Electronic Supplementary Material (ESI) for Dalton Transactions

Complexation of novel diglycolamide functionalized calix[4]arenes: Unusual extraction behaviour, transport, and fluorescence studies

Prasanta K. Mohapatra, Mudassir Iqbal, Dhaval R. Raut, Willem Verboom, Jurriaan Huskens and Shrikant V. Godbole

Supporting Information

Experimental

Materials

General

TODGA was procured from Thermax Ltd, Pune, India. The extractants were characterized by NMR, HPLC, and GC-MS. PTFE membranes used in the present study were procured from Sartorius, Germany. All reagents were of AR grade and were used without further purification. Stock solutions of ^{241}Am, Pu (mostly ^{239}Pu), and ^{233}U tracers were used while ^{152,154}Eu, ^{85,89}Sr and ^{137}Cs tracers were purchased from BRIT, Mumbai. The actinides were purified prior to their use by ion-exchange methods[1] and the purity was checked by alpha-spectrometry. Pu(III) was prepared by reducing Pu to the +3 state using a mixture of hydroxyl amine (in the nitrate form) and hydrazine hydrate (in the nitrate form). Conversion of Pu to the +3 state was ascertained by UV-visible spectrophotometry. Pu(IV) stock solution was prepared by oxidizing Pu to Pu(IV) using $NaNO_2$ followed by TTA extraction from a feed made in 0.5 M HNO_3. The loaded TTA phase was subsequently stripped using 8 M HNO_3 and was used as stock solution for Pu(IV). The stability of the oxidation state was monitored intermittently by both TTA extraction method (a dependence of 4 in the log-log plot of distribution coefficient of Pu and TTA concentration was ensured) and spectrophotometry.

Assaying of ^{241}Am, ^{152,154}Eu, ^{137}Cs, and ^{85,89}Sr was done by gamma counting using a NaI(Tl) scintillation counter, while nuclides such as ^{239}Pu, ^{237}Np, and ^{233}U were assayed by liquid scintillation counting.

Synthesis of ligands

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. All known compounds *viz.* **1**[2], **3**[3], **5**[4], and **7**[5] were prepared according to literature procedures. Solvents were dried according to standard procedures and stored over molecular sieves. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) chemical shift values are reported as δ using the residual solvent signal as an internal standard. All NMR measurements are recorded in $CDCl_3$ as a solvent. Electrospray

Ionization (positive mode) mass spectra and high resolution mass spectra were recorded on a WATERS LCT mass spectrometer. Analytical TLC was performed using Merck prepared plates (silica gel 60 F-254 on aluminum). Column chromatography was carried out with Merck silica gel 60 (230–400 mesh).

***p*-Nitrophenol activated DGA (2).** A solution of *N,N*-dioctylglycolic acid **(1)** (2.00 g, 5.6 mmol), *p*-nitrophenol (0.81 g, 5.7 mmol), and DCC (1.22 g, 5.8 mmol) in pyridine (60 mL) was stirred overnight at room temperature. The solvent was evaporated and the residue was dissolved in *n*-hexane, filtered and the filtrate was washed with 4% $NaHCO_3$ solution (2 x 50 mL). The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2:MeOH, 98:2) to afford *p*-nitrophenol activated DGA **(2)** (2.16 g, 81%) as a light yellow oil. ^{1}H NMR: δ 0.81-0.93 (m, 6H, CH_3), 1.14-1.38 (m, 20H, $CH_3(CH_2)_5$), 1.45-1.60 (m, 4H, NCH_2CH_2), 3.18 and 3.31 (t, 2H J = 7.5 Hz, NCH_2), 4.37 (s, 2H, OCH_2), 4.58 (s, 2H, OCH_2), 7.33 (d, 2H, J = 9.0 Hz, ArH), 8.28 (d, 2H, J = 9.0 Hz, ArH); ^{13}C NMR: δ 14.3, 22.8, 29.5, 31.9, 60.1, 68.2, 69.4, 122.5, 125.5, 126.3, 145.9, 169.1; HRMS: *m/z* 479.3130 $(M+H)^+$, calculated: 479.3121.

