Electronic Supplementary Material (ESI) for ChemComm.

Ditopic CMPO-pillar[5]arenes as unique receptors for efficient separation of americium(III) and europium(III)

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Supporting Information

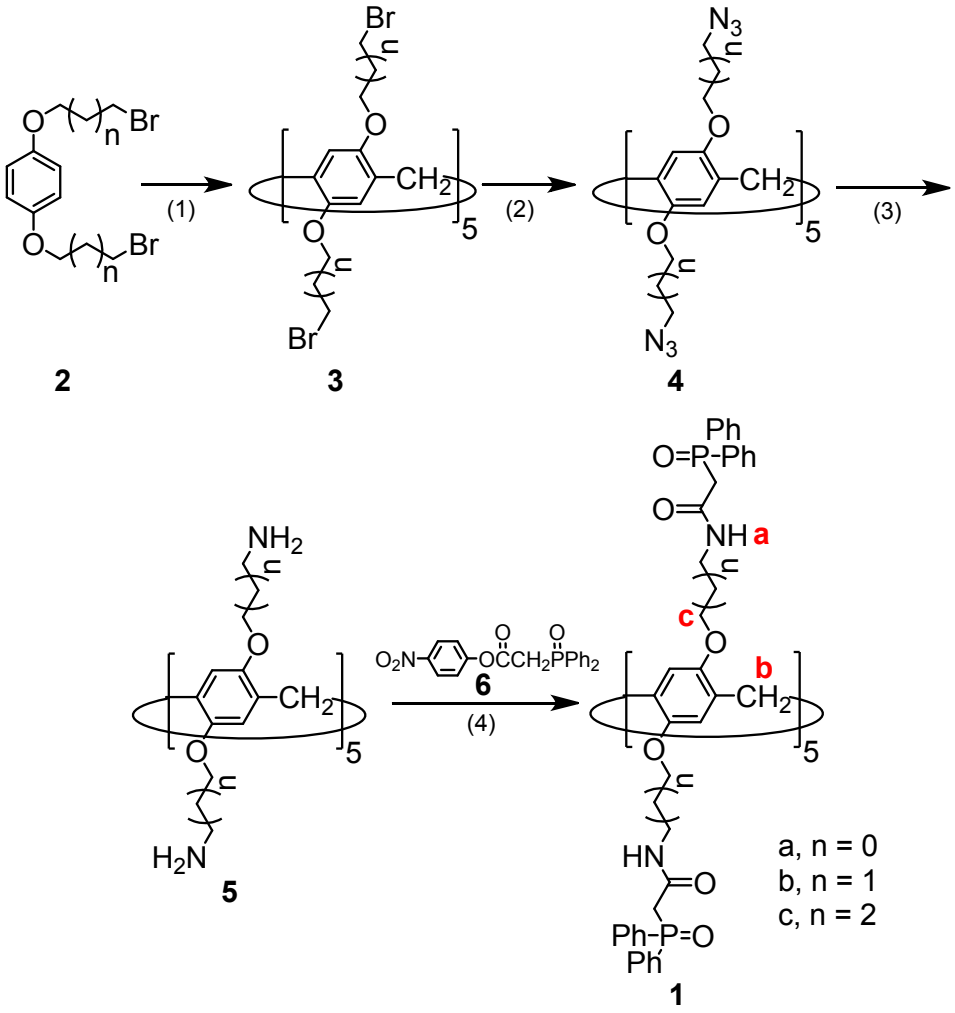
Contents

1. General information

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz; ^{31}P: 163 MHz). Chemical shifts are reported in δ values in ppm using tetramethlysilane (TMS) and coupling constants (J) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, dd = double doublet and m = multiplet. High resolution mass (HRMS) data were obtained by WATERS Q-TOF Premier. Solvents for extraction and chromatography were reagent grade. CH_2Cl_2 was distilled from CaH_2. $CDCl_3$ and DMSO-d_6 were from Cambridge Isotope Laboratories (CIL)

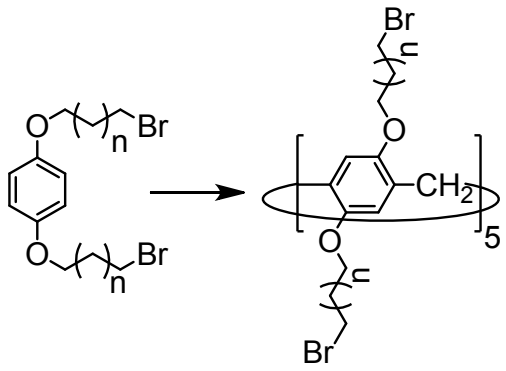
2. Synthesis and characterization

Synthetic route



Scheme S1 Synthesis of CMPO-functionalized pillar[5]arenes **1a-c**. Reagents: (1) $(CH_2O)_n$, BF_3•OEt_2, CH_2Cl_2, r.t.; (2) NaN_3, DMF, 90 °C; (3) H_2, Pd/C, CH_3OH, 48 h, 50 °C; (4) **6**, $CHCl_3$, NEt_3, 48 h, reflux.

Synthesis of compound 3



2 **3**

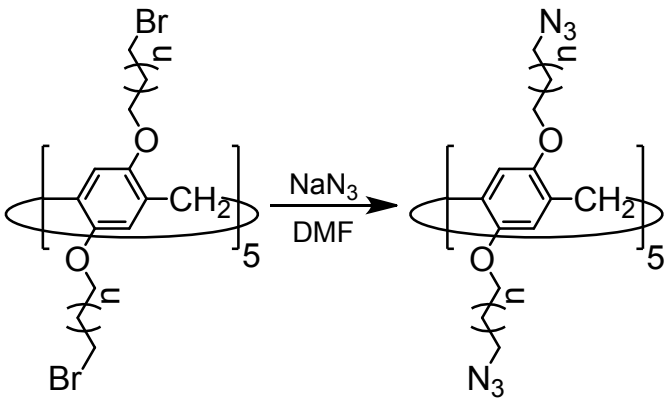
The general procedure for compounds **3b-c** was exemplified by the synthesis of **3a**: To a solution of **2a** (3.03 g, 9.34 mmol) in dry dichloromethane (80 mL) was added paraformaldehyde (291 mg, 9.34 mmol) under nitrogen atmosphere. Then boron trifluoride diethyl etherate (1.32 g, 11.5 mmol) was added to the solution and the mixture was stirred at room temperature for 2 h. Water (100 mL) was added to quench the reaction. The organic layer was washed twice with H_2O (2 × 100 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The obtained solid was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:1, v/v) as the eluent to afford a white powder.

3a[S1]: Yield 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 10 H), 4.23 (t, J = 5.5 Hz, 20 H), 3.84 (s, 10 H), 3.64 (t, J = 5.5 Hz, 20 H).

3b[S2]: Yield 40%.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (s，10 H), 3.99 (t, J = 5.7 Hz, 20 H), 3.76 (s, 10 H), 3.52 (t, J = 6.4 Hz, 20 H), 2.23 (m, 20 H).

3c[S3]: Yield 36%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 10 H), 3.93 (t, J = 5.8 Hz, 20 H), 3.75 (s, 10 H), 3.43 (t, J = 6.5 Hz, 20 H), 2.05 (m, 20 H), 1.92 (m, 20 H).

Synthesis of compound 4



3 **4**

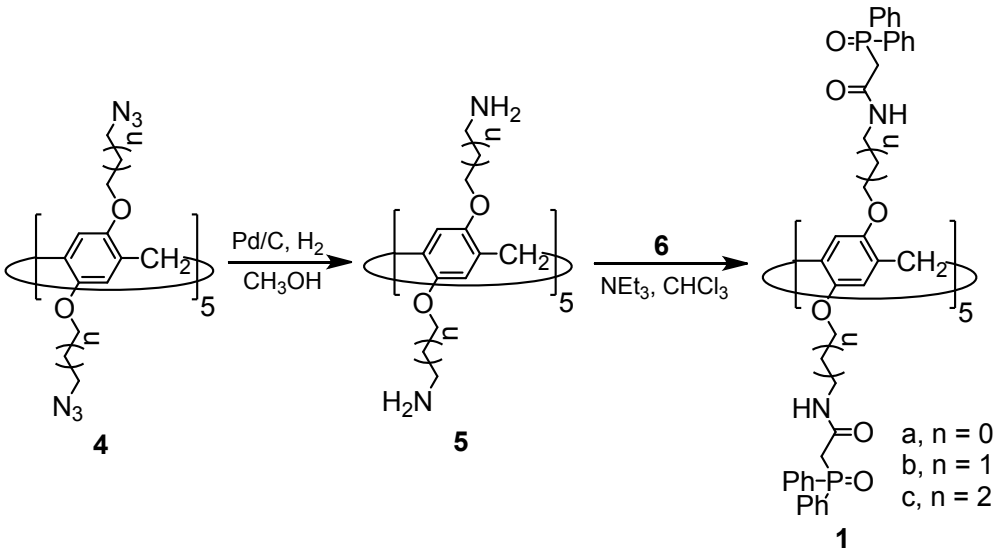
The general procedure for compounds **4b-c** was exemplified by the synthesis of **4a**: To a solution of **3a** (3.03 g, 1.80 mmol) in dry DMF (80 mL) was added sodium azide (1.41 g, 21.6 mmol) under nitrogen atmosphere. The mixture was stirred at 90 °C for 12 h and cooled to room temperature. After slow addition of ice water to the solution, the precipitate was collected by filtration, and washed with water (2 × 100 mL) and methanol (2 × 100 mL) to afford a white solid.

4a[S4]: Yield 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 10 H), 4.01 (t, J = 4.8 Hz, 20 H), 3.84 (s, 10 H), 3.55 (t, J = 4.7 Hz, 20 H).

4b: Yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 10 H), 3.91 (t, J = 5.9 Hz, 20 H), 3.75 (s, 10 H), 3.43 (t, J = 6.7 Hz, 20 H), 1.97 (m, 20 H).^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 128.6, 115.3, 65.5, 48.4, 29.8, 29.1. ESI-HRMS (m/z) calcd. for $C_{65}H_{80}N_{30}O_{10}$ $[M+Na]^+$ 1463.6571; found $[M+Na]^+$ 1463.6572.

4c: Yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 10 H), 3.90 (t, J = 4.7 Hz, 20 H), 3.75 (s, 10 H), 3.34 (t, J = 6.3 Hz, 20 H), 1.82 (m, 40 H).^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 128.4, 115.1, 67.9, 51.3, 29.6, 27.1, 26.0. ESI-HRMS (m/z) calcd. for $C_{75}H_{100}N_{30}O_{10}$ $[M+Na]^+$ 1063.8136; found $[M+Na]^+$ 1063.8134.

Synthesis of compound 1



The general procedure for compounds **1b-c** was exemplified by the synthesis of **1a**: A mixture of **4a** (2.00 g, 1.54 mmol) and Pd/C (400 mg, 20% w.t.) in methanol was stirred at 50 °C under hydrogen atmosphere (0.4 MPa) for 48 h. After removal of the catalyst by filtration, the solvent was concentrated under reduced pressure to give the amine **5a** as a white solid which was used without further purification. The resulting solid **5a** was dissolved together with *p*-nitrophenyl(diphenylphosphoryl) acetate **6**[S5] (8.81 g, 23.1 mmol) and triethylamine (2.34 g, 23.1 mmol) in ethanol-free dry chloroform (120 mL) at 60 °C for 48 h. Water (100 mL) was added to quench the reaction. The organic layer was washed repeatedly with 5% Na_2CO_3 (3 × 100 mL), water (3 × 100 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The obtained pale yellow solid was washed with cold ethyl acetate (3 × 20 mL) and purified by column chromatography on silica gel with dichloromethane/methanol (15:1, v/v) as the eluent to afford a white powder.

1a: Yield 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 10 H), 7.75 (m, 40 H), 7.38 (m, 60 H), 6.50 (s, 10 H), 3.59 (s, 10 H), 3.37-3.50 (m, 40 H), 3.28 (m, 20 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 149.9, 132.2, 131.0, 128.8, 128.7, 128.6, 115.9, 67.2, 39.5, 38.7, 29.3. ESI-HRMS (m/z) calcd. for $C_{195}H_{190}O_{30}P_{10}N_{10}$ $[M+2Na]^{2+}$ 1754.5444; found $[M+2Na]^{2+}$ 1754.5402.

1b: Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 10 H), 7.75 (dd, 40 H), 7.34 (m, 60 H), 6.60 (s, 10 H), 3.62 (t, J = 6.0 Hz, 20 H), 3.52 (m, 10 H), 3.41 (m, 30 H),

3.29 (m, 10 H), 1.77 (m, 20 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 149.7, 132.3, 130.9, 130.8, 128.8, 128.7, 115.0, 66.2, 39.5, 38.9, 37.3, 29.3. ESI-HRMS (m/z) calcd. for $C_{205}H_{210}O_{30}P_{10}N_{10}$ $[M+2Na]^{2+}$ 1824.6226; found $[M+2Na]^{2+}$ 1824.6232.

1c: Yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 10 H), 7.76 (m, 40 H), 7.39 (m, 60 H), 6.69 (s, 10 H), 3.72 (m, 10 H), 3.67 (s, 10 H), 3.60 (m, 10 H), 3.18 (m, 20 H), 1.67 (m, 40 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 149.8, 132.2, 131.3, 130.9, 128.8, 128.2, 115.0, 67.9, 39.6, 38.8, 29.3, 27.1, 26.1. ESI-HRMS (m/z) calcd. for $C_{215}H_{230}O_{30}P_{10}N_{10}$ $[M+2Na]^{2+}$ 1894.1992; found $[M+2Na]^{2+}$ 1894.1949.

3. NMR and ESI-HRMS spectra

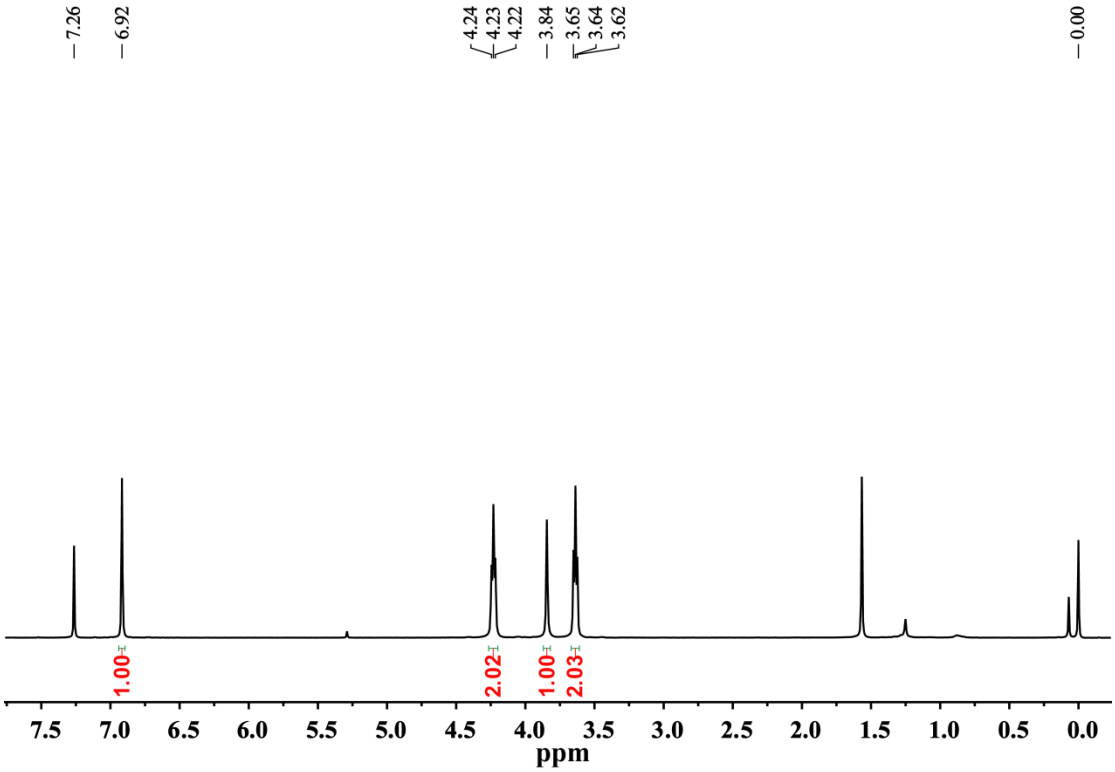


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a** at 298 K.

