

Pillar[5]arene-based diglycolamides for highly efficient separation of americium(III) and europium(III)

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Supporting Information

was stirred at 50 °C under hydrogen atmosphere (0.5 MPa) for 48 h. The resulting mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by crystallization from chloroform to produce **2b** as a white solid (1.18g, 86.5%). ESI-HRMS (m/z) calcd. for [M+H]⁺ 1321.9267; found [M+H]⁺ 1321.9266.

Compound 2c: Following the procedure for **2b**, reaction of the compound **1c** (1.30 g, 0.583 mmol) with sodium azide (379 mg, 5.83 mmol) in 50 mL DMF for 10 h provided the product **2c** (844 mg, 90.6%) as a white solid. ESI-HRMS (m/z) calcd. for [M+Na]⁺ 1603.2430; found [M+Na]⁺ 1603.2429.

Compound 4: To the solution of **3** (500 mg, 2.30 mmol) in dry 30 mL dichloromethane were added p-nitrophenol (320 mg, 2.3 mmol), DCC (570 mg, 2.76 mmol) and DMAP (67.4 mg, 0.276 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 10 h. The resulting mixture was washed with cold sodium bicarbonate solution (3×20 mL) and the solvent was evaporated under reduced pressure to give a yellow oil. Column chromatography (silica gel; dichloromethane: methanol =50:1) afforded a light yellow solid **4** (560 mg, 72.1%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.29 (d, *J* = 8.9 Hz, 2 H), 7.35 (d, *J* = 8.9 Hz, 2 H), 4.56 (s, 2 H), 4.31 (s, 2 H), 3.89 (m, 1 H), 3.46 (m, 1 H), 1.43 (d, *J* = 6.6 Hz, 6 H), 1.22 (d, *J* = 6.4 Hz, 6 H).

L-I: To the solution of **2a** (50 mg, 0.042 mmol) in 30 mL dry dichloromethane was added a mixture of **4** (284 mg, 0.84 mmol) and triethylamine (85 mg, 0.84 mmol) under nitrogen atmosphere. After refluxing for 48 h, the mixture was washed with 2 M NaOH aqueous (3×50 mL), 1 M HCl aqueous (3×50 mL) and water (3×50 mL), respectively. Then, the solvent was evaporated under reduced pressure to give the crude product. Column chromatography (silica gel; dichloromethane: methanol = 30:1) afforded a light yellow solid **L-I** (77 mg, 57.7%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.98 (s, 10 H), 6.83 (s, 10 H), 4.24-4.15 (m, 20 H), 4.11 (s, 20 H), 3.97-3.97 (m, 20 H), 3.71-3.66 (m, 40 H), 3.43 (s, 10 H), 1.36 (s, 60 H), 1.16 (s, 60 H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 20.40, 20.74, 38.62, 45.97, 47.54, 66.24, 70.86, 71.28, 113.96, 127.99, 149.01, 167.19, 169.95. ESI-HRMS (m/z) calcd. for [M+Na]⁺ 3055.8075; found [M+Na]⁺ 3055.8062.

L-II: Following the procedure for **L-I**, reaction of compound **2b** (2.0 g, 1.51 mmol) and **4** (6.14 g, 18.2 mmol) in presence of triethylamine (1.84 g, 18.2 mmol) in dichloromethane for 48 h provided the

compound **L-II** (3.10 g, 62.0 %) as a light yellow solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.90 (s, 10 H), 6.78 (s, 10 H), 4.20 (s, 20 H), 4.08 (s, 20 H), 3.98 (s, 10 H), 3.78 (m, 10 H), 3.71 (s, 20H), 3.46 (m, 10 H), 3.38 (d, $J = 5.4$ Hz, 2 H), 1.83 (s, 40 H), 1.39 (d, $J = 6.2$ Hz, 60 H), 1.19 (d, $J = 6.2$ Hz, 60 H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 169.60, 167.26, 149.12, 127.79, 113.45, 71.49, 70.83, 67.14, 47.44, 45.96, 38.76, 27.41, 26.46, 20.72, 20.40. ESI-HRMS (m/z) calcd. for $\text{C}_{175}\text{H}_{290}\text{N}_{20}\text{O}_{40}$ $[\text{M}+\text{H}]^+$ 3315.1419, $[\text{M}+\text{Na}]^+$ 3337.1238; found $[\text{M}+\text{H}]^+$ 3315.1282, $[\text{M}+\text{Na}]^+$ 3337.1570.

