

Iron(II) complexes utilising terpyridine containing [2]rotaxanes as ligands

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A terpyridine chelating group is incorporated into a cationic (dipyridinium)ethane axle and self-assembly synthesis used to create three [2]rotaxanes utilising 24-membered crown ether wheels: 24-crown-8, dibenzo-24-crown-8 and dinaphtho-24-crown-8 ether. The resulting [2]rotaxanes are characterised by ^1H NMR spectroscopy, X-ray crystallography and mass spectrometry. The ability of these rotaxanes to act as ligands is demonstrated by the formation of bis(terpy) chelate complexes of Fe(II). The effect of using a rotaxane as a ligand is probed by UV-vis absorption spectroscopy of the Fe(II) complexes.

Introduction

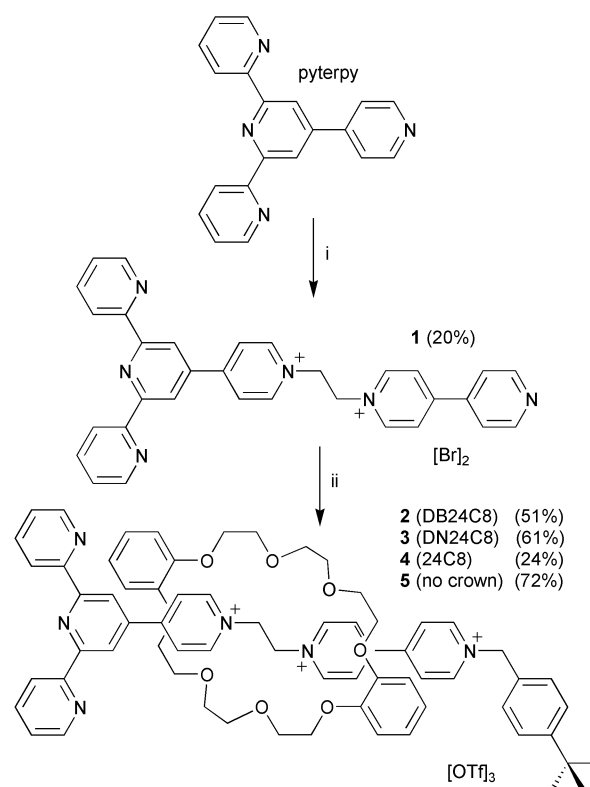
The investigation of mechanically linked molecules as prototypical molecular machines has resulted in the synthesis of a variety of interlocked systems;^{1–18} in particular [2]rotaxanes.¹⁹ One of the most common reasons for incorporating a metal ion has been as a stopper to trap the wheel on the axle.^{20–23} An example of an exception is the inclusion of $[\text{Ru}(\text{bipy})_3]^{2+}$ units for powering light driven molecular shuttles.²⁴ One of the shortcomings of any self-assembly strategy for metal ion incorporation is that formation of the metal ligand bonds must be compatible with maintaining the weaker non-covalent interactions between axle and wheel (ion-dipole, H-bonding and π -stacking). A way to circumvent this problem would be to incorporate a good chelating ligand as a permanent stopper allowing for *post*-rotaxane addition of a metal centre. In such situations, once formed, the rotaxane could be treated like any other ligand and subjected to reaction conditions not normally compatible with [2]pseudorotaxane formation. We describe herein the synthesis and characterisation of terpyridine capped [2]rotaxanes and their utilisation as ligands for the formation of Fe(II) complexes.

Results and discussion

The ligand 4'-(4''-pyridyl)-2,2':6',2''-terpyridine (pyterpy) was chosen as the source of a terpy unit for eventual inclusion into a rotaxane axle. The synthesis of pyterpy proceeded smoothly *via* the condensation of 2-acetylpyridine with 4-pyridinecarboxaldehyde in the presence of base to form the corresponding 1,5-diketone. Subsequent ring closure of the 1,5-diketone *in situ* with NH_4OAc produced the desired compound as previously reported.²⁵ *N*-alkylation of the 4-pyridyl group with 1-bromo-2-(4,4'-dipyridinium)ethane bromide, in MeCN over seven days, produced compound **1** in relatively low yield, but high purity, as the dibromide salt. The ^1H NMR spectrum of **1** in D_2O showed the expected resonances; in particular those for the new dipyridiniumethane link, H_n and H_i , were a clearly distinguishable multiplet at 5.47 ppm.