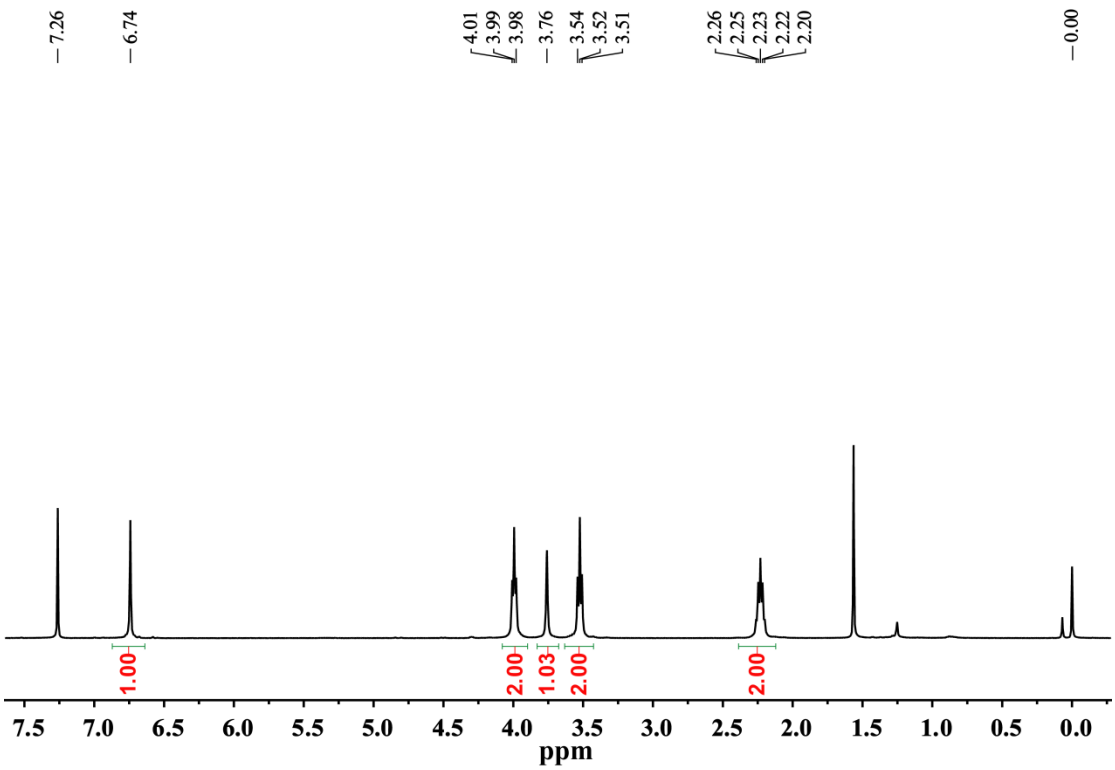


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b** at 298 K.

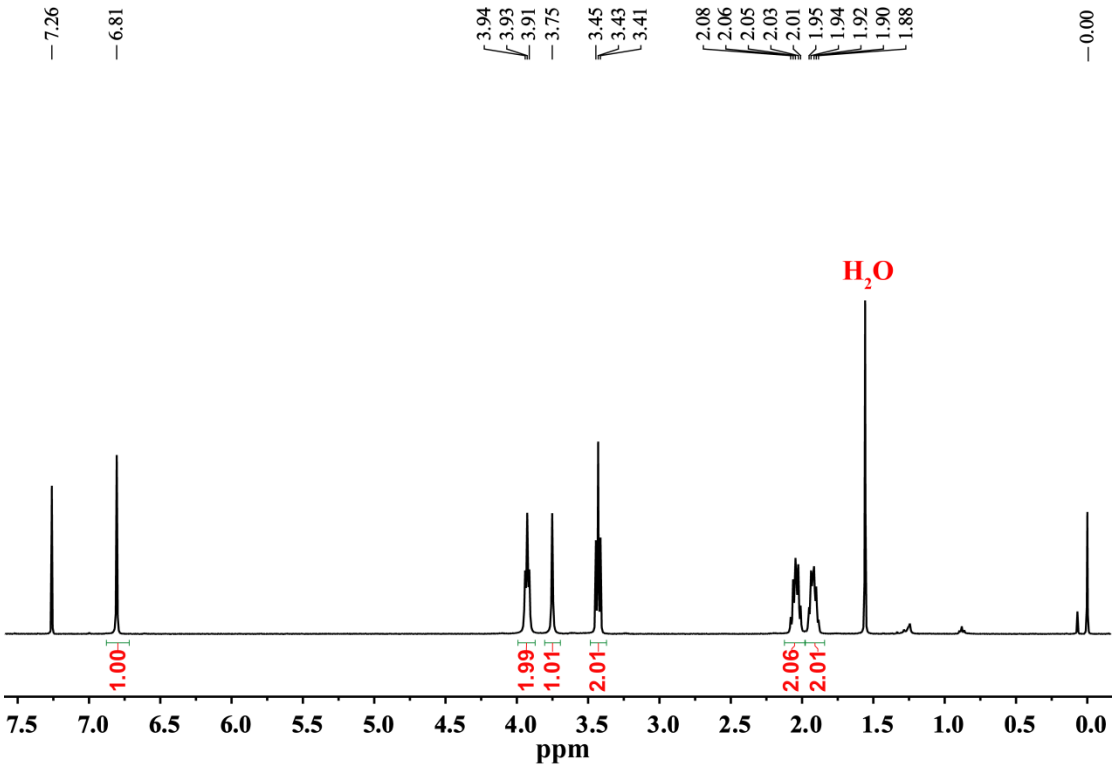


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3c** at 298 K.

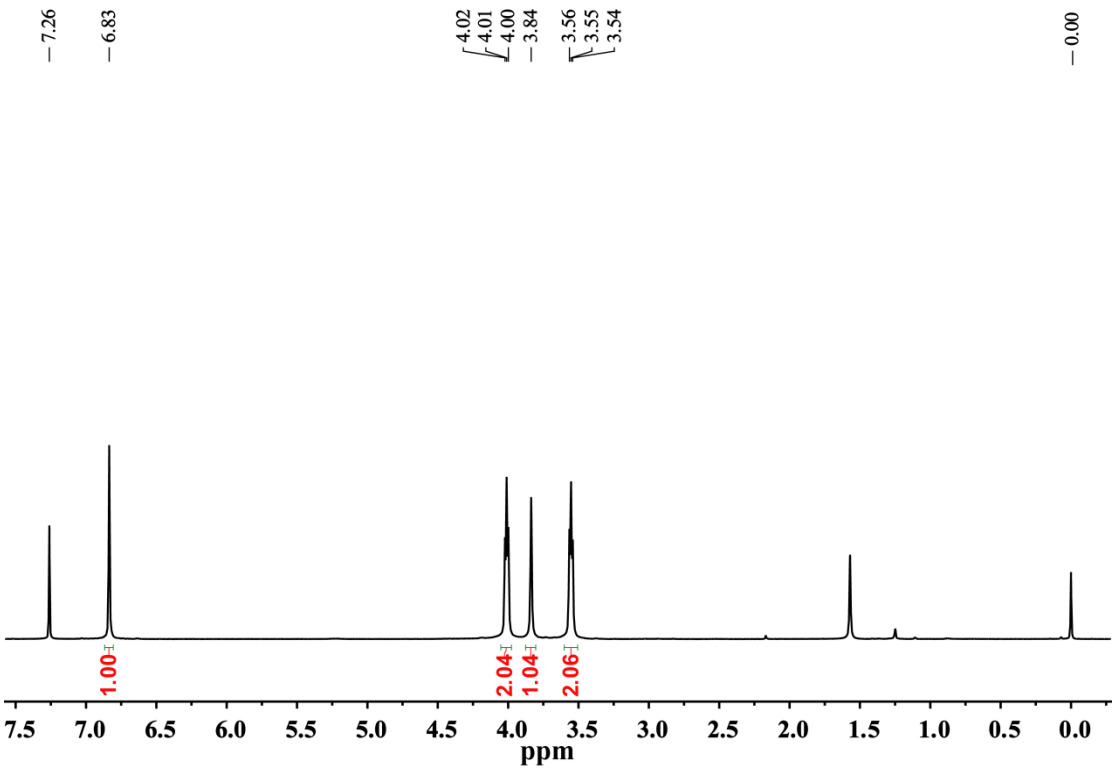


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a** at 298 K.

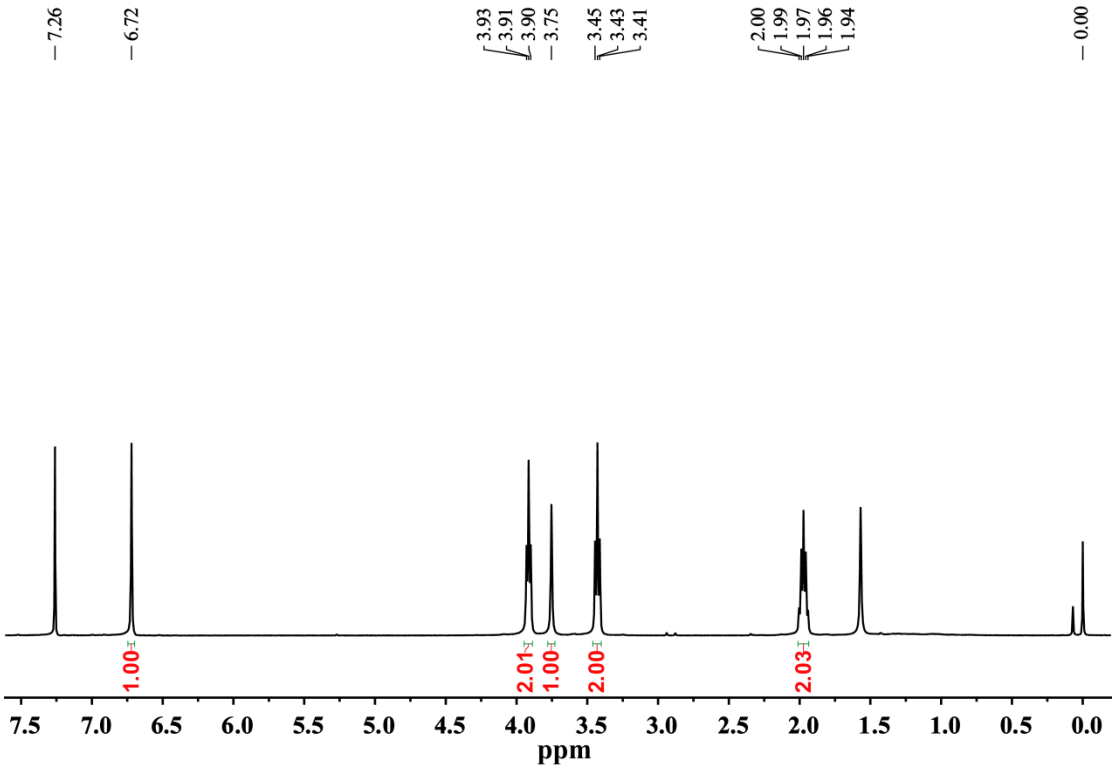


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b** at 298 K.

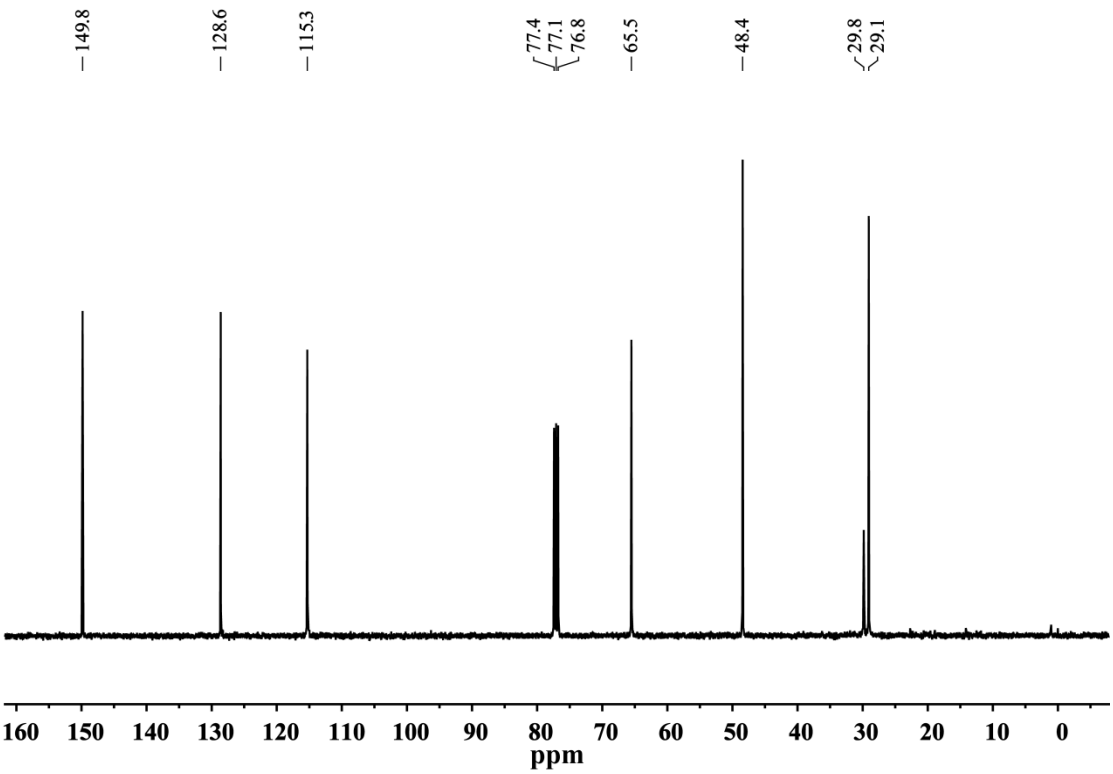


Figure S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4b** at 298 K.

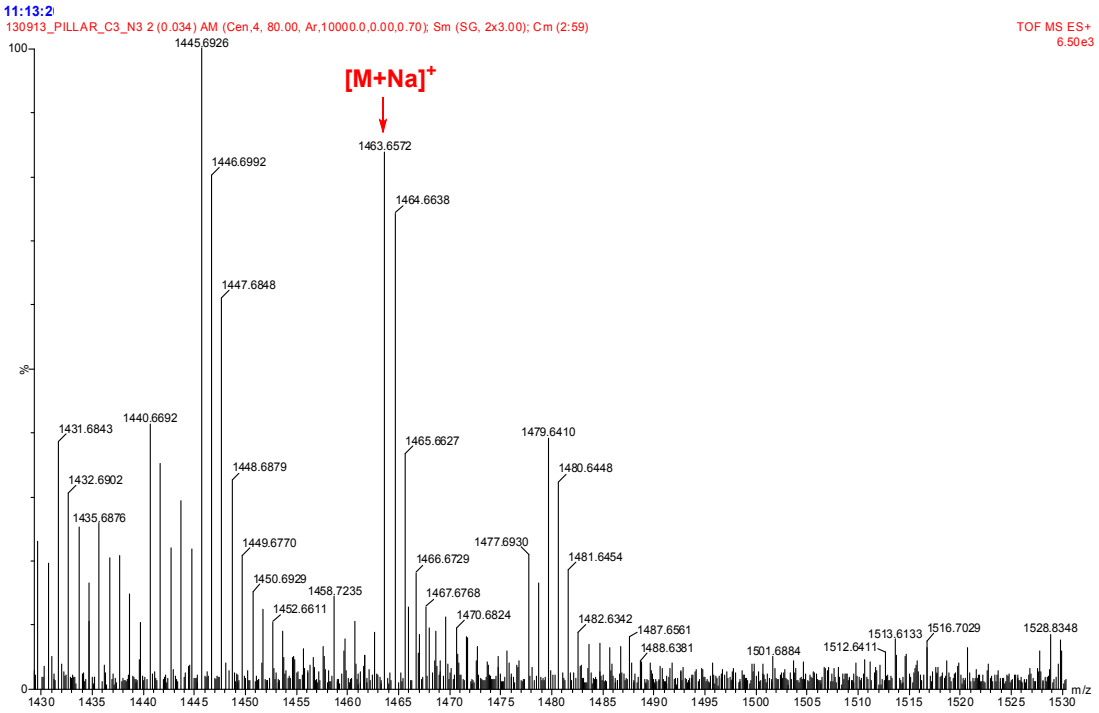


Figure S7. ESI-HRMS spectrum of **4b**.