L-III: Following the procedure for **L-I**, reaction of compound **2c** (2.0 g, 1.25 mmol) and **4** (5.07 g, 15 mmol) in presence of triethylamine (1.52 g, 15 mmol) in dichloromethane for 48 h provided the compound **L-II** (3.20 g, 71.2%) as a light yellow solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.78 (s, 10 H), 6.80 (s, 10 H), 4.19 (s, 20 H), 4.06 (s, 20 H), 3.97 (m, 10 H), 3.85 (m, 30 H), 3.47 (m, 10 H), 3.30 (dd, $J = 13.2$ Hz, 20 H), 1.83-1.82 (m, 40 H), 1.62-1.59 (m, 40 H), 1.40 (d, $J = 6.6$ Hz, 60 H), 1.21 (d, $J = 6.6$ Hz, 60 H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 169.29, 167.00, 149.54, 127.95, 114.26, 71.46, 70.84, 68.13, 53.38, 47.50, 46.09, 39.01, 29.90, 29.72, 29.55, 27.03, 26.18, 20.78, 20.45. ESI-HRMS (m/z) calcd. for $\text{C}_{175}\text{H}_{290}\text{N}_{20}\text{O}_{40}$ $[\text{M}+\text{H}]^+$ 3595.4549, $[\text{M}+\text{Na}]^+$ 3616.4334; found $[\text{M}+\text{H}]^+$ 3595.4541, $[\text{M}+\text{Na}]^+$ 3616.3938.

1.3 ^1H NMR and ^{13}C NMR spectra of new compounds

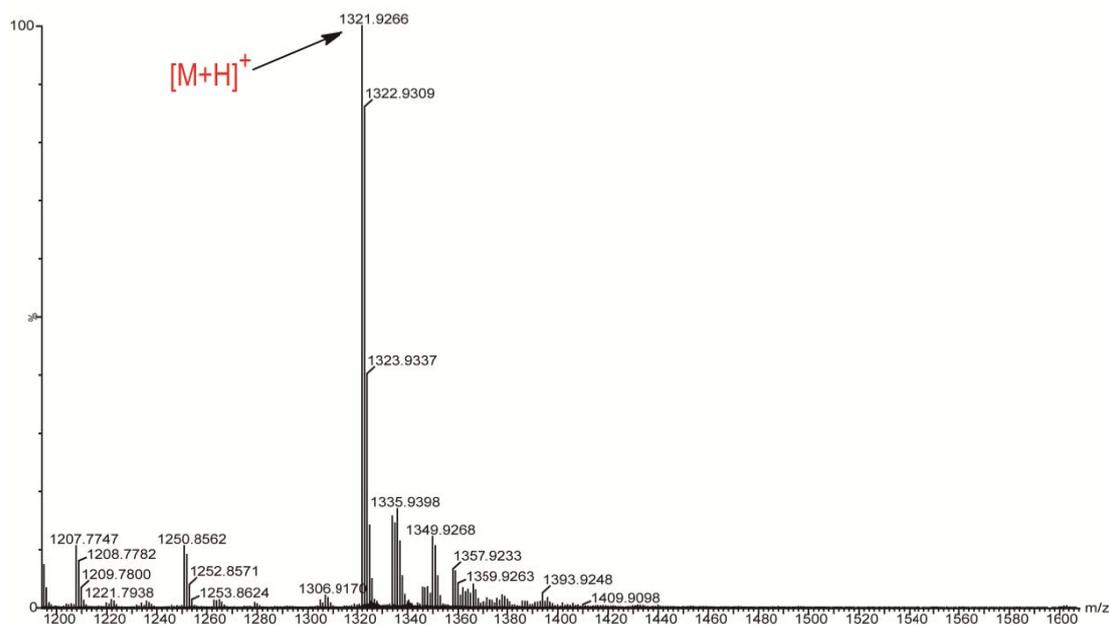


Fig. S1 ESI-HRMS spectrum of compound 2b.

