Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Lanthanide-cation templated synthesis of rotaxanes

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TABLE OF CONTENTS

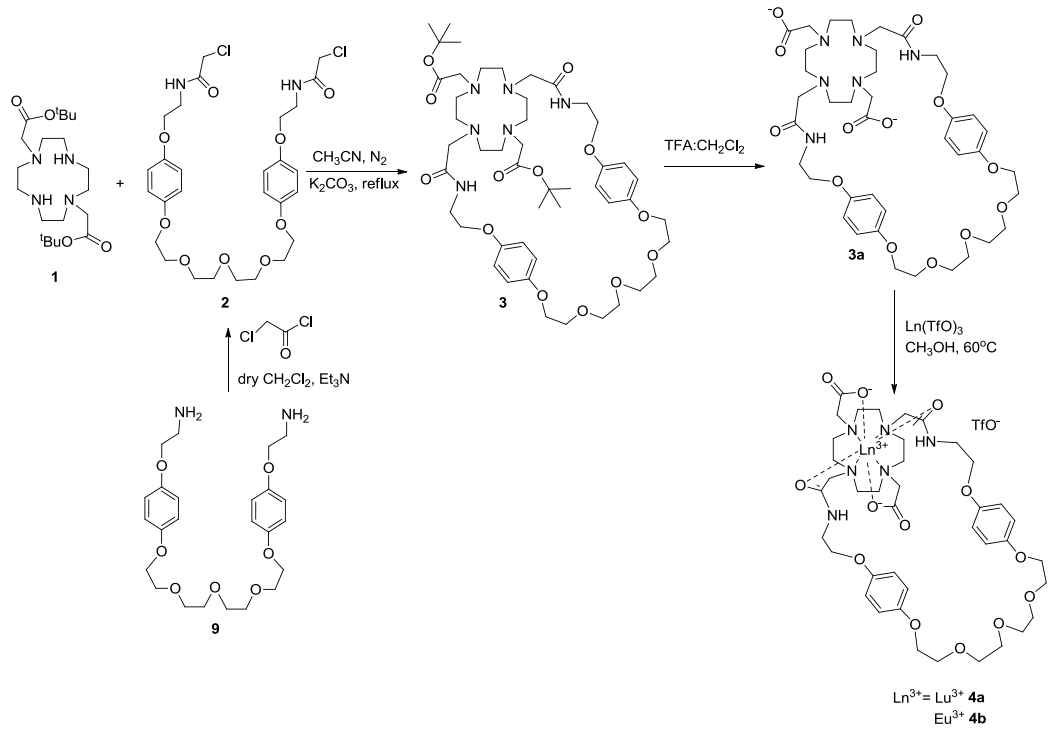
Part I: Experimental Procedures.

General Considerations

All solvents and reagents were purchased from commercial suppliers and used as received unless otherwise stated. Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H_2O was de-ionised and micro filtered using a Milli-Q ® Millipore machine. TBA salts were stored in a vacuum desiccator containing phosphorus pentoxide prior to use. Triethylamine was distilled from and stored over potassium hydroxide. Size exclusion chromatography was carried out using Biobeads SX-3, with $CHCl_3$ as the eluent. NMR spectra were recorded on Varian Mercury 300 with ^1H NMR operating at 300 MHz, ^{13}C (all proton decoupled) at 75.5 MHz and Varian Unity Plus 500 spectrometer, operating at 500 MHz. Mass spectra were carried out on a Waters Micromass LCT and Bruker microTOF spectrometers.

Synthesis

Lanthanide macrocycle complexes. Compounds **1**[1] and **9**[2] were synthesized using the procedure described in the literature.



Scheme SI 1. *Synthesis of lanthanide macrocycle complexes*

General procedure for the preparation of compound 2. Compound **9** (2.00 g, 4.31 mmol) and Et_3N (4 ml) were dissolved in dry CH_2Cl_2 (100 ml). A solution of 2-chloroacetylchloride (0.8 ml, 9.48 mmol) in dry CH_2Cl_2 (20 ml) was added dropwise and the mixture was stirred for 6h. The mixture was allowed to room temperature and washed with HCl 10% (3x30 ml) and then with $NaHCO_3$ (2x50 ml) and water (1x100 ml). The organic phase was dried over $MgSO_4$, filtered and the solvent removed. Finally the residue was recristallized from diethyl ether (yield 84 %). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.97 (2H, bs), 6.78 (4H, d, *J* = 9 Hz), 6.74 (4H, d, *J* = 9 Hz), 4.03-3.98 (8H, m), 3.94 (4H, t, *J* = 6 Hz), 3.76 (4H, t, *J* = 6 Hz), 3.64-3.62 (12H, m); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.8, 145.2, 119.9, 71.4, 69.9, 68.3, 42.4, 37.2; **MS (ESI)**: *m/z* calc. for $[M + Cl]^-$ 653.1, found 653.1.

General procedure for the preparation of macrocycle 3. Compound **2** (500 mg, 1.24 mmol) was dissolved in dry CH_3CN (415 ml) and compound **8** (767 mg, 1.24 mmol) and K_2CO_3 (2.40 g) were added, the mixture was heated at 70 ^oC for 3 days under N_2. The reaction mixture was then filtered, and the solvent was removed from the filtrate in *vacuo*. The solid residue was recrystallized from diethyl ether and dried under vacuum to afford the title compound as orange solid (yield 70%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.41 (2H, bs), 6.83-6.74 (8H, m), 4.05-3.93 (8H, m), 3.83-3.80 (4H, m), 3.70-3.59 (12H, m), 3.19-2.51 (24H, m), 1.41 (18H, s); **^{13}C NMR** (125 MHz, $CDCl_3$/CD_3OD) δ 172.2, 170.3, 153.0, 152.8, 81.2, 70.8, 7.07, 69.8, 69.7, 68.2, 68.0, 66.8, 65.8, 64.3, 62.2, 59.4, 56.6, 54.3, 52.7, 39.7, 39.3, 39.0, 38.5, 28.2. **HRMS** (ES +ve) *m/z* calc for $[M + H]^+$ 945.5579, found 945.5543).