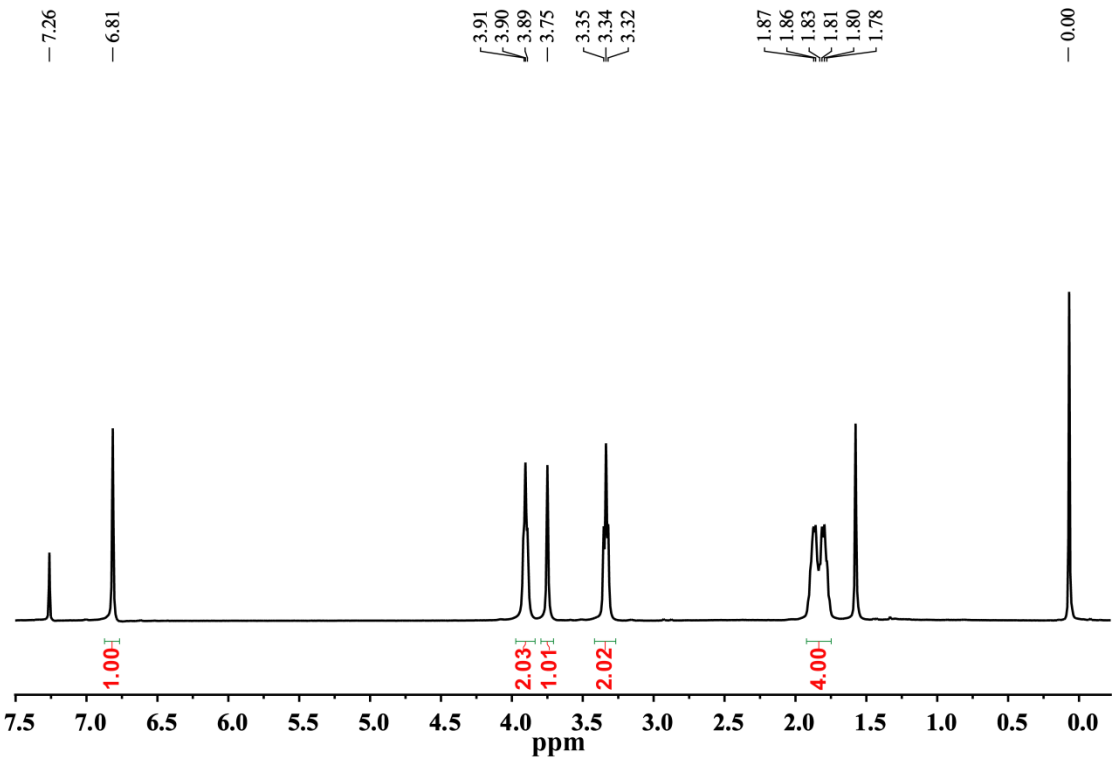


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4c** at 298 K.

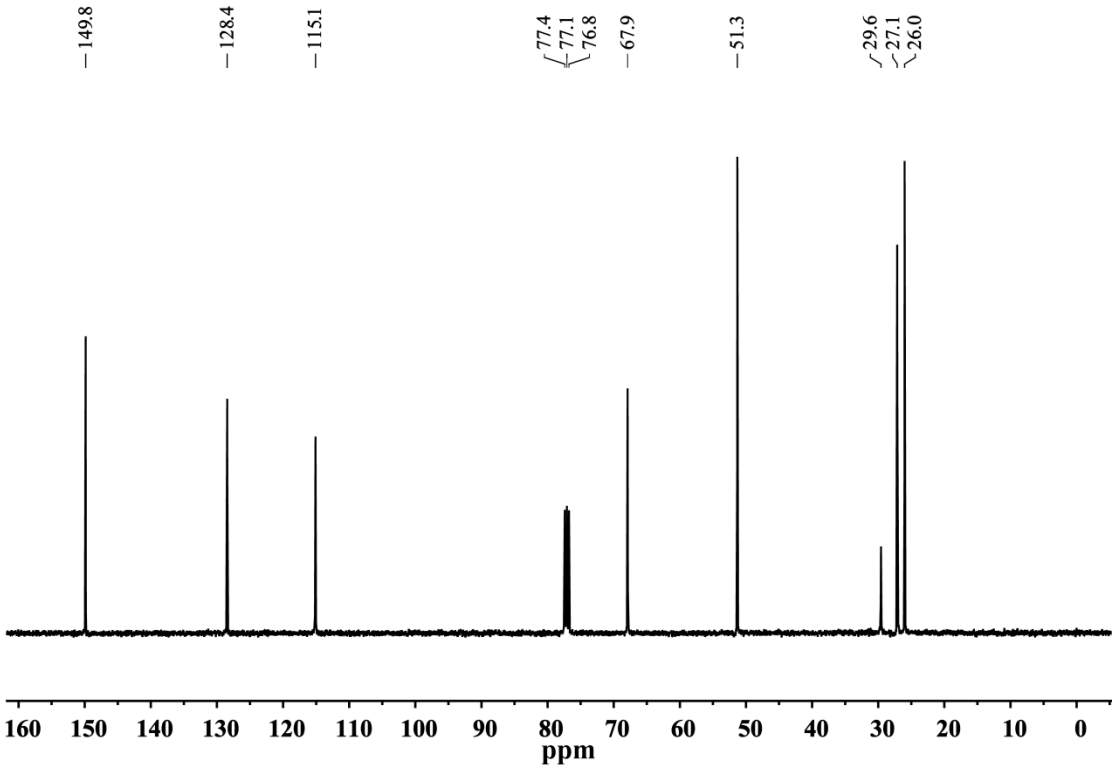


Figure S9. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4c** at 298 K.

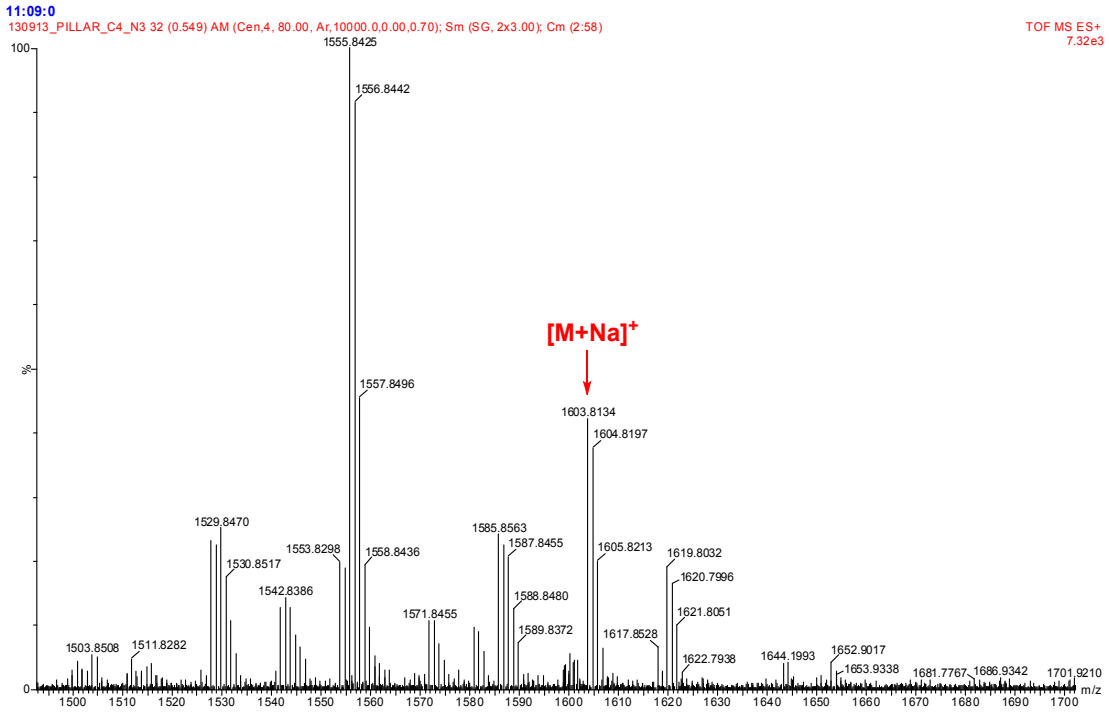


Figure S10. ESI-HRMS spectrum of **4c**.

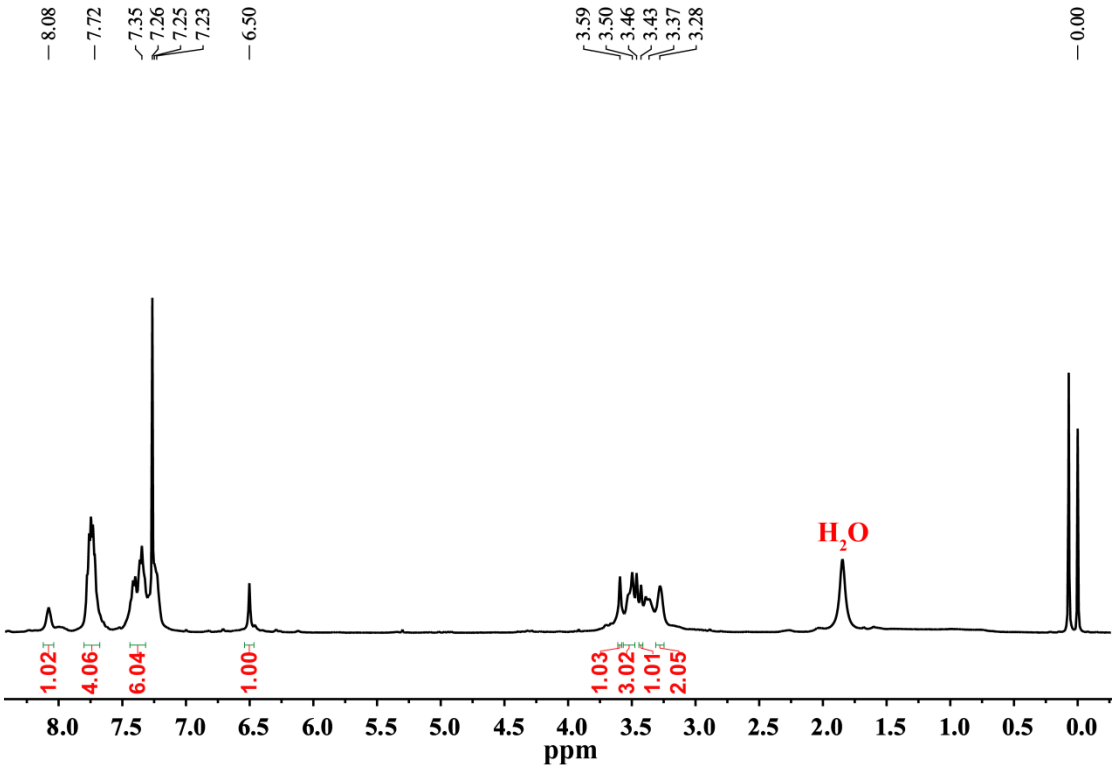


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a** at 298 K.

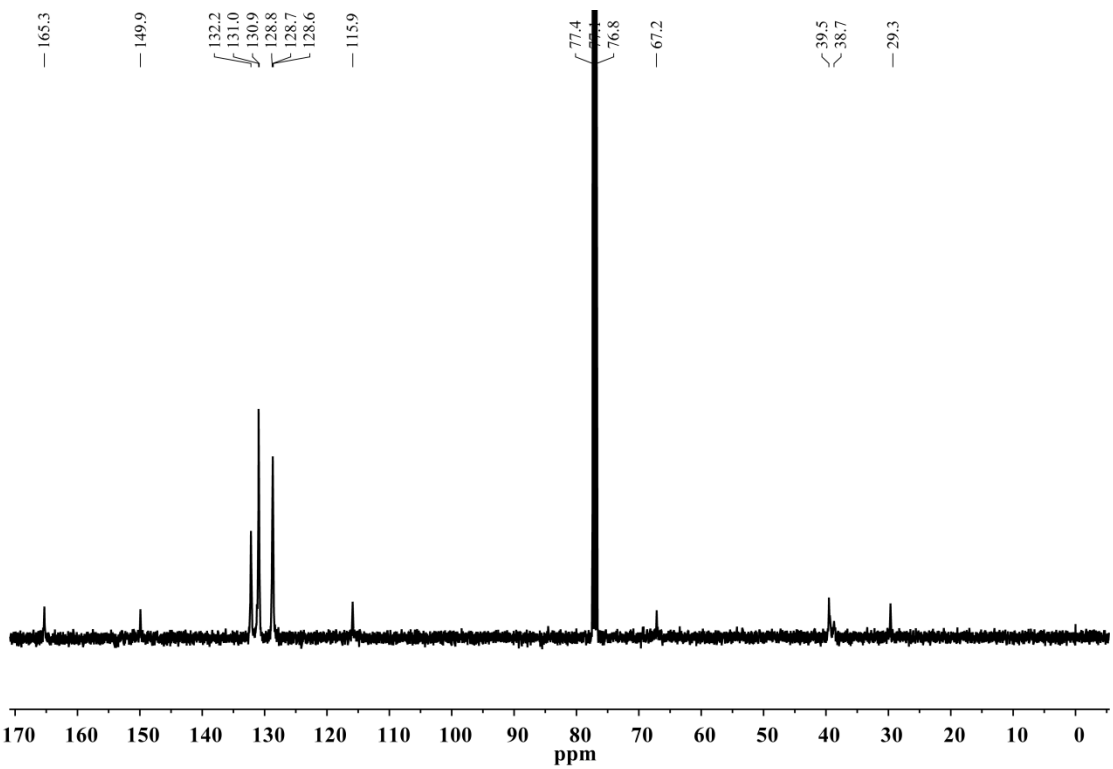


Figure S12. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1a** at 298 K.

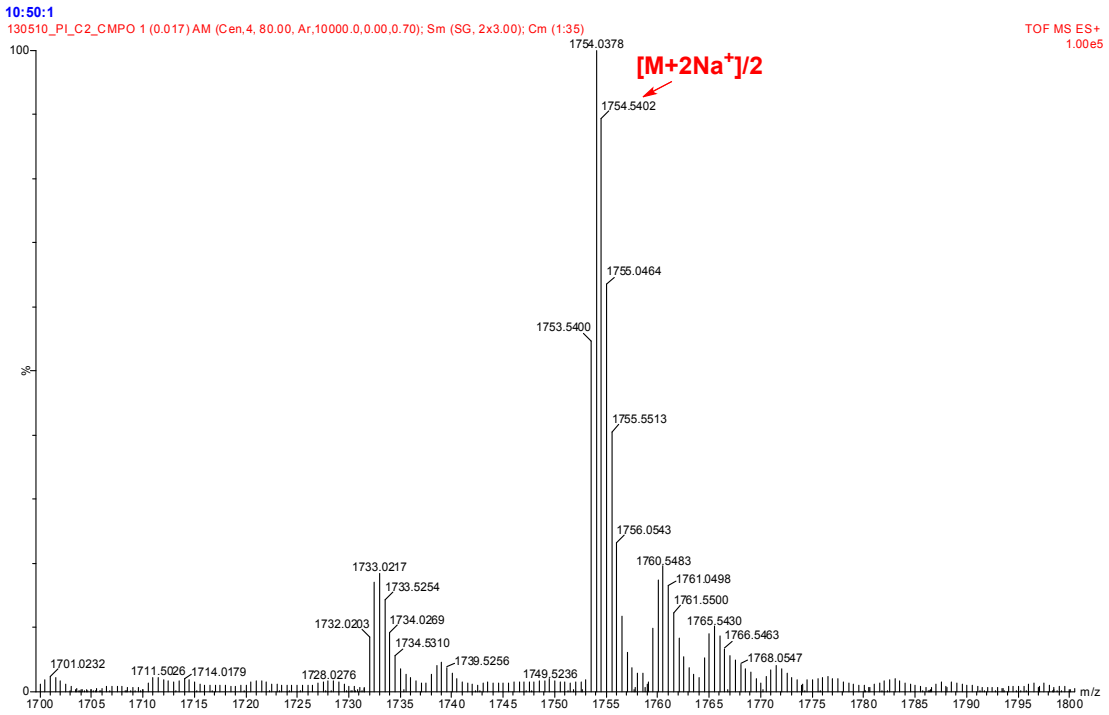


Figure S13. ESI-HRMS spectrum of **1a**.

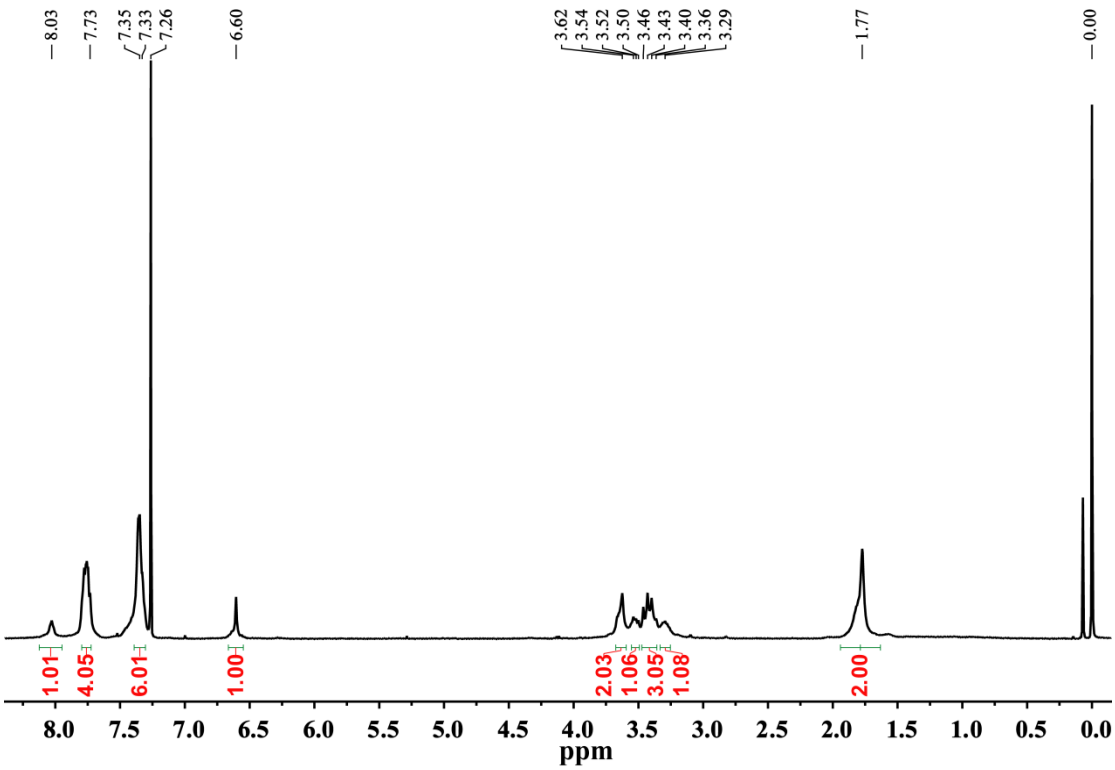


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b** at 298 K.