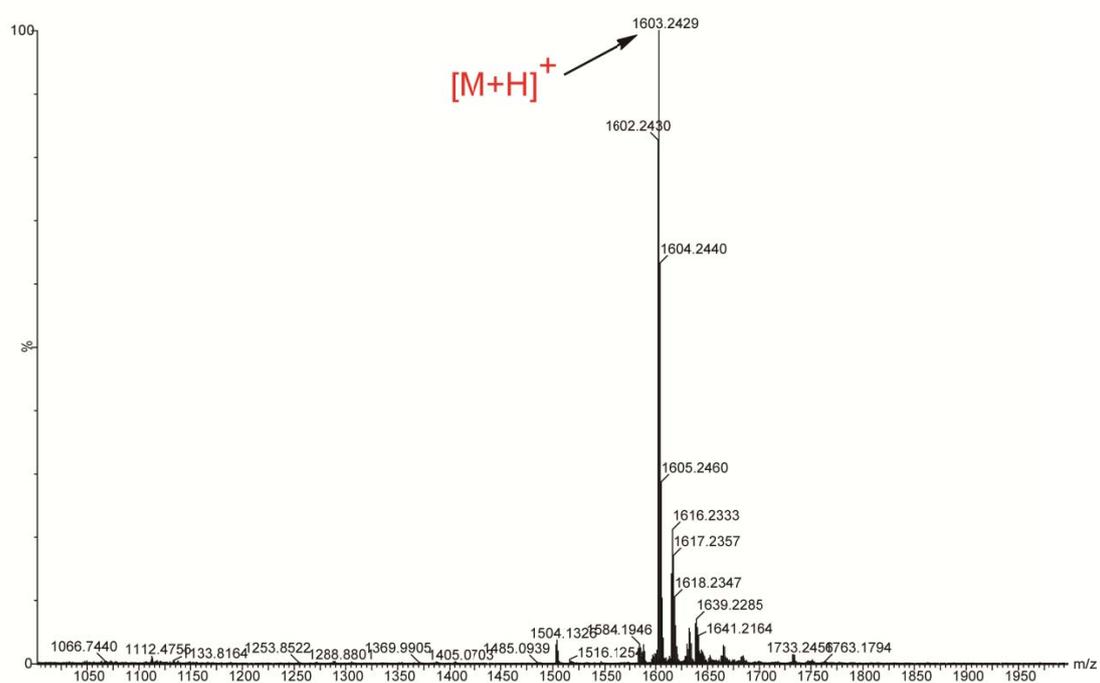


Fig. S2 ESI-HRMS spectrum of compound 2c.