Calix[4]arene 4-DGA (4). A mixture of **3** (0.45 g, 0.5 mmol), *p*-nitrophenol activated DGA (**2**) (1.20 g, 2.5 mmol) and triethylamine (0.25 g, 2.5 mmol) in chloroform (50 mL) was refluxed overnight. The crude reaction mixture was successively washed with 2M NaOH solution (3 x 50 mL), 1M HCl (3 x 50 mL), and water (2 x 50 mL). The organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2:MeOH, 96:4) to afford calix[4]arene 4-DGA **(4)** (1.10 g, 71%) as a dense oil. ^{1}H NMR: δ 0.81-0.93 (m, 24H, CH_3), 1.07 (s, 36H, *t*-Bu), 1.17-1.35 (m, 80H, $CH_3(CH_2)_5$), 1.43-1.60 (m, 16H, NCH_2CH_2), 2.25 (pentet, 8H, J = 6.0 Hz, OCH_2CH_2), 3.04-3.16 (m, 12H, $ArCH_2Ar$ and NCH_2), 3.27 (t, 8H, J = 7.5 Hz, NCH_2), 3.46 (t, 8H, J = 6.0 Hz, $NHCH_2$), 3.89 (t, 8H, J = 6.0 Hz, $ArOCH_2$), 4.09 (s, 8H, OCH_2CO), 4.27 (s, 8H, OCH_2CO), 4.34 (d, 4H, J = 12.0 Hz, $ArCH_2Ar$), 6.75 (s, 8H,

ArH), 7.97-8.07 (m, 4H, NH); ^{13}C NMR: δ 14.3, 22.9, 27.1, 29.5, 31.6, 32.0, 34.0, 36.7, 46.3, 47.0, 60.1, 133.9, 144.8, 153.5, 168.4, 170.0; MS: *m/z* 2234.7 $(M+H)^+$, calculated: 2234.8.

Calix[4]arene 2-DGA (6) was prepared in an analogous way as **4** starting from **5** (1.60 g, 2.1 mmol) and *p*-nitrophenol activated DGA (**2**) (2.11 g, 4.4 mmol) in the presence of triethylamine (0.46 g, 4.5 mmol), and purified by column chromatography (CH_2Cl_2:MeOH, 96:4) in 77% yield (2.20 g) as a dense oil. ^{1}H NMR: δ 0.83-0.93 (m, 12H, CH_3), 0.99 (s, 18H, *t*-Bu), 1.18-1.38 (m, 58H, *t*-Bu and $CH_3(CH_2)_5$), 1.42-1.57 (m, 8H, NCH_2CH_2), 2.26 (pentet, 4H, J = 6.0 Hz, OCH_2CH_2), 3.03 (t, 4H, J = 7.5 Hz, NCH_2), 3.21-3.33 (m, 8H, $ArCH_2Ar$ and NCH_2), 3.74 (t, 4H, J = 6.0 Hz, $NHCH_2$), 4.05 (t, 4H, J = 6.0 Hz, $ArOCH_2$), 4.11 (s, 4H, OCH_2CO), 4.16 (s, 4H, OCH_2CO), 4.25 (d, 4H, J = 12.0 Hz, $ArCH_2Ar$), 6.83 (s, 4H, ArH), 7.02 (s, 4H, ArH), 7.68 (s, 2H, ArOH), 8.09-8.18 (m, 2H, NH); ^{13}C NMR: δ 14.3, 22.9, 27.3, 29.5, 31.3, 32.0, 34.1, 34.2, 69.7, 71.7, 125.7, 127.9, 132.9, 141.8, 147.2, 149.7, 150.7, 168.6, 170.4; HRMS: *m/z* 1441.0741 $(M+H)^+$, calculated: 1441.0882.

