

Selected Luminescence Titrations

A 3 ml dry dichloromethane solution of macrocycle **1** at concentration $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ was prepared and placed in a quartz cuvette (path length 1 cm). A luminescence emission profile was recorded following excitation at 400 nm. A 0.50 ml dry dichloromethane solution of the guest compound (TBA Cl, **2a** or **3a**) was prepared at a concentration of $0.075 \text{ mol dm}^{-3}$. Luminescent emission spectra were recorded after addition of aliquots of $2.0 \mu\text{l}$ (0.2 molar equivalents of guest) up to 2 equivalents, and then further aliquots to give guest equivalents of 2.5, 3.0, 4.0, 5.0, 7.0 and 10.0. Aliquots were added using a $10.0 \mu\text{l}$ microsyringe. The titration data (Figures 1 and 2) was fitted using the Specfit¹ software package and binding constants determined (estimated errors in all cases less than 10%).

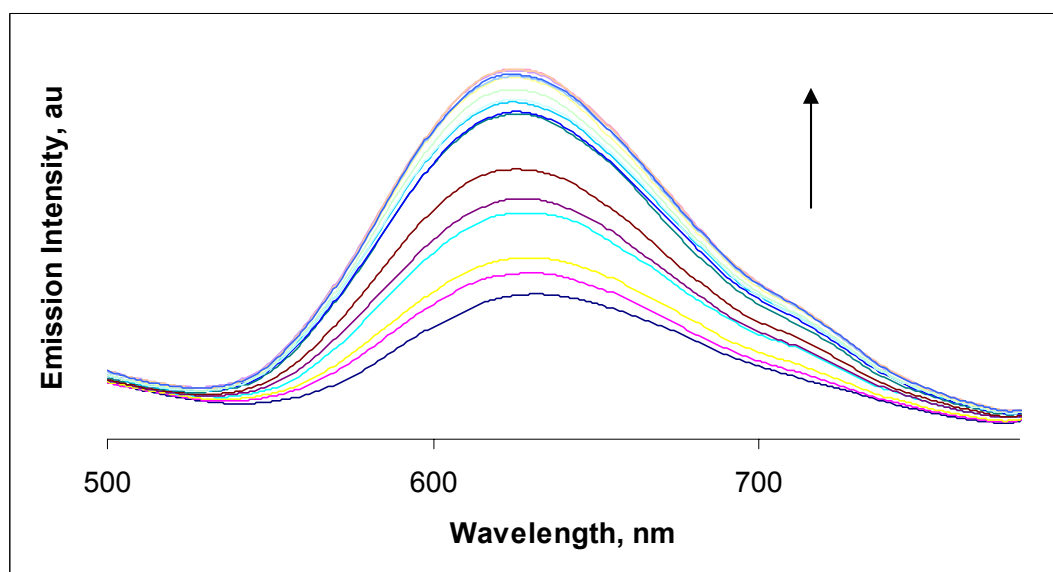


Figure 1: Luminescence titration profile for macrocycle **1** with TBA chloride guest in dichloromethane at 293K ($\lambda_{\text{ex}} = 400 \text{ nm}$)

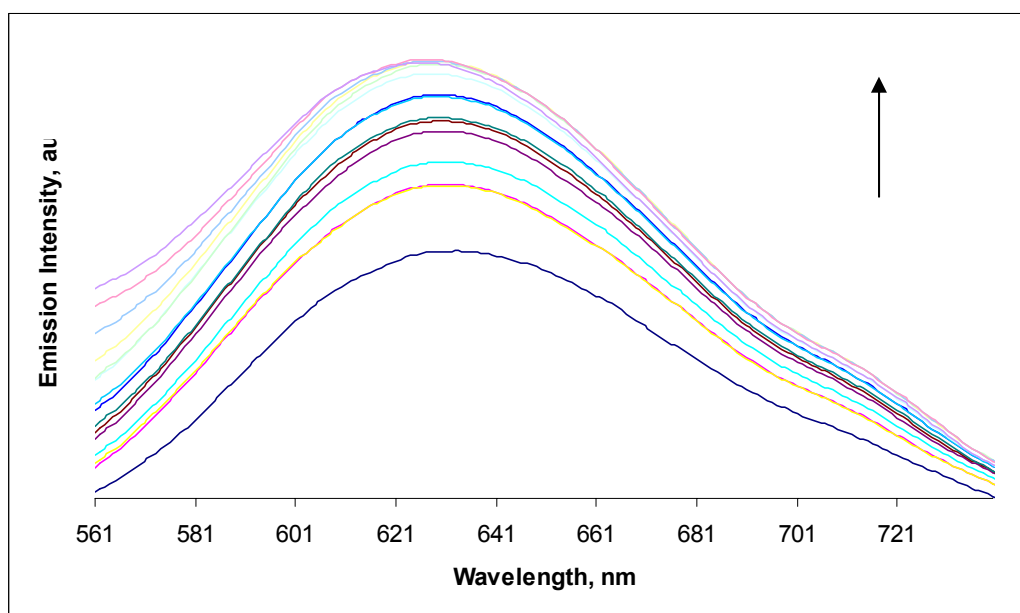


Figure 2: Luminescence titration profile for macrocycle **1** with thread **2a** in dichloromethane at 293K ($\lambda_{\text{ex}} = 400$ nm)

Selected Photophysical Experiments

An enhancement in Re(I) ³MLCT luminescence emission is observed upon addition of tetrabutyl ammonium chloride (TBA Cl) and gadolinium imidazolium thread **2a**. In contrast, quenching of the luminescence emission is observed upon addition of neodymium imidazolium thread **2b** (Figure 3).