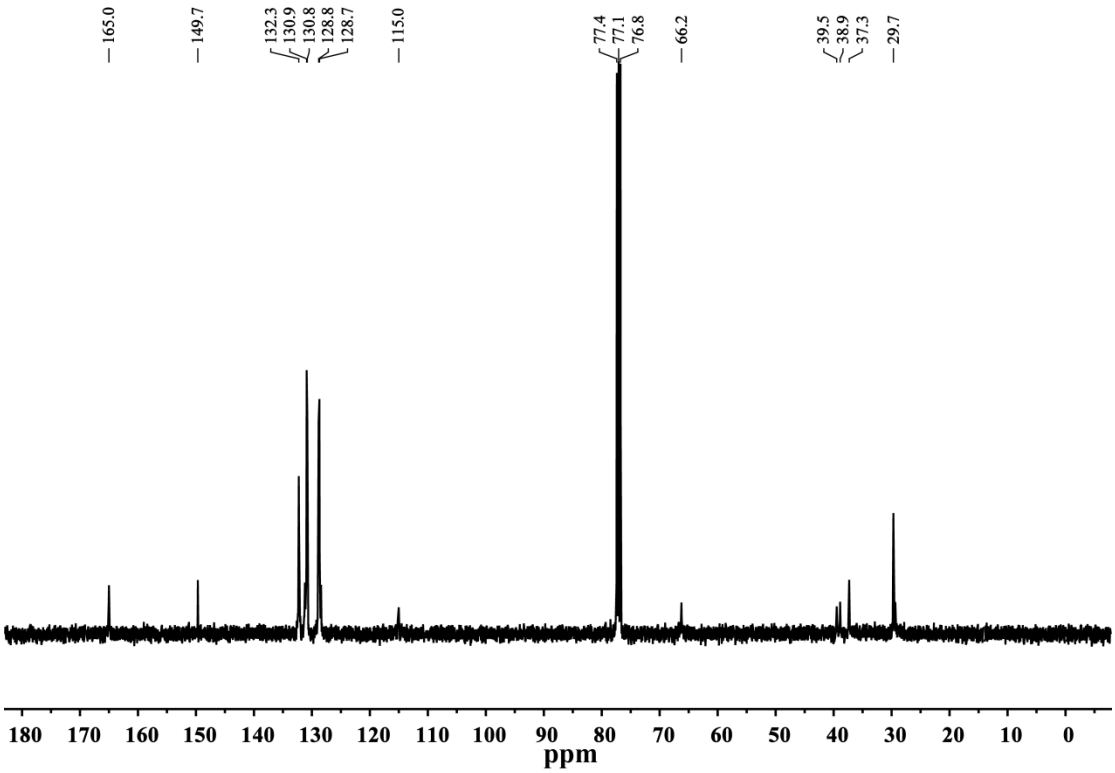


Figure S15. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1b** at 298 K.

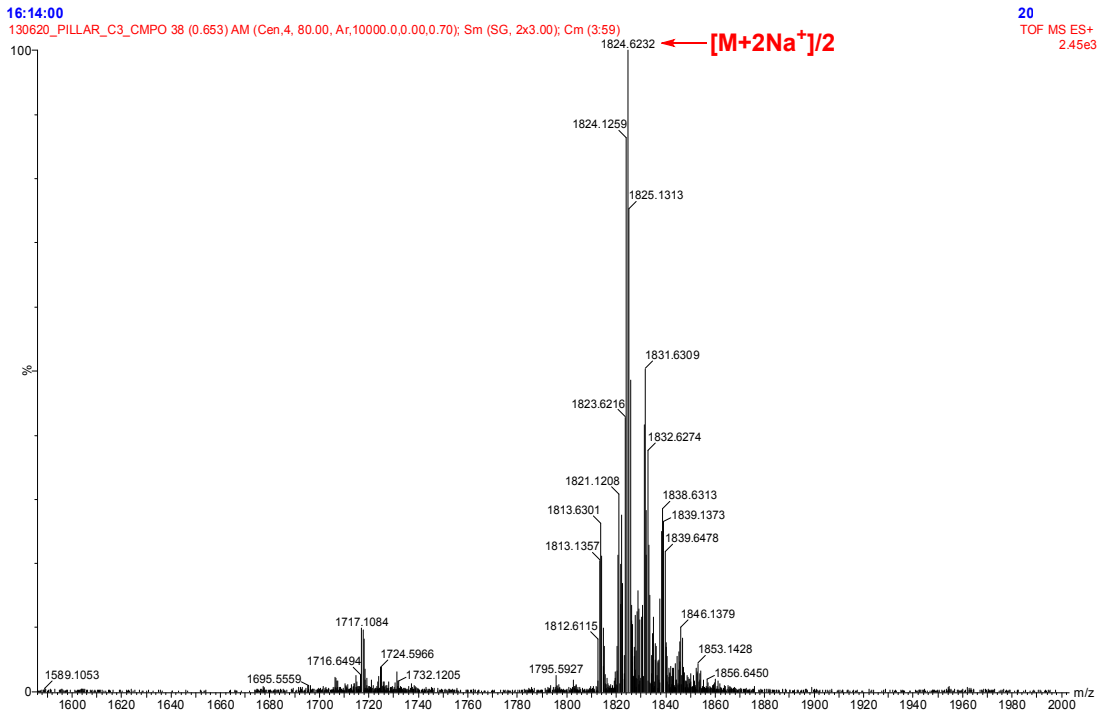


Figure S16. ESI-HRMS spectrum of **1b**.

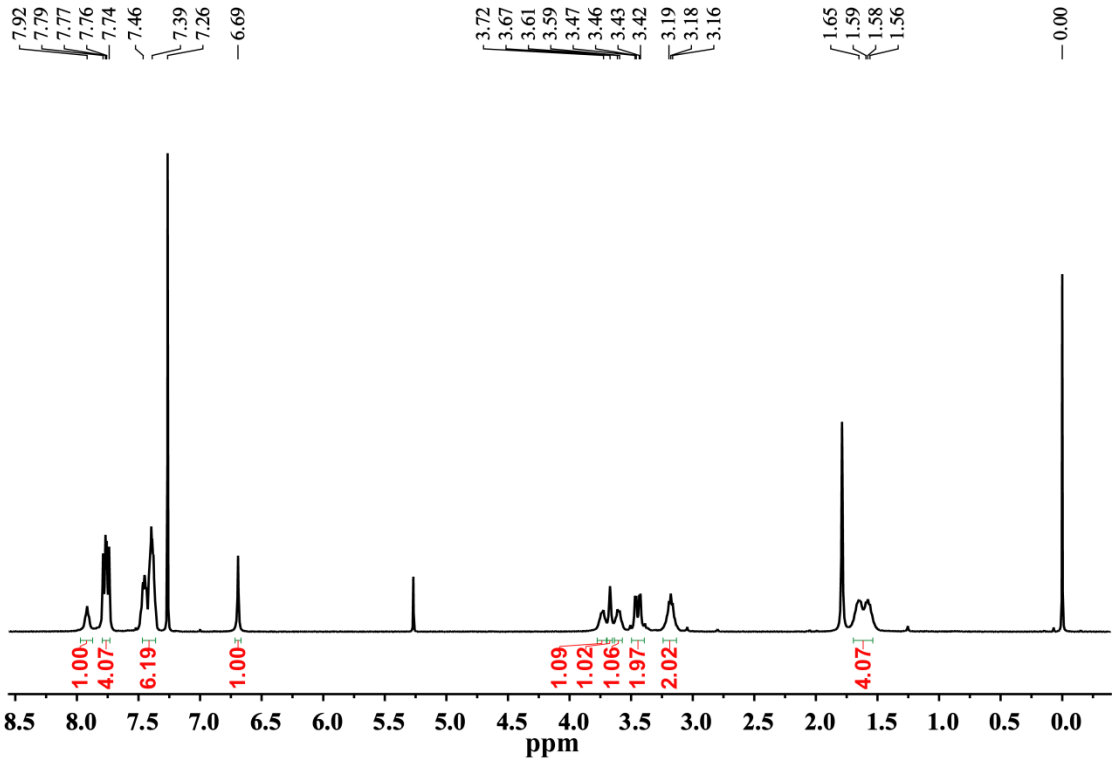


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1c** at 298 K.

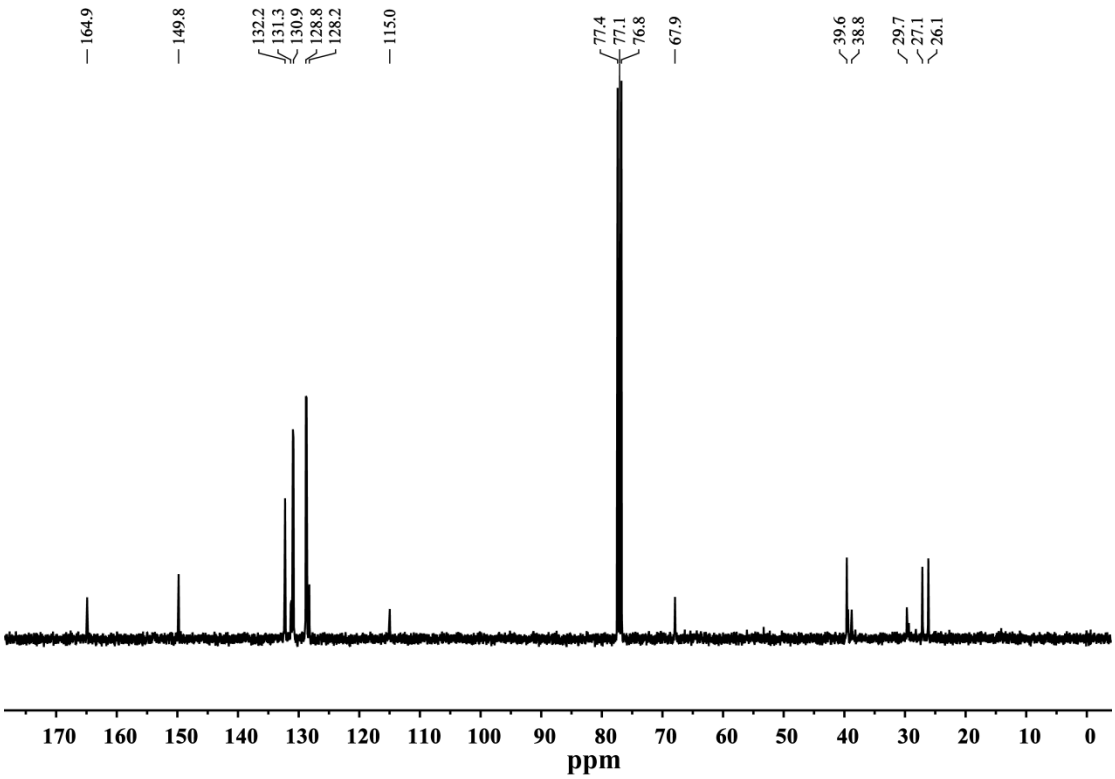


Figure S18. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1c** at 298 K.

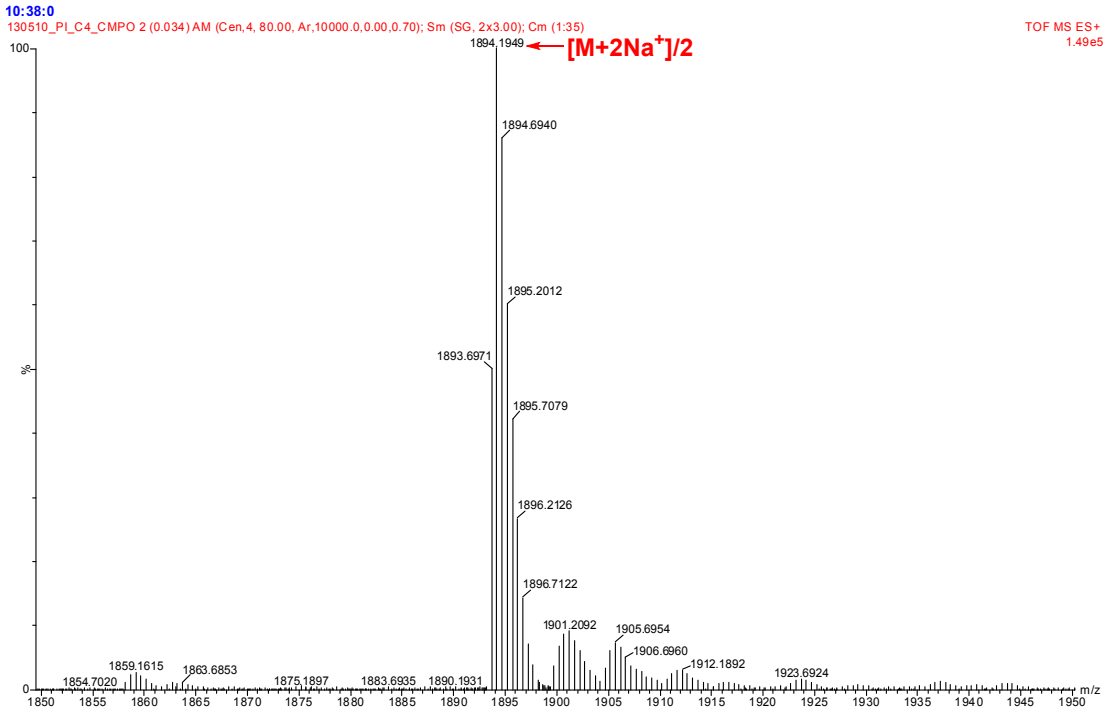


Figure S19. ESI-HRMS spectrum of **1c**.

4. ESI-HRMS for complexes

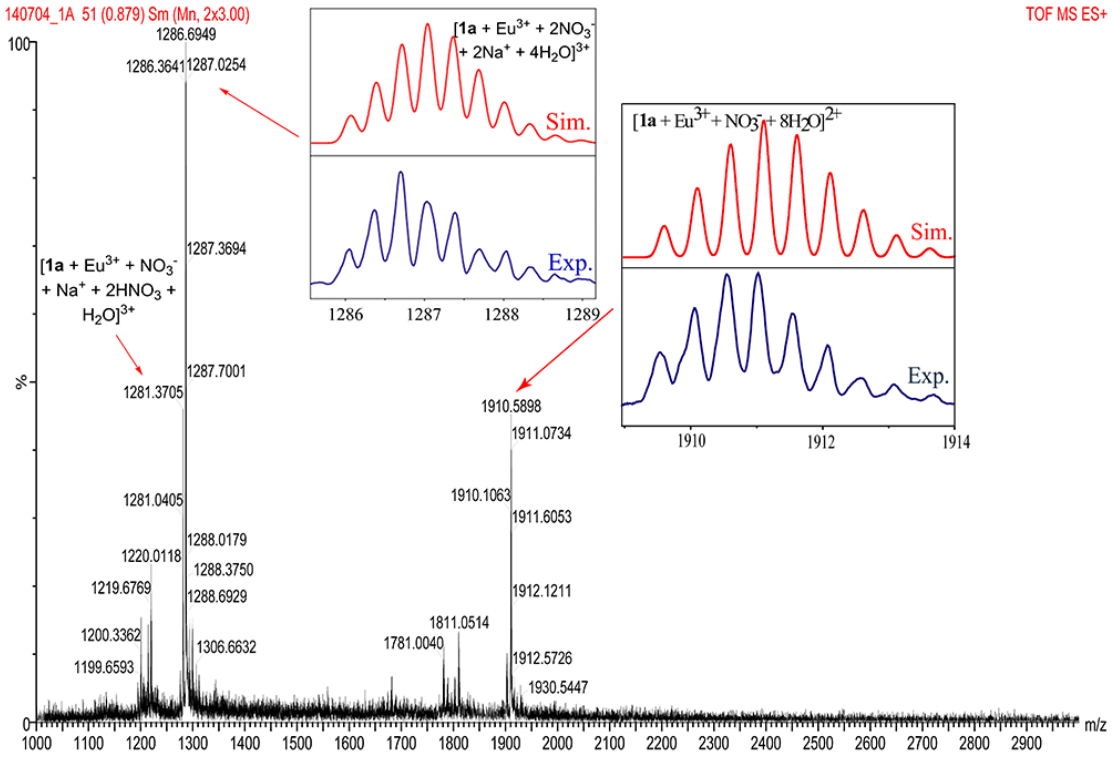


Figure S20. ESI-HRMS spectrum of the 1:1 (M:L) complex formed between **1a** and Eu^{3+} on addition of 1 equiv. of $Eu(NO_3)_3$ (inset: experimental isotope distribution (blue) and computer simulation (red)).