Treatment of the bromide salt of **1** with excess crown ether in a two-phase $\text{MeNO}_2/\text{NaOTf}(\text{aq})$ mixture at room temperature resulted in a pale yellow to orange MeNO_2 layer indicative of [2]pseudorotaxane $[\text{1C}(\text{crown})]^{2+}$ formation. This mixture was then reacted with 4-*t*-butylbenzylbromide to produce the [2]rotaxanes **2–4** as the OTf salts in moderate to good yield; see Scheme 1.

The ^1H NMR spectra in MeCN-d_3 revealed shifts to higher frequency for H_n and H_i of the axle due to hydrogen bonding with the mechanically linked crown ether component (see Fig. 1



Scheme 1 (i) 0.35 equivalents of 1-bromo-2-(4,4'-dipyridinium)ethane bromide in MeCN at reflux for 7 days, (ii) 6 equivalents of crown ether in $\text{MeNO}_2/\text{NaOTf}(\text{aq})$ at room temperature for 72 h.

for the labelling scheme). The presence of a singlet at ~ 5.8 ppm for H_n also indicated alkylation of the terminal nitrogen had occurred and this was further confirmed by a shift to higher frequency for H_m . The naked axle **5** was also prepared with this method by eliminating the crown ether from the reaction.

In addition to resonances which are diagnostic of the capping process and rotaxane formation in general, the ^1H NMR spectra of compounds **2–5** exhibit some interesting trends that result from the interaction of the two mechanically linked components. Firstly, shifts of 0.14–0.41 ppm to higher frequency of H_n and H_i for rotaxanes **2–4** compared to axle **5**, are attributable to $\text{C-H}\cdots\text{O}$ interactions between these protons and the oxygens of the crown ether. Secondly, the presence of two separate resonances for H_i and H_n at 6.68 and 6.54 ppm, compared to 6.93 ppm for free DB24C8, are indicative of π -stacking between pairs of electron-poor pyridinium and electron-rich crown aromatic rings. The three aromatic

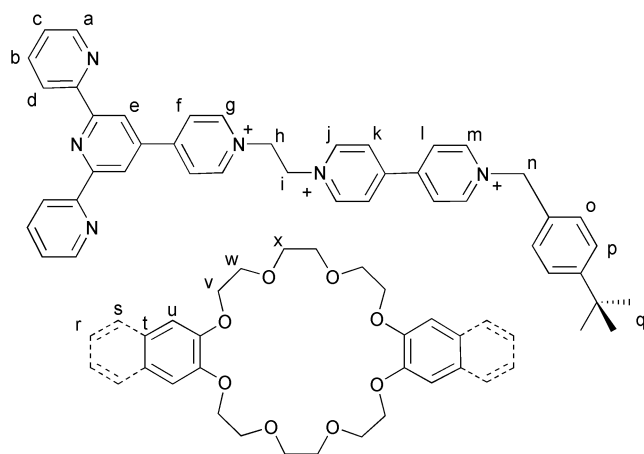


Fig. 1 The basic labelling scheme used for all NMR spectral data is shown for the terpyridine based axle and the three crown ethers used, 24-crown-8 (24C8), dibenzo-24-crown-8 (DB24C8) and dinaphtho-24-crown-8 ether (DN24C8).

resonances for **3** at 7.22, 6.97 and 6.72 ppm for H_s , H_u and H_r , respectively, are also shifted to lower frequency relative to free DN24C8; 7.64, 7.04 and 7.35 ppm. Thirdly, the shift to lower frequency of H_e on increasing the size of the aromatic ring of the crown ether from DB24C8 (0.22 ppm) to DN24C8 (0.40 ppm) can be taken as a measure of the increased efficiency of the larger naphthyl ring to engage in π -stacking.