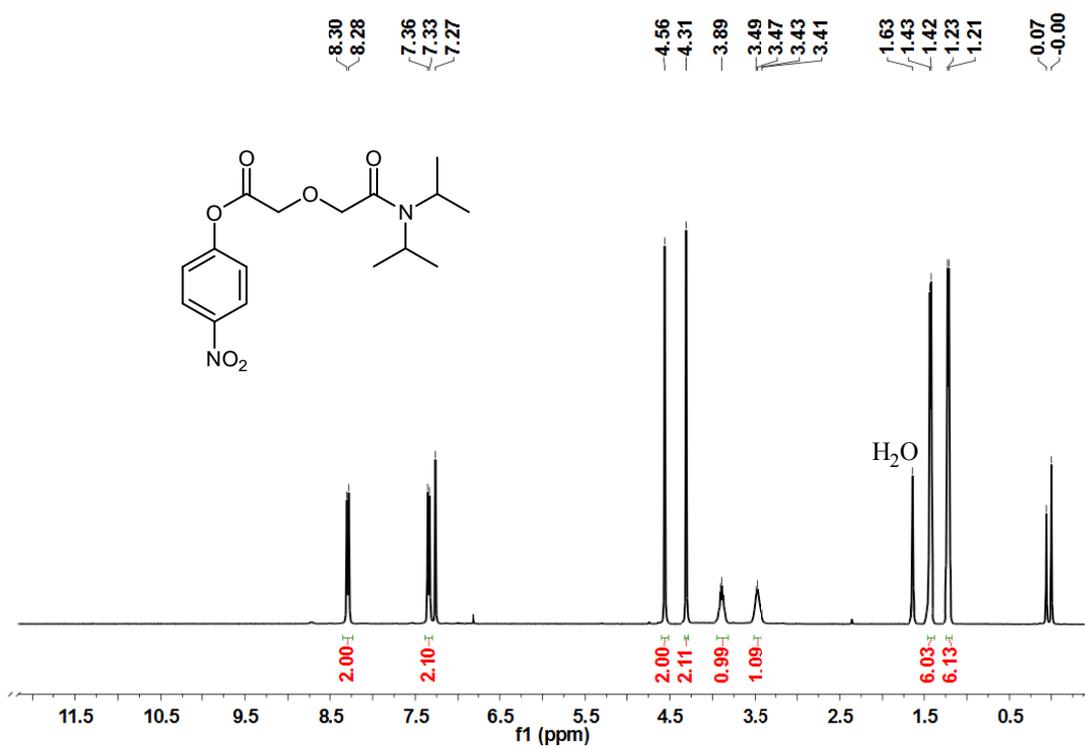


Fig. S3 ^1H NMR spectrum (400 Hz, CDCl_3 , 298 K) of compound 4.

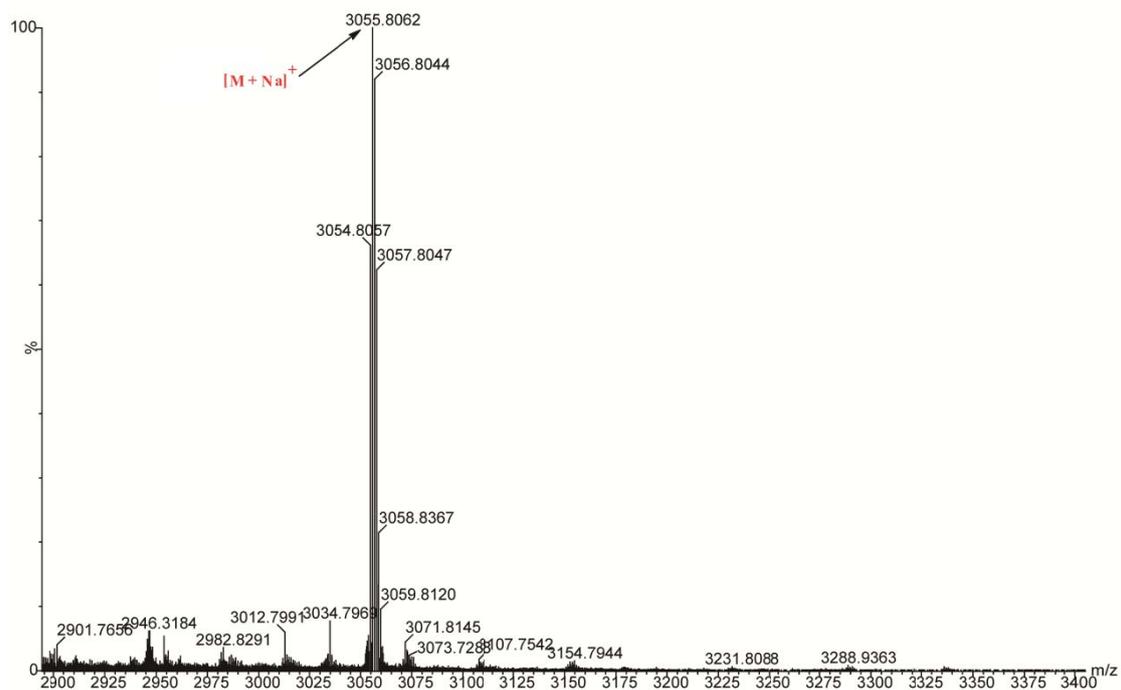


Fig. S6 ESI-HR MS spectrum of compound L-I.