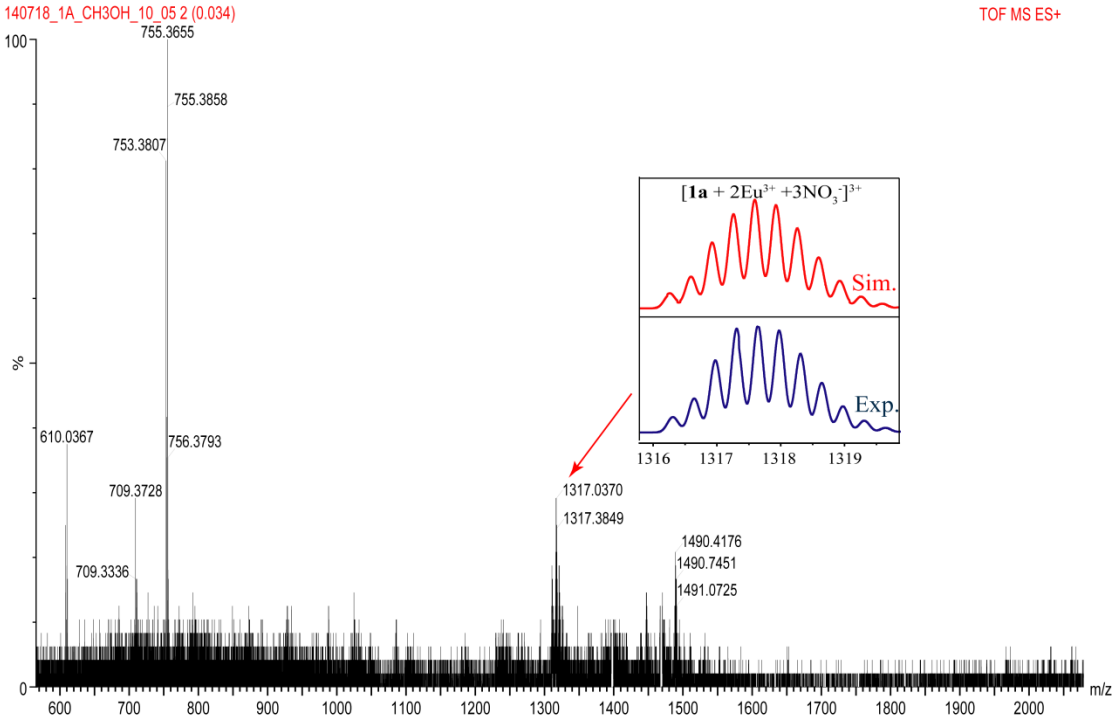


Figure S21. ESI-HRMS spectrum of the 2:1 (M:L) complex formed between **1a** and Eu^{3+} on addition of 3 equiv. of $Eu(NO_3)_3$ (inset: experimental isotope distribution (blue) and computer simulation (red)).

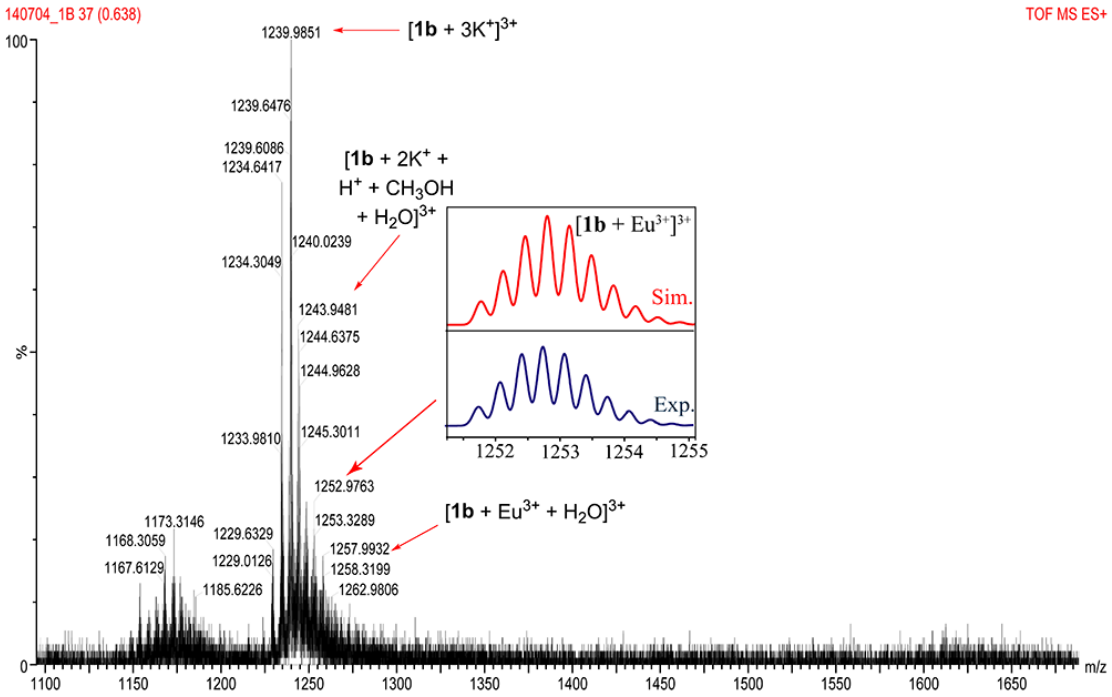


Figure S22. ESI-HRMS spectrum of the 1:1 (M:L) complex formed between **1b** and Eu^{3+} on addition of 1 equiv. of $Eu(NO_3)_3$ (inset: experimental isotope distribution (blue) and computer simulation (red)).

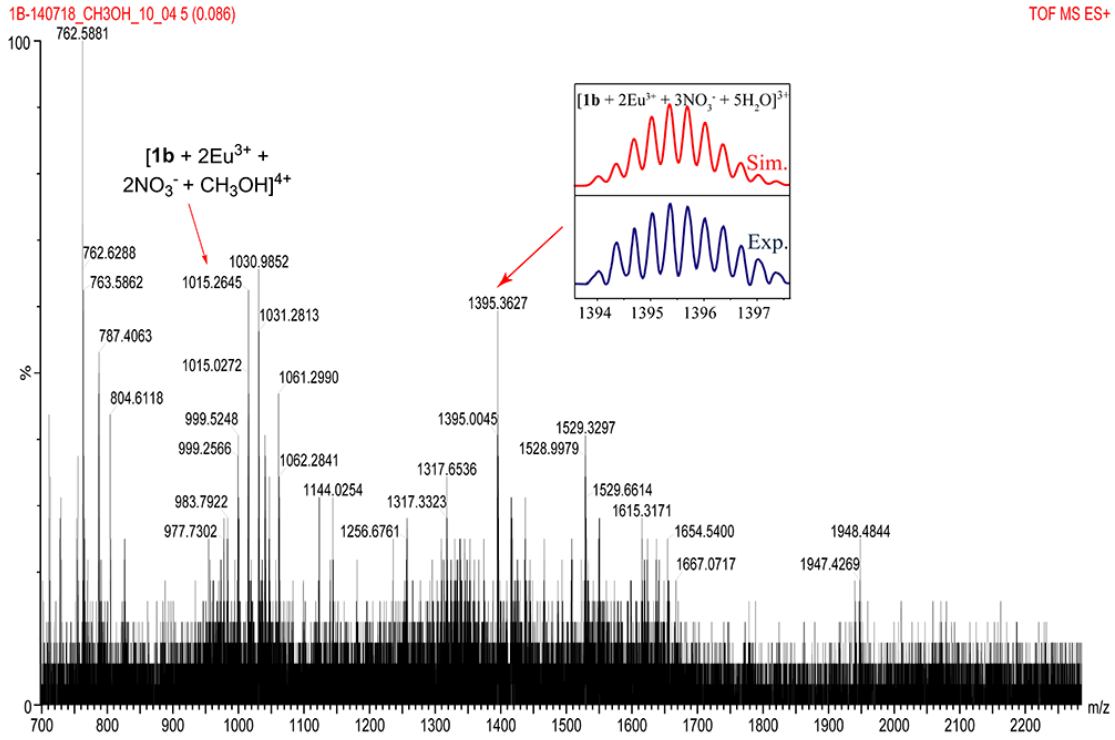


Figure S23. ESI-HRMS spectrum of the 2:1 (M:L) complex formed between **1b** and Eu^{3+} on addition of 3 equiv. of $Eu(NO_3)_3$ (inset: experimental isotope distribution (blue) and computer simulation (red)).

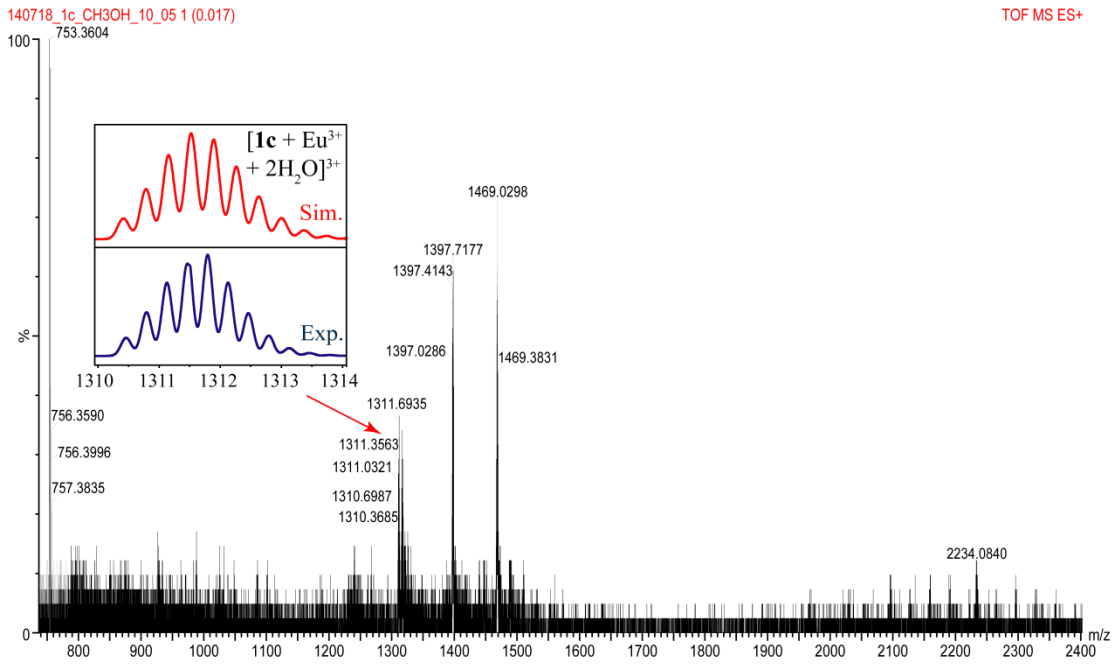


Figure S24. ESI-HRMS spectrum of the 1:1 (M:L) complex formed between **1c** and Eu^{3+} on addition of 1 equiv. of $Eu(NO_3)_3$ (inset: experimental isotope distribution (blue) and computer simulation (red)).

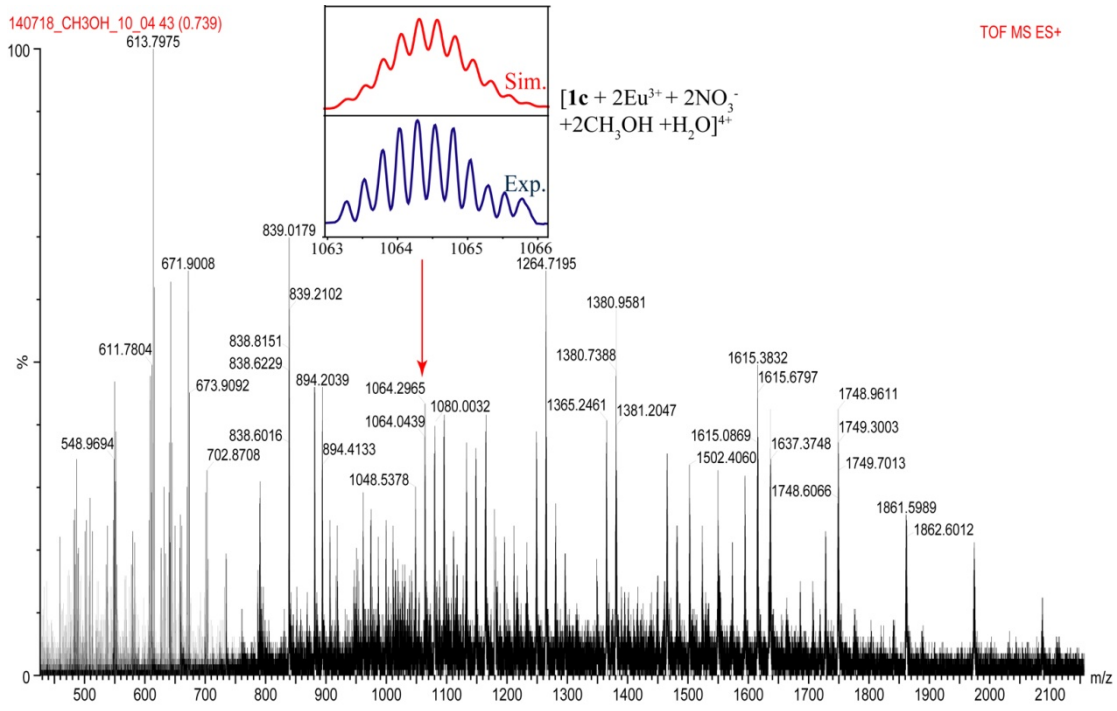


Figure S25. ESI-HRMS spectrum of the 2:1 (M:L) complex formed between **1c** and Eu^{3+} on addition of 3 equiv. of $Eu(NO_3)_3$ (inset: experimental isotope distribution (blue) and computer simulation (red)).

5. NMR titration of 1 with La^{3+}

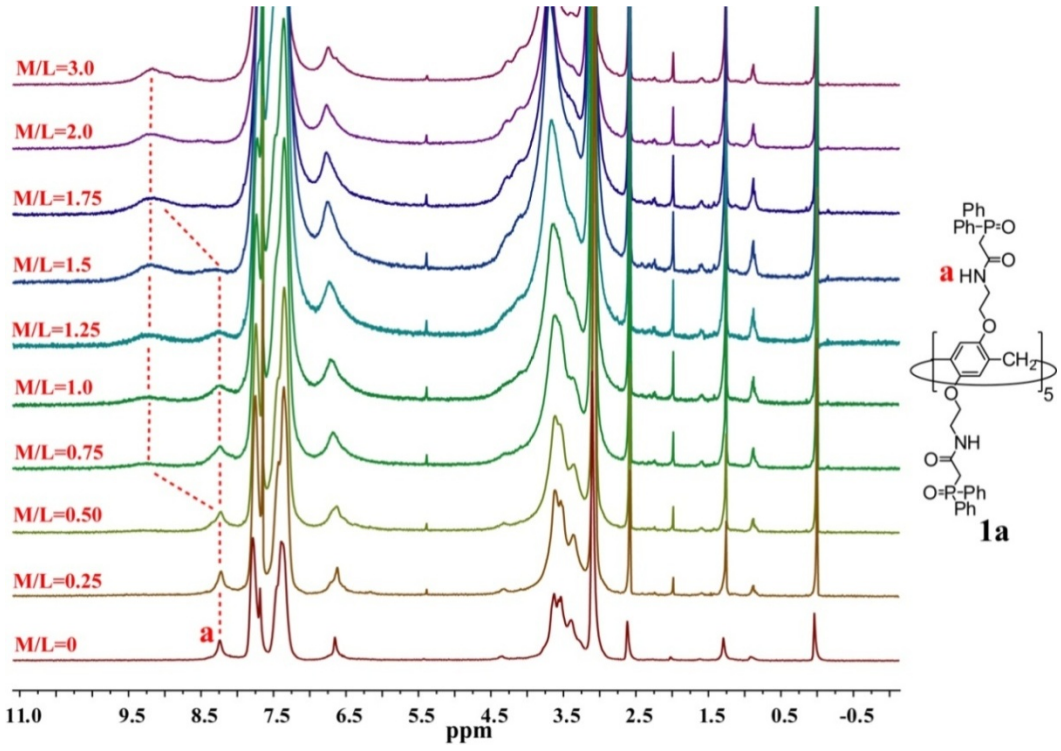


Figure S26. Titration of a **1a** solution (4.0 mM) by La^{3+} in $CDCl_3$/DMSO-d_6 (4:1, v/v) as monitored by ^1H NMR spectroscopy at 298 K.