1,3-Dibutoxy-2,4-bis(phthalimidopropoxy)calix[4]arene (8). A suspension of **7** (2.50 g, 3.3 mmol) in DMF (60 mL) was stirred under argon for 30 min. NaH (60% in oil, 1.00 g, 26.2 mmol) was added and stirring was continued for 1 h. *N*-(3-Bromopropyl) phthalimide (3.51 g, 13.1 mmol) was then added and the mixture was stirred for 3 d at room temperature. After addition of water (100 mL) the resulting precipitate was collected, dissolved in chloroform (100 mL) and washed with 15% HCl (50 mL). Evaporation of the solvent, after drying ($MgSO_4$), followed by precipitation from chloroform–methanol gave the target product **8** (2.46 g, 66%) as a white solid. M.p. 108-110 ^{o}C; ^{1}H NMR: δ 0.92 (s, 18H, *t*-Bu), 0.99 (t, 6H, *J* = 7.5 Hz, CH_3), 1.21 (s, 18H, *t*-Bu), 1.43 (sextet, 4H, *J* = 7.5 Hz, CH_3CH_2(Bu)), 1.86 (pentet, 4H, *J* = 7.5 Hz, OCH_2CH_2(Bu)), 2.52 (pentet, 4H, *J* = 7.5 Hz, OCH_2CH_2(PrPhth)), 3.10 (d, 4H, *J* = 12 Hz, $ArCH_2Ar$), 3.75 (t, 4H, *J* = 7.5 Hz, CH_2Phth), 3.89 (t, 4H, *J* = 7.5 Hz, OCH_2(Bu)), 4.07 (t, 4H, *J* = 7.5 Hz, OCH_2(PrPhth)), 4.36 (d, 4H, *J* = 12 Hz, $ArCH_2Ar$), 6.57 (s, 4H, ArH), 6.93 (s, 4H, ArH), 7.66-7.71 (m, 2H, ArPhth), 7.79-7.86 (m, 2H, ArPhth); ^{13}C NMR: δ 14.2, 19.5, 29.9, 31.3, 31.5, 31.9, 32.5, 33.9, 34.2, 81.8, 103.1, 123.4, 125.1, 129.4, 132.5, 132.9, 135.0, 144.2, 144.9, 153.2, 154.3, 168.5; HRMS: *m/z* 1135.6779 $(M+H)^+$, calculated: 1135.6775.

1,3-Dibutoxy-2,4-bis(aminopropyl)calix[4]arene (9). Hydrazine hydrate (10 mL, 200 mmol) was added to a suspension of **8** (2.00 g, 1.7 mmol) in ethanol (50 mL). The mixture was refluxed for 12 h, cooled and then diluted with water (100 mL). A precipitate formed which was extracted into dichloromethane (4 × 50 mL). The organic layer was then dried ($MgSO_4$) and the solvent was evaporated to give **9** (1.51 g, 98%) as

a white solid. M.p. 73-75 ^{o}C; ^{1}H NMR: δ 0.98-1.02 (m, 24H, (CH_3 and *t*-Bu), 1.16 (s, 18H, *t*-Bu), 1.41 (sextet, 4H, *J* = 7.5 Hz, CH_3CH_2(Bu)), 1.93 (pentet, 4H, *J* = 7.5 Hz, OCH_2CH_2(Bu)), 2.18 (pentet, 4H, *J* = 7.5 Hz, OCH_2CH_2($PrNH_2$)), 3.10 (t, 4H, *J* = 7.5 Hz, CH_2NH_2), 3.16 (d, 4H, *J* = 12 Hz, $ArCH_2Ar$), 3.93 (t, 4H, *J* = 7.5 Hz, OCH_2(Bu)), 4.02 (t, 4H, *J* = 7.5 Hz, OCH_2($PrNH_2$)), 4.37 (d, 4H, *J* = 12 Hz, $ArCH_2Ar$), 6.74 (s, 4H, ArH), 6.91 (s, 4H, ArH); ^{13}C NMR: δ 14.5, 19.5, 29.9, 31.6, 32.4, 34.1, 39.1, 60.1, 73.0, 76.8, 125.4, 133.7, 134.3, 144.5, 144.9, 152.9, 153.6; HRMS: *m/z* 875.6639 $(M+H)^+$, calculated: 875.6666.