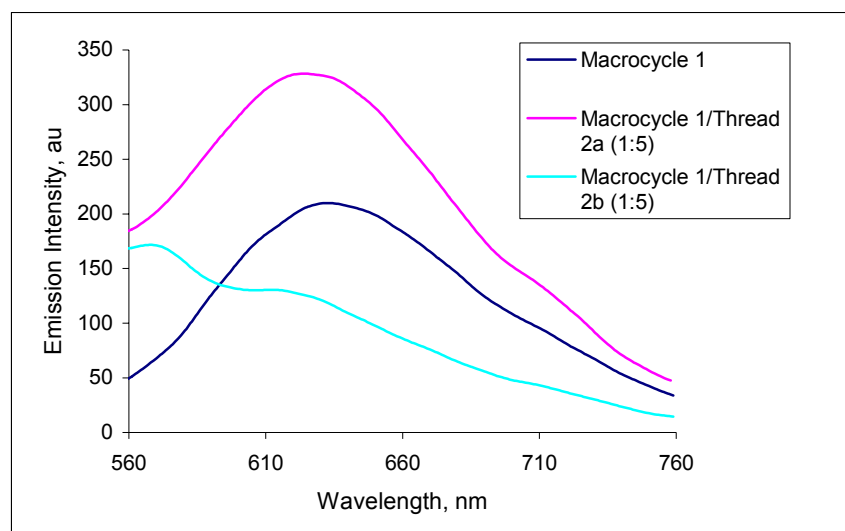


Figure 3: Observed enhancement and quenching of Re(I) ³MLCT luminescent emission upon addition of 5 equivalents of threads **2a** and **2b** to macrocycle **1** in CH₂Cl₂ at 293K ($[1] = 5.0 \times 10^{-5}$ M; $[2] = 2.5 \times 10^{-4}$ M)

Excitation of the neodymium thread **2b** using radiation of 337 nm gives a typical luminescent decay profile from emission at 880 nm with a lifetime of 916 ns. Upon

addition of 1 equivalent of the rhenium macrocycle **1** an increase in neodymium near-Infrared (NIR) emission is observed (Figure 4).

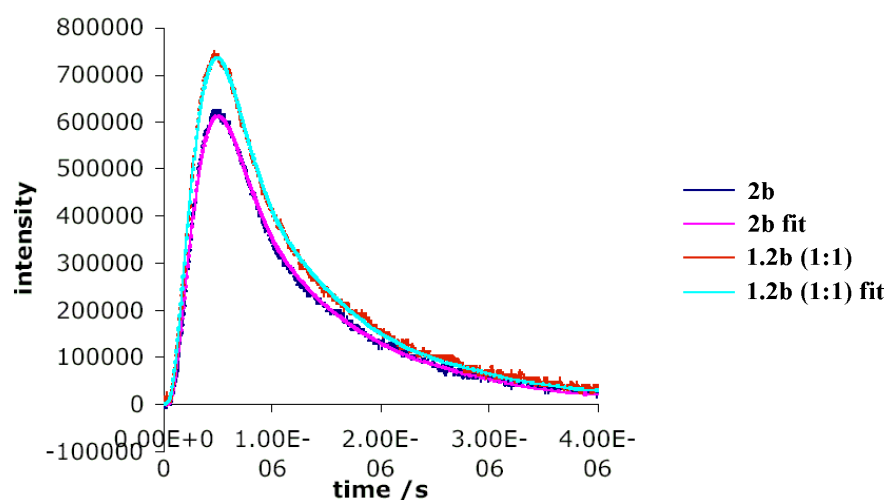


Figure 4: NIR emission at 880 nm from neodymium thread **2b** in the absence and presence of 1 equivalent of macrocycle **1**

Monitoring the neodymium NIR emission in thread **3b** after excitation at 337 nm also gave a substantial increase in intensity upon addition of 1 equivalent of macrocycle **1** (Figure 5).