Single crystals of **3** suitable for X-ray analysis were grown by slow diffusion of isopropyl ether into an MeCN solution of the compound. Fig. 2 shows a ball-and-stick representation of the structure of the cationic portion of **3**. The terpy capped dipyrindiniummethane thread adopts an *anti* conformation at the central NCH_2CH_2N unit²⁶ while the DN24C8 wheel exhibits a typical S-shaped conformation.²⁷ The cationic axle interpenetrates the central cavity of the wheel and the aromatic rings of the crown π -stack over the pyridinium rings. The terpy portion of the axle is essentially planar and exhibits an all *transoid* disposition for the three pyridine ring nitrogen atoms.^{28–29}

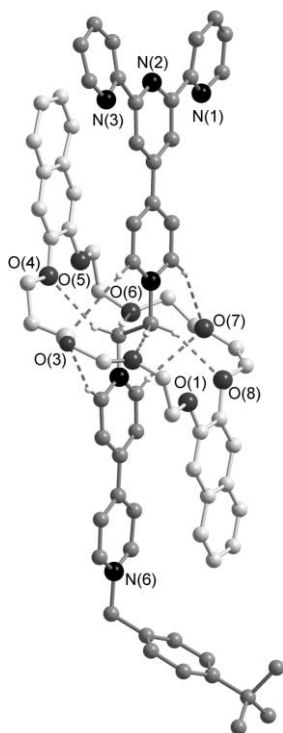


Fig. 2 A ball-and-stick representation of the X-ray structure of **3**⁺ showing the basic labelling scheme and hydrogen bond network. The pyridinium axle is shown with darker shaded bonds and the crown ether wheel with lighter shaded bonds.

These structural details are consistent with the solution NMR data and have been observed in related compounds.^{20,30} Fig. 3 shows a space-filling model which emphasises how the axle and wheel components interact. Alternating electron-rich and electron-poor aromatic rings in the [2]rotaxanes stack side-by-side in layers in the solid state.

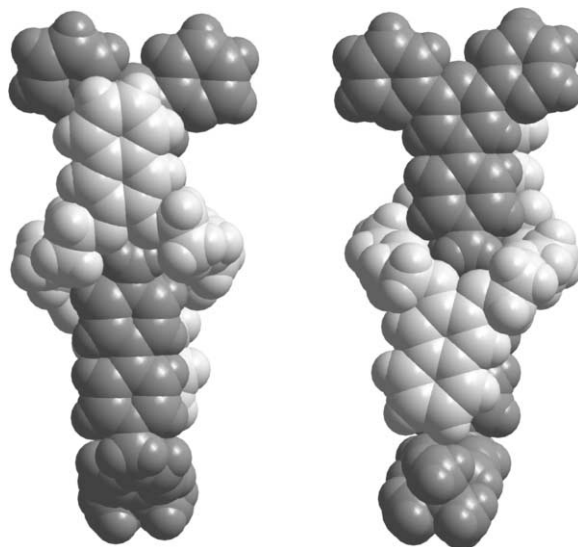


Fig. 3 Space-filling models of the X-ray structure of **3**⁺ showing the relative orientations of the terpy based axle (dark gray) and DN24C8 wheel (light gray). The two views are of opposite faces of the [2]rotaxane ligand.

The [2]rotaxanes **2** and **3** are an orange-red colour in the solid state and solutions in MeCN are orange. The UV-vis absorption spectra of these compounds show absorption shoulders at 397 and 401 nm respectively, as a result of charge transfer (CT) interactions between the electron-rich aromatic rings of the crown ether wheel and the electron-deficient axle. This interaction provides a low energy π^* orbital and results in CT transitions being observed in the visible region.