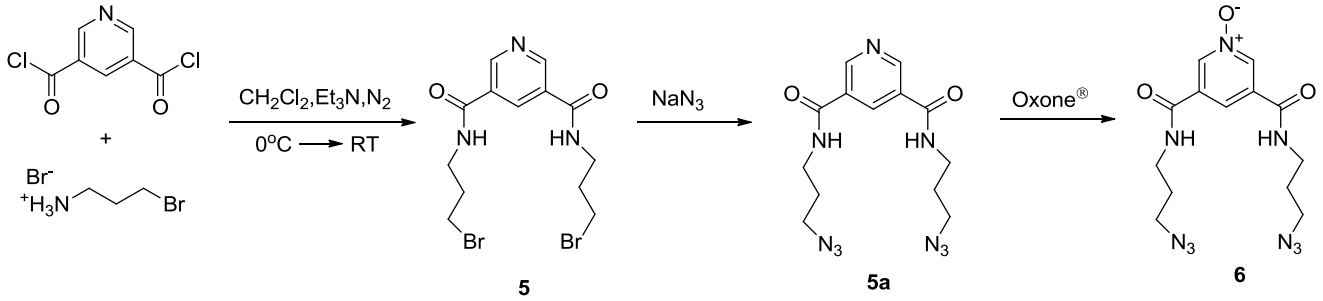
General procedure for the preparation of macrocycle 3a. Macrocycle **3** (250 mg, 0.249 mmol) was dissolved in dichloromethane (5 ml) and trifluoroacetic acid (5 ml) was dropwise added. This was left to stir at room temperature for 48 hours, after which all volatiles were evaporated under reduced pressure yielding an orange oil; this was tritured in diethyl ether until a orange solid was obtained (quant.). **^{1}H NMR** (300 MHz, CD_3OD) δ 6.84-6.72 (8H, m), 4.05-3.95 (12H, m), 3.86-3.76 (10H, m), 3.69-3.64 (16H, m), 3.52-3.44 (10H, m) ; **MS (ESI)**: *m/z* calc. for $[M + H]^+$ 833.4308, found 833.4291

General procedure for the preparation of lanthanide macrocycles complexes 4a and 4b. Macrocycle **3a** (1 equiv, 0.05 M) and the corresponding lanthanide triflate (1 equiv) were dissolved in methanol (3 ml); the mixture was stirred for 48 hours at 60 ^{o}C. The solvent was removed under reduced pressure and diethyl ether was added until a solid was obtained, affording the lanthanide complexes **4a** and **4b.**

Compound 4a: ^{1}H NMR (500 MHz, CD_3OD) δ 6.86-6.80 (8H, m), 4.04-4.0 (10H, m), 3.82-3.78 (8H, m), 3.69-3.65 (12H, m), 3.49-3.40 (10H, m), 2.79-2.73 (4H, m), 2.57-2.38 (4H, m). **^{13}C NMR** (125 MHz, CD_3OD δ 177.9, 172.9, 154.9, 154.6, 154.5, 154.1, 154.0, 125.6, 123.1, 120.5, 71.7, 71.6, 70.9, 70.8, 69.4, 69.3, 69.2, 68.4, 67.4, 67.1, 66.9, 65.6, 62.1, 57.6, 57.2, 56.7, 56.3, 41.7, 41.5, 41.3, 41.0, 40.6. **MS (ESI)**: *m/z* calc. for $[M]^+$ 1005.3453, found 1005.3464.

Compound 4b: ^{1}H NMR (500 MHz, CD_3OD) δ excluding region between 0 and 10 ppm 31.61, 30.81, -0.43, -0.93, -2.28, -4.07, -6.24, -8.03, -9.63, -14.38, -15.25, -18.9. **MS (ESI)**: *m/z* calc. for $[M]^+$ 981.3260, found 981.3255.

Pyridine N-oxide thread component



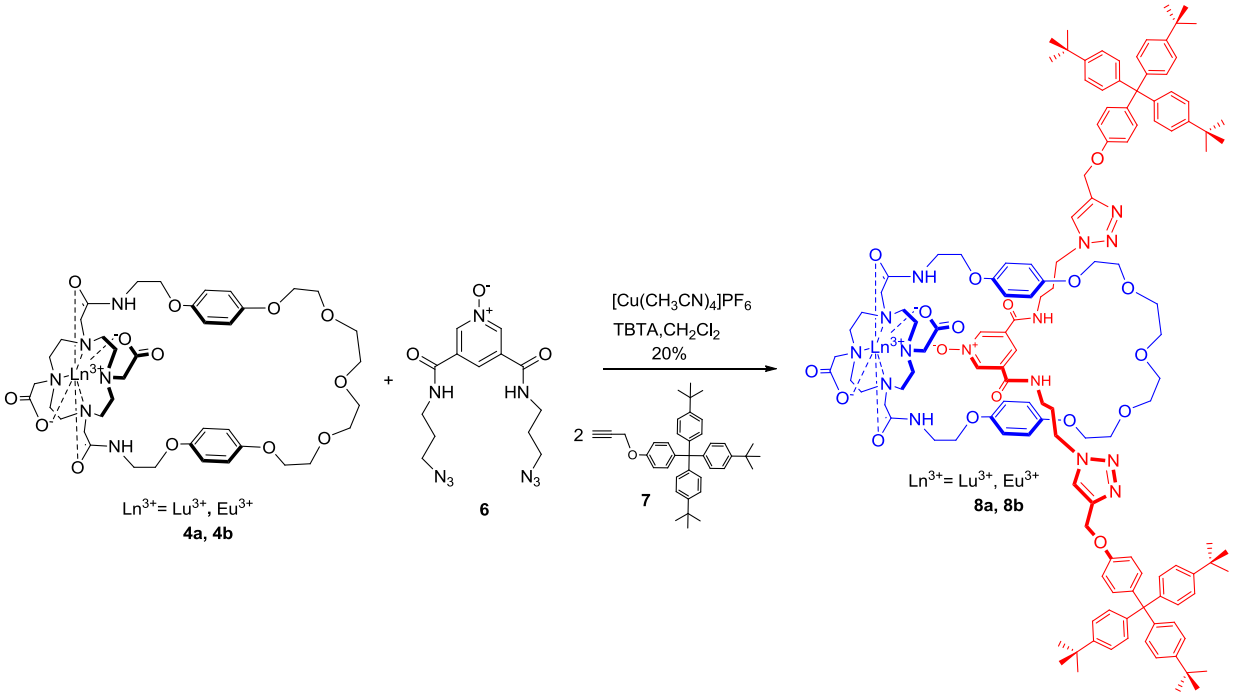
Scheme SI 2. *Synthesis of Pyridine N-oxide thread component*