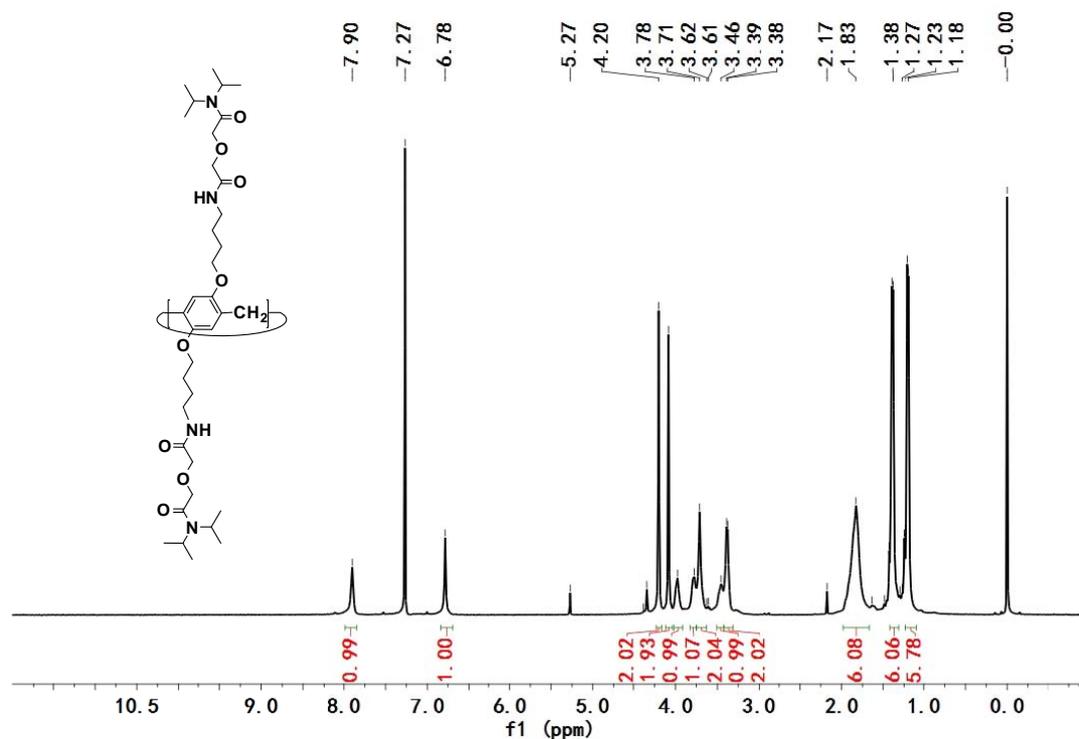


Fig. S7 ^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of compound L-II.