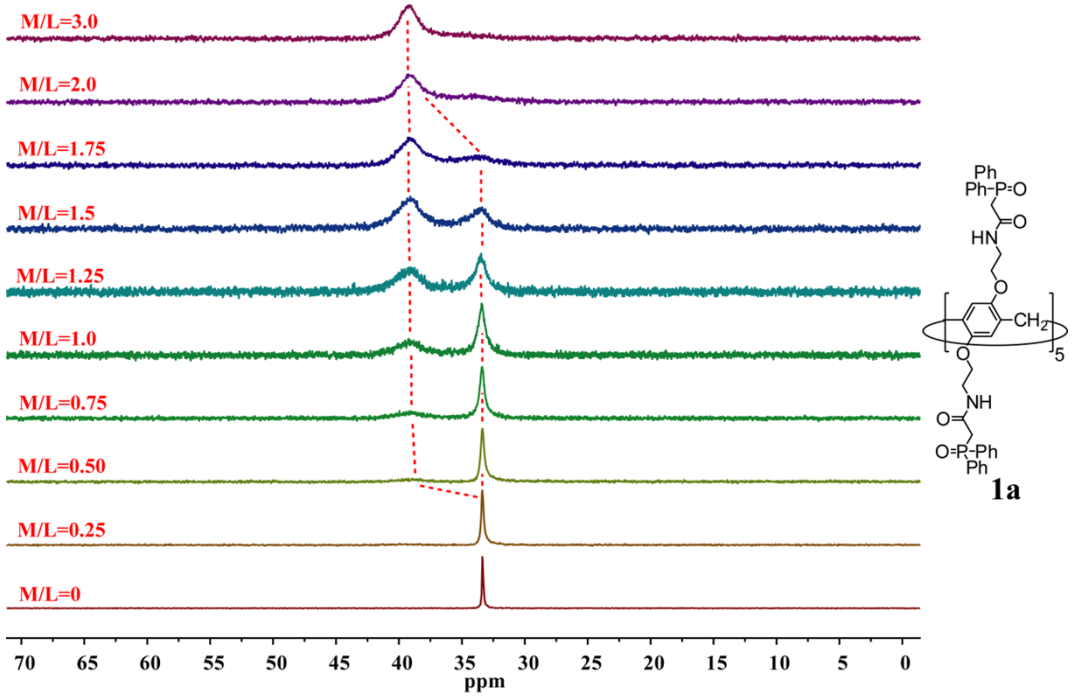


Figure S27. Titration of a **1a** solution (4.0 mM) by La^{3+} in $CDCl_3$/DMSO-d_6 (4:1, v/v) as monitored by ^{31}P NMR spectroscopy at 298 K.

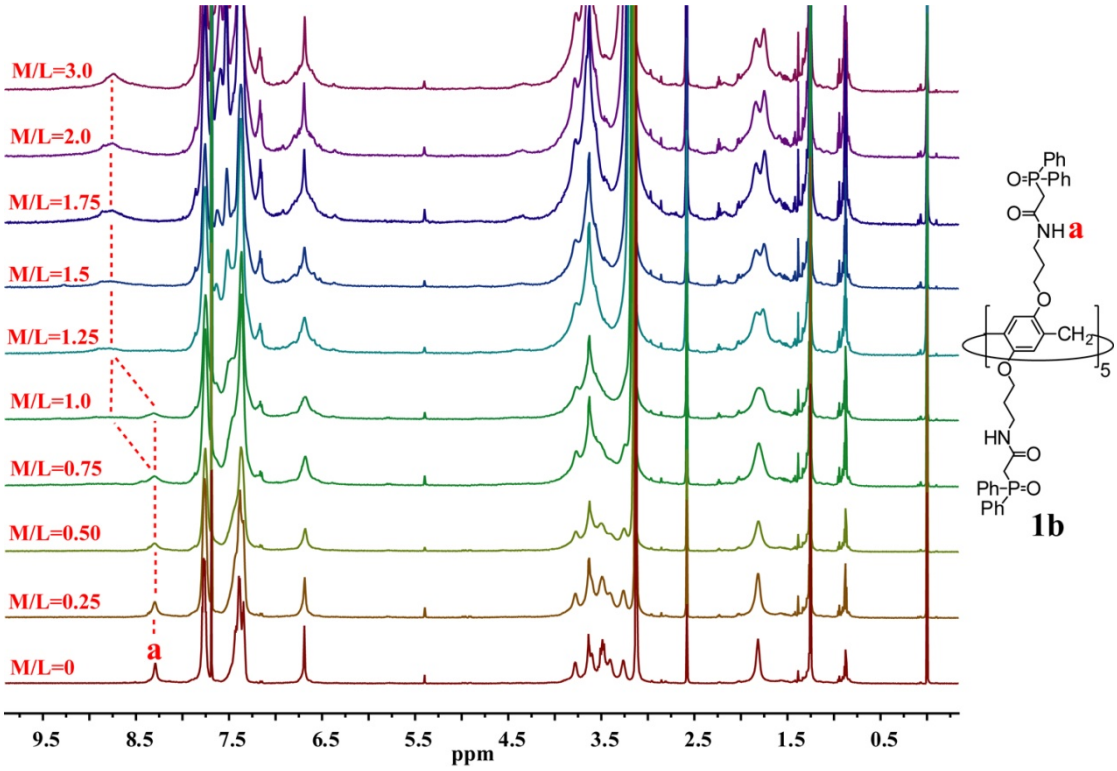


Figure S28. Titration of a **1b** solution (4.0 mM) by La^{3+} in $CDCl_3$/DMSO-d_6 (4:1, v/v) as monitored by ^1H NMR spectroscopy at 298 K.

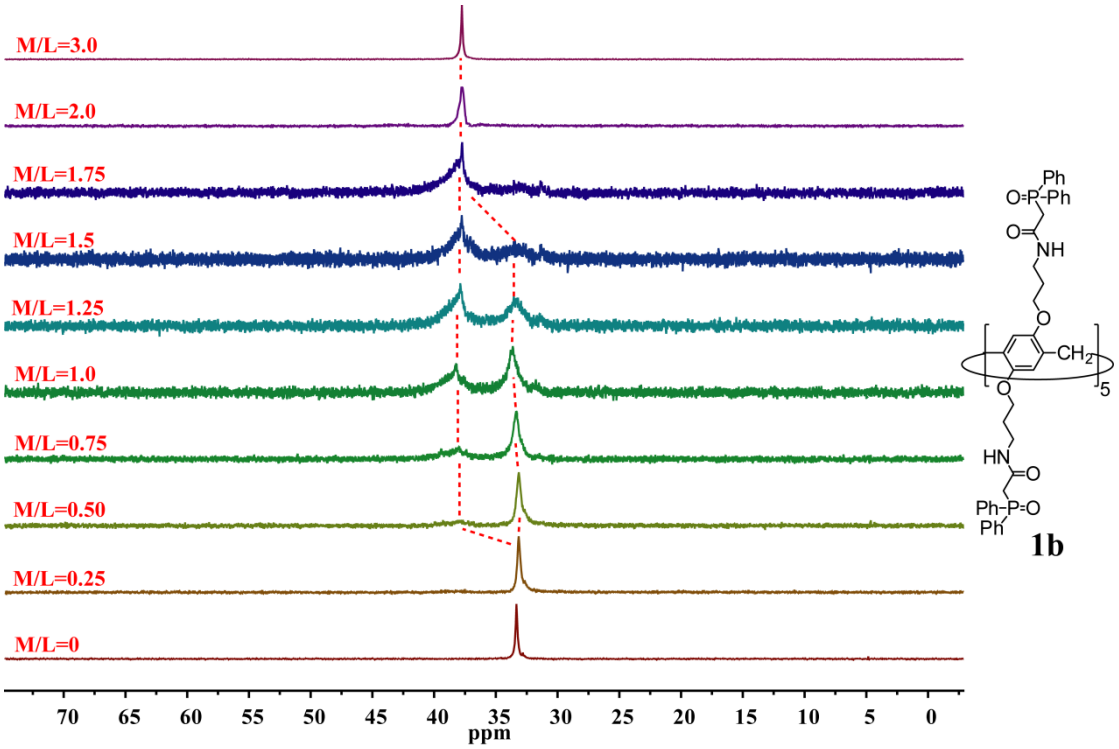


Figure S29. Titration of a **1b** solution (4.0 mM) by La^{3+} in $CDCl_3$/DMSO-d_6 (4:1, v/v) as monitored by ^{31}P NMR spectroscopy at 298 K.

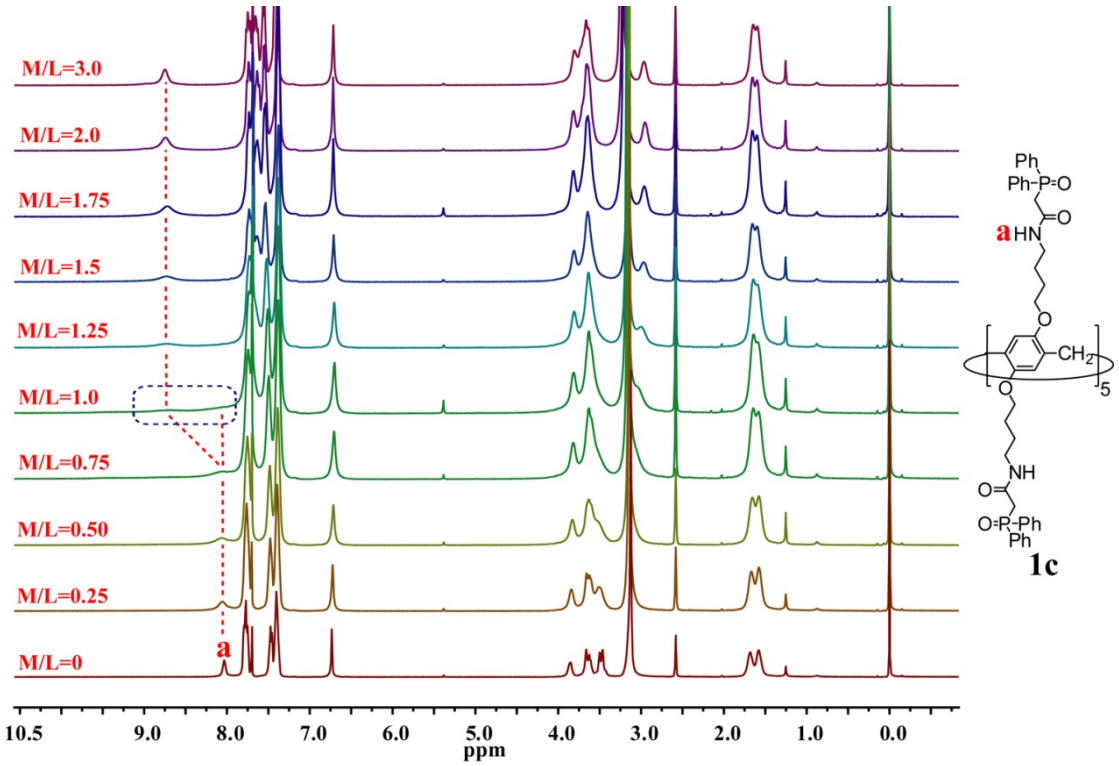


Figure S30. Titration of a **1c** solution (4.0 mM) by La^{3+} in $CDCl_3$/DMSO-d_6 (4:1, v/v) as monitored by ^1H NMR spectroscopy at 298 K.

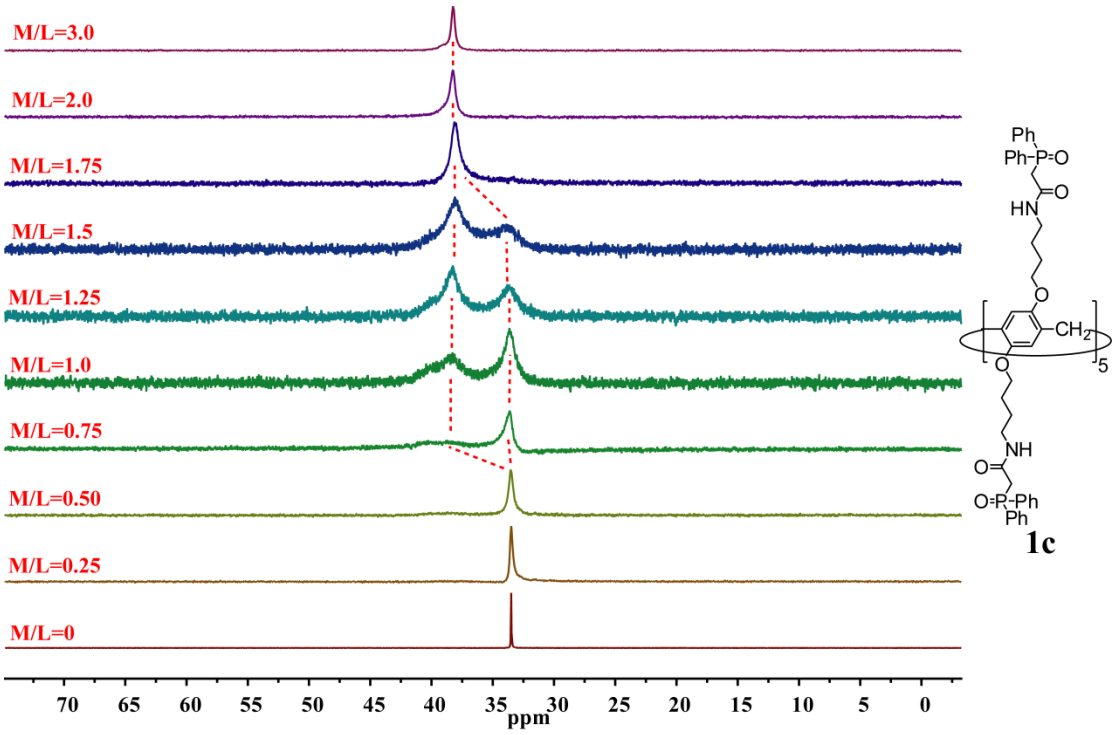


Figure S31. Titration of a **1c** solution (4.0 mM) by La^{3+} in $CDCl_3$/DMSO-d_6 (4:1, v/v) as monitored by ^{31}P NMR spectroscopy at 298 K.

6. Fluorescencetitration of Eu^{3+} with 1

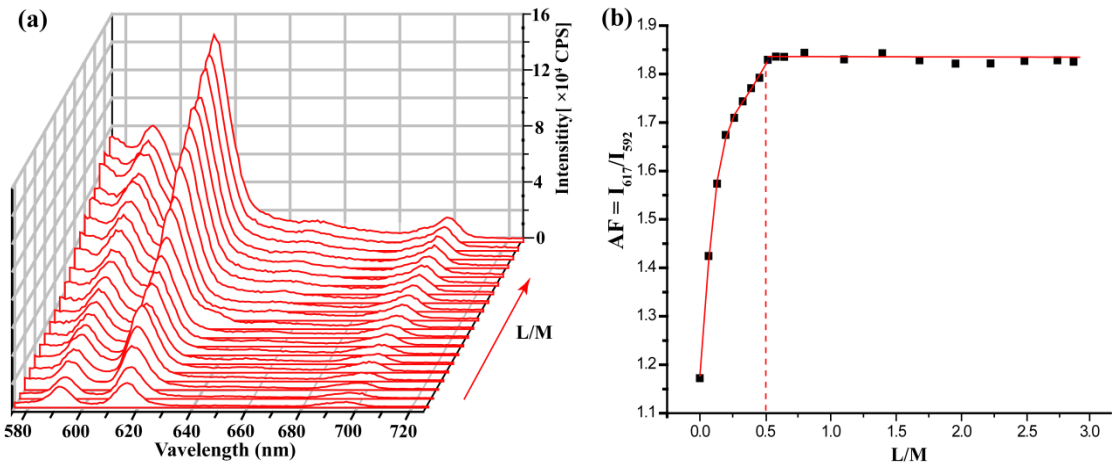


Figure S32. (a) Fluorescence titration of $Eu(NO_3)_3$ (2×10^{-4} M) with ligand **1a** in

CH_3OH; (b) Corresponding asymmetry factors (AF = I_{617} / I_{592}) as a function of [**1a**]/[M] mole ratio (λ_{ex} = 394 nm).

