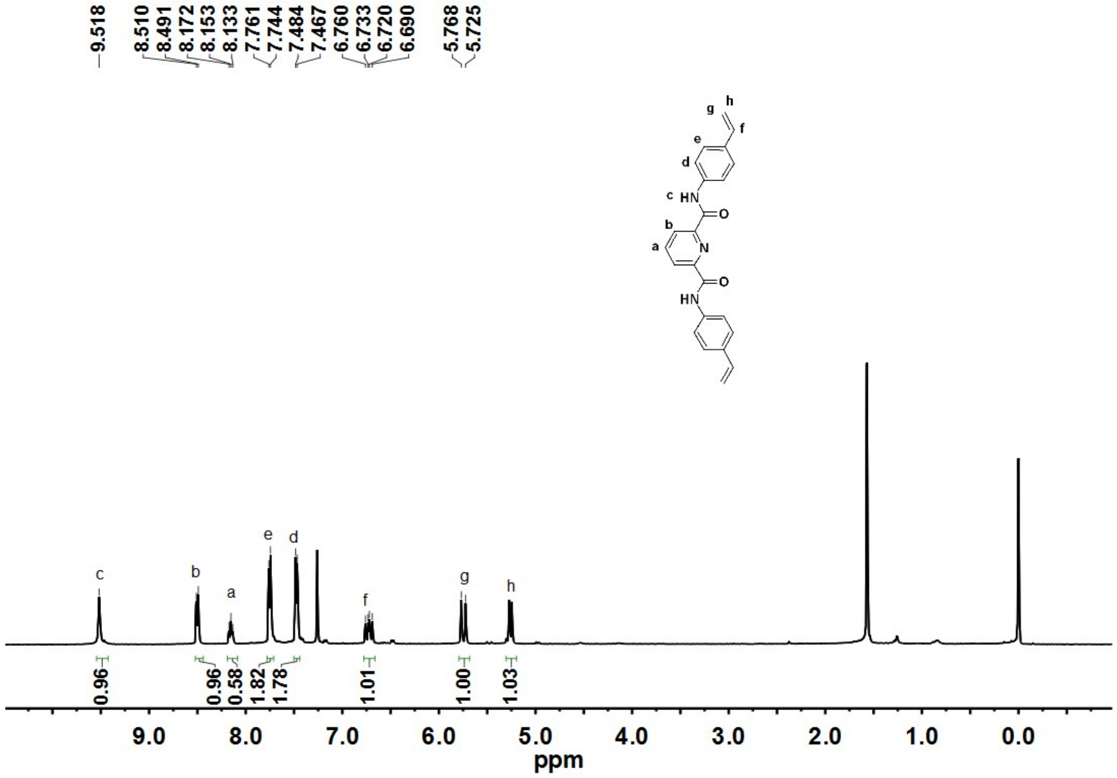


Figure S8. ^{1}H NMR spectrum of ligand **L′** (400MHz, $CDCl_3$, 298K).

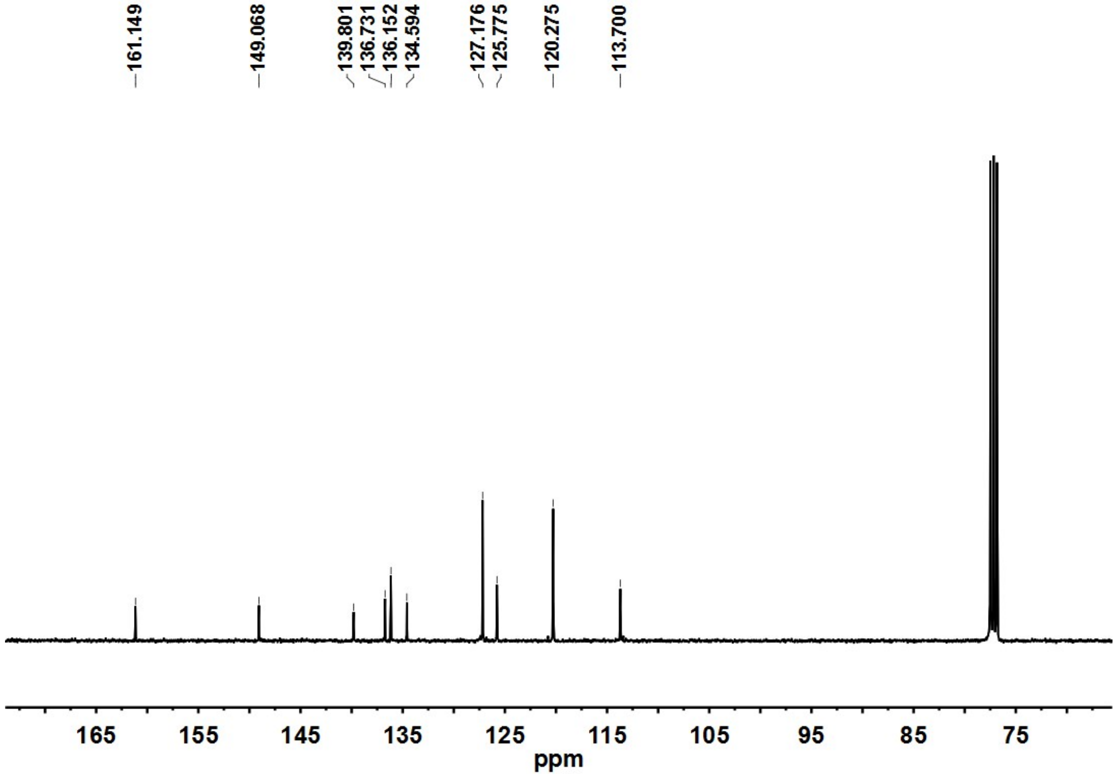


Figure S9. ^{13}C NMR spectrum of ligand **L′** (100MHz, $CDCl_3$, 298K).

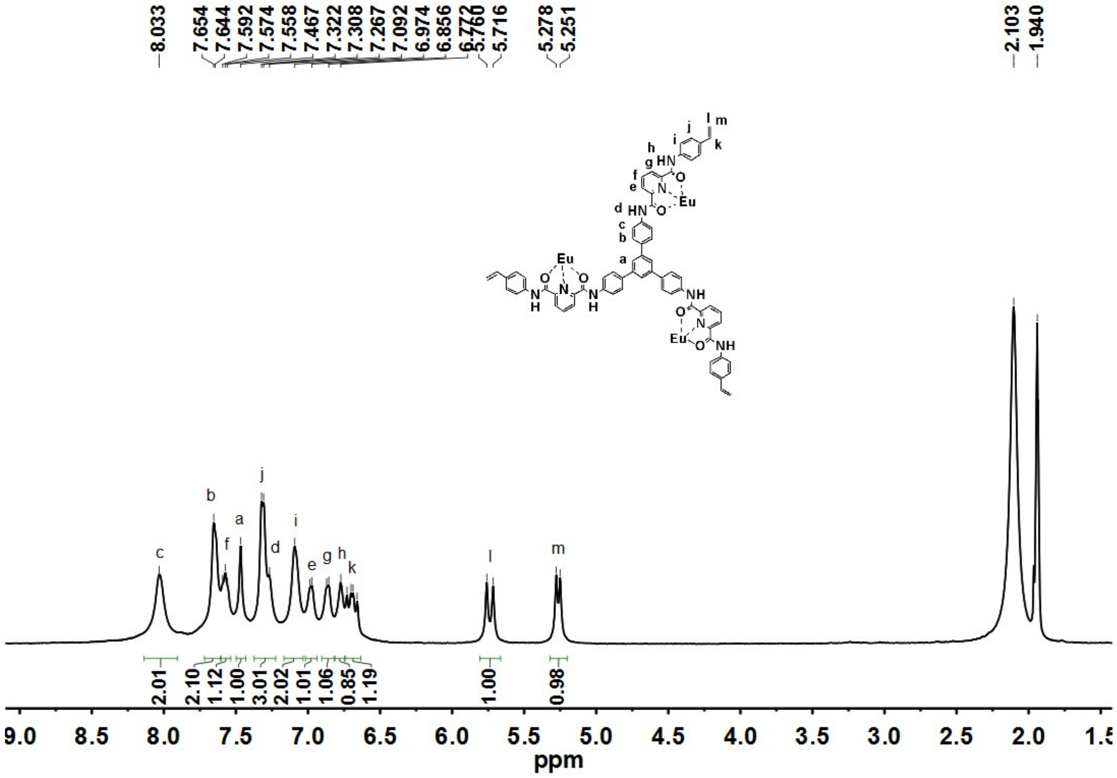


Figure S10. ^{1}H NMR spectrum of the self-assembly complex of **L** and $Eu(OTf)_3$ (400 MHz, CD_3CN, 298 K).