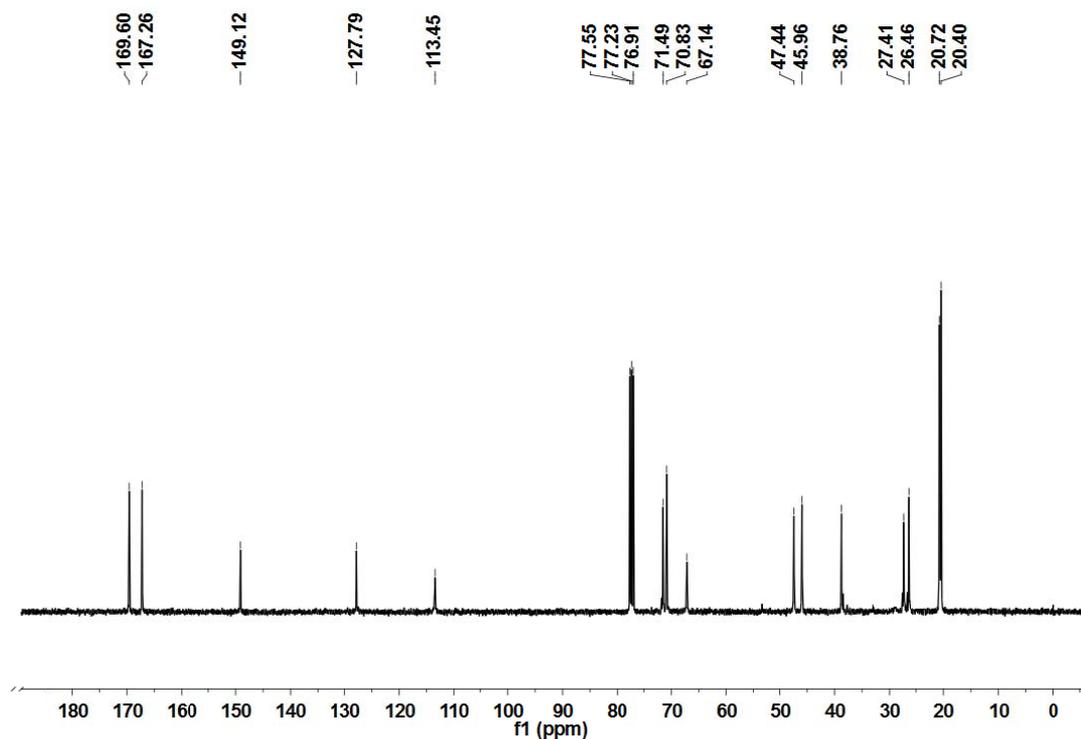


Fig. S8 ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of compound L-II.

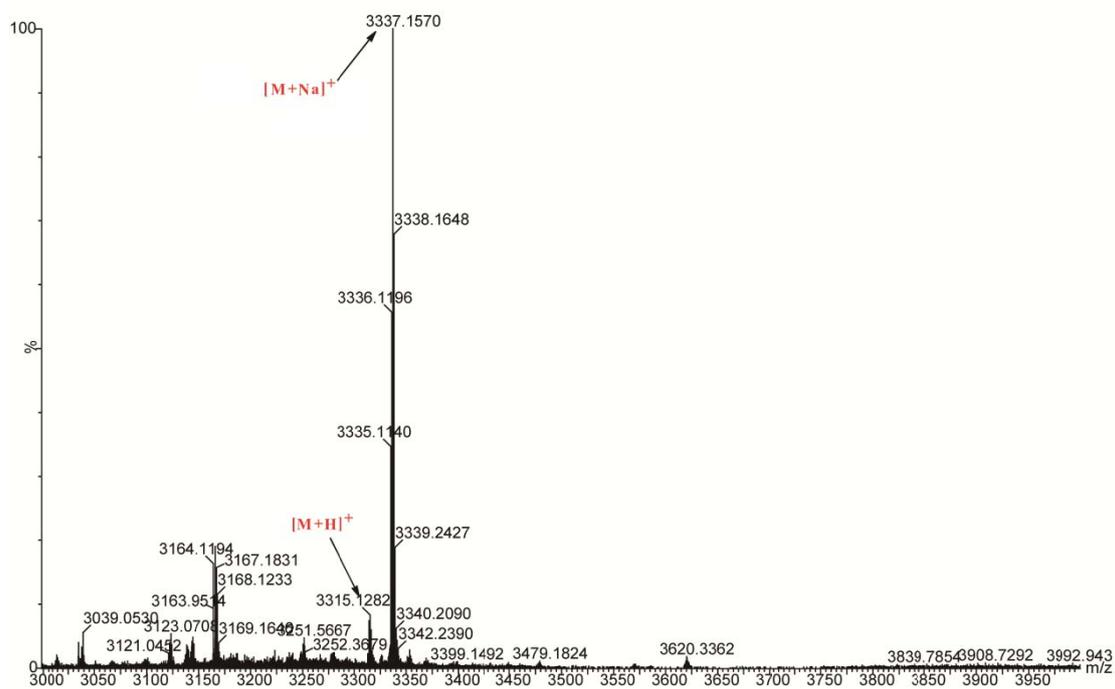


Fig. 9 ESI-HRMS spectrum of compound L-II.