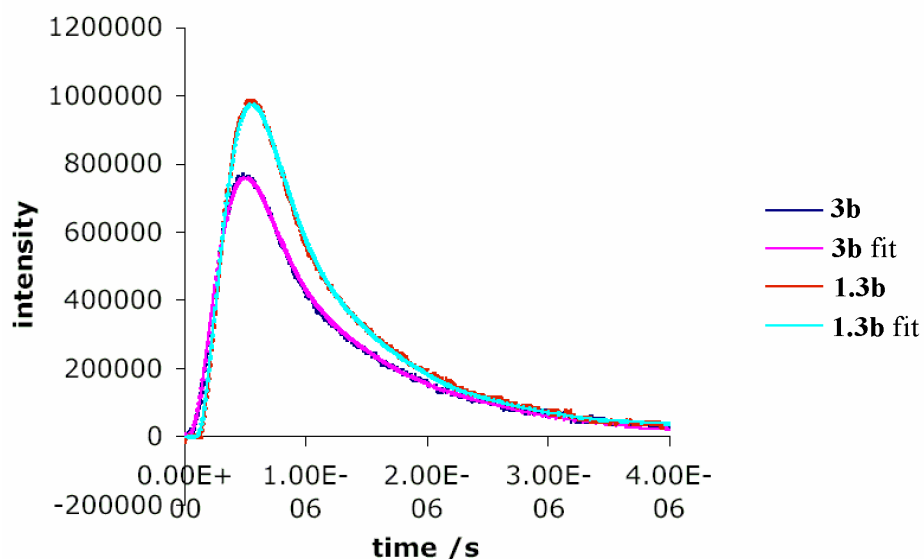
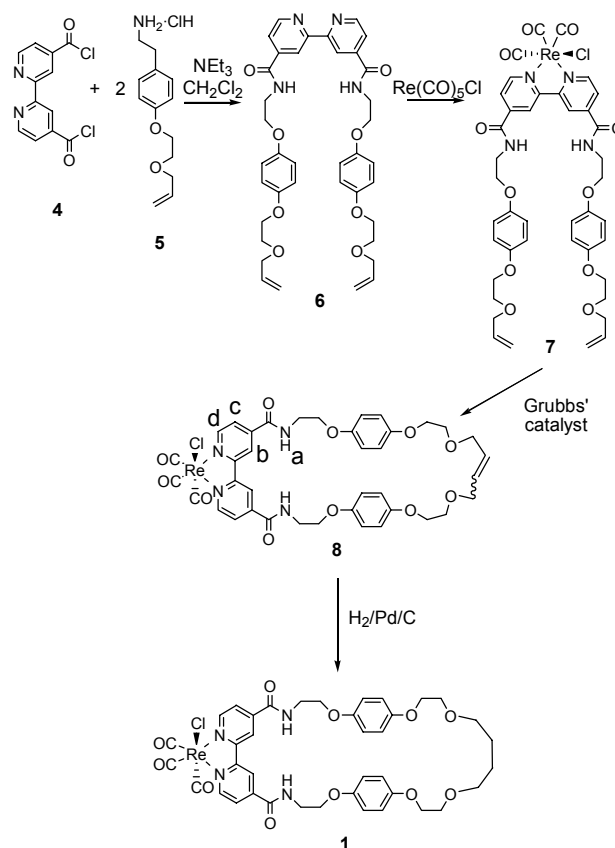


Figure 5: NIR emission at 880 nm from neodymium thread **3b** in the absence and presence of 1 equivalent of macrocycle **1**

Experimental Data

Unless otherwise stated all reagents were used as received and without further purification. Triethylamine was distilled and stored over potassium hydroxide. Solvents were dried according to standard laboratory procedures. All reactions were carried out under a nitrogen atmosphere unless otherwise stated. NMR Spectra were recorded on a Varian Mercury 300 or Varian Unity Plus 500 instrument. UV/vis spectra were recorded on a Perkin-Elmer Lambda 6 Spectrophotometer. The lanthanide complexes $\text{Ln}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}^2$, 5-bromo-methyl-2,2'-bipyridine³ and synthon **5**⁴ were prepared according to literature procedures.



Scheme 1: Synthesis of macrocycle **1**

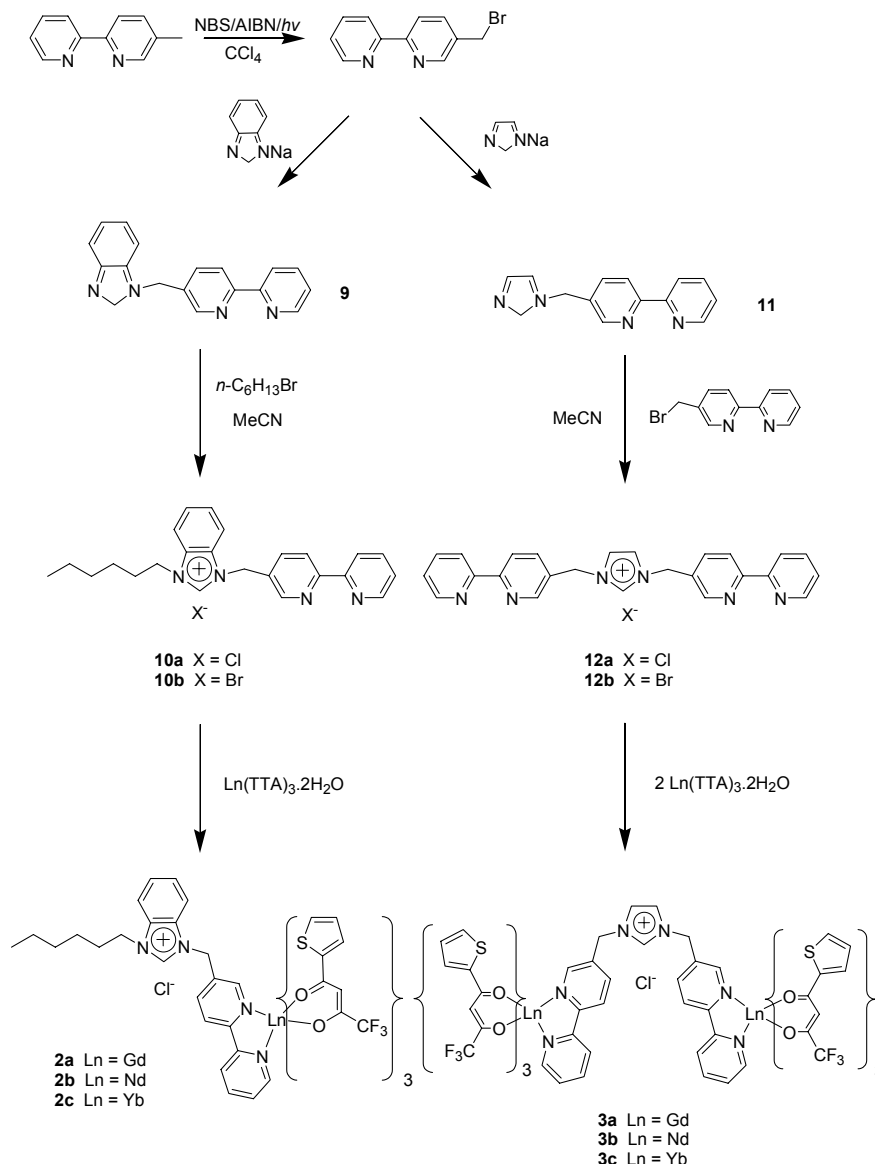
6: A solution of **4** (0.44 g, 1.83 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a solution of **5** (1.1 g, 4.02 mmol) and triethylamine (1.7 ml) in CH_2Cl_2 (25 ml) at room temperature. The mixture was stirred overnight. A precipitate was formed which was then filtered and washed with dichloromethane and diethylether to give the pure product (1.79 g, 98 %). $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, TMS) δ = 3.66 (8H, b), 3.99-4.08 (12H, m, $-\text{NHCH}_2\text{CH}_2\text{OAr-}$ & $-\text{ArOCH}_2\text{CH}_2-$ & $-\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$), 5.11-5.27 (4H, m, $-\text{CH}=\text{CH}_2$), 5.85 (2H, b, $-\text{CH}=\text{CH}_2$), 6.86 (8H, bs, CH_{Ar}), 7.84 (2H, bs, $\text{CH}_{(5,5')} \text{ bipy}$), 8.78 (2H, bs, $\text{CH}_{(3,3')} \text{ bipy}$), 8.84 (2H, m, $\text{CH}_{(6,6')} \text{ bipy}$), 9.16 (2H, b, NH). $^{13}\text{C-NMR}$