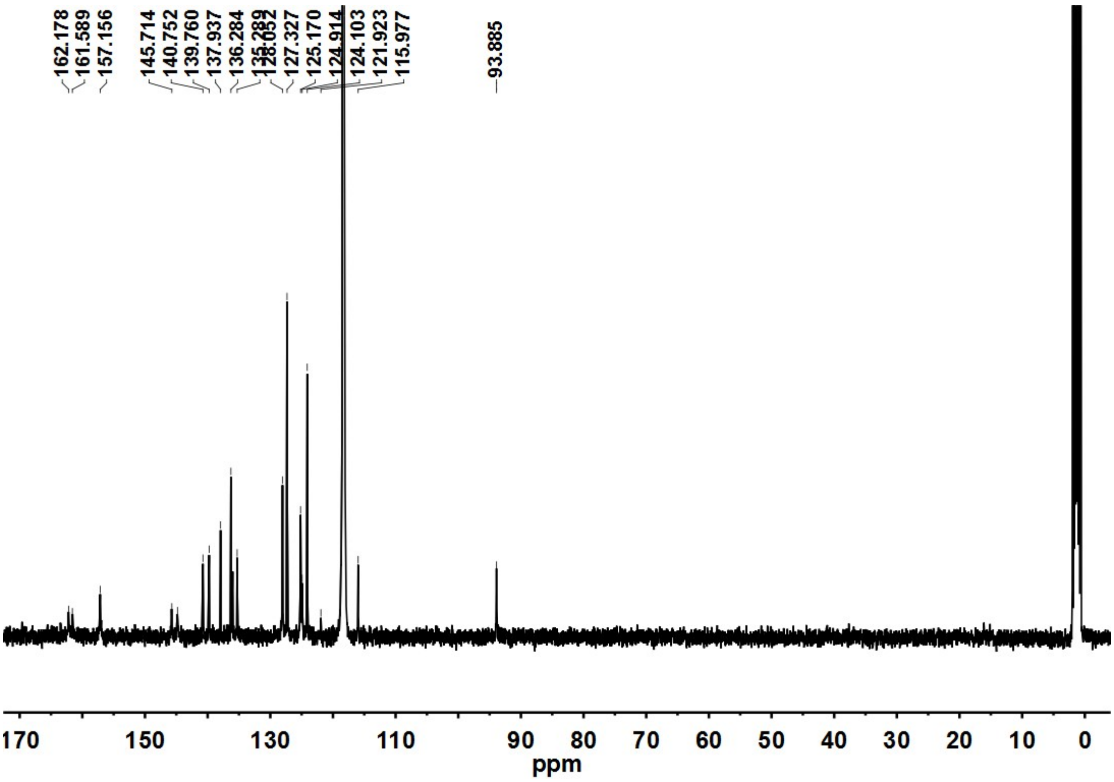


Figure S11. ^{13}C NMR spectrum of the self-assembly complex of **L** and Eu(OTf)$_3$ (100 MHz, CD$_3$CN, 298 K).

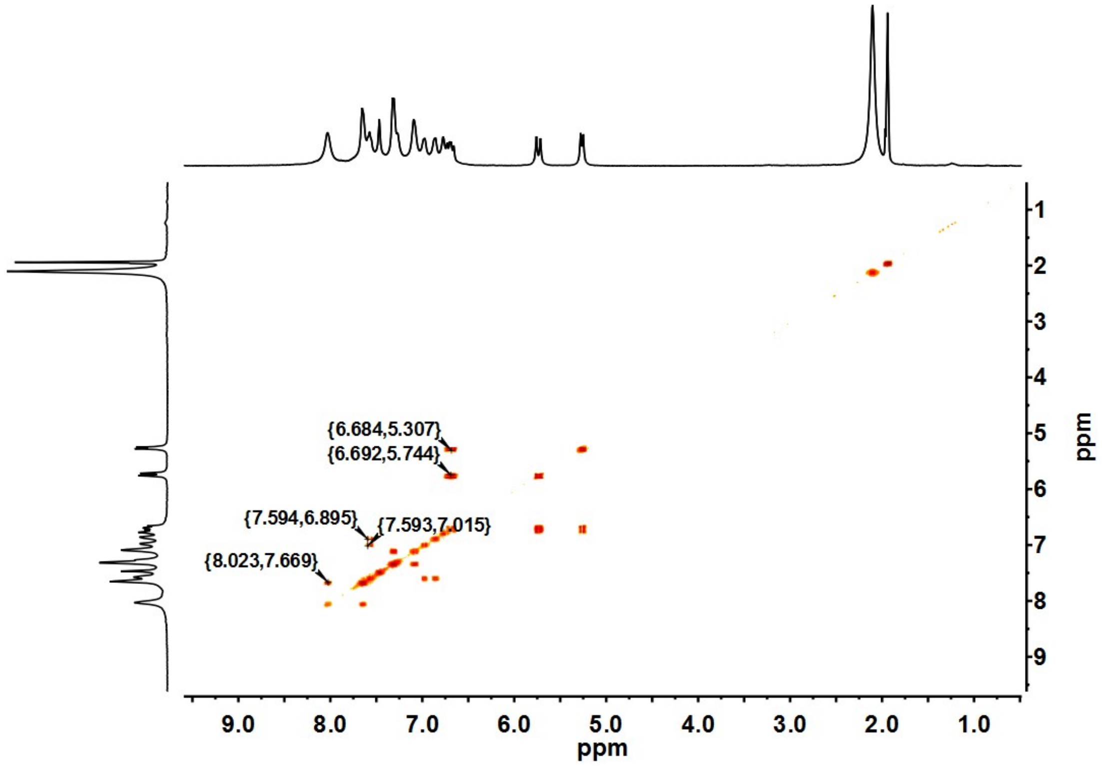


Figure S12. ^{1}H-^{1}H COSY spectrum of the self-assembly complex of **L** and Eu(OTf)$_3$ (400 MHz, CD$_3$CN, 298 K).

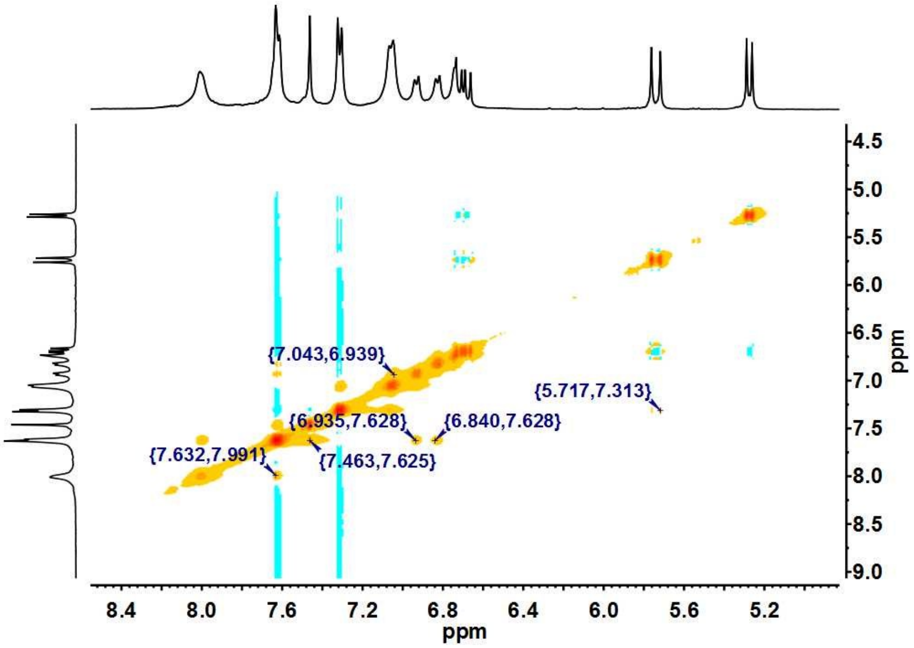
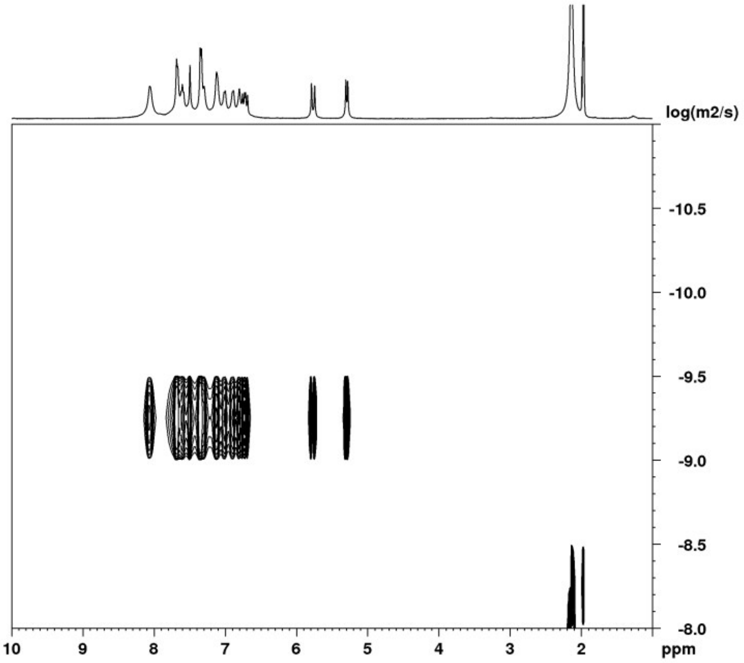


Figure S13. ^1H-^1H NOESY spectrum of the self-assembly complex of **L** and Eu(OTf)$_3$ (400 MHz, CD_3CN, 298 K).