The synthesis of [2]rotaxanes using a bulky *tert*-butyl unit in conjunction with a terpyridyl group as stoppers provides a stable interlocked molecule suitable as a ligand for complexation to transition metals in a wide variety of competitive solvent systems.³¹ To initially investigate the coordination ability of these unique ligands, we prepared homoleptic iron(II)-terpyridine complexes. The expectation was that these complexes would contain a 2 : 1 ligand to metal ratio and exhibit diamagnetic features characteristic of d^6 low spin system.

For ligands **2–5**, the homoleptic Fe(II) complexes were synthesised with relative ease. Unfortunately, due to the lability of such Fe(II) complexes, heteroleptic versions employing these ligands could not be prepared. As outlined in Scheme 2, two equivalents of the rotaxane ligand in an MeCN/MeOH solution were added to one equivalent of $[Fe(H_2O)_6][BF_4]_2$; a dark blue colour instantly developed. Purification by column chromatography yielded the complexes **6–9** with formula $[Fe(L)_2][OTf]_2$ ($L = 2–5$) in excellent yields.

The ¹H NMR spectra of **6–9** show characteristic shifts attributable to the coordination of a terpyridine ligand to Fe(II). In order to chelate to the iron atom, the terpy ligand must rotate the two 2-pyridyl units from the *transoid* conformation seen in the crystal structure of **3**, to the *cisoid* conformation. Chemical shift changes for proton resonances $H_a–H_d$ are attributed to the electronic effects of metal ligation and this change in conformation. In particular, the shift to a lower frequency of H_a from 8.79 ppm for the uncomplexed rotaxane to 7.20 ppm for the complexed rotaxane is characteristic of terpy coordination. These diagnostic shifts are clearly observed in Fig. 4 which shows the NMR spectra of naked axle **5**, rotaxane **3** and Fe