(300MHz, DMSO-*d*₆, TMS) δ = 39.25, 66.26, 67.44, 68.18, 71.07, 115.23, 115.35, 116.40, 118.14, 121.87, 134.99, 142.49, 149.93, 152.28, 152.46, 155.32, 164.71. FAB MS $[M + H]^+$: m/z = 683.

7: Compound **6** (0.44 g, 0.64 mmol) and Re(CO)₅Cl (0.25 g, 0.69 mmol) were heated under reflux for 12 hours in THF (80 ml) and the reaction mixture was observed to turn orange. The solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography (SiO₂; CH₂Cl₂/MeOH 9:1). The Re(I) complex was isolated as a bright yellow solid (0.57 g, 90%). ¹H-NMR (300 MHz, CDCl₃, TMS) δ = 3.74 (4H, t, J = 4.5 Hz, -NHCH₂-), 4.00-4.07 (12H, m, -NHCH₂CH₂OAr- & -ArOCH₂CH₂- & -CH₂CH₂Oallyl), 4.18-4.31 (4H, m, -CH₂OCH₂CH=CH₂), 5.18 (2H, dd, J_{cis} = 10.2 Hz, J_{gem} = 1.5 Hz, -CH=CH₂), 5.28 (2H, dd, J_{trans} = 17.4 Hz, J_{gem} = 1.5 Hz, -CH=CH₂), 5.93 (2H, ddd, J_{trans} = 17.4 Hz, J_{cis} = 10.2 Hz, J_{vic} = 5.4 Hz, -CH=CH₂), 6.84 (4H, d, J_{ortho} = 9.0 Hz, CH_{Ar}), 6.91 (4H, d, J_{ortho} = 9.0 Hz, CH_{Ar}), 7.63 (2H, bs, NH), 7.83 (2H, d, J_{ortho} = 5.4 Hz, CH_(5,5') bipy), 8.43 (2H, s, CH_(3,3') bipy), 8.91 (2H, d, J_{ortho} = 5.4 Hz, CH_(6,6') bipy). ¹³C-NMR (300MHz, CDCl₃, TMS): δ = 40.53, 66.82, 68.03, 68.60, 72.40, 115.67, 115.86, 117.40, 120.26, 126.47, 134.46, 143.20, 152.51, 153.35, 153.70, 155.04, 161.75, 187.21, 195.89. ESI MS $[C_{41}H_{42}ClN_4O_{11}Re + Na]^+$: m/z observed 1011.2134, calc. 1011.1994; $[C_{41}H_{42}N_4O_{11}Re - Cl]^+$: m/z observed 953.2458, calc. 953.2408.

Macrocycle 8: Grubbs' catalyst (0.03 g) was added to a solution of **7** (0.3 g, 0.30 mmol) in dichloromethane (20 ml) under nitrogen atmosphere. After six hours a second aliquot of catalyst (0.03 g) was added and the mixture was stirred overnight. The solvent was evaporated under reduced pressure and the crude was purified by column chromatography (SiO₂; Acetone/CH₂Cl₂, 1:1). The product was isolated as a bright yellow solid (0.12 g, 40%). ¹H-NMR (300 MHz, DMSO-*d*₆, TMS) δ = 3.60-3.69 (8H, m, -NHCH₂- & -CH₂CH₂OCH₂-), 3.94 (8H, bs, -NHCH₂CH₂OAr- & -ArOCH₂CH₂-), 4.08 (4H, bs, -CH₂OCH₂CH=CH-), 5.73 (2H, bs, -CH=CH-), 6.78-6.86 (8H, m, CH_{HQ}), 8.05 (2H, d, J_{ortho} = 5.1 Hz, CH_(5,5') bipy), 9.07 (2H, s, CH_(3,3') bipy), 9.12 (2H, d, J_{ortho} = 5.1 Hz, CH_(6,6') bipy), 9.41 (2H, b, NH). ¹³C-NMR (300MHz, DMSO-*d*₆, TMS) δ = 38.62, 66.36, 67.70, 68.15, 69.97, 115.38, 115.55, 122.20, 125.76, 128.79, 144.37, 152.36, 152.82, 153.79, 155.69, 163.38, 189.38, 197.46. ESI MS $[C_{39}H_{38}N_4ClO_{11}Re + Na]^+$: m/z observed 983.1716, calc. 983.1681; $[C_{39}H_{38}N_4O_{11}Re - Cl]^+$: m/z observed 925.2086, calc. 925.2095.