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EXPNO                  6
PROCNO                 1

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PULPROG        stebpgp1s
TD                 16384
SOLVENT            CD3CN
NS                    16
DS                     2
SWH             6393.862 Hz
FIDRES          0.390250 Hz
AQ             1.2812288 sec
RG                102.35
DW                78.200 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
D16           0.00020000 sec
D20           0.10000000 sec

======== CHANNEL f1 ========
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NUC1                  1H
P1                  9.90 usec
P2                 19.80 usec
PLW1         16.00000000 W

====== GRADIENT CHANNEL =====
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GPNAM[7]        sine.100
GPZ6              100.00 %
GPZ7              -17.13 %
P19               600.00 usec
P30              1800.00 usec

F1 - Acquisition parameters
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SFO1            400.1328 MHz
FIDRES        250.000000 Hz
SW                 4.998 ppm
FnMODE                QF

F2 - Processing parameters
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SF           400.1300000 MHz
WDW                   EM
SSB        0
LB                  0.30 Hz
GB         0
PC                  1.00

F1 - Processing parameters
SI                    16
MC2                   QF
SF           400.1300000 MHz
WDW                   no
SSB        0
LB         0 Hz
GB         0
```

Figure S14. ^1H DOSY spectrum of the self-assembly complex of **L** and Eu(OTf)$_3$ (logD = -9.251, r = 11.34 Å, 400 MHz, CD_3CN, 298 K).

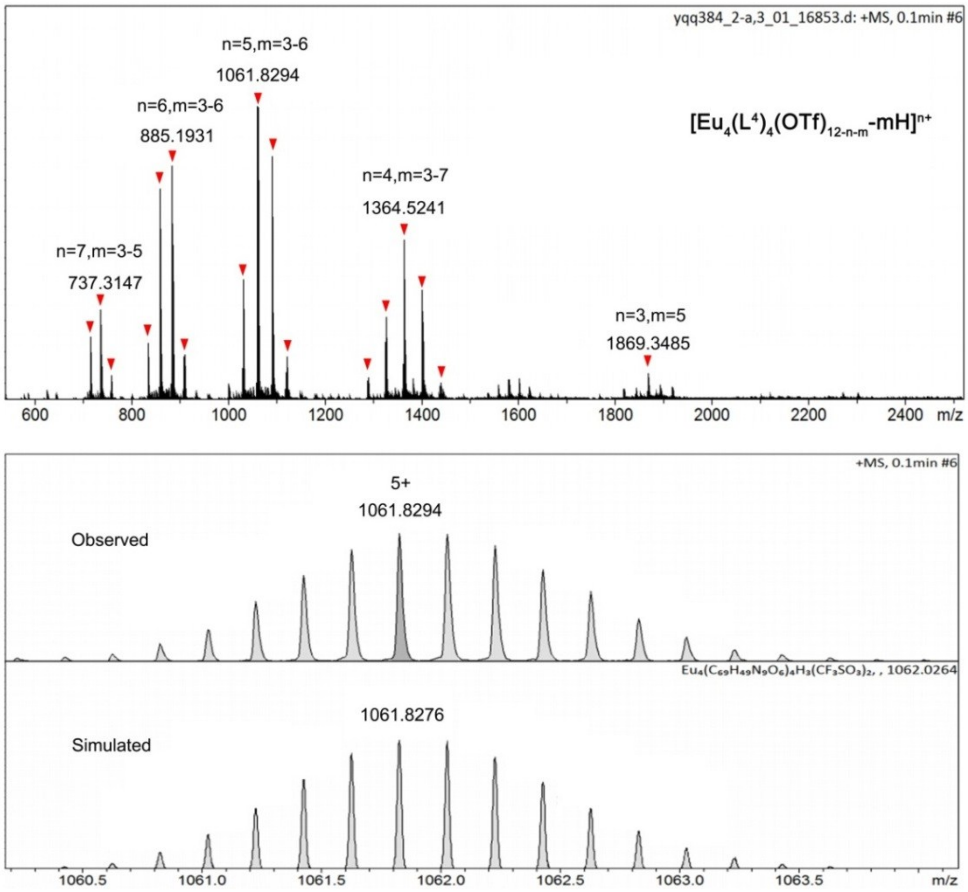


Figure S15. ESI-TOF-MS of the self-assembly complex of **L** and Eu(OTf)$_3$.

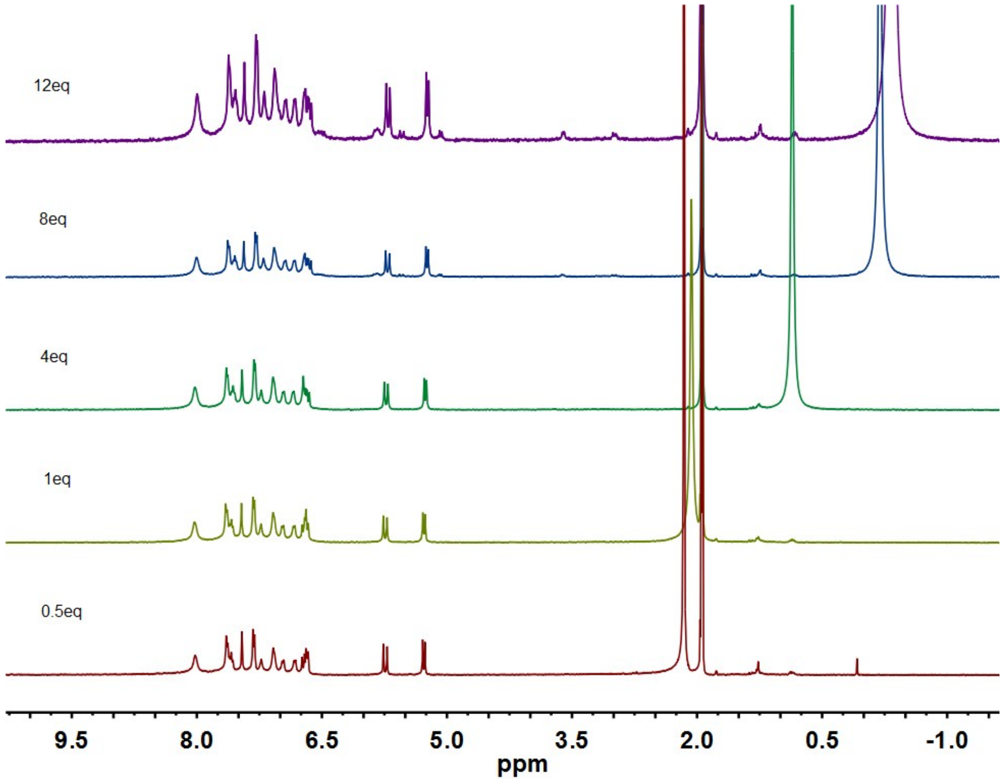


Figure S16. ^{1}H NMR titration spectra of titrating **L** with Eu(OTf)$_3$ (400 MHz, CD$_3$CN, 298 K).