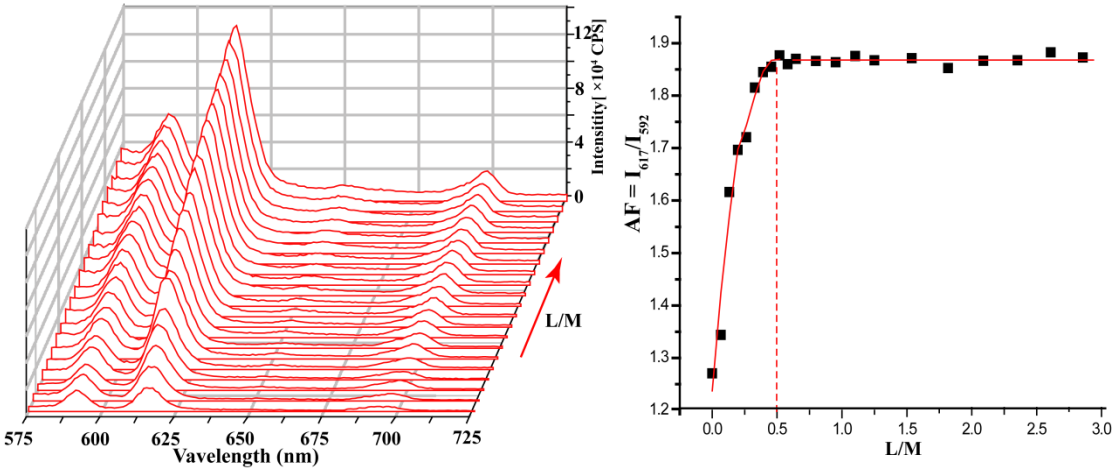


Figure S33. (a) Fluorescence titration of $Eu(NO_3)_3$ (2×10^{-4} M) with ligand **1b** in CH_3OH; (b) Corresponding asymmetry factors (AF = I_{617} / I_{592}) as a function of [**1b**]/[M] mole ratio (λ_{ex} = 394 nm).

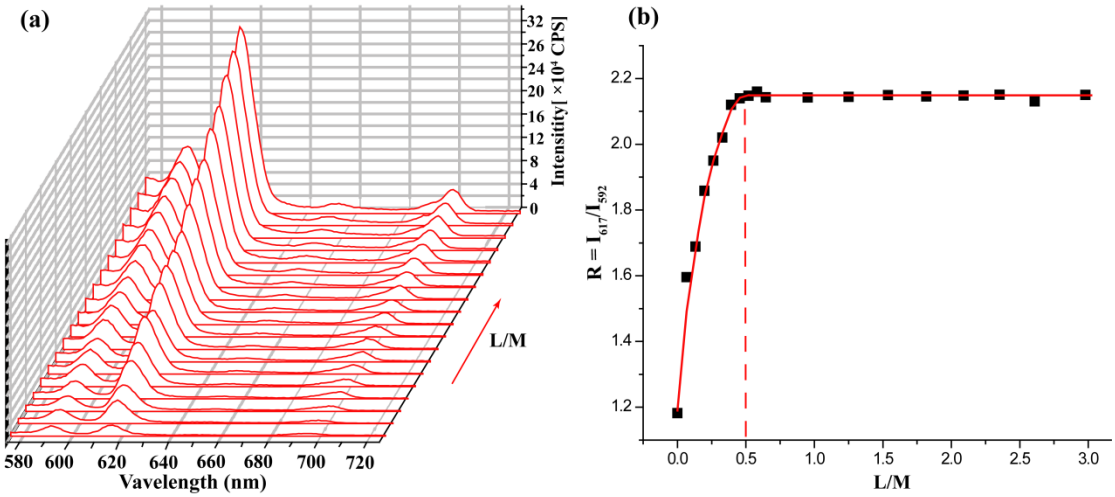


Figure S34. (a) Fluorescence titration of $Eu(NO_3)_3$ (2×10^{-4} M) with ligand **1c** in CH_3OH; (b) Corresponding asymmetry factors (AF = I_{617} / I_{592}) as a function of [**1c**]/[M] mole ratio (λ_{ex} = 394 nm).

7. Job's plot of 1 and Eu^{3+}

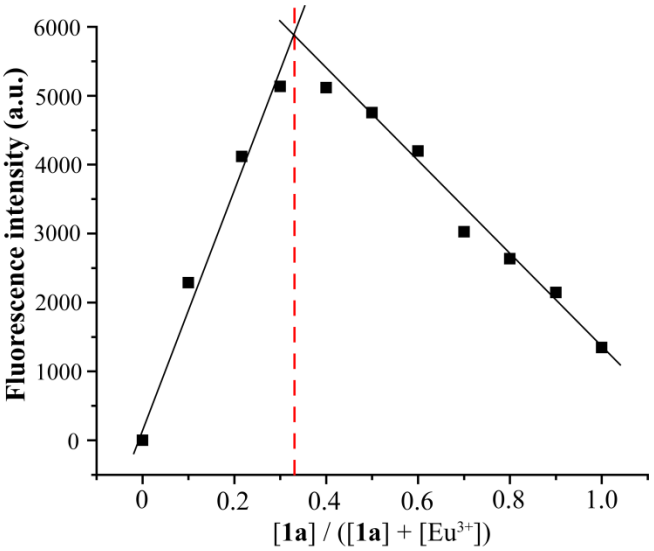


Figure S35. Job's plot of **1a** and Eu^{3+} in CH_3OH. The emission intensity at 617 nm is plotted against the molar fraction of [**1a**] to ([**1a**] + [Eu^{3+}]) at a fixed total concentration 2.0×10^{-4} M (λ_{ex} = 394 nm).

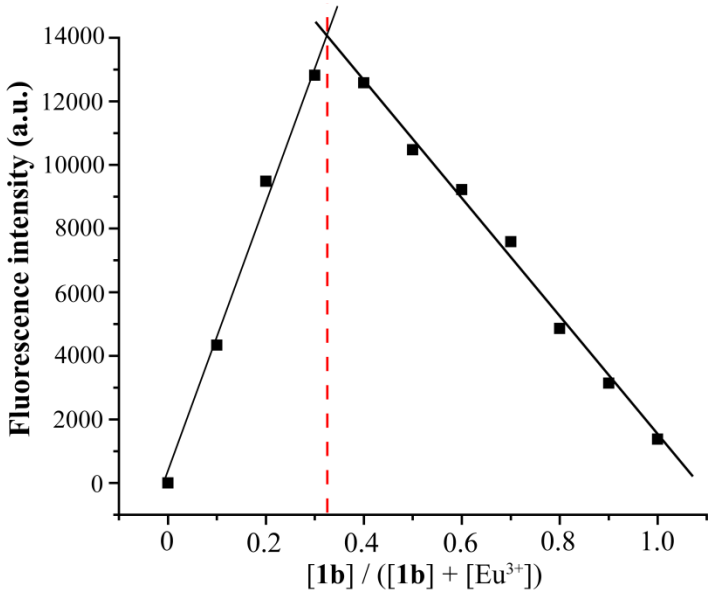


Figure S36. Job's plot of **1b** and Eu^{3+} in CH_3OH. The emission intensity at 617 nm is plotted against the molar fraction of [**1b**] to ([**1b**] + [Eu^{3+}]) at a fixed total concentration 2.0×10^{-4} M (λ_{ex} = 394 nm).

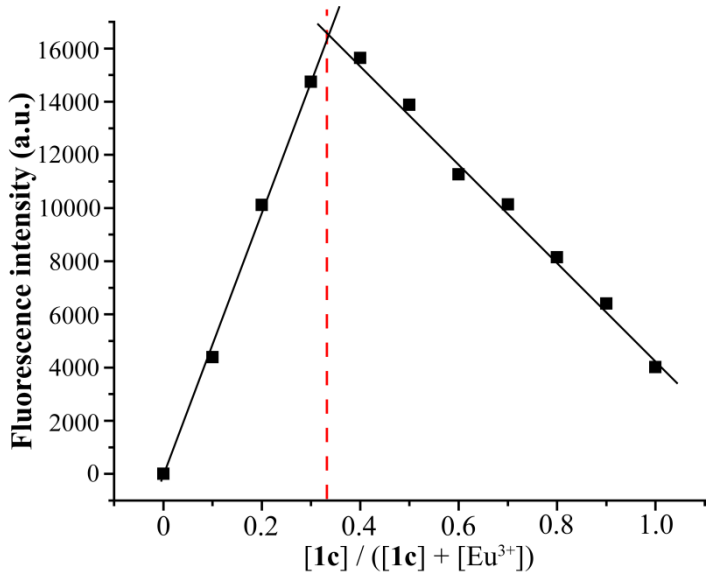


Figure S37. Job's plot of **1c** and Eu^{3+} in CH_3OH. The emission intensity at 617 nm is plotted against the molar fraction of [**1c**] to ([**1c**] + [Eu^{3+}]) at a fixed total concentration 2.0×10^{-4} M (λ_{ex} = 394 nm).

8. UV-vis spectrophotometric titration of 1 with Eu^{3+}

The stability constants β defined as the concentration ratio ($\beta = [M_xL_y{}^{n+}]^x/[M^{n+}]^x[L]^y$) were determined in methanol by UV-vis spectrophotometric titration at 25 °C. The concentration of ligand **1** in methanol was 4.0×10^{-5} M and 0.01 M tetraethylammonium nitrate (Et_4NNO_3) was added to control the ionic strength. The experiments were carried out in a 1.0 cm quartz cell. Factor analysis and mathematical treatment of the spectrophotometric data were performed and fitted with the ReactLab EQUILIBRIA software.[S6]

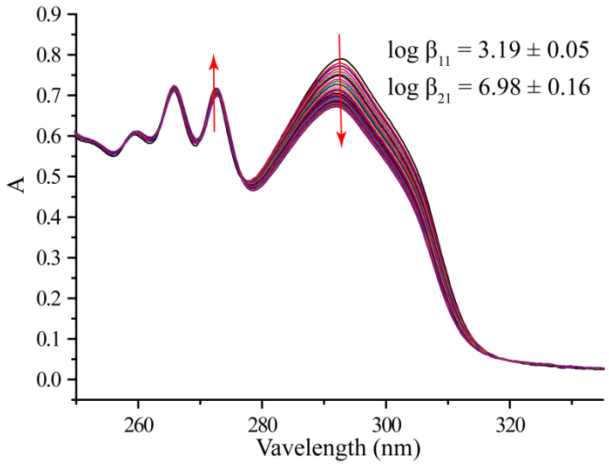


Figure S38. UV-vis spectrophotometric titration of **1a** (4.0×10^{-5} M) with $Eu(NO_3)_3$ in methanol ($0 \leq R = C_M/C_L \leq 5$).

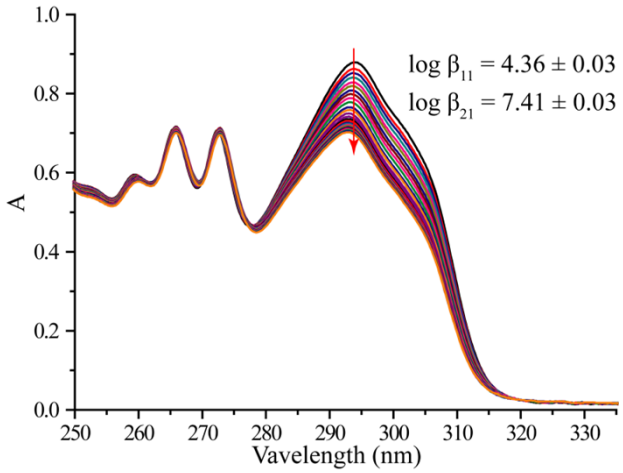


Figure S39. UV-vis spectrophotometric titration of **1b** (4.0×10^{-5} M) with $Eu(NO_3)_3$ in methanol ($0 \leq R = C_M/C_L \leq 5$).

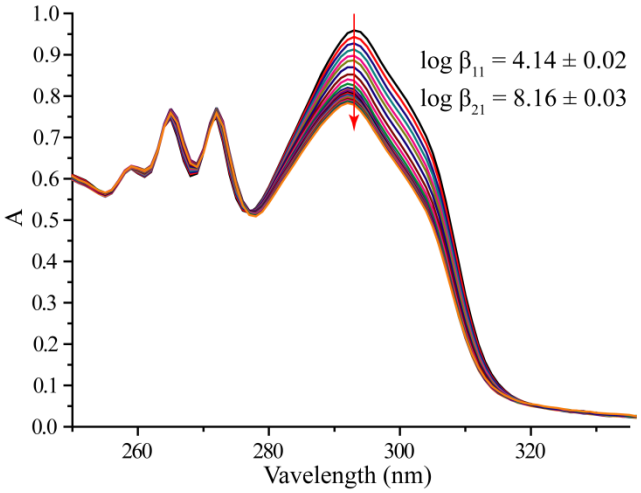


Figure S40. UV-vis spectrophotometric titration of **1c** (4.0×10^{-5} M) with $Eu(NO_3)_3$

in methanol ($0 \leq R = C_M/C_L \leq 4$).

9. FT-IR spectra of free and Eu^{3+}-loaded 1

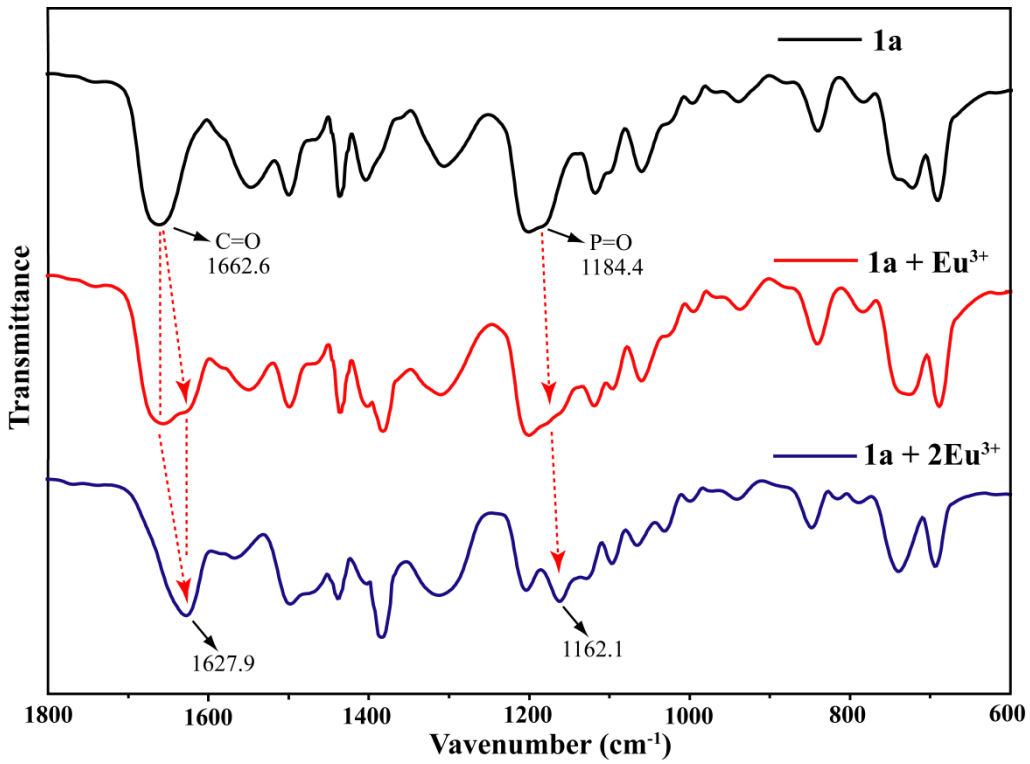


Figure S41. FT-IR spectra of **1a** in the absent and present of different equivalent of $Eu(NO_3)_3$.

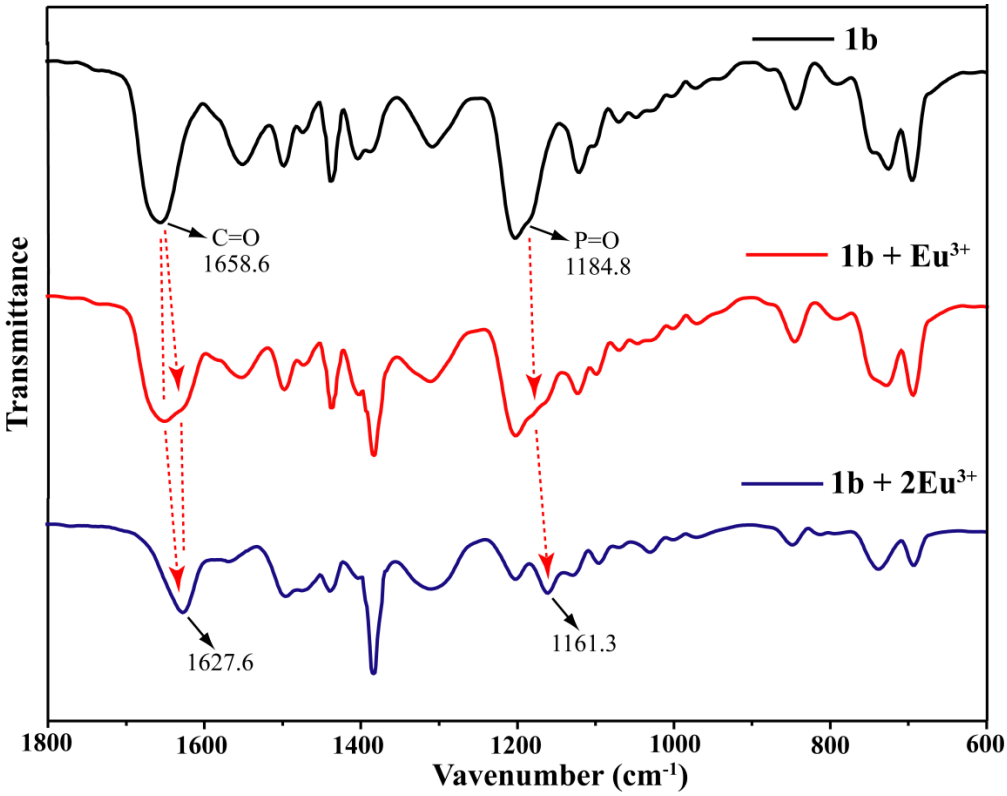


Figure S42. FT-IR spectra of **1b** in the absent and present of different equivalent of $Eu(NO_3)_3$.