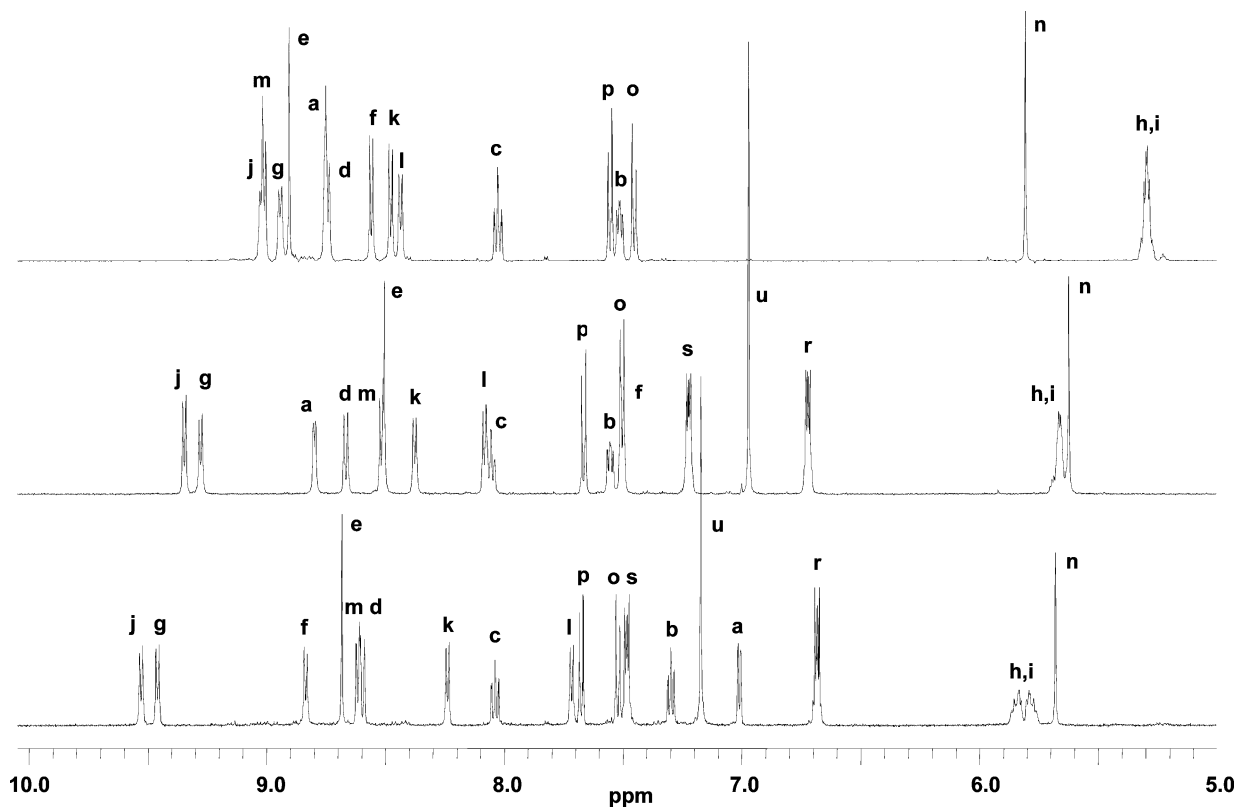
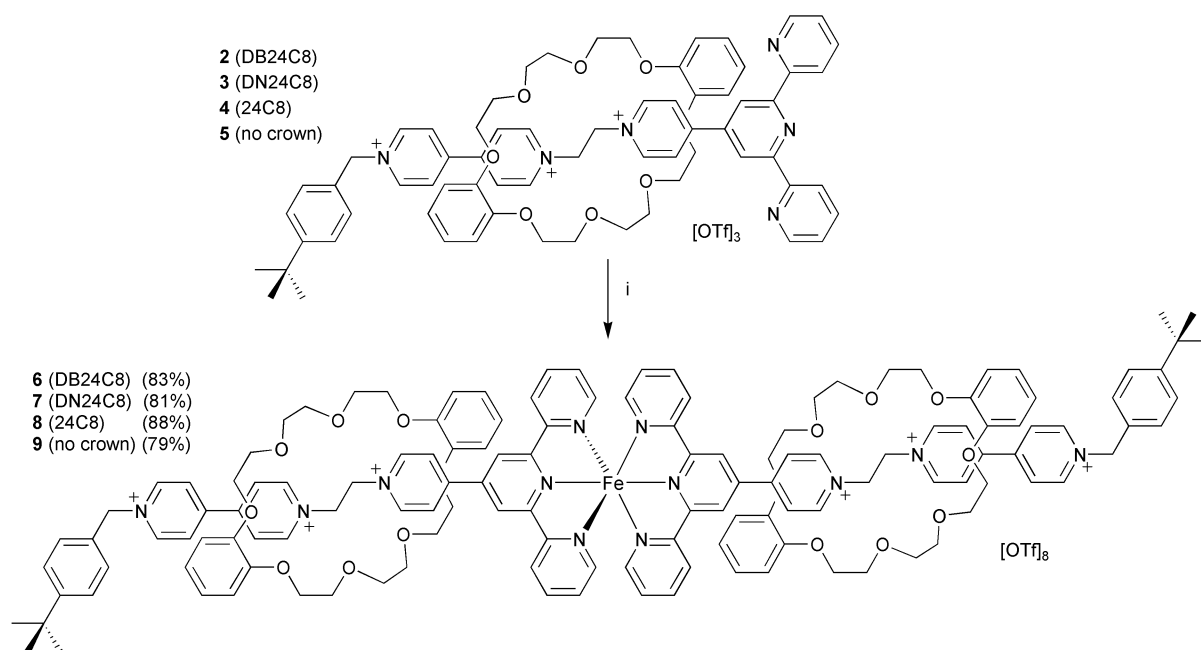


Fig. 4 NMR spectra in MeCN- d_3 of, from top to bottom, naked axle 5, rotaxane 3 and Fe complex 7.

complex 7 allowing sequential comparison of rotaxane formation and subsequent coordination of Fe(II).