Macrocycle 1: Compound **8** (0.2 g, 0.21 mmol) was dissolved in a suspension 10% Palladium on activated carbon (0.025 g) in methanol (40 ml) and the resulting reaction mixture was stirred under a hydrogen atmosphere (1 atm.) overnight. The solution was filtered through celite and washed with THF (2 x 15 ml). The solvent was evaporated under reduced pressure to yield the pure product (0.19 g, 96%) as a yellow solid. ¹H-NMR (300 MHz, DMSO-*d*₆, TMS) δ = 1.52 (4H, bs, -OCH₂CH₂CH₂CH₂-), 3.43 (4H, bs, -NHCH₂CH₂OAr), 3.63 (4H, bs, -OCH₂CH₂CH₂CH₂-), 3.73 (4H, bs, -OCH₂CH₂CH₂-), 3.98 (4H, bs), 4.14 (4H, bs), 6.86 (4H, d, J = 7.5 Hz, CH_{HQ}), 6.92 (4H, d, J = 7.5 Hz, CH_{HQ}), 8.13 (2H, bs, CH_(5,5') bipy), 9.21 (2H, bs, CH_(6,6') bipy), 9.38 (2H, s, CH_(3,3') bipy), 9.60 (2H, b, NH). ¹³C-NMR (300MHz, DMSO-*d*₆, TMS): δ = 25.81, 39.68, 66.59, 67.82, 67.96, 68.82, 70.34, 116.20, 116.40, 123.00, 126.77, 145.27, 153.58, 153.95, 155.03, 156.95, 164.44, 191.08, 199.21. ESI MS $[M]^+$: m/z 985.



Scheme 2: Synthesis of lanthanide complexes

5-(N-Benzimidazolyl)methyl-2,2'-bipyridine 9. Sodium hydride (52.1 mg, 2.17mmol) was suspended in dry THF (20ml) and cooled to 0°C. A solution of benzimidazole (0.26g, 2.17mmol) in dry THF (15 ml) was added slowly until no further gas production was observed. A solution of 5-bromomethyl-2,2'bipyridine (0.54 g, 2.17mmol) in dry THF (40 ml) was added dropwise over 30 minutes and the solution stirred for a further 12 hours during which time it was allowed to warm to room temperature. The resulting reaction mixture was filtered and the solvent removed to give an oily residue. Precipitation with hexane allowed the product to be isolated by filtration as an orange solid (0.53 g, 85%). ¹H NMR (300 MHz, CDCl₃, TMS) δ = 8.66 (1H, br d, J = 4.5Hz, ArH), 8.62 (1H, br m, ArH), 8.36 (2H, d, J = 8.1Hz, ArH), 8.02 (1H, s, ArH), 7.79-7.85 (2H, m, ArH), 7.65 (1H, dd, J = 3.2, 5.9Hz, ArH), 7.57 (1H, dd, J = 2.1, 8.1Hz, ArH), 7.29 (4H, m, ArH), 5.44 (2H, s, H). ESI MS [C₁₈H₁₄N₄ + H]⁺: m/z observed 287.1284, calc 287.1297.

Compound 10b. Compound 9 (0.45 g, 1.57 mmol) and *n*-hexylbromide (1.3 g, 7.86 mmol) were heated under reflux in dry acetonitrile (100 ml) for 48 hours. After cooling

to room temperature the solvent was removed and the resulting red solid washed with ether and dried under a stream of nitrogen to give the pure product (0.40 g, 56%). ^1H NMR (300 MHz, CDCl_3 , TMS) δ = 10.55 (1H, s, NCHN), 8.86 (1H, br d, ArH), 8.62-8.67 (1H, m, ArH), 8.35 (2H, d, J = 8.1Hz, ArH), 8.28 (1H, d, J = 7.8Hz, ArH), 8.13 (1H, d, J = 8.1Hz, ArH), 7.78-7.87 (2H, m, ArH), 7.67 (2H, m, ArH), 7.13 (1H, m, ArH), 5.60 (2H, s, ArCH₂N), 4.57 (2H, m, NCH₂), 2.07 (2H, m, NCH₂CH₂), 1.30-1.42 (6H, m, CH₂CH₂CH₂), 0.84 (3H, m, CH₃). ESI MS [$\text{C}_{24}\text{H}_{27}\text{N}_4 - \text{Br}$]⁺: m/z observed 371.2238, calc 371.2236.