1,3-Dibutoxycalix[4]arene 2-DGA (10) was prepared in an analogous way as **4** starting from **9** (1.05 g, 1.2 mmol) and *p*-nitrophenol activated DGA (**2**) (1.40 g, 2.8 mmol) in the presence of triethylamine (0.30 g, 2.8 mmol), and purified by column chromatography ($CHCl_3$:MeOH, 97:3) in 64% yield (1.20 g) as a dense oil. ^{1}H NMR: δ 0.83-0.93 (m, 12H, CH_3), 0.99 (t, 6H, *J* = 7.5 Hz, (CH_3(Bu)), 1.07 (s, 18H, *t*-Bu), 1.08 (s, 18H, *t*-Bu), 1.20-1.35 (m, 40H, $CH_3(CH_2)_5$), 1.42 (sextet, 4H, *J* = 7.5 Hz, CH_3CH_2(Bu)), 1.45-1.60 (m, 8H, NCH_2CH_2), 1.97 (pentet, 4H, *J* = 7.5 Hz, OCH_2CH_2(Bu)), 2.26 (pentet, 4H, *J* = 7.5 Hz, OCH_2CH_2), 3.04-3.18 (m, 8H, NCH_2 and $ArCH_2Ar$), 3.28 (t, 4H, *J* = 7.5 Hz, NCH_2) , 3.49 (t, 4H, *J* = 7.5 Hz, $NHCH_2$), 3.89 (pentet, 8H, *J* = 7.5 Hz, $ArOCH_2$), 4.08 (s, 4H, OCH_2CO), 4.24 (s, 4H, OCH_2CO), 4.38 (d, 4H, *J* = 12.0 Hz, $ArCH_2Ar$), 6.75 (s, 4H, ArH), 6.77 (s, 4H, ArH), 7.75-7.83 (m, 2H, NH); ^{13}C NMR: δ 14.4, 19.6, 23.0, 27.1, 29.5, 31.6, 32.1, 34.0, 69.8, 72.1, 81.8, 103.2, 125.1, 134.0, 144.5, 153.6, 168.3, 169.7; HRMS: *m/z* 1554.2200 $(M+H)^+$, calculated: 1554.2213.

Methods

Distribution studies

The distribution studies were carried out by mixing 1 mL of the ligand solution in the suitable diluent mixture with an equal volume of the aqueous phase containing the required concentration of HNO_3 and spiked with the required tracer in a thermostated water bath at 25±0.1 ^{o}C for about 0.5 h. After centrifugation, the phases were separated and assayed radiometrically as mentioned above. The distribution ratio, D_M was defined as the ratio of the activity per unit volume in the organic phase to that in the aqueous phase. Typically, the concentrations of Am and Pu were in the range of 10^{-6} M, that of U was 10^{-5} M and those of Eu, Sr and Cs were around 10^{-4} M. The experiments were carried out in duplicate and the precision was within ± 5%.

Transport studies

PTFE membrane filters (0.45 μm pore size) were used for the supported liquid membrane (SLM) studies. The membrane thickness was measured (Mitutoyo Digital micrometer) to be 65 μm, while its porosity, measured by an Electroscan 2020

environmental scanning electron microscope (ESEM), was determined as 64%. The effective area of transport on the basis of the porosity data was calculated to be 3.14 cm^2. The SLM transport studies were carried out using 20 mL glass transport cells with feed / strip solutions stirred at 200 rpm. The micro porous PTFE membranes were soaked in the carrier solution (usually, $1.13x10^{-3}$ M C4DGA in *n*-dodecane) 30 minutes prior to use. A previous report has indicated that at least 10 min of soaking time was required to give reproducible results[6]. Subsequently, the membrane was removed from the solution and wiped carefully with a tissue paper to remove the excess fluid on its surface and mounted in a two compartment cell with 20 mL feed as well as receiver phase capacity.