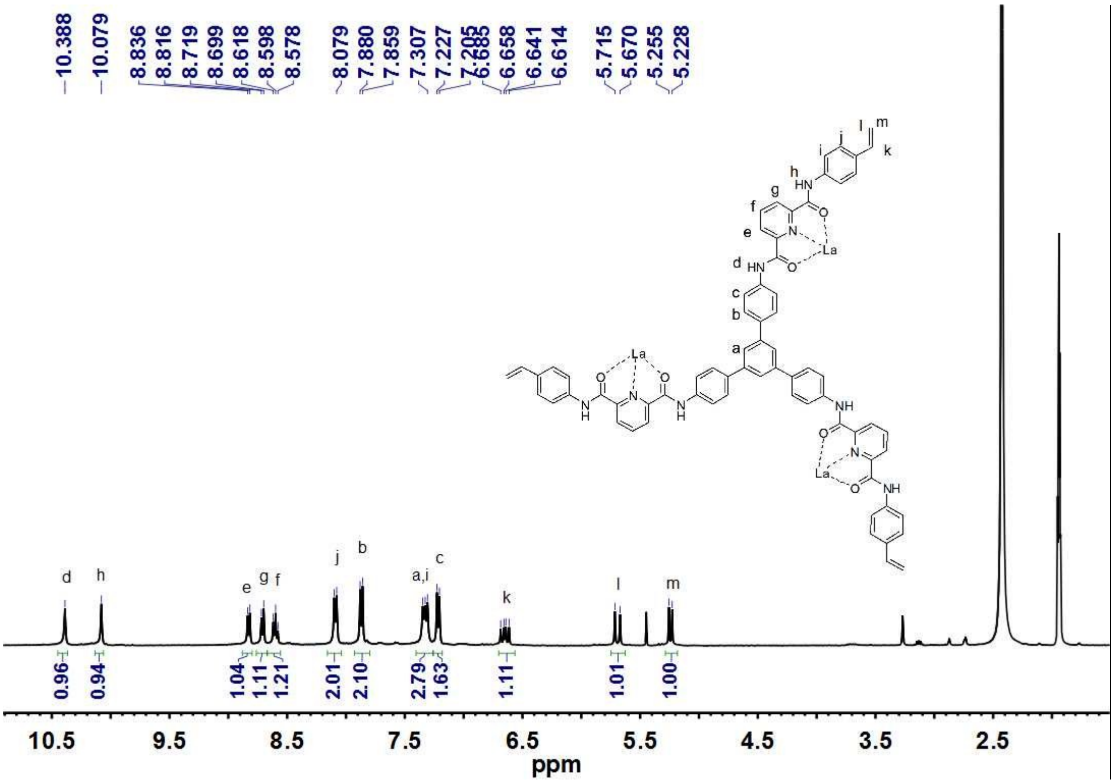


Figure S17. ^{1}H NMR spectrum of the self-assembly complex of **L** and La(OTf)$_3$ (400 MHz, CD$_3$CN, 298 K).

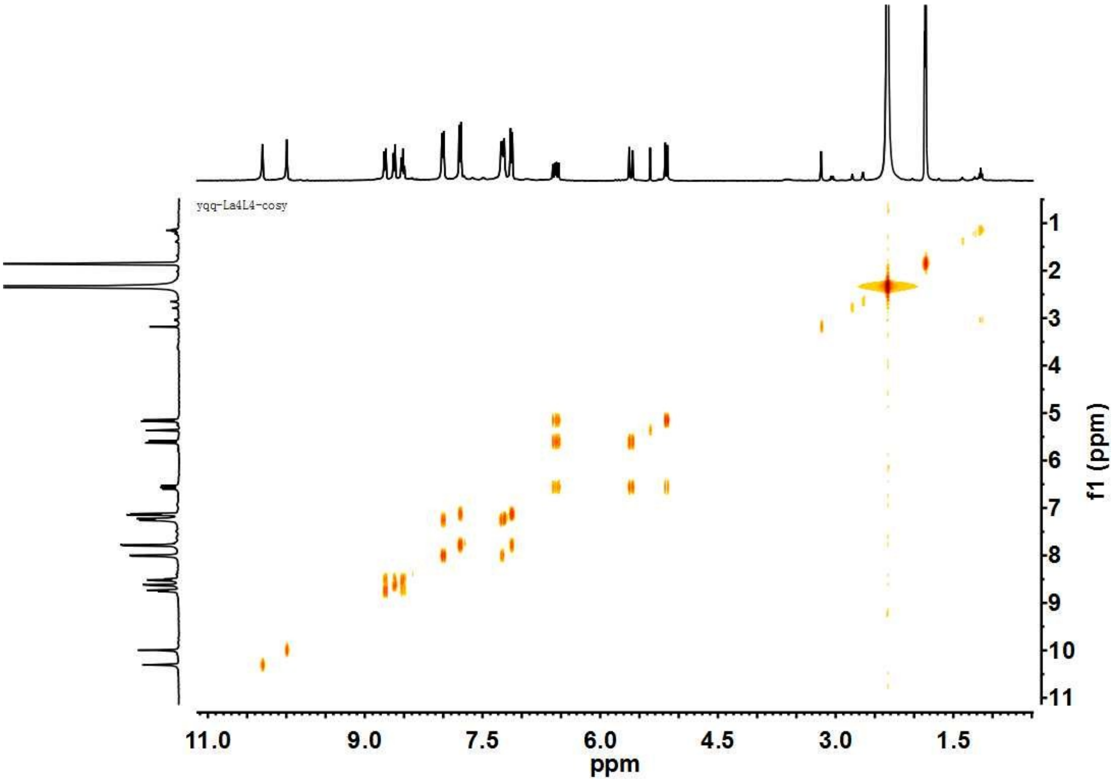
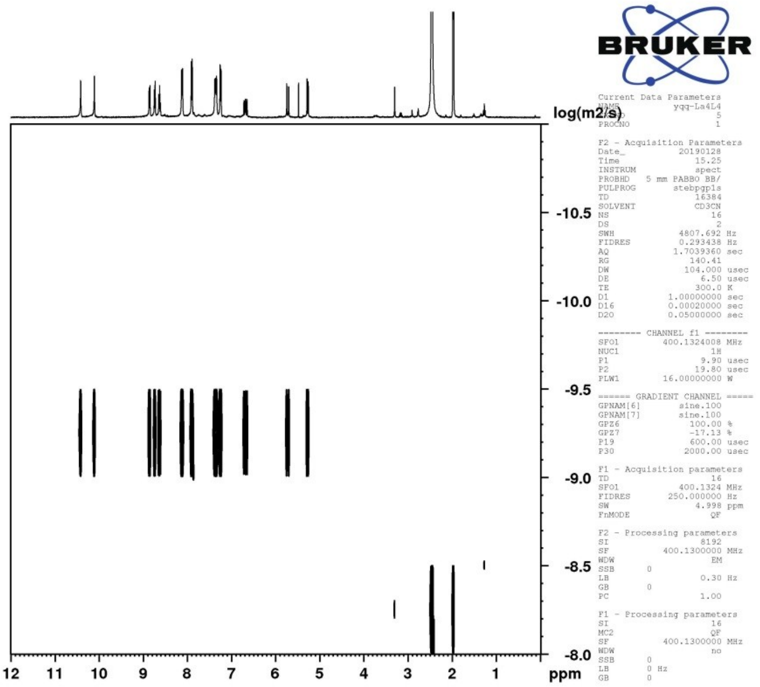


Figure S18. ^{1}H-^{1}H COSY spectrum of the self-assembled La$_4$L$_4$ complex from **L** and La(OTf)$_3$ (400 MHz, CD$_3$CN, 298 K).



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PROCNO                   1

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PULPROG          stebpgp1s
TD                   16384
SOLVENT              CD3CN
NS                      16
DS                       2
SWH               4807.692 Hz
FIDRES            0.293438 Hz
AQ               1.7039360 sec
RG                  140.41
DW                 104.000 usec
DE                    6.50 usec
TE                   300.0 K
D1              1.00000000 sec
D16             0.00020000 sec
D20             0.05000000 sec

======== CHANNEL f1 ========
SFO1          400.1324008 MHz
NUC1                    1H
P1                    9.90 usec
P2                   19.80 usec
PLW1           16.00000000 W

====== GRADIENT CHANNEL =====
GPNAM[6]          sine.100
GPNAM[7]          sine.100
GPZ6                100.00 %
GPZ7                -17.13 %
P19                 600.00 usec
P30                2000.00 usec

F1 - Acquisition parameters
TD                      16
SFO1              400.1324 MHz
FIDRES          250.000000 Hz
SW                   4.998 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    8192
SF             400.1300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00

F1 - Processing parameters
SI                      16
MC2                     QF
SF             400.1300000 MHz
WDW                     no
SSB      0
LB       0 Hz
GB       0
```

Figure S19. ^{1}H DOSY spectrum of the self-assembled La_4L_4 complex from **L** and $La(OTf)_3$ (logD = -9.251, r = 11.34 Å, 400 MHz, CD_3CN, 300 K).