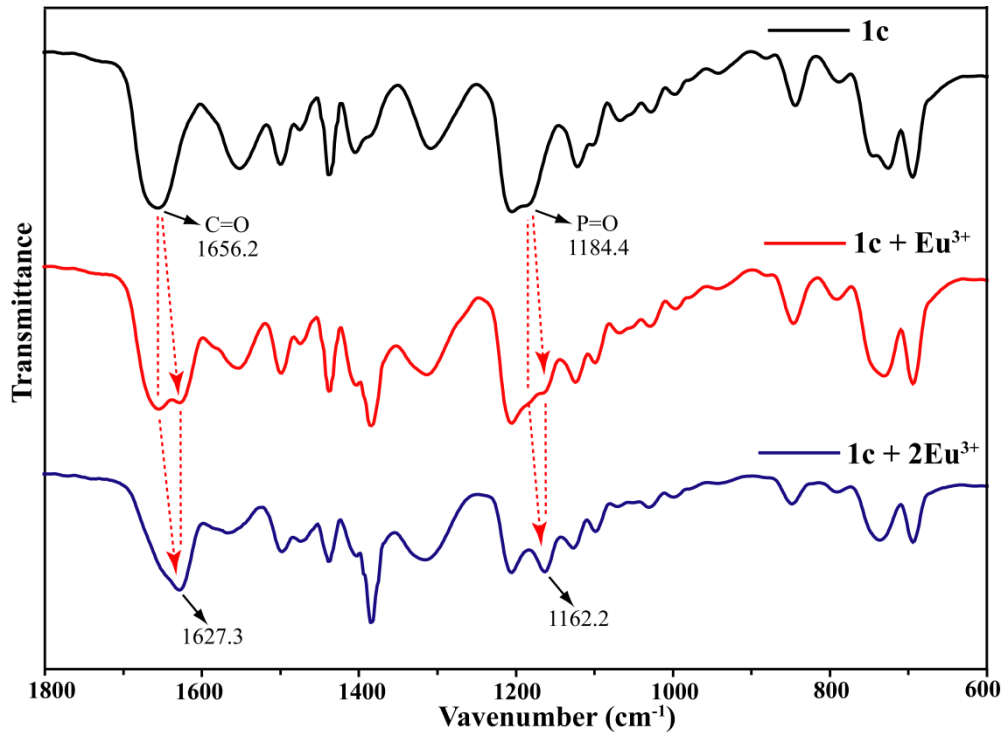


Figure S43. FT-IR spectra of **1c** in the absent and present of different equivalent of $Eu(NO_3)_3$.

10. Extraction properties of Am(III) and Eu(III)

The ligands (1.0×10^{-3} M) were dissolved in a mixed solvent system consisting of *m*-nitro(trifluoromethyl)benzene and *n*-octanol (*m*-NTFB/*n*-octanol, 95:5, v:v). The organic phase was mixed with an aqueous phase containing europium(III) nitrate ($C_{Eu} = 10^{-5}$ M) with ^{241}Am(III) or ^{152}Eu(III) (radiochemical purity, *ca.* 1.0×10^{-7} mol•L^{-1}) as well as HNO_3 at different concentrations (0.1, 1.0, 2.0, 3.0 and 4.0 M). Liquid-liquid extraction experiments were performed by shaking 1 mL of organic phase and 1 mL of aqueous phase in a stoppered tube immersed in a thermostated bath at 25 ± 0.5 °C for 1 hour which is long enough to reach the extraction equilibrium. After separation of the two phases, 0.5 mL of each phase was collected and the concentration was determined by gamma counting (NaI(Tl) well detector). The distribution ratios D_M were calculated as the ratio of the cation gamma activity in the organic phase to the cation gamma activity in the aqueous phase. The selectivity for Am(III) over Eu(III) is expressed as $SF_{Am/Eu} = D_{Am}/D_{Eu}$. The reported D_M values are the averages of at least two experiments. The errors in the extraction percentages of the duplicate experiments are less than 5%.

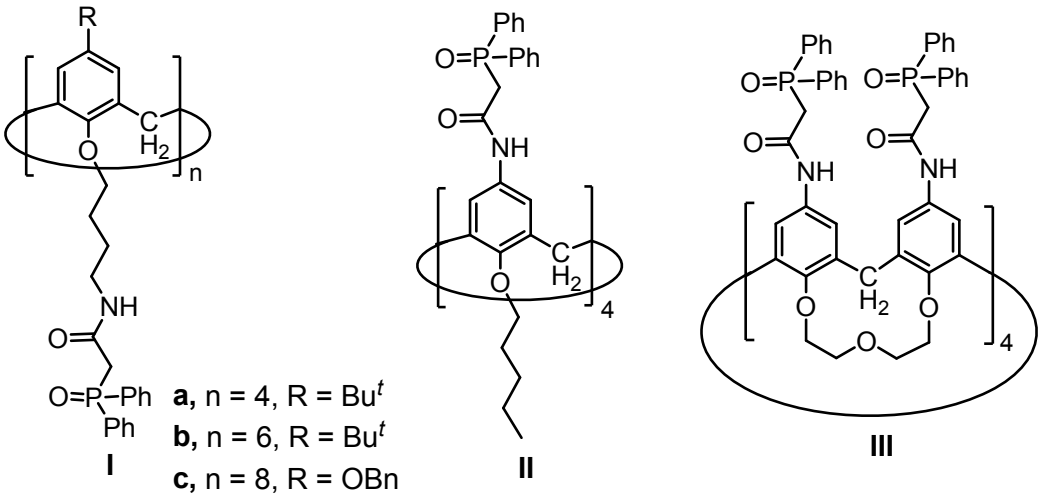


Figure S44. Chemical structures of CMPO-functionalized calixarenes **I**-**III**.

Table S1 Extraction data of Am(III) and Eu(III) from different HNO_3 solution by the ligands **1a-c** (1 mM) and CMPO **2** (10 mM) into *m*-NTFB/*n*-octanol (95:5, v:v) at 25 °C.

Compounds		HNO_3 / mol•L^{-1}				
		0.1	1.0	2.0	3.0	4.0
1a	D_{Am}	4.30	8.69	2.66	0.69	0.13
	D_{Eu}	2.10	4.54	1.30	0.44	0.12
	$SF_{Am/Eu}$	2.05	1.91	2.05	1.57	1.08
1b	D_{Am}	4.46	10.7	3.30	0.78	0.43
	D_{Eu}	2.12	6.17	1.37	0.47	0.19
	$SF_{Am/Eu}$	2.10	1.73	2.41	1.66	2.26
1c	D_{Am}	57.7	171	5.10	1.56	0.50
	D_{Eu}	7.54	13.1	2.90	1.16	0.34
	$SF_{Am/Eu}$	7.65	13.0	1.76	1.34	1.47
I-a[a]	D_{Am}	48	51	61	63	nr
	D_{Eu}	28	33	44	48	nr
	$SF_{Am/Eu}$	1.7	1.5	1.4	1.3	--
I-b[a]	D_{Am}	11.1	> 100	> 100	> 100	> 100
	D_{Eu}	5.1	26.4	27.7	35.5	26.6
	$SF_{Am/Eu}$	2.2	> 3	> 3	> 3	> 3
I-c[a]	D_{Am}	18.3	32.8	nd	nd	nd
	D_{Eu}	9.2	21.9	nd	nd	nd
	$SF_{Am/Eu}$	2.0	1.5	nd	nd	nd
II[a]	D_{Am}	19	195	275	150	100
	D_{Eu}	2.3	30	52	37	19
	$SF_{Am/Eu}$	8.3	6.5	5.3	4.0	5.26
III[b]	D_{Am}	397	nd	$> 10^3$	nd	nd
	D_{Eu}	93	nd	$> 10^3$	nd	nd
	$SF_{Am/Eu}$	4.27	--	--	--	--
2	D_{Am}	<0.01	<0.01	0.04	0.02	<0.01
	D_{Eu}	<0.01	<0.01	0.03	<0.01	<0.01

[a] The data were obtained from the literature [S7]; [b] The data were obtained from the literature [S8] ([ligands] = 1 mM; the diluent: *o*-nitrophenylhexyl ether, NPHE). nd: not determined.

Table S2 Multiple extractions of Am(III) and Eu(III) from 3 M HNO_3 solution by the ligands **1c** (1 mM) into *m*-NTFB/*n*-octanol (95:5, v:v) at 25 °C.

Compounds	Extraction No.	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
1c	1	1.56	1.16	1.34
	2	12.0	2.97	4.04
	3	103	6.63	15.5

11. Fluorescence studies

General

$Eu(NO_3)_3 \cdot 6H_2O$ (spectroscopic grade, >99.99%) was procured from Alpha Biochem and the solutions were made using Suprapur (Merck) nitric acid and HPLC grade methanol. Sample solutions for time resolved laser induced fluorescence spectroscopy (TRLFS) measurements were prepared by taking suitable aliquots of Eu(III) stock in the present (or absent) of **1a-c** in the mixed solvent system of $MeOH/H_2O$ (5:1, v/v, pH = 3.0).

TRLFS studies of the Eu^{3+}-solvent and Eu^{3+}-**1** complexes, in dilute nitric acid (pH = 3.0) as well as in the solvent, were carried out using a spectrometer (Edinburgh Analytical Instruments, UK) controlled by CD 920 controller and equipped with OPO laser. While the samples were excited at 394 nm, the emission spectra were recorded in the range of 575-750 nm. The emission decay curves were fitted into the exponential function to obtain the lifetimes/decay rates of the excited states using inbuilt software GEM/3 (Edinburgh) with reproducibility of lifetimes of the excited states within ± 3 μs. The life time of the $^5D_0$ emitting level of Eu^{3+} depends on the number of OH oscillators linked to the cations.[S9] An empirical relation has been established between primary hydration number of Eu^{3+} ion (N_{H_2O}) and the lifetime of its $^5D_0$ emitting level:

$$N_{H_2O} = 1.06/\tau - 0.19$$

The number of water molecules in the inner coordination sphere calculated from

the lifetime has an uncertainty of ± 0.5 in these measurements.

Table S3 Life time and number of inner-sphere water molecules (N_{H_2O}) of Eu^{3+}-**1** complexes when mixing 1.0 equiv. of **1** (λ_{ex} = 394 nm; λ_{em} =617 nm).

System	Life time (ms)	No. of inner-sphere water molecules
Eu^{3+}-solvent	τ = 0.144	7
Eu^{3+}-**1a**	τ_1 = 0.225 (61%)	4.5
	τ_2 = 0.619 (39%)	1.5
Eu^{3+}-**1b**	τ_1 = 0.246 (9.0%)	4.0
	τ_2 = 0.411 (91%)	2.0
Eu^{3+}-**1c**	τ_1 = 0.335 (22%)	3.0
	τ_2 = 0.673 (78%)	1.5

Table S4 Life time and number of inner-sphere water molecules (N_{H_2O}) of Eu^{3+}-**1** complexes when mixing 0.5 equiv. of **1** (λ_{ex} = 394 nm; λ_{em} =617 nm).

System	Life time (ms)	No. of inner-sphere water molecules
Eu^{3+}-**1a**	τ = 0.334	3
Eu^{3+}-**1b**	τ = 0.401	2.5
Eu^{3+}-**1c**	τ = 0.578	1.6

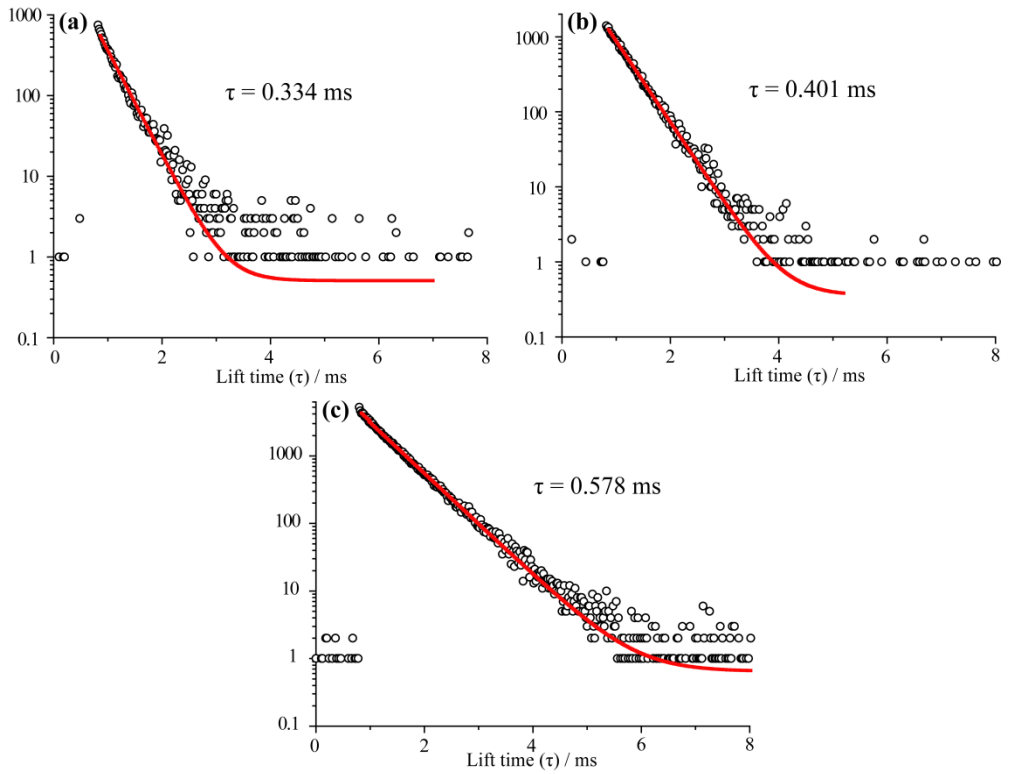


Figure S44. Fluorescence decay profiles of Eu^{3+}-**1** complexes on addition of 0.5 equiv. of **1** in methanol/water (5:1, v/v, pH=3.0); (a) Eu^{3+}-**1a** complex; (b) Eu^{3+}-**1b** complex; (c) Eu^{3+}-**1c** complex.

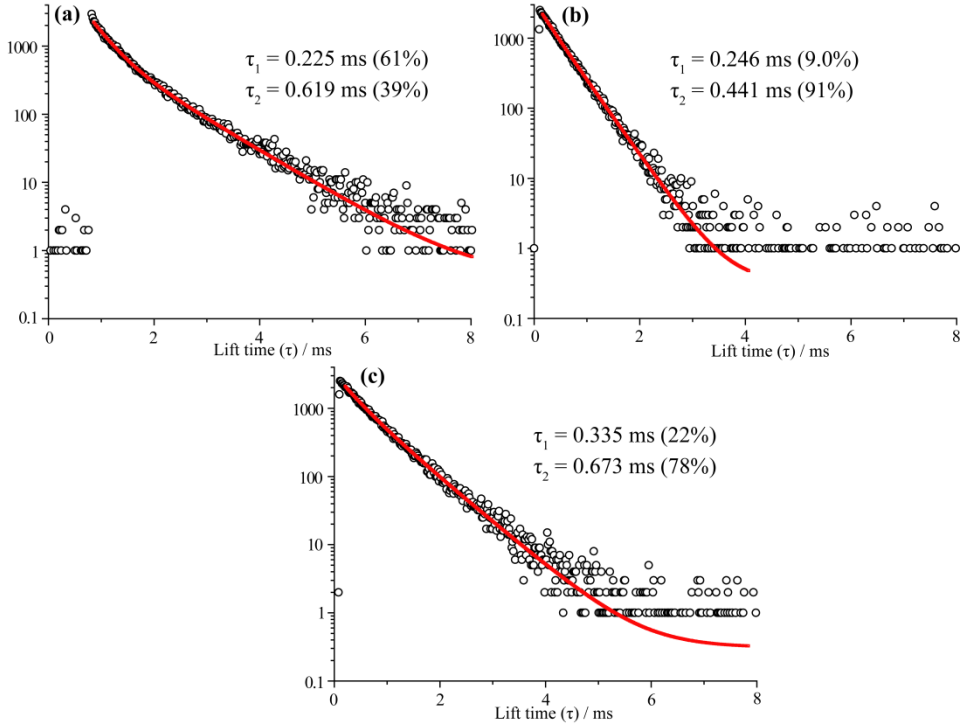


Figure S45. Fluorescence decay profiles of Eu^{3+}-**1** complexes on addition of 1.0

equiv. of **1** in methanol/water (5:1, v/v, pH=3.0); (a) Eu^{3+}-**1a** complex; (b) Eu^{3+}-**1b** complex; (c) Eu^{3+}-**1c** complex.

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