Usually, the feed compartment contained ^{241}Am tracer in 3.0 M HNO_3 while the strip solution was a 0.01 M EDTA solution (pH 2.0). An assay of the radiotracer was made as described above from the feed as well as the receiver compartment at different time intervals to calculate the permeability coefficients and % transport data. The concentrations of the metal ions are similar to those mentioned in the solvent extraction studies. The transport studies were carried out at ambient temperature (24 ± 1^oC). The material balance in these studies was found to be within $\pm$ 5%.

Fluorescence studies

Spectroscopic grade crystals of $Eu(NO_3)_3 \cdot 6H2O$ (>99.99%) was procured from Alpha Biochem and the solutions were made using Suprapur (Merck) nitric acid and HPLC grade acetonitrile (Merck). Deionized water from a milli-Q purification system (Millipore) was used for all dilutions. All the other reagents employed were AR grade. Sample solutions for time resolved laser induced fluorescence spectroscopy (TRLIFS) measurements were prepared by taking suitable aliquots of Eu^{3+} stock with/without C4DGA ($\mathbf{L_I}$), C2DGA ($\mathbf{L_{II}}$) and C2DGA-Bu ($\mathbf{L_{III}}$) in the desired medium.

TRLIFS measurements

These measurements were carried out using Edinburgh CD-920 (controller system for lamp monochromator) luminescence spectrometer equipped with OPO laser as the excitation sources. The excitation wavelength was fixed at 230 nm, while emission spectrum was recorded in the range of 575–750 nm. The luminescence decay curves were

fitted into the exponential function to obtain the lifetimes/decay rates of the excited states using inbuilt software GEM/3 (Edinburgh). The reproducibility of lifetimes of the excited states was within ±3_s.

References

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Solvent extraction data

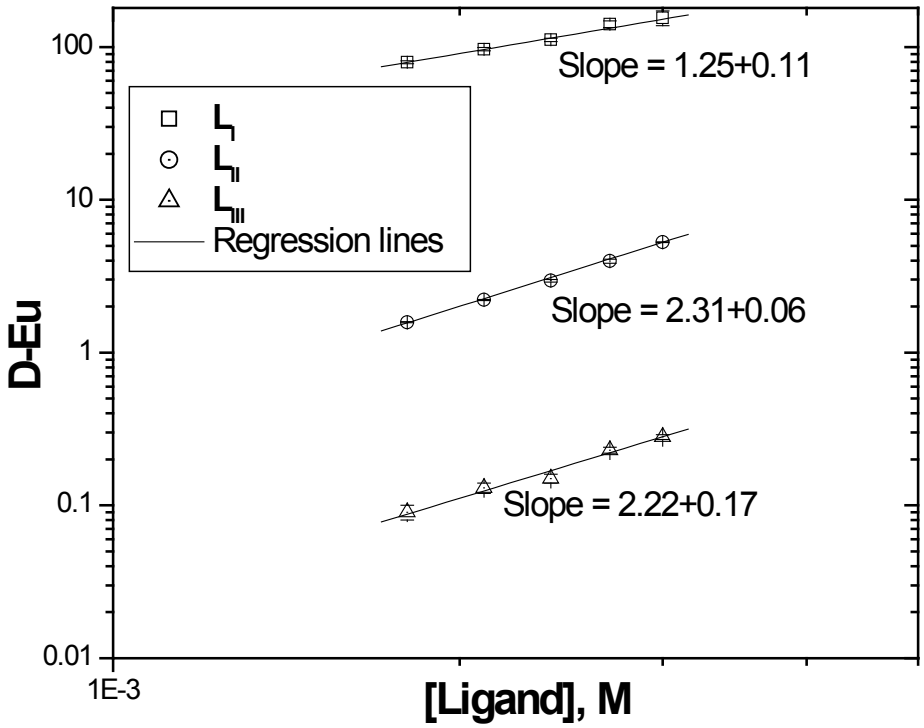

Fig. S-1: Dependence of D-Eu values on the concentration of the ligands. Aqueous phase: 3 M HNO3