General procedure for the preparation of compound 5. A solution of pyridine-3,5-dicarbonyl dichloride (2.30 g, 11.3 mmol), freshly prepared from 3,5-pyridinedicarboxylic acid and thionyl chloride, was dissolved in CH_2Cl_2 (40 ml). This was added dropwise to a cooled suspension of Bromopropylamine hydrobromide (4.94 g, 22.6 mmol) in CH_2Cl_2 (100 ml) and NEt_3 (9.4 ml, 60 mmol). The reaction mixture was left to stir for 2h before washing with 10% $HCl_{(aq)}$ (2x50 ml) and the aqueous phase was neutralized with saturated $NaHCO_{3(aq)}$ to give a white precipitate which was filtered and washed with H_2O (5x20 ml). The solid was then dried under high vacuum affording compound **5** as a pale yellow solid (2.29 g, 50%). **^{1}H NMR** (300 MHz, d^6-DMSO) δ 9.10 (d, 2H, ^4J = 3.7 Hz, Ar*H*), 8.87 (t, 2H, ^3J = 5.3 Hz, CON*H*), 8.59 (t, 1H, ^4J = 2.1 Hz, Ar*H*), 3.60, (t, 4H, ^3J = 6.5 Hz, CH_2Br), 3.42, (m, 4H, CONHCH_2), 2.09 (quint, 4H, ^3J = 6.6 Hz, $CH_2CH_2CH_2$); **^{13}C NMR** (75 MHz, d^6-DMSO) δ 164.5, 150.4, 134.0, 129.6, 37.9, 32.5, 32.1; **MS (ESI)** *m/z* calc. for $[M+Cl]^-$ 441.94, found 441.93.

General procedure for the preparation of compound 5a. Compound **5** (1.00 g, 2.45 mmol) was dissolved in dry degassed DMF (50 ml) and sodium azide (0.48 g, 7.37 mmol) was added at room temperature before being left to stir for 24 hours at 80^{o}C under N_2. H_2O (50 ml) was then added and the product extracted into CH_2Cl_2 (6 x 20 ml). The organic layer was then dried over $MgSO_4$, filtered and the solvent removed in *vacuo*. The crude product was recrystallised from chloroform/hexane to give **5a** as an off- white solid in 91% yield (740 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.10 (s, 2H, Ar*H*), 8.50 (t, 1H, ^{4}J = 2.1 Hz, Ar*H*), 7.33 (t, 2H, ^{3}J = 5.9 Hz), 3.59 (m, 4H, CONHCH_2), 3.47 (t, 4H, ^{3}J = 6.5 Hz, CH_2N_3), 1.93 (quint, 4H, ^{3}J = 6.6 Hz, $CH_2CH_2CH_2$); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.1, 150.5, 143.7, 133.6, 49.4, 38.0, 28.6; **MS (ESI)** *m/z*: calc. for $[M+Cl]^-$ 366.12, found 366.11.

General procedure for the preparation of compound 6. A saturated solution of Oxone® (2.22 g, 3.61 mmol) in H_2O (11 mL) was added dropwise to a vigorously stirred mixture of **5a** (0.400 g, 1.20 mmol) and $NaHCO_3$ (3 g, 3.61 mmol) in 1:1 H_2O/butanone at room temperature. After stirring for 2 hours, NaCl (12.45 g, 222 mmol) was added prior to the product being extracted into $CHCl_3$ (3 x 50 mL). The organic phase was then dried over $MgSO_4$, filtered, and solvent removed *in vacuo* to give the product as a yellow solid (0.377 g, 90%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.98 (s, 2H, Ar*H*), 8.37 (s, 1H, Ar*H*), 8.15 (t, 2H, ^{3}J = 5.3 Hz, CON*H*), 3.7 (m, 4H, CONHCH_2), 3.46 (t, 4H, ^{3}J = 6.5 Hz, CH_2N_3), 1.95 (quint, 4H, ^{3}J = 6.6 Hz, $CH_2CH_2CH_2$); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 162.4, 148.5, 140.3, 133.9, 49.1, 38.1, 28.4 **MS (ESI)** *m/z:* calc. for $[M+Cl]^-$ 382.11, found 382.11.

Lanthanide Rotaxanes. Compound **7** was synthesized using the procedure described in the literature.[3]



Scheme SI 3.*Synthesis of lanthanide rotaxanes* ***8a*** *and* ***8b***

General procedure for the preparation of Rotaxanes 8a and 8b. To a solution of the corresponding lanthanide complex (1 equiv, 0.3 M) in a dry mixture of 5:1 acetonitrile /dichloromethane, compound **6** (1.2 equiv, 0.3 M) was added (dissolved in a mixture 5:1 CH_2Cl_2/CH_3CN,). The reaction mixture was stirred for 30 min and then stopper alkyne (2.2 equiv), Cu[$(CH_3CN)_4PF_6$] (0.4 equiv), TBTA (0.4 equiv), and diisopropylethylamine (3 equiv) were added. The reaction was stirred for 3 days at RT under N_2. After this time the solvent was evaporated under reduced pressure, the crude was dissolved in CH_2Cl_2, and washed with aqueous EDTA (2 x 5 ml) and then with water (10 ml). The organic phase was dried over $MgSO_4$ and solvent removed in *vacuo*. The resulting solid wash purified by using size exclusion chromatography with chloroform to give the rotaxane in 20% yield.

Rotaxane 8a. **^{1}H NMR** (500 MHz, $CDCl_3/CD_3OD$) δ 8.85 (2H, s), 8.27 (1H, s), 7.59 (2H, s), 7.23-7.04 (28H, m), 6.87-6.79 (4H, m), 6.56 (4H, d, *J* = 10 Hz), 6.31 (4H, d, *J* = 10 Hz), 4.02-3.36 (48H, m), 2.80-2.17 (20H, m), 1.24 (54H, s) ; **^{13}C NMR** (125 MHz, $CDCl_3/CD_3OD$ δ 157.5, 153.9, 153.8, 153.4, 149.8,

145.5, 133.7, 132.0, 125.4, 117.1, 117.0, 116.8, 116.1, 116.0, 114.5, 72.2, 72.2, 72.0, 71.9, 71.4, 71.1, 71.1, 69.5, 69.4, 69.0, 67.9, 67.7, 66.9, 66.6, 65.8, 65.1, 64.8, 64.5, 62.9, 57.8, 57.6, 56.9, 56.4, 56.3, 56.0, 35.6, 33.2, 31.0, 30.7. **MS (ESI)** *m/z:* 1230.0967 calc. for $[M+Na-CF_3SO_3^-]^{2+}$, found 1230.0954.

Rotaxane 8b. ^{1}**H NMR** (500 MHz, 1 :1 CD_2Cl_2/CD_3OD) δ excluding region between 0 and 10 ppm. 34.95, 33.70, 32.74, 32.39, 30.27, 27.28, 20.72, 13.26, 12.52, -0.04, -3.04, -3.69, -4.35, -4.82, -5.79, -6.09, -7.24, -7.92, -9.39, -10.16, -12.36, -13.45, -14.00, -15.73, -17.00, -17.55, -18.20. **MS (ESI)** *m/z:* 1219.0836 calc. for $[M+Na-CF_3SO_3^-]^{2+}$, found 1219.0859.