Previously, Constable *et al.* have shown that the addition of electron withdrawing and/or electron donating substituents to the back of a terpyridine based ligands, coordinated to Ru(II), lowered the energy of the LUMO (π^* of the ligand) resulting in a red shift of the MLCT band as compared to the parent complex, $\text{Ru}(\text{terpy})_2^{2+}$. Similarly, Constable *et al.* have also shown that *N*-alkylation of pyterpy complexed to Fe(II) also resulted in a red shift of ~ 25 nm, as compared to $[\text{Fe}(\text{terpy})_2]^{2+}$.^{25,32–34} Similar trends were observed for compounds 6–9. Fig. 5 shows that 6 undergoes a red shift when compared to $[\text{Fe}(\text{terpy})_2]^{2+}$ and the $[\text{Fe}(\text{pyterpy})_2]^{2+}$. This shift to lower energy can once

again be attributed to the lowering of the ligand based π^* orbital upon alkylation. Interestingly, the λ_{max} of 8 and 9 are indistinguishable at 603 nm, as the hydrogen bonding within 8 is not expected to affect the MLCT. However, the introduction of a dibenzo-24-crown-8 ether to the iron(II) complex, 6, produces a λ_{max} of 604 nm as a result of alkylation and the addition of stabilisation due to π -stacking. Finally, the λ_{max} of 7 at 606 nm is a result of the two naphthalene fragments causing the further stabilisation of the MLCT as seen by the shift to higher wavelength. Within this new series of rotaxane iron(II) complexes, a very slight but reproducible shift in the λ_{max} can be viewed as fine tuning the MLCT by the addition of a stabilising influence within the rotaxane component.

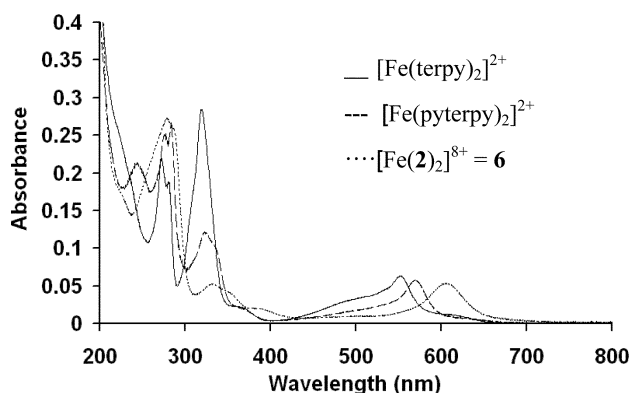


Fig. 5 UV-visible absorption spectra for $[\text{Fe}(\text{terpy})_2]^{2+}$ type complexes.

Conclusions

The idea of creating an interlocked molecule with a chelating group as an integral part of the axle was realized by incorporating a pyterpy group into a dipyrindiniumethane axle and forming [2]rotaxanes with 24-membered crown ethers. It was demonstrated that these ligands can be used as simple terpy chelators to form octahedral bis-ligand Fe(II) complexes. Preliminary results show that varying one of the interlocked components, in our case the crown ether wheel, might be a viable method to fine tune the physical and/or optical properties of the parent complex.

Experimental

General methods

Chemicals were obtained from Aldrich and used as received. Acetonitrile was dried using Innovative Technologies Solvent Purification Systems. 1-bromo-2-(4,4'-dipyridinium)ethane bromide,³⁵ 4'-(4''-pyridyl)-2,2':6',2''-terpyridine,²⁵ 24-crown-8^{36,37} and dinaphtho-24-crown-8^{36,37} were synthesized using literature methods. Thin layer chromatography (TLC) were done on Merck Silica gel 60 F₂₅₄ plates and viewed under UV light. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230–400 mesh). ¹H NMR spectra were obtained on a Bruker Avance 500 instrument operating at 500.1 MHz (using the deuterated solvent as the lock and the residual solvent or tetramethylsilane as the internal reference). Conventional 2-D NMR (¹H-¹H COSY and NOESY) were used to assign all peaks. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. High-resolution mass spectra were recorded in 50/50 MeCN/H₂O on a Micromass LCT Electrospray TOF mass spectrometer. UV-vis absorption spectra were run on an Agilent 8453E spectrometer. The absorption spectra were recorded in acetonitrile (EM Science OmniSolv[®] High Purity Solvent) at concentrations of 2.0×10^{-3} for compounds 2–5 and 2.0×10^{-6} for compounds 6–9 and all other related Fe(II) complexes.