Fluorescence data

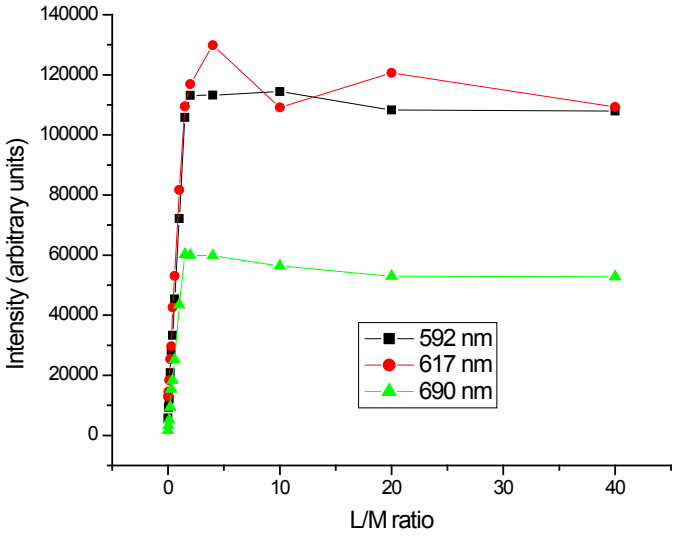

Fig. S-2: Fluorimetric titration data. Intensity vs L:M ratio for the three major emission lines as seen with $\mathbf{L_I}$.

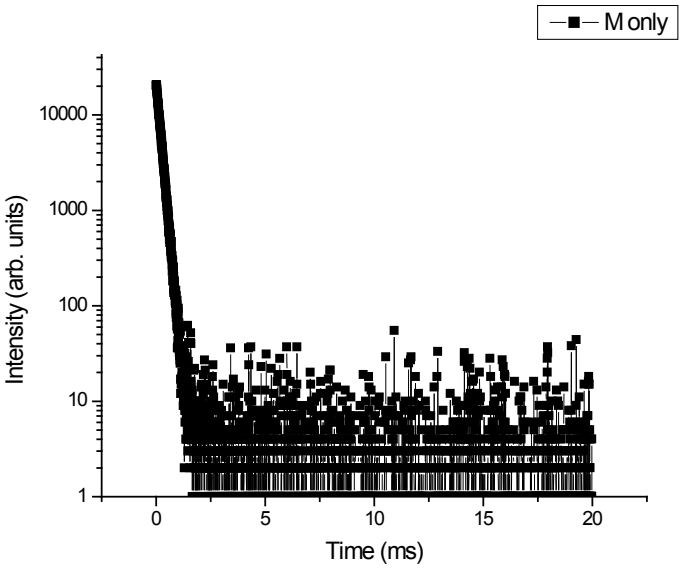

Fig. S-3: Decay profile for Eu^{3+} in 3 M HNO_3 (5:1 acetonitrile: water)