HRMS (ES +ve) *m/z*: 1219.0836 $(M+Na-CF_3SO_3^-)^{2+}$, $C_{133}H_{167}EuN_{15}O_{18}$ requires 1219.0859).

Part II: High Resolution Mass Spectra

Lanthanide macrocycles complexes

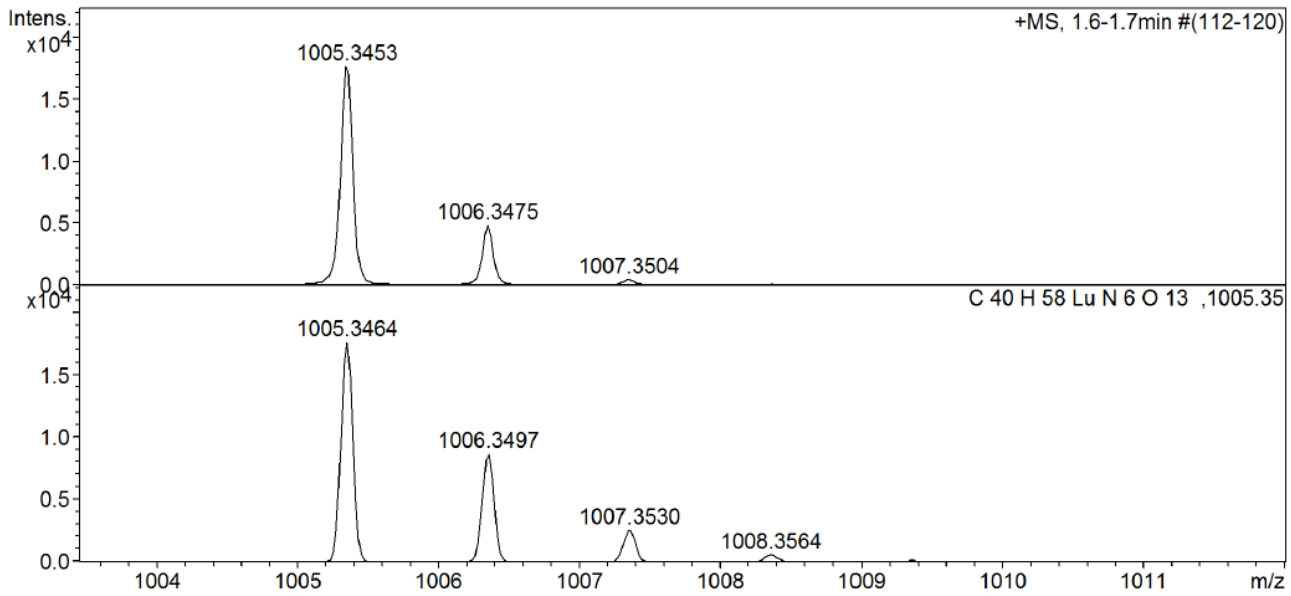


Figure SI 1. *High resolution electrospray ionization mass spectrum of lanthanide macrocycle complex* ***4a****.*

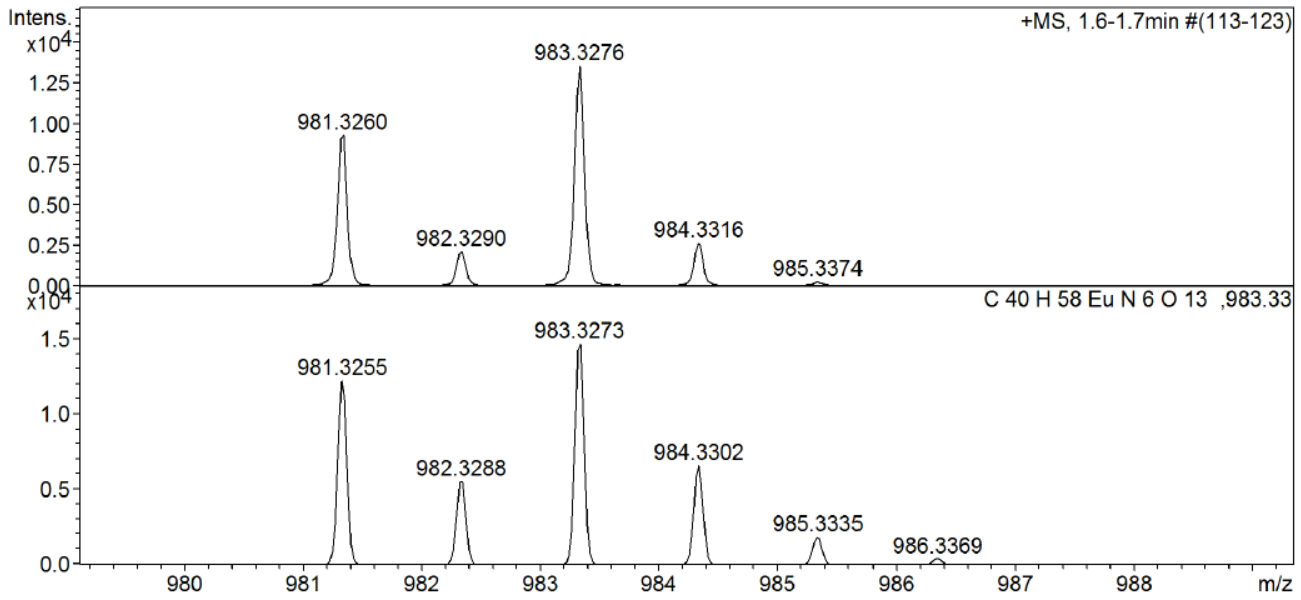


Figure SI 2.*High resolution electrospray ionization mass spectrum of lanthanide macrocycle complex* ***4b***

