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

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Supporting Information
1. Synthesis and Characterization

1.1 General. All moisture-sensitive reactions were carried out under an argon atmosphere. The solvents and all reagents were obtained from commercial sources and used without further purification. Solvents for extraction and chromatography were reagent grade. Solvents were dried according to standard procedures and stored over molecular sieves. 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). High resolution mass (HRMS) data were obtained by WATERS Q-TOF Premier. UV-spectra were measured by SHIMADZU UV-2450. Column chromatography was carried out with Merck silica gel 60 (230-400 mesh).

1.2 Synthesis procedure

Scheme 1 The synthesis route of compounds P5DGA.

All known compounds viz. $1a^1$, $1b^2$, $1c^2$, $2a^2$, $3^2$ and TiPrDGA$^3$ were prepared according to literature procedures.

Compound 2b: To the solution of $1b$ (2.00 g, 1.03 mmol) in dry 50 mL DMF was added sodium azide (667 mg, 10.3 mmol). The reaction mixture was stirred at 85 °C for 10 h under nitrogen atmosphere. The mixture was cooled to room temperature and poured into water (100 mL). The precipitate was collected by filtration, and washed with water to yield a white solid. To a solution of dried product got from the over reaction in methanol, about Pd/C (10%, 180 mg) was added. Then, the reaction mixture
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. $^1$H 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 C$_{175}$H$_{390}$N$_{20}$O$_{40}$ [M+H]$^+$ 3315.1419, [M+Na]$^+$ 3337.1238; found [M+H]$^+$ 3315.1282, [M+Na]$^+$ 3337.1570.

L-III: Following the procedure for L-I, reaction of compound 2e (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. $^1$H 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 C$_{175}$H$_{390}$N$_{20}$O$_{40}$ [M+H]$^+$ 3595.4549, [M+Na]$^+$ 3616.4334; found [M+H]$^+$ 3595.4541, [M+Na]$^+$ 3616.3938.

1.3 $^1$HNMR 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 $^1$H NMR spectrum (400 Hz, CDCl$_3$, 298 K) of compound 4.
**Fig. S4** $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound L-I.

**Fig. S5** $^{13}$C NMR spectrum (100 Hz, CDCl$_3$, 298 K) of compound L-I.
**Fig. S6** ESI-HR MS spectrum of compound L-I.

**Fig. S7** $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) 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. S10** $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound L-III.

**Fig. S11** $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, 298 K) 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 (Cₑᵤ = 10⁻⁵ M) with ²⁴¹Am and ¹⁵⁴,¹⁵²Eu (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 (DM) 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. DM is presented as the following equation:

\[ DM = \frac{(C_i - C_f)}{(C_i)} \]

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 ±5%.
3. Fluorescence Studies.

3.1 General. Spectroscopic grade crystals of Eu(NO₃)₃·6H₂O (>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 Eu³⁺ stock with/without L-I, L-II and L-III in the mixed solvent system of EtOH/H₂O (5:1, v/v).

Emission spectroscopic studies of the Eu³⁺-solvent (4.0 × 10⁻⁶ M) and Eu³⁺-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/H₂O (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 ±3μs. The life time of the ⁵D₀ emitting level of Eu³⁺ 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 Eu³⁺ ion (N₁,H₂O) and the lifetime of its ⁵D₀ emitting level:

\[ N_{1,H_2O} = (1.06/\tau) - 0.19 \quad (1) \]

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>
<thead>
<tr>
<th>System</th>
<th>Asymmetry factor</th>
<th>Life time (ms)</th>
<th>No. of inner-sphere water molecules</th>
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<tr>
<td>Eu-solventᵃ</td>
<td>1.103</td>
<td>0.144ᵇ</td>
<td>9</td>
</tr>
<tr>
<td>Eu-L-I complex</td>
<td>2.864</td>
<td>0.807</td>
<td>1</td>
</tr>
<tr>
<td>Eu-L-II complex</td>
<td>2.676</td>
<td>1.507</td>
<td>0</td>
</tr>
<tr>
<td>Eu-L-III complex</td>
<td>2.562</td>
<td>1.506</td>
<td>0</td>
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ᵃ Solvent: ethanol/H₂O (5:1, v/v); pH=3.0 (HNO₃); 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.

**References**