Compound 10a. Compound **10b** (0.25 g, 5.54 mmol) was dissolved in water (20 ml) and passed down a chloride charged Amberlite anion exchange column. The solvent was removed, the product precipitated with diethyl ether and isolated as a red solid by filtration (0.14 g, 62%). ^1H NMR (300 MHz, CDCl_3 , TMS) δ = 9.85 (1H, s, NCHN), 9.03 (1H, br d, ArH), 8.84 (1H, d, J = 5.4Hz, ArH), 8.60-8.74 (2H, m, ArH), 8.46 (1H, d, J = 8.4Hz, ArH), 8.22 (1H, d, J = 8.4Hz, ArH), 8.01 (2H, m, ArH), 7.56-7.68 (3H, m, ArH), 5.98 (2H, ArCH₂N), 4.53 (2H, m, NCH₂), 2.00 (2H, m, NCH₂CH₂), 1.30 (6H, m, CH₂CH₂CH₂), 0.84 (3H, m, CH₃).

Thread 2a. Method as for complex **2b**, using Gd(TTA)₃.2H₂O (42 mg, 0.0049 mmol). Product obtained as off-white solid (50 mg, 83%). UV/vis data (CH_2Cl_2): λ_{max} (10^{-3} ϵ) = 272 (74.3), 340nm (50.3M⁻¹cm⁻¹). FAB MS [$\text{C}_{48}\text{H}_{39}\text{F}_9\text{GdN}_4\text{O}_6\text{S}_3$]⁺: m/z observed 1192.38, calc 1192.11.

Thread 2b. Compound **10a** (20 mg, 0.0049 mmol) and Nd(TTA)₃.bishydrate (41 mg, 0.0049 mmol) were refluxed in dry acetonitrile (50 ml) overnight. The solvent was removed and the reaction residue dissolved in dry dichloromethane (50 ml) and filtered. The organic solvent was removed and the product precipitated in hexane to give a white solid (50 mg, 84%). UV/vis data (CH_2Cl_2): λ_{max} (10^{-3} ϵ) = 270 (31.4), 340nm (54.4M⁻¹cm⁻¹). FAB MS [$\text{C}_{48}\text{H}_{39}\text{F}_9\text{NdN}_4\text{O}_6\text{S}_3 - \text{Cl}$]⁺: m/z observed 1178.07, calc. 1178.10.

Thread 2c. Method as for complex **2b**, using Yb(TTA)₃.2H₂O (43 mg, 0.0049 mmol). Product obtained as an off-white solid (41 mg, 67%). UV/vis data (CH_2Cl_2): λ_{max} (10^{-3} ϵ) = 269 (25.4), 337nm (47.0M⁻¹cm⁻¹). FAB MS [$\text{C}_{48}\text{H}_{39}\text{F}_9\text{N}_4\text{O}_6\text{S}_3\text{Yb}$]⁺: m/z observed 1204.19, calc 1124.12.

5-Imidazolemethyl-2,2'-bipyridine 11. Sodium hydride (48 mg, 2.01 mmol) was suspended in dry THF (20 ml) and cooled to 0°C. A solution of imidazole (0.14g, 2.01 mmol) in dry THF (15 ml) was slowly added until no further gas production was observed. A solution of 5-bromomethyl-4,4'-bipyridine, **9**, (0.5 g, 2.01 mmol) in dry THF (40 ml) was added dropwise over 30 minutes and the solution stirred for 12 hours. The resulting reaction mixture was filtered and the solvent removed to give an oily residue. Trituration with hexane gave the product as an orange solid (0.40 g, 100%). ^1H NMR (300 MHz, CDCl_3 , TMS) δ = 8.67 (1H, dq, J = 0.9, 4.8Hz, ArH), 8.54 (1H, dd, J = 0.6, 2.1Hz, ArH), 8.38 (1H, m, ArH), 7.82 (1H, td, J = 1.8, 7.5Hz, ArH), 7.55-7.60 (2H, m, ArH), 7.32 (1H, ddd, J = 1.2, 4.8, 7.5Hz, ArH), 7.09-7.12 (2H, m, ArH), 6.93 (1H, t, J = 1.5Hz, ArH). ESI MS [$\text{C}_{14}\text{H}_{12}\text{N}_4 + \text{H}$]⁺: m/z observed 237.1131, calc 237.1140.

N,N'-Bis[5-(2,2'-bipyridyl)methyl]imidazolium Chloride 12a. Compound **12b** (0.4 g, 1.63 mmol), was passed down an Amberlite anion exchange column charged with chloride anions using water as eluent. The solvent was removed to give the product as a pale yellow waxy solid (0.33 g, 100%). ¹H NMR (300 MHz, DMSO-*d*₆, TMS) δ = 9.73 (1H, s, *ArH*), 8.89 (2H, d, J = 1.8 Hz, *ArH*), 8.75 (2H, d, J = 4.8 Hz, *ArH*), 8.49-8.52 (4H, m, *ArH*), 8.12-8.17 (4H, m, *ArH*), 7.99 (2H, d, J = 1.5 Hz, *ArH*), 7.63 (2H, m, *ArH*), 5.64 (4H, s, *H*).

N,N'-Bis[5-(2,2'-bipyridyl)methyl]imidazolium Bromide 12b. 5-Imidazolomethyl-2,2'-bipyridine **11** (0.42 g, 2.16 mmol) and 5-bromomethyl-2,2'-bipyridine **9** (0.54 g, 2.16 mmol) were heated under reflux in dry acetonitrile (50 ml) for 48 hours. The reaction mixture was cooled to room temperature and the solvent removed *en vacuo*. Addition of dichloromethane to the residue gave rise to the formation of a yellow precipitate which was collected by filtration as the pure product (0.55 g, 63%). ¹H NMR (300 MHz, DMSO-*d*₆, TMS) δ = 9.54 (1H, s, *ArH*), 8.82 (2H, br s, *ArH*), 8.71 (2H, br s, *ArH*), 8.43 (4H, t, J = 8.7 Hz, *ArH*), 7.96-8.06 (6H, m, *ArH*), 7.50 (2H, m, *ArH*), 5.59 (4H, s, *H*). ESI MS [C₂₅H₂₁N₆ - Br]⁺: *m/z* observed 405.1837, calc 405.1828.