Lanthanide Rotaxane

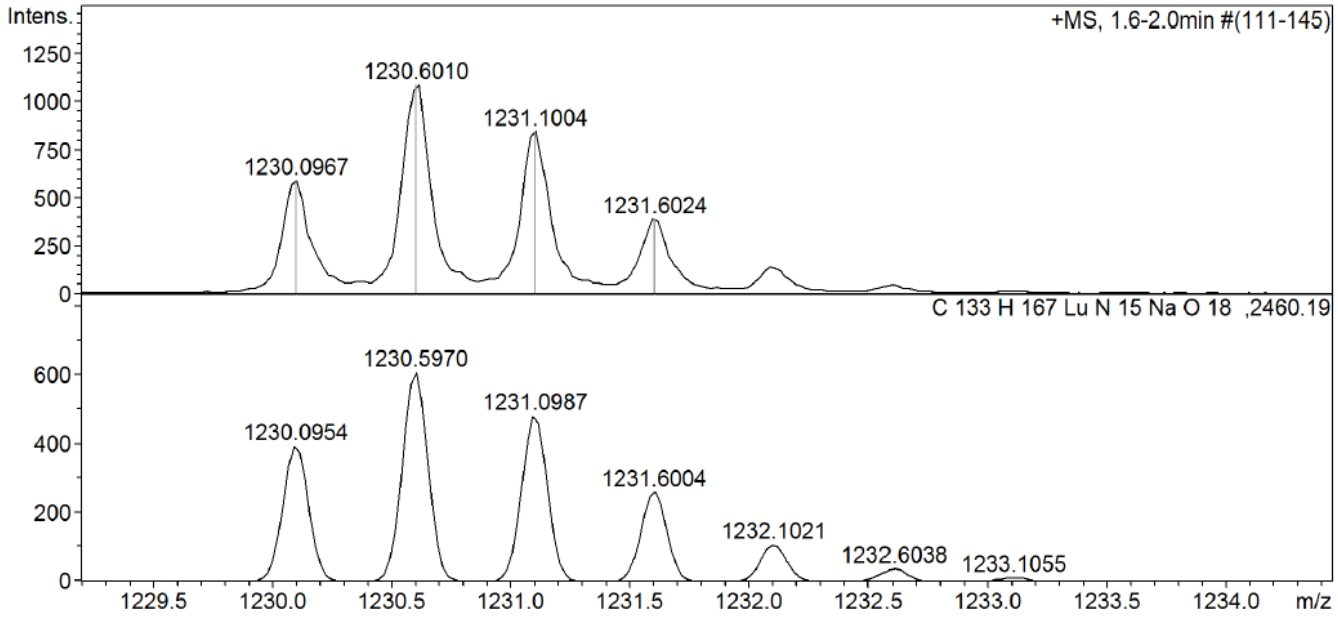


Figure SI 3. *High resolution electrospray ionization mass spectrum of [2]rotaxane* ***8a****.*

Part III: Additional NMR

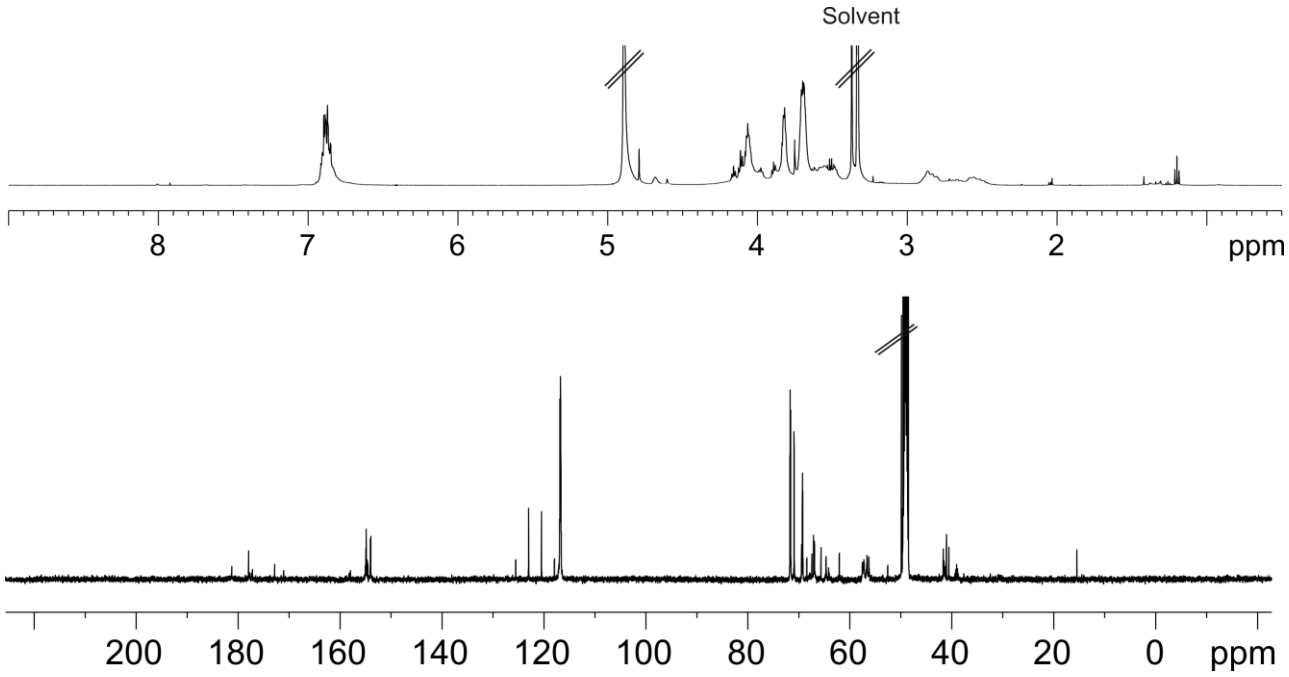


Figure SI 4. *NMR spectra of macrocycle* ***4a****. Top:* ^{1}*H NMR (*CD_3OD*, 500 MHz, 298K); bottom 13C NMR (*CD_3OD*, 125 MHz, 298K)*