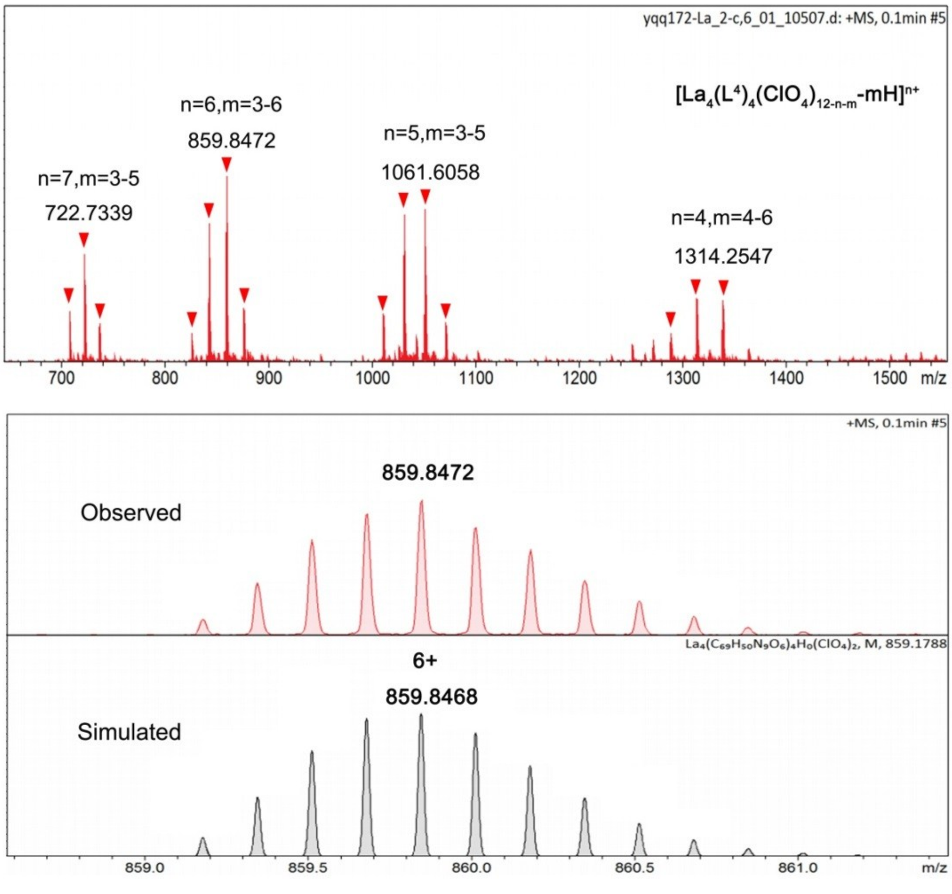


Figure S20. ESI-TOF-MS of the self-assembly complex of **L** and $La(ClO_4)_3 \cdot 6H_2O$.

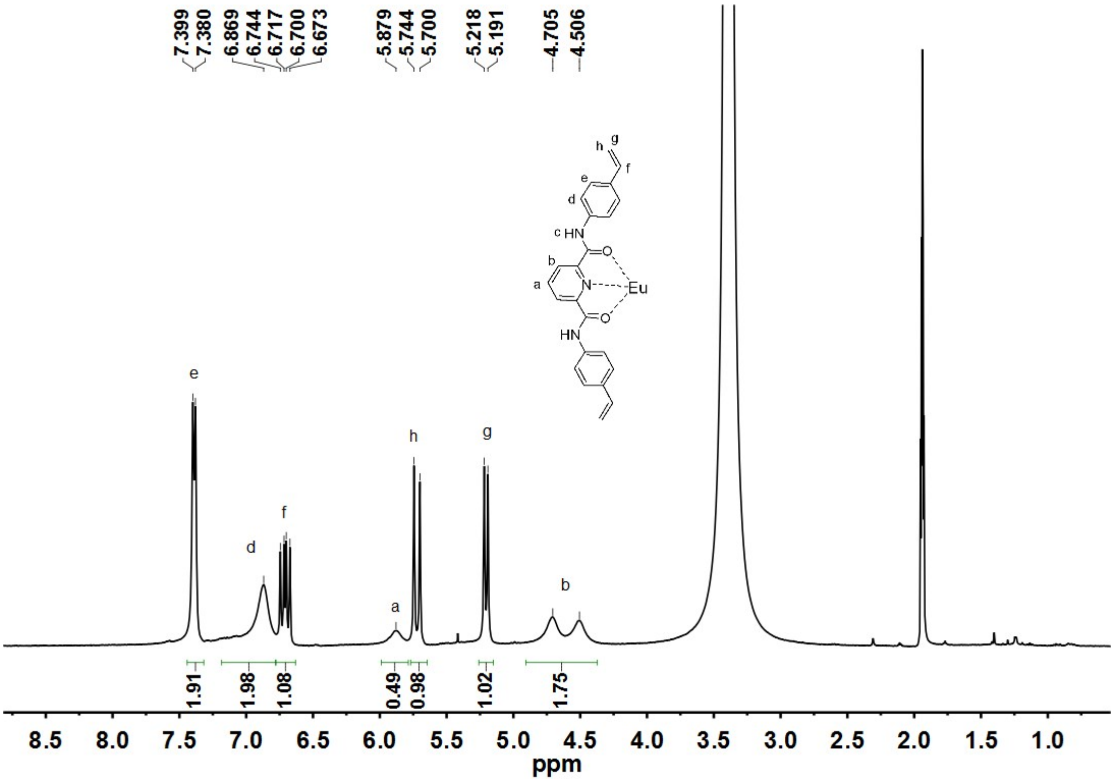


Figure S21. ^{1}H NMR spectrum of the self-assembly complex of **L′** and Eu(OTf)$_3$ (400 MHz, CD$_3$CN, 298 K).

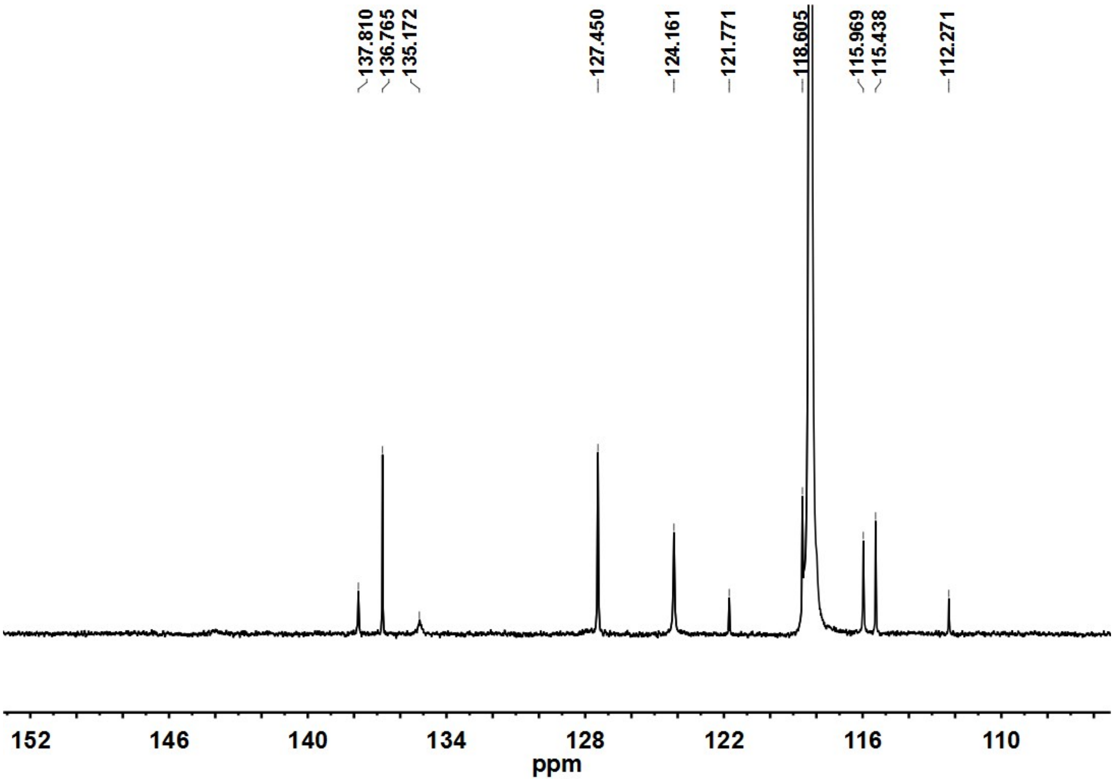


Figure S22. ^{13}C NMR spectrum of the self-assembly complex of **L′** and Eu(OTf)$_3$ (100 MHz, CD$_3$CN, 298 K).