1[Br]₂: to a solution of 1-bromo-2-(4,4'-dipyridinium)ethane[BF₄]⁻ (2.0 g, 5.7 mmol) dissolved in 500 mL of dry MeCN was added 4'-(4''-pyridyl)-2,2':6',2''-terpyridine (7.0 g, 22.5 mmol). The resulting mixture was refluxed for 168 h, allowed to cool to room temperature and the precipitated solid collected by suction filtration. The solid was washed with 75 mL of CHCl₃ to remove any excess terpyridine. The resulting solid was then recrystallised from H₂O as an off-white powder (0.748 g, 20%). δ_{H} (500 MHz; solvent D₂O) 9.05 (d, 2H, 6.5 Hz H_g), 9.03 (d, 2H, 6.6 Hz, H_i), 8.77 (d, 2H, 6.5 Hz, H_m), 8.60 (d, 2H, 4.7 Hz, H_a), 8.55 (m, 4H, H_e and H_p), 8.50 (d, 2H, 6.5 Hz, H_j), 8.37 (d, 2H, 7.8 Hz, H_d), 8.04 (ddd, 2H, 7.6 Hz, H_l), 7.92 (d, 2H, 6.6 Hz, H_k), 7.56 (ddd, 2H, 5.8 Hz, H_b), 5.47 (m, 4H, H_n and H_q). HRESI, *m/z*: calc. for C₃₂H₂₆N₆F₄B [M-BF₄]⁺, 581.2248; found, 581.2236.

General synthesis of [2]rotaxanes

2[OTf]₃: to a solution of MeNO₂ layered with an aqueous solution of NaOTf was added 1[Br]₂ (0.150 g, 0.23 mmol) and dibenzo-24-crown-8 ether (0.614 g, 1.37 mmol). The resulting pseudorotaxane was observed in the MeNO₂ layer and stirred for a further 10 min to allow equilibrium to be reached. To this mixture, was added 4-*tert*-butylbenzylbromide (0.057 g, 0.25 mmol) and stirring continued for 48 h at room temperature. Subsequently, the MeNO₂ layer was removed and washed with 3 portions of H₂O, dried and concentrated to 10 mL. The addition of 50 mL of diethyl ether induced precipitation of the triflate salt which was collected by vacuum filtration as an orange solid (0.181 g, 51%). δ_{H} (500 MHz, CD₃CN): 9.41 (d, 2H, 6.5 Hz, H_j), 9.35 (d, 2H, 6.5 Hz, H_g), 8.98 (d, 2H, 6.7 Hz, H_m), 8.79 (d, 2H, 4.2 Hz, H_a), 8.72 (d, 2H, 7.9 Hz, H_d), 8.68 (s, 2H, H_e), 8.59 (m, 4H, H_k and H_i), 8.23 (d, 2H, 6.5 Hz, H_p), 7.98 (ddd, 2H, 6.2 Hz, H_c), 7.56 (d, 2H, 8.4 Hz, H_p), 7.46 (m, 4H, H_o and H_b), 6.68 (m, 4H, H_l), 6.54 (m, 4H, H_u), 5.81 (s, 2H, H_n), 5.68 (s, 4H, H_h and H_i), 4.00–4.18 (m, 24H, H_v, H_w and H_x), 1.34 (s, 9H, H_q). UV-vis (MeCN), $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 234 (1.5×10^3), 339 (4.5×10^3), 397 (8.5×10^2). HRESI, *m/z*: calc. for C₆₉H₇₃N₆O₁₄F₆S₂ [M-OTf]⁺, 1387.4530; found, 1387.4513.