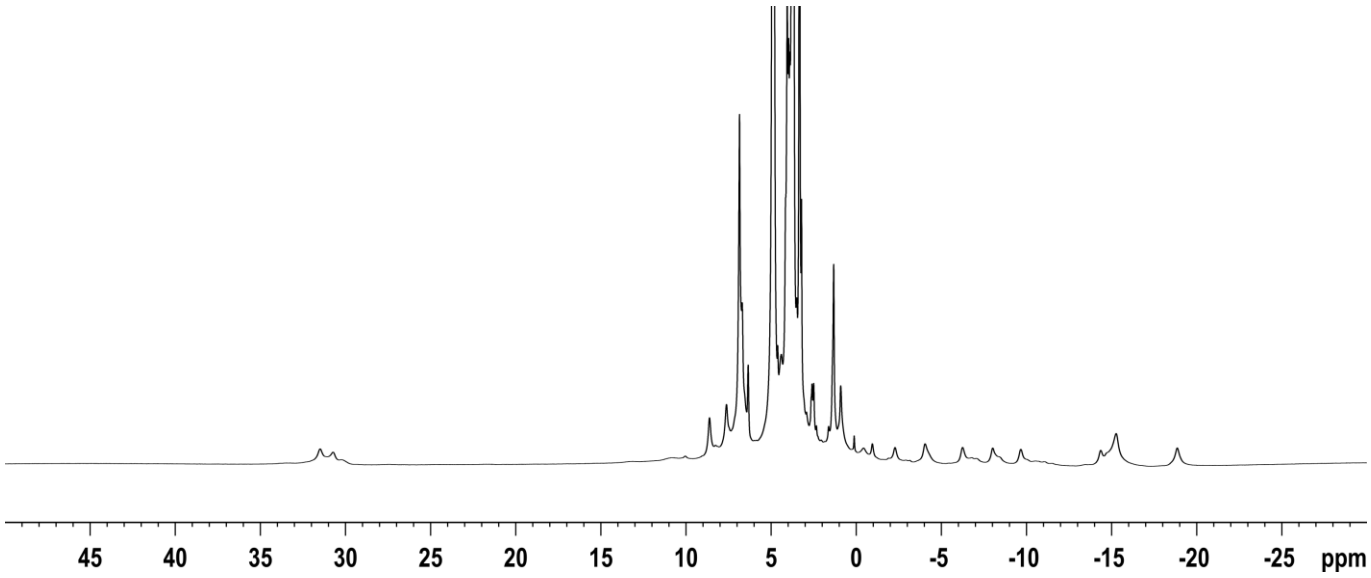


Figure SI 5. ^{1}*H NMR spectra of macrocycle* ***4b****. Top:* ^{1}*H NMR (*CD_3OD*, 500 MHz, 298K);*

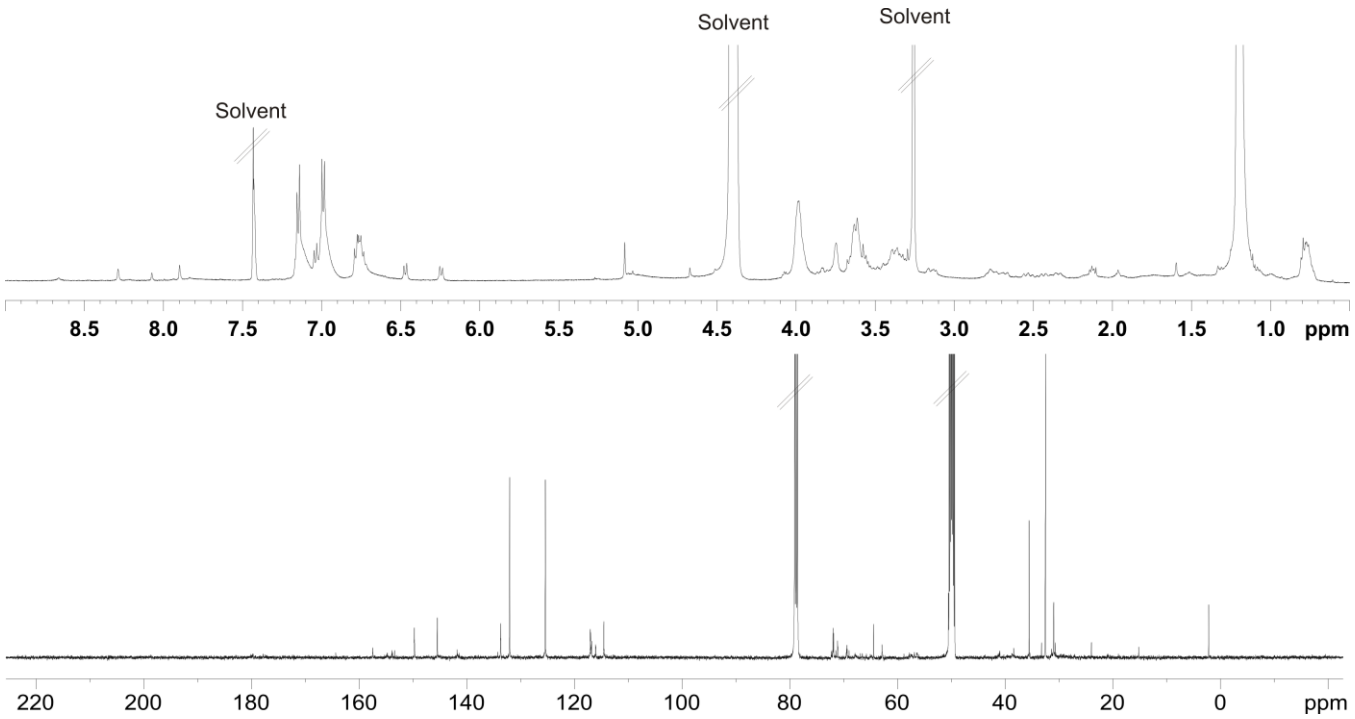


Figure SI 6. *^{1}H NMR spectra of rotaxane* ***8a****. Top: ^{1}H NMR (1:1 $CDCl_3$/CD_3OD, 500 MHz, 298K); bottom 13C NMR (1:1 $CDCl_3$/CD_3OD, 125 MHz, 298K)*