Thread 3a. Compound **12a** (11 mg, 2.45 × 10⁻⁵ mol) and Gd(TTA)₃.2H₂O (42 mg, 0.0049 mmol) were heated under reflux in acetonitrile (25 ml) for 12 hours. The solvent was removed *en vacuo* to give a yellow residue which was dissolved in dichloromethane and filtered. The product was precipitated using pentane and collected by filtration (22 mg, 45%). UV/vis (CH₂Cl₂): λ_{max} (10⁻³ ε) = 267.6 (41.7), 306.7 (61.0), 340.0 nm (83.6 M⁻¹ cm⁻¹). FAB MS [C₇₃H₄₅F₁₈Gd₂N₆O₁₂S₆ - Cl]⁺: *m/z* observed 2047.03, calc 2046.96.

Thread 3b. Method as for complex **3a** using Nd(TTA)₃.2H₂O (42 mg, 0.0049 mmol) to give the product as a yellow solid (30 mg, 61%). UV/vis (CH₂Cl₂): λ_{max} (10⁻³ ε) = 264.6 (43.0), 307.7 (63.0), 340.0 nm (101.0 M⁻¹ cm⁻¹). FAB MS [C₇₃H₄₅F₁₈N₆Nd₂O₁₂S₆ - Cl]⁺: *m/z* observed 2018.82, calc 2018.93.

Thread 3c. Method as for complex **3a** using Yb(TTA)₃.2H₂O (42 mg, 0.0049 mmol) to give the product as a yellow solid (32 mg, 60%). UV/vis (CH₂Cl₂): λ_{max} (10⁻³ ε) = 266.6 (41.2), 309.7 (65.2), 339.0 nm (88.0 M⁻¹ cm⁻¹). FAB MS [C₇₃H₄₅F₁₈N₆O₁₂S₆Yb₂ - Cl]⁺: *m/z* observed 2079.07, calc 2078.99.

Typical Mass Spectrometry Isotope Patterns

The following two fast-atom bombardment (FAB) mass spectra for compounds **2a** (Figure 6) and **3a** (Figure 7) illustrate the typical isotope patterns obtained for both the mono- and bis-lanthanide containing imidazolium thread molecules. In all cases the experimentally obtained isotope distribution matches closely to the calculated one.