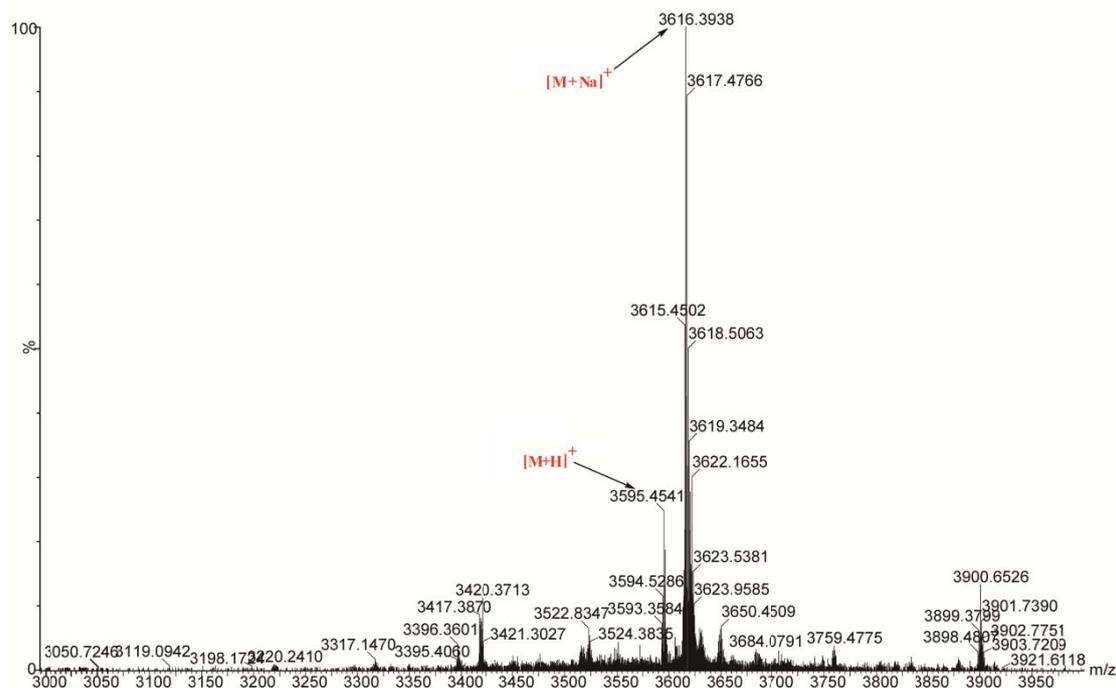


Fig. S12 ESI-HR MS spectrum of compound L-III.

2. Distribution Studies

The distribution studies were carried out by mixing 1 mL of the ligand (1 mM P5DGA or 10 mM TiPrDGA) solution in 1-octanol with an equal volume of the aqueous phase containing the required concentration of HNO₃ and spiked with the stock solution containing europium(III) nitrate ($C_{Eu} = 10^{-5}$ M) with ²⁴¹Am and ^{154,152}Eu (radiochemical purity) in a thermostated water bath at 25 ± 1.0 °C for about 2 h. After centrifugation, 0.5 mL of aqueous phase was collected and the concentration was determined by gamma counting (NaI(Tl) well detector).

For the calculation of the distribution ratio (D_M) of a particular metal ion M, defined as the ratio of the cation gamma activity in the organic phase to that in the aqueous phase, aliquots were removed from the aqueous phase only before and after the extraction experiments. D_M is presented as the following equation:

$$D_M = (C_i - C_f) / (C_f)$$

where, C_i and C_f are the initial and final concentrations of the metal ion, respectively. The selectivity for Eu(III) over Am(III) is expressed as $SF_{Eu/Am} = D_{Eu} / D_{Am}$. The experiments were carried out in duplicate and the precision was within $\pm 5\%$.

3. Fluorescence Studies.

3.1 General. Spectroscopic grade crystals of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (>99.99%) was procured from Alpha Biochem and the solutions were made using Suprapur (Merck) nitric acid and HPLC grade ethanol. Sample solutions for time resolved laser induced fluorescence spectroscopy (TRLIFS) measurements were prepared by taking suitable aliquots of Eu^{3+} stock with/without L-I, L-II and L-III in the mixed solvent system of EtOH/ H_2O (5:1, v/v).