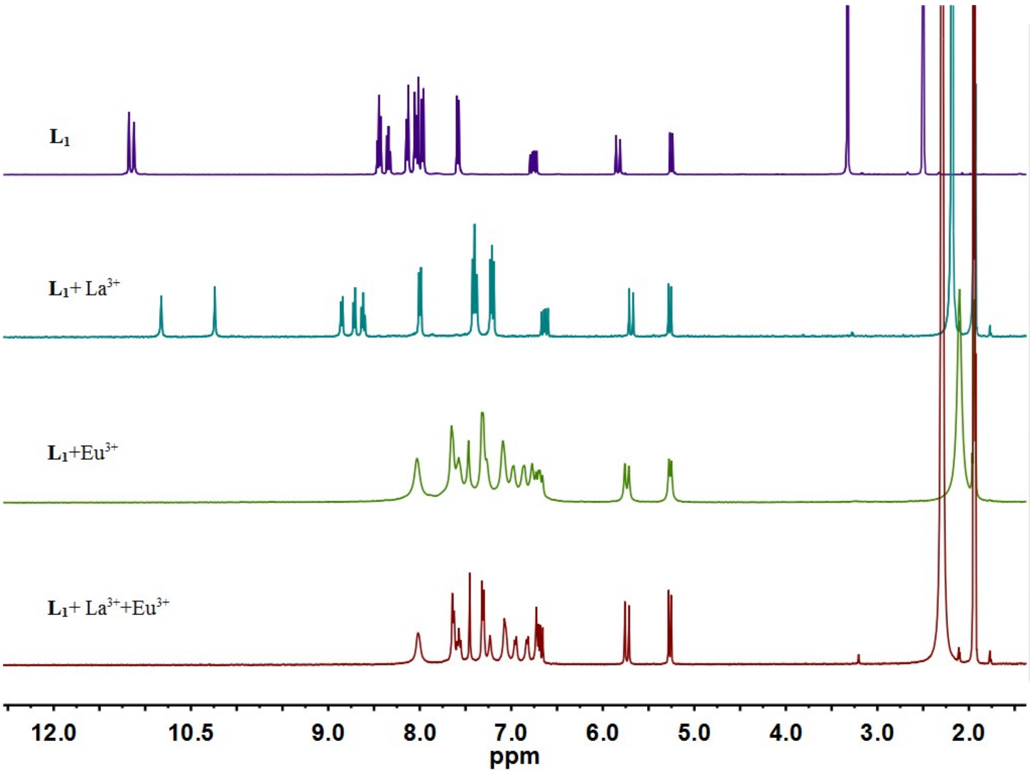


Figure S23. ^{1}H NMR spectra for the mixed-metal self-sorting studies of $Ln_4(\mathbf{L})_4$ (400 MHz, CD_3CN, 298 K).

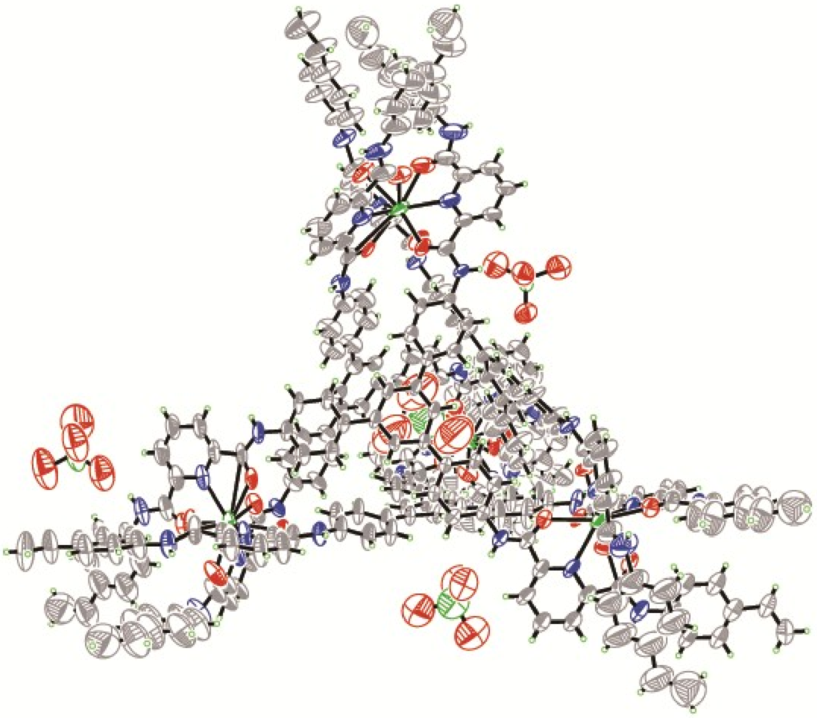


Figure S24. Ortep-drawing for the crystal structure of $Eu_4\mathbf{L}_4(ClO_4)_{12}$.

Table S1. Crystal data and structure refinement for $Eu_4\mathbf{L}_4(ClO_4)_{12}$.

Identification code	fddd_sq	
Empirical formula	C276 H204 Cl11 Eu4 N36 O68	
Formula weight	6110.53	
Temperature	293(2) K	
Wavelength	0.7388 Å	
Crystal system	Orthorhombic	
Space group	Fddd	
Unit cell dimensions	a = 15.1924(19) Å	α= 90°.
	b = 62.679(10) Å	β= 90°.
	c = 95.062(13) Å	γ = 90°.
Volume	90523(22) Å^3	
Z	8	
Density (calculated)	0.897 Mg/m^3	
Absorption coefficient	0.730 mm^{-1}	
F(000)	24760	
Crystal size	0.05 x 0.03 x 0.03 mm^3	
Theta range for data collection	0.891 to 15.298°.	
Index ranges	-10<=h<=10, -44<=k<=44, -67<=l<=67	
Reflections collected	57632	
Independent reflections	4284 [R(int) = 0.1376]	
Completeness to theta = 15.298°	99.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4284 / 1528 / 785	
Goodness-of-fit on F^2	2.478	
Final R indices [I>2sigma(I)]	R1 = 0.1634, wR2 = 0.4469	
R indices (all data)	R1 = 0.1914, wR2 = 0.4808	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.029 and -0.517 e.Å^{-3}	

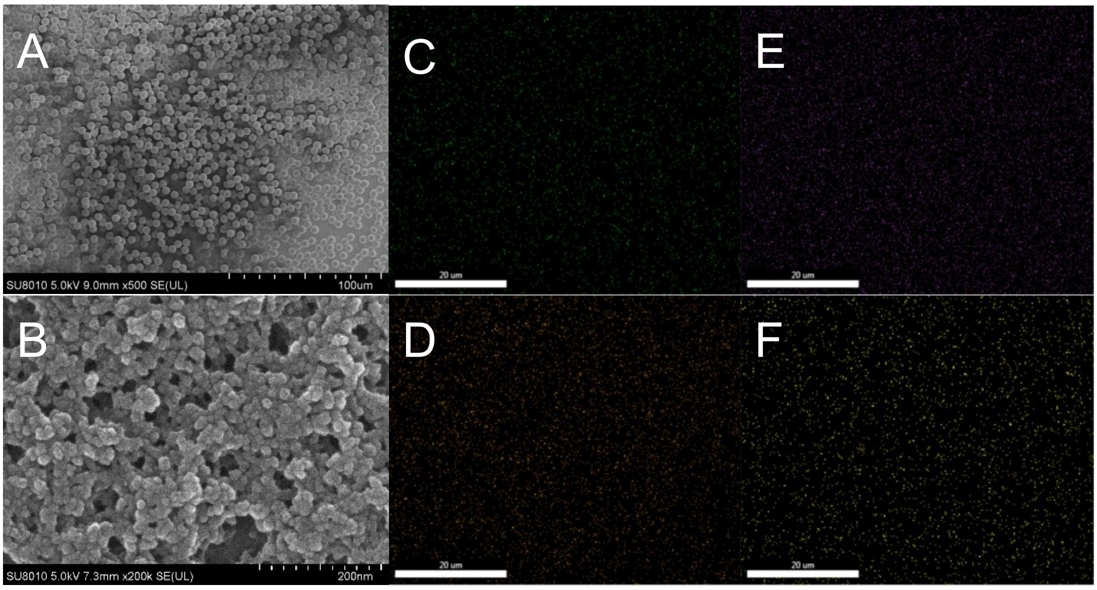
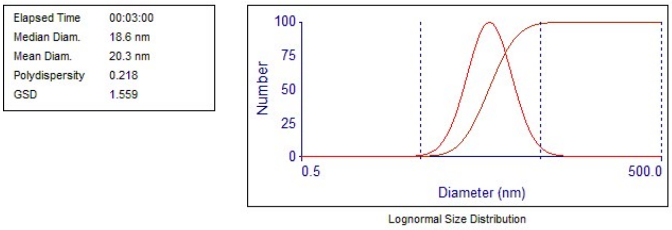


Figure S25. SEM images of A) PDVB and B) PDVB-Eu_4**L**$_4$; EDS mapping of C) N, D) S, E) F and F) Eu of PDVB-Eu_4**L**$_4$



```
Elapsed Time      00:03:00
Median Diam.      18.6 nm
Mean Diam.        20.3 nm
Polydispersity    0.218
GSD               1.559
```

Figure S26. DLS size distribution by Volume of PDVB-Eu_4**L**$_4$.