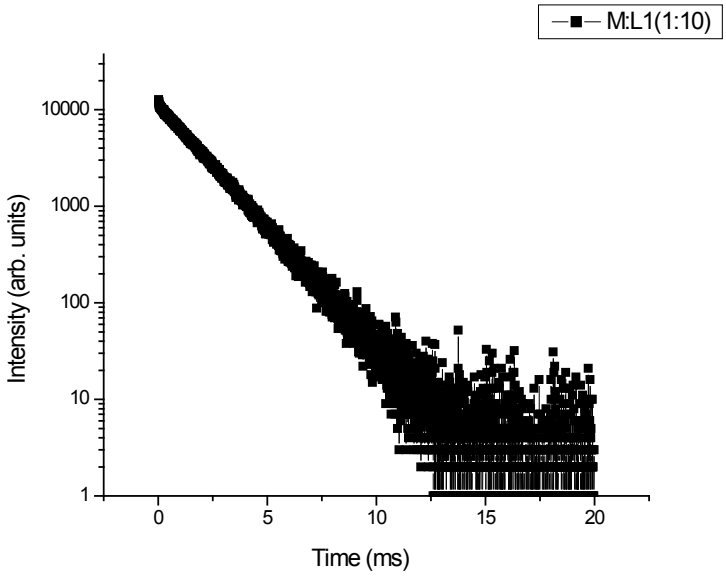

Fig. S-4: Decay profile for Eu^{3+} + $\mathbf{L_I}$ in 3 M HNO_3 (5:1 acetonitrile: water)

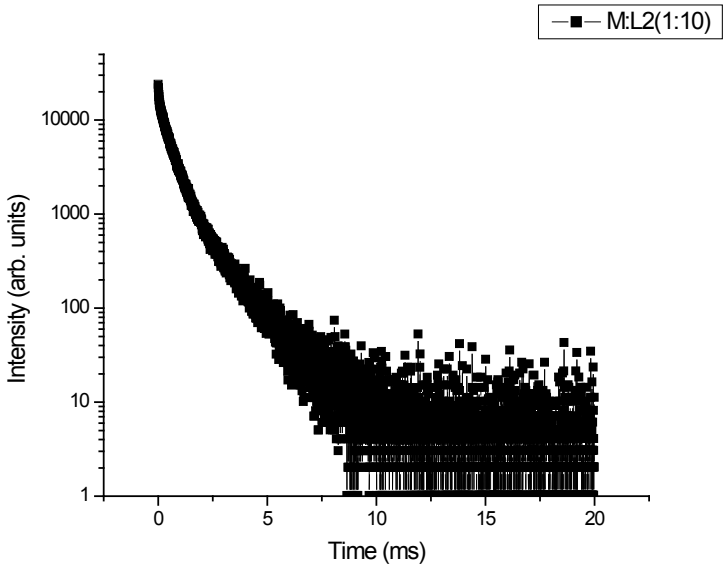

Fig. S-5: Decay profile for Eu^{3+} + $\mathbf{L_{II}}$ in 3 M HNO_3 (5:1 acetonitrile: water)

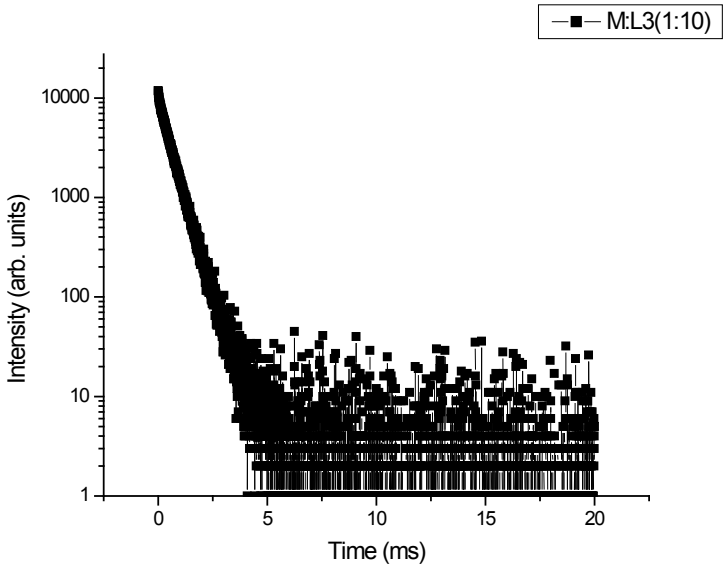

Fig. S-6: Decay profile for Eu^{3+} + $\mathbf{L_{III}}$ in 3 M HNO_3 (5:1 acetonitrile: water)