Emission spectroscopic studies of the Eu^{3+} -solvent (4.0×10^{-6} M) and Eu^{3+} -P5DGA (4.0×10^{-6} M) 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. The solvent is the solution containing ethanol/ H_2O (5:1, v/v). 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 $\pm 3\mu\text{s}$. The life time of the $^5\text{D}_0$ emitting level of Eu^{3+} depends on the number of OH oscillators linked to the cations. This is because of non-radiative deexcitation phenomenon through OH bonds vibrations, which is suppressed when hydrogen atoms are replaced by deuterium isotopes. The luminescence lifetime only depends on the radiative and various non-radiative decay processes, and has no correlations with the environment.⁴ An empirical relation has been established between primary hydration number of Eu^{3+} ion ($N_{\text{H}_2\text{O}}$) and the lifetime of its $^5\text{D}_0$ emitting level:

$$N_{\text{H}_2\text{O}} = (1.06/\tau) - 0.19 \quad (1)$$

The calculation of the number of water molecules in the inner coordination sphere from the lifetime has an uncertainty of ± 0.5 in these measurements.

3.2 The results of fluorescence studies

Table S1 The asymmetry factor, life time and number of inner-sphere water molecules of the Eu^{3+} -P5DGA complexes. Excitation wavelength: 258 nm; Emission wavelength: 614 nm.

System	Asymmetry factor	Life time (ms)	No. of inner-sphere water molecules
Eu-solvent ^a	1.103	0.144 ^b	9
Eu-L-I complex	2.864	0.807	1
Eu-L-II complex	2.676	1.507	0
Eu-L-III complex	2.562	1.506	0

^a Solvent: ethanol/ H_2O (5:1, v/v); pH=3.0 (HNO_3); ^b The data were obtained from the literature⁵.

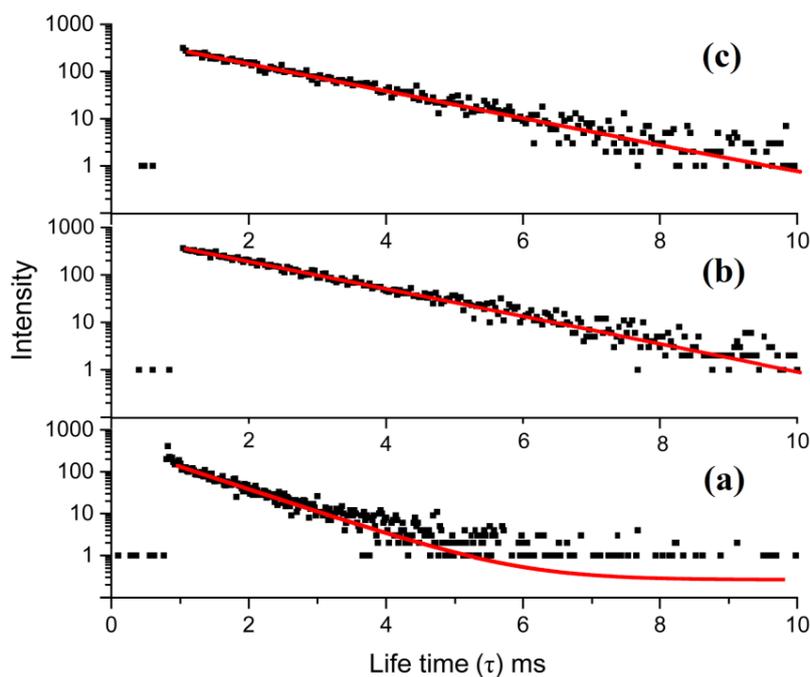


Fig. S13 Fluorescence decay profiles of Eu^{3+} -P5DGA complexes in the medium of ethanol/water (5:1,v/v) at pH=3; (a) L-I- Eu^{3+} complex; (b) L-II- Eu^{3+} complex; (c) L-III- Eu^{3+} complex.

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