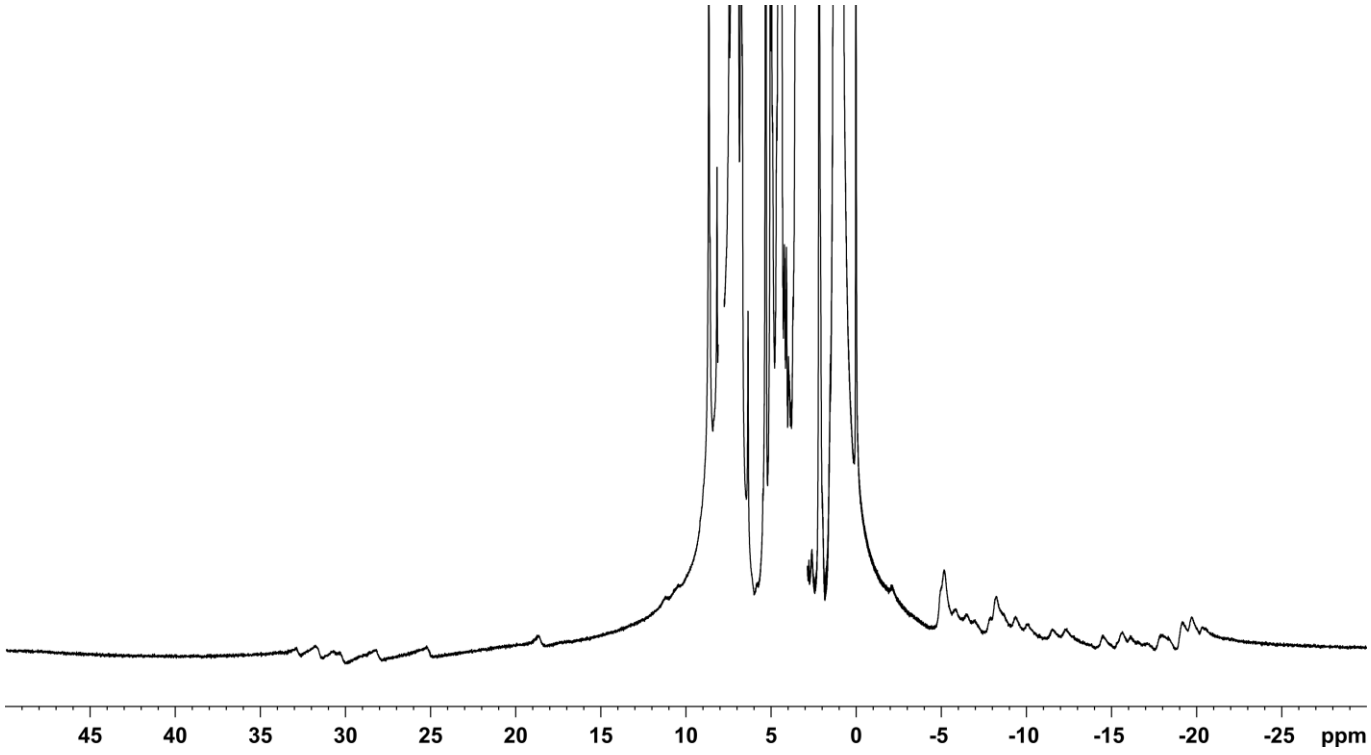


Figure SI 7. *^{1}H NMR spectra of rotaxane* ***8b****. Top: ^{1}H NMR (1:1 CD_2Cl_3/CD_3OD, 500 MHz, 298K)*

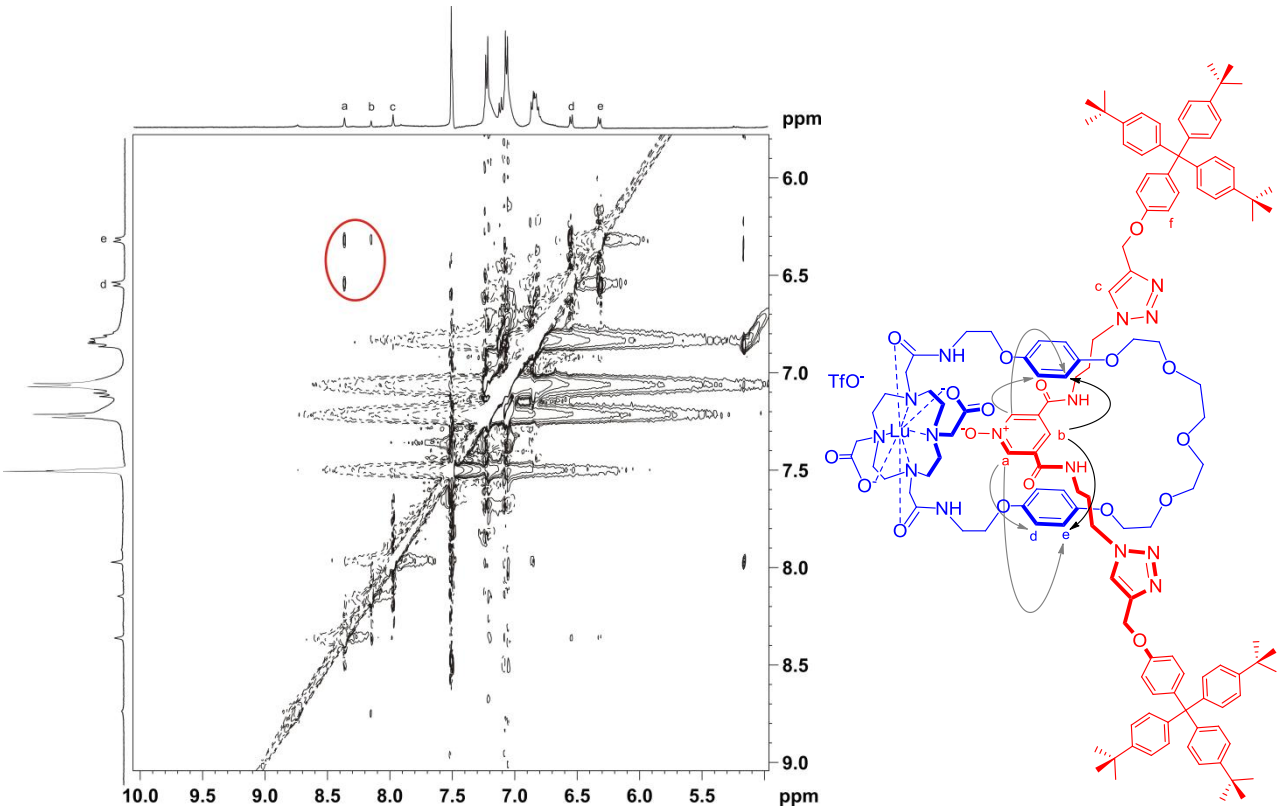


Figure SI 8. Section of the ^{1}H NMR ROESY spectrum of rotaxane **8a** (500 MHz, 1:1 $CDCl_3/CD_3OD$). Cross peaks between the pyridine-noxide protons of the axle (*a* and *b*), and the hydroquinone protons of the interlocked macrocycle (*d* and *e*) are highlighted (red).

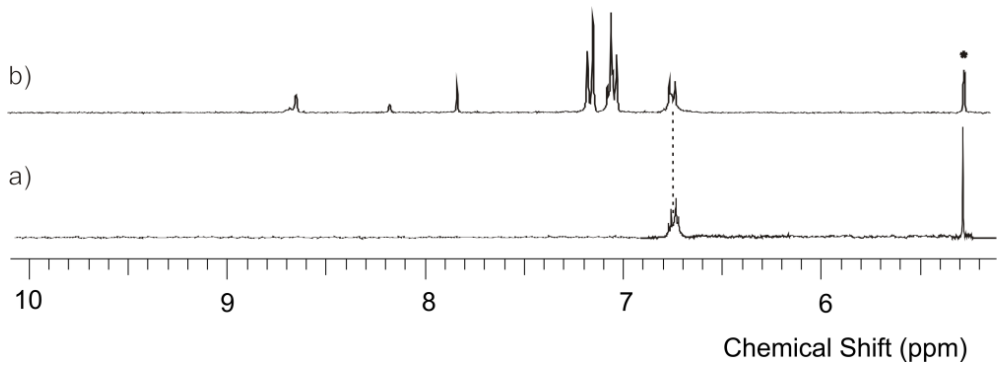


Figure SI 9. ^{1}H NMR spectra of (a) Macrocycle **4a** and (b) 1:1 macrocycle **4a** / axle (1:1 CD_2Cl_2 / CD_3OD, 300 MHz). * residual CD_2Cl_2 signal. No perturbations of the macrocycle hydroquinone protons (δ = 6.75 ppm) indicates that upon addition of the axle to a solution of macrocycle **4a,** no interpenetration of the axle component occurs, due to the large size of the stopper components.