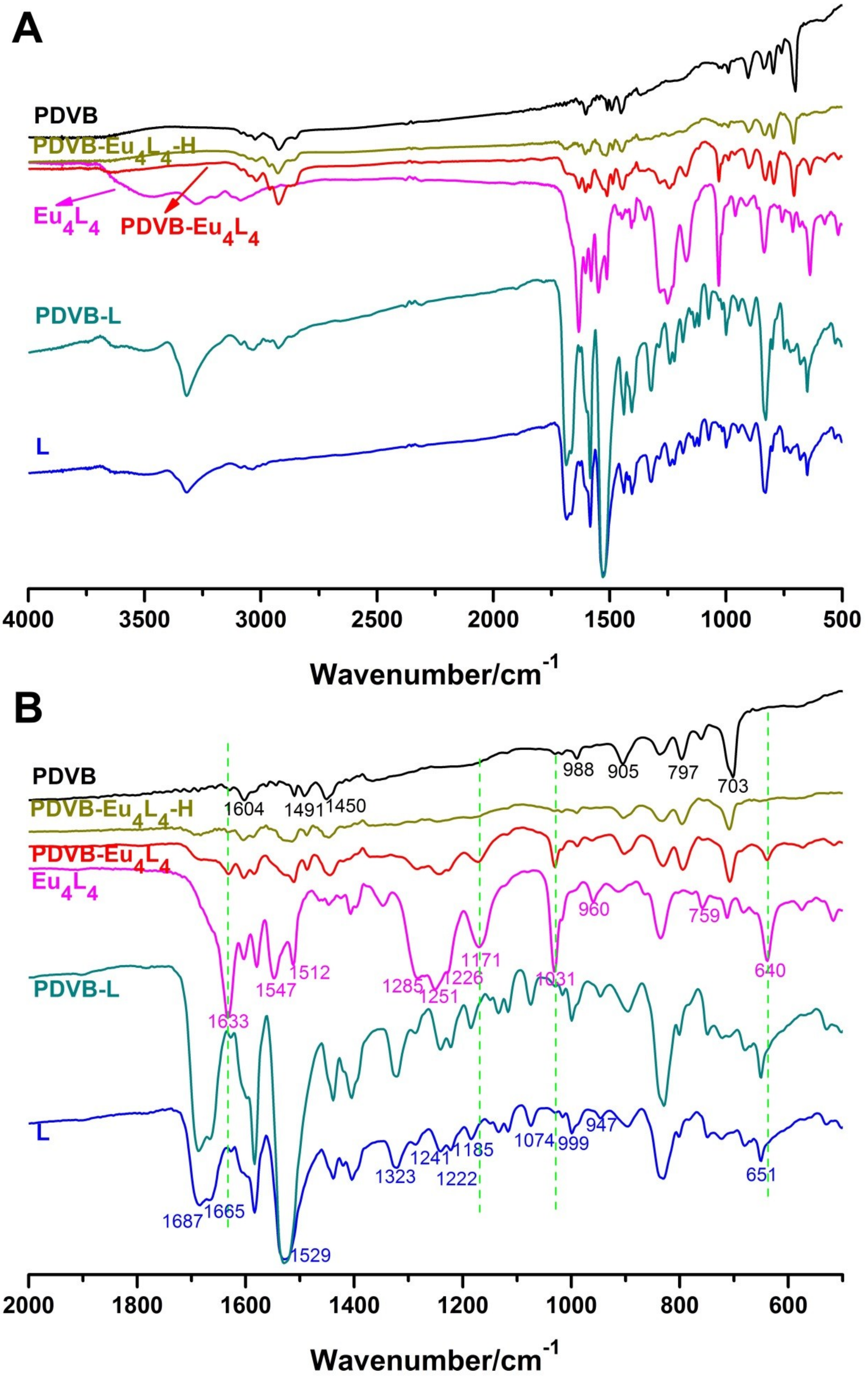


Figure S27. FT-IR spectra (A) and partial enlarged FT-IR spectra of **L**, PDVB-**L**, Eu_4**L**$_4(OTf)_{12}$, PDVB-Eu_4**L**$_4$, PDVB-Eu_4**L**$_4$-H, and PDVB.

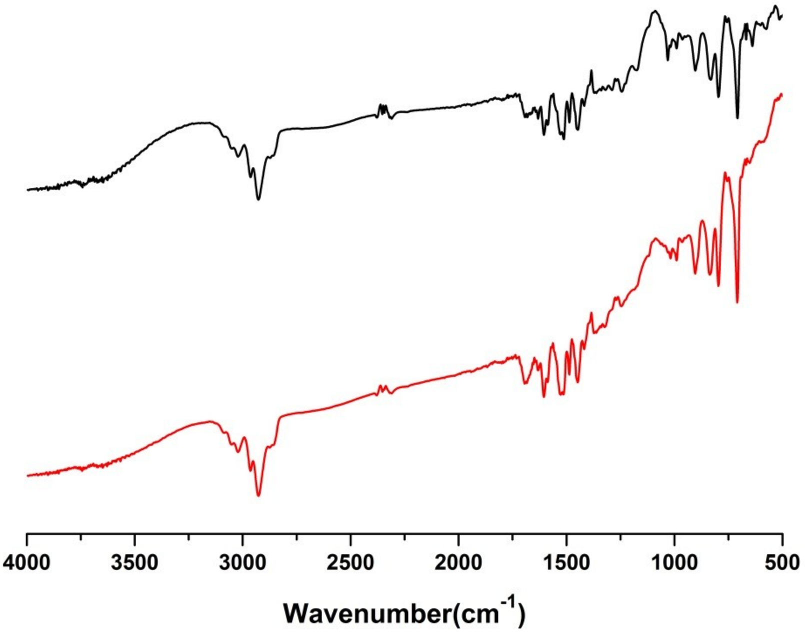


Figure S28. FT-IR spectra of PDVB-Eu$\mathbf{L}'_3$ (black line) and PDVB-Eu$\mathbf{L}'$-H (red line).

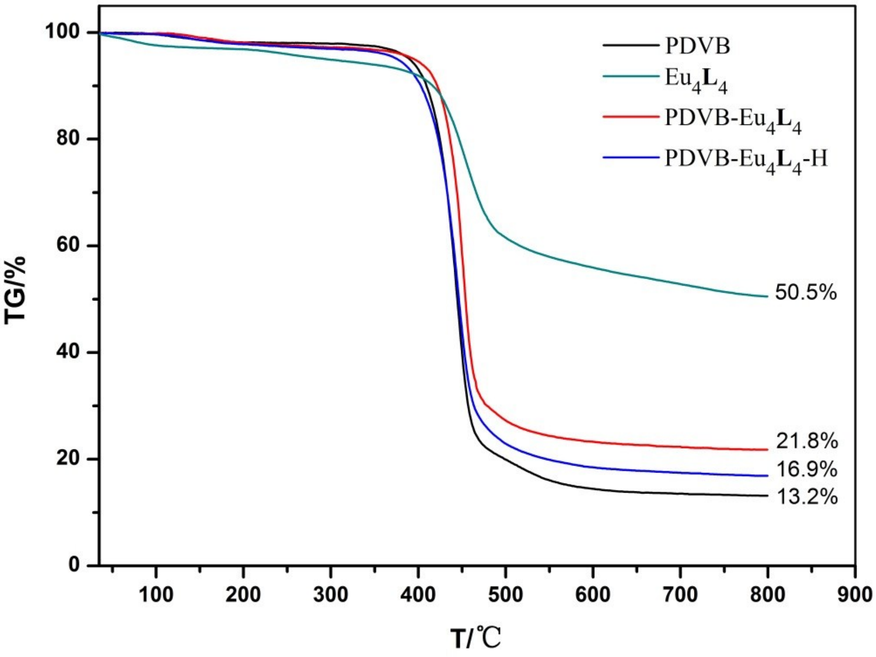


Figure S29. TGA profiles of PDVB, Eu$_4$$\mathbf{L}_4$, PDVB-Eu$_4$$\mathbf{L}_4$, PDVB-Eu$_4$$\mathbf{L}_4$-H.