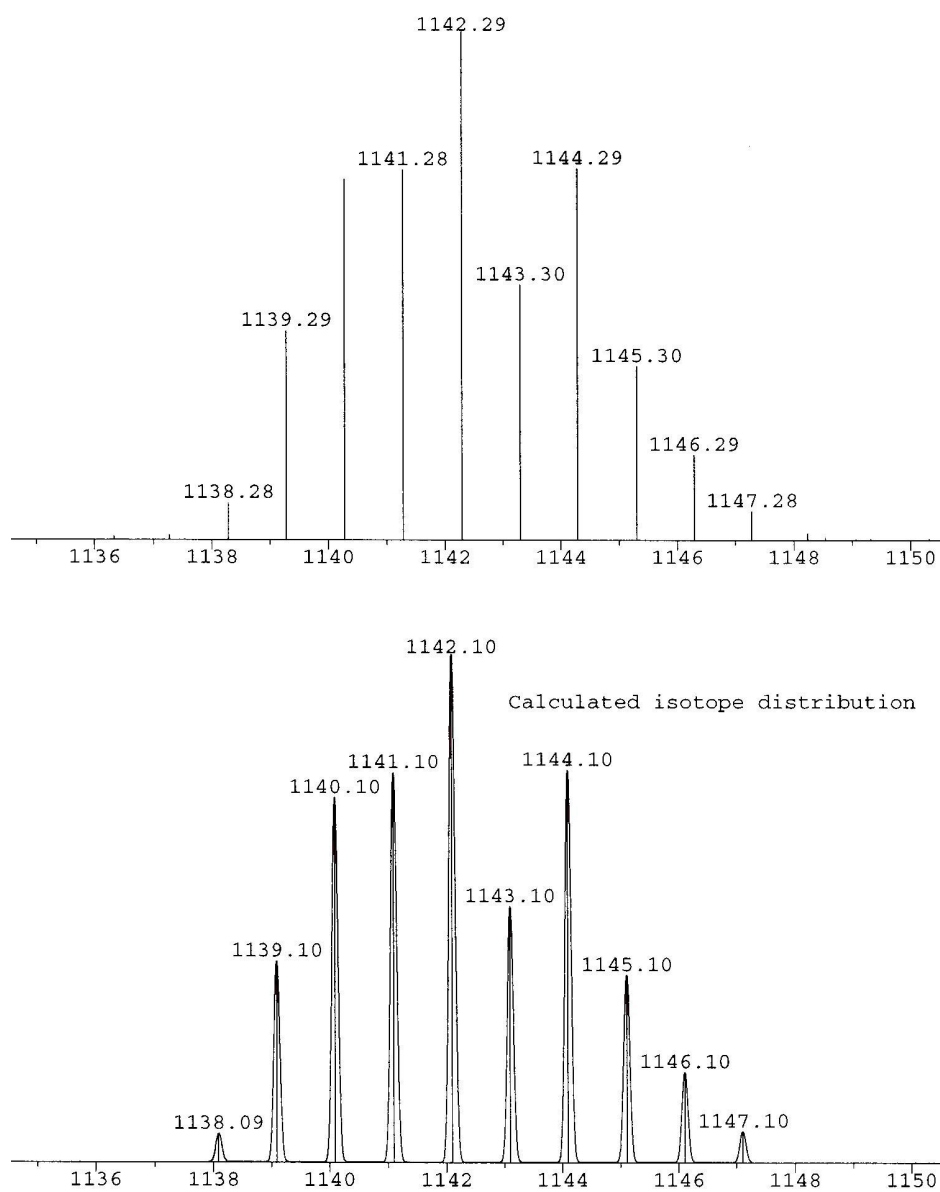


Figure 6: Top: Observed isotopic distribution pattern for **2a** by FAB MS
Bottom: Calculated isotopic distribution pattern

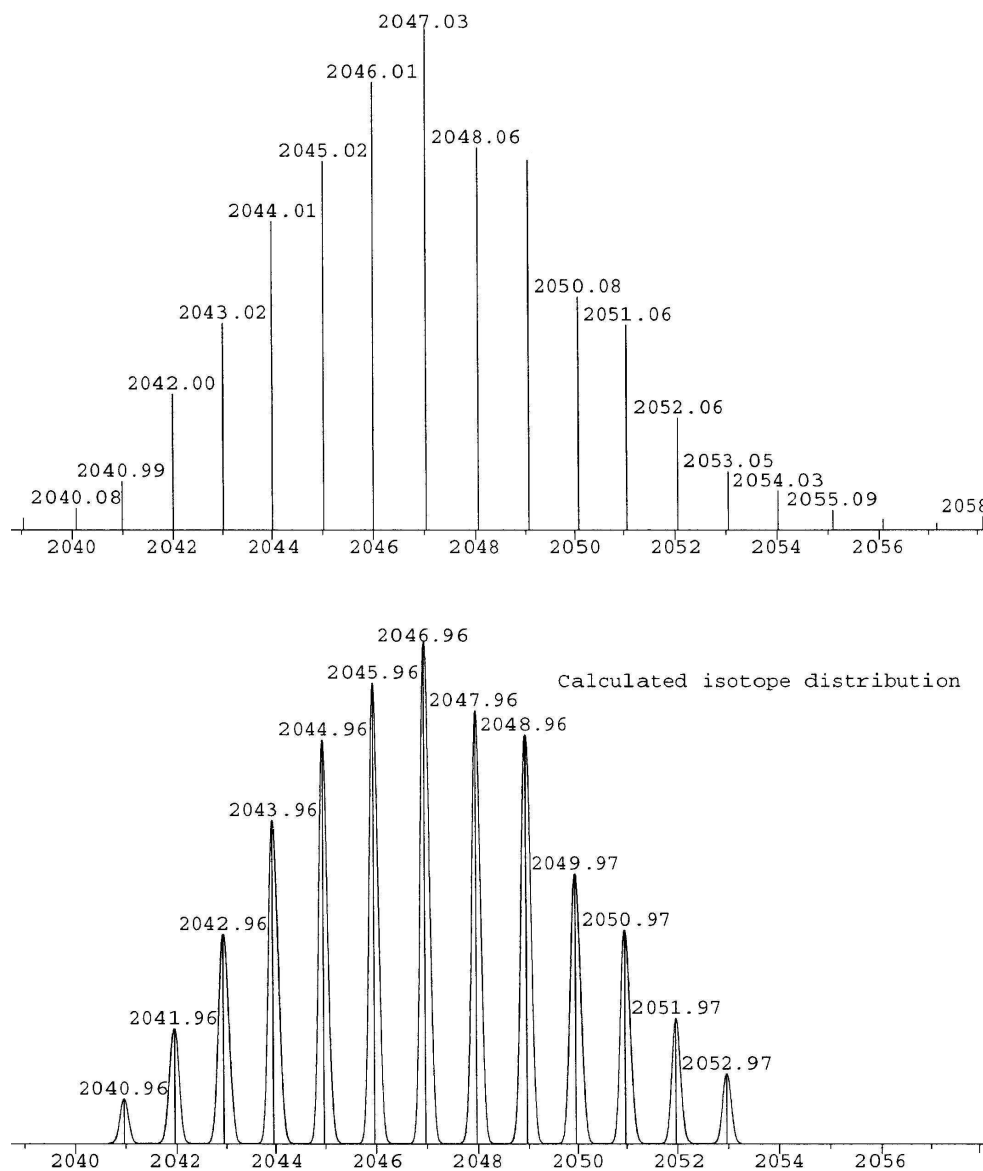


Figure 8: Top: Observed isotopic distribution pattern for **3a** by FAB MS
Bottom: Calculated isotopic distribution pattern

¹ Binstead, R.A.; Zuberbühler, A.D. *Specfit Global Analysis Version 2.90X*

² Voloshin, A.I.; Shavaleev, N.M.; Kazakov, V.P. *J. Luminescence* **2000**, *91*, 49-58.

³ Polin, J.; Schmohel, E.; Balzani, V. *Synthesis* **1999**, 321-324.

⁴ Sambrook, M.R.; Beer, P.D.; Wisner, J.A.; Paul, R.L.; Cowley, A.R. *J. Am. Chem. Soc.* **2004**, *126* (47), 15364-15365.