Part IV: Luminescence studies

General Procedures

All luminescence spectra and lifetimes were obtained using a Horiba Fluorolog 3.

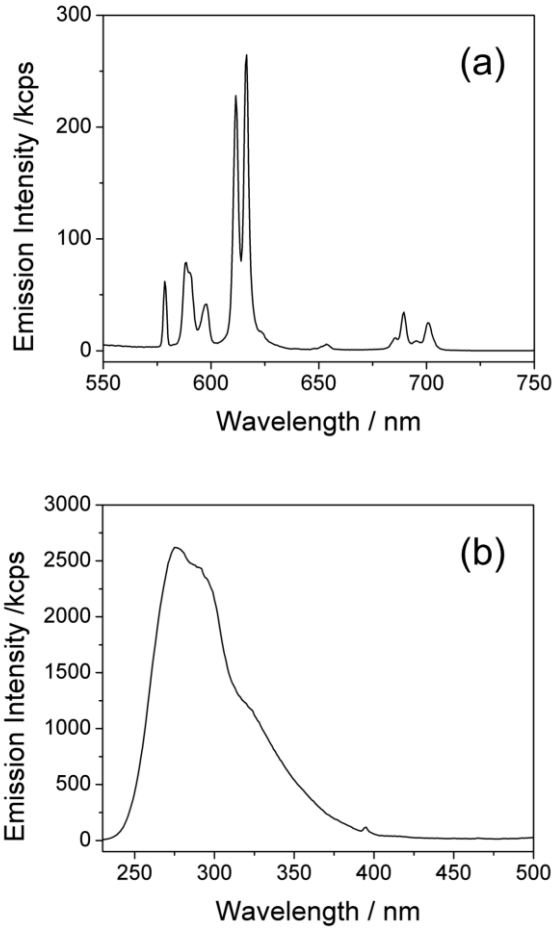


Figure SI 10. (a) Emission spectrum (λ_{ex} = 270 nm, excitation slit = 14 nm, emission slit = 1 nm), and (b) excitation spectrum (λ_{em} = 618 nm, excitation slit = 2 nm, emission slit = 5 nm) of europium-containing rotaxane **8b** recorded in fluorescence mode (1:1 CH_2Cl_2:CH_3OH).

Lifetimes

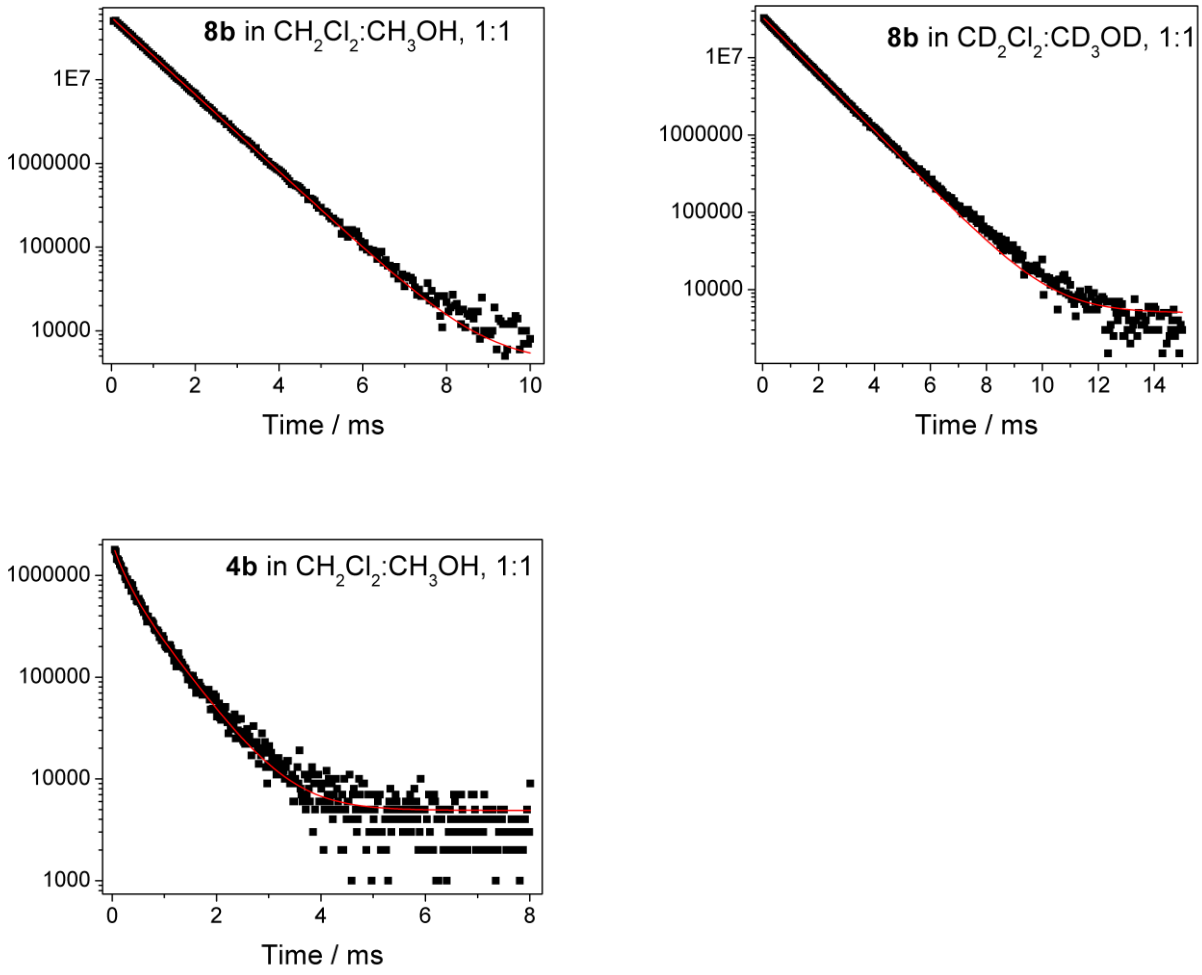


Figure SI 11. Lifetime data and fits (red lines) for rotaxane **8b** and macrocycle **4b** in the specified solvent mixtures, exciting at 397 nm and observing at 616 nm.

References

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3. V. Ancagne, K. D. Hanni, D. A. Leigh, P. J. Lurby, D. B. Walker, *J. Am. Chem. Soc*., **2006**, *128*, 2186-2187.