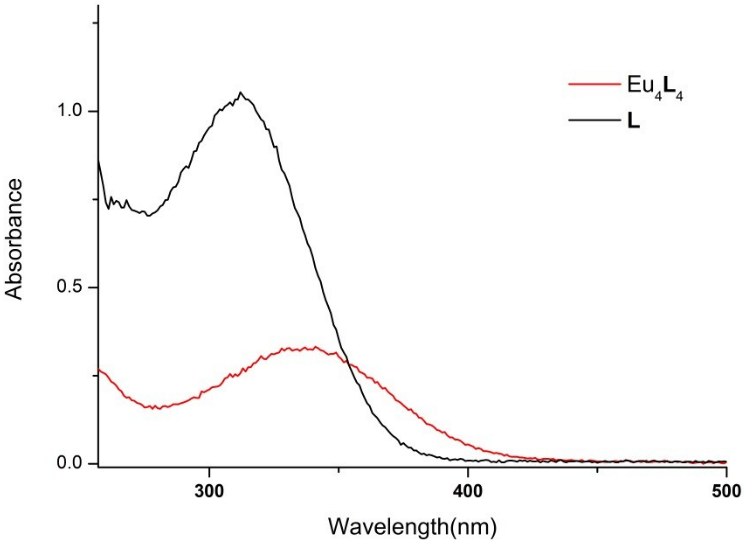


Figure S30. UV-Vis spectra of **L** (1×10^{-5} M in DMSO) and Eu$_4$**L**$_4$(OTf)$_{12}$ (0.25×10^{-5} M in CH_3CN)

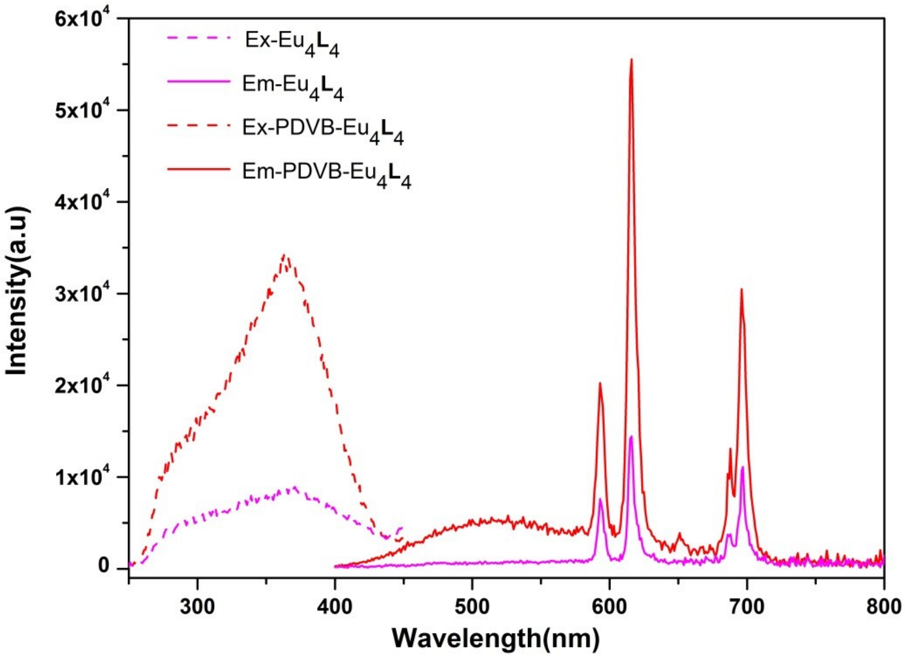
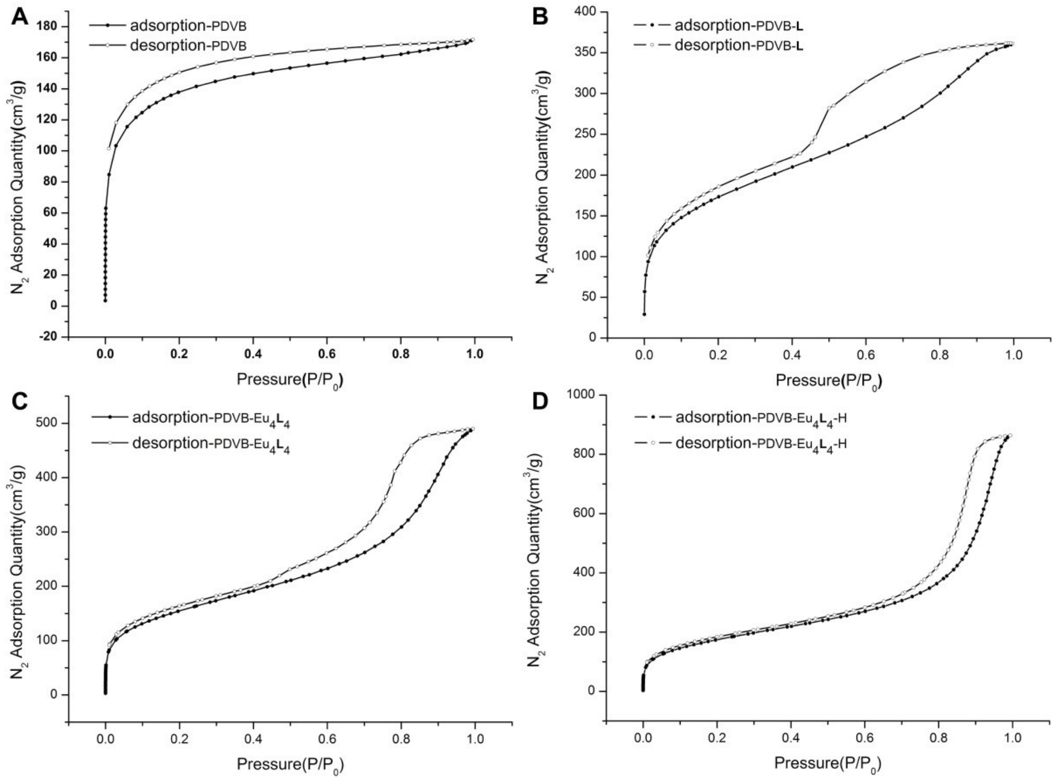


Figure S31. Excitation spectrum (λ_{em}= 615nm) and emission spectrum (λ_{ex}= 369 nm for PDVB-Eu$_4$**L**$_4$ and λ_{ex}= 366 nm for PDVB-Eu$_4$**L**$_4$) of Eu$_4$**L**$_4$(OTf)$_{12}$ and PDVB-Eu$_4$**L**$_4$ in solid (298K).



FigureS32. N_2 abosorpotion of A) PDVB, B) PDVB-**L**, C) PDVB-Eu_4**L**$_4$ and D) PDVB-Eu_4**L**$_4$-H.

Table S2. Summary of N_2 abosorpotion of PDVB, PDVB-**L**, PDVB-Eu_4**L**$_4$ and PDVB-Eu_4**L**$_4$-H.

	PDVB	PDVB-**L**	**PDVB-Eu$_4$L$_4$**	**PDVB-Eu$_4$L$_4$-H**
Maximum N_2 abosorpotion (m^3/g)	171.791	361.248	489.989	863.671
BET Surface Area (m^2/g)	467.936	597.996	548.215	626.608
BET Adsorption average pore width (nm)	2.271	3.697	5.530	8.528
BJH Adsorption average pore width (nm)	3.197	4.443	6.327	9.164
BJH Desorption average pore width (nm)	2.384	3.671	5.739	8.866

Table S3. The extraction coefficient of PDVB-**L**, PDVB-Eu**L**′$_3$-H and PDVB-Eu_4**L**$_4$-H.

	E(%)		Q(mg/g)		D		$S_{Eu/La}$
	La	Eu	La	Eu	La	Eu	
PDVB-L	6.11	29.42	0.7776	3.9016	5.21	33.34	6.40
PDVB-EuL′$_3$-H	18.78	41.13	2.39	5.45	18.50	55.89	3.02
PDVB-Eu$_4$L$_4$-H	30.82	58.44	3.92	7.75	35.64	112.49	3.16

6. References

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