3[OTf]₃: 61%; δ_{H} (500 MHz, CD₃CN): 9.34 (d, 2H, 6.7 Hz, H_j), 9.27 (d, 2H, 6.7 Hz, H_g), 8.79 (d, 2H, 4.4 Hz, H_a), 8.66 (d, 2H, 7.9 Hz, H_d), 8.50 (m, 4H, H_m and H_e), 8.37 (d, 2H, 6.7 Hz, H_k), 8.08 (d, 2H, 6.8 Hz, H_i), 8.05 (ddd, 2H, 6.6 Hz, H_c), 7.66 (d, 2H, 8.4 Hz, H_p), 7.55 (ddd, 2H, 6.9 Hz, H_b), 7.54 (m, 4H, H_o and H_r), 7.22 (m, 4H, H_s), 6.97 (s, 4H, H_u), 6.72 (m, 4H, H_v), 5.68 (m, 4H, H_h and H_i), 5.62 (s, 2H, H_n), 4.30–4.05 (m, 24H, H_w, H_x and H_y), 1.37 (s, 9H, H_q); UV-vis (MeCN), $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 233 (20.0×10^3), 336 (4.2×10^3), 401 (1.0×10^3). HRESI, *m/z*: calc. for C₇₇H₇₇N₆O₁₄F₆S₂ [M-OTf]⁺, 1487.4843; found, 1487.4805.

4[OTf]₃: 24%; δ_{H} (500 MHz, CD₃CN): 9.37 (d, 6.7 Hz, 2H, H_j), 9.25 (d, 2H, 6.5 Hz, H_m), 9.06 (d, 2H, 6.7 Hz, H_g), 8.99 (s, 2H, H_e), 8.80 (m, 4H, H_a and H_d), 8.52 (d, 2H, 6.7 Hz, H_p), 8.49 (d, 2H, 6.7 Hz, H_k), 8.45 (d, 2H, 6.5 Hz, H_i), 8.10 (m, 2H, H_c), 7.57 (m, 4H, H_b and H_r), 7.45 (d, 2H, 8.3 Hz, H_o), 5.84 (s, 2H, H_n), 5.45 (m, 4H, H_h and H_i), 3.70 (s, 32H, H_v), 1.36 (s, 9H, H_q); UV-vis (MeCN), $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 236 (7.4×10^3), 339 (4.2×10^3). HRESI, *m/z*: calc. for C₆₁H₇₃N₆O₁₄F₆S₂ [M-OTf]⁺, 1291.4530; found, 1291.4474.

5[OTf]₃: 72%; prepared similarly to that described above but in the absence of crown ether. The compound was isolated as an off-white powder. δ_{H} (500 MHz, CD₃CN): 9.03 (d, 2H, 6.9 Hz, H_j), 9.01 (d, 2H, 6.9 Hz, H_m), 8.95 (d, 2H, 6.7 Hz, H_g), 8.90 (s, 2H, H_e), 8.75 (m, 4H, H_a and H_d), 8.55 (d, 2H, 6.7 Hz, H_p), 8.48 (d, 2H, 6.9 Hz, H_k), 8.46 (d, 2H, 6.9 Hz, H_i), 8.02 (ddd, 2H, 7.7 Hz, H_c), 7.54 (d, 2H, 8.4 Hz, H_p), 7.52 (ddd, 2H, 7.2 Hz, H_b), 7.45 (d, 2H, 8.4 Hz, H_o), 5.80 (s, 2H, H_n), 5.27 (m, 4H, H_h and H_i), 1.36 (s, 9H, H_q); UV-vis (MeCN), $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 341 (8.0×10^5). Anal. Found: C, 50.28; H, 3.72; N, 7.54%. C₄₆H₄₁F₉N₆O₉S₃ requires C, 50.73; H, 3.79; N, 7.72%. HRESI, *m/z*: calc. for C₄₅H₄₁N₆O₆F₆S₂ [M-OTf]⁺, 939.2433; found, 939.2473.

General preparation of iron(II) complexes

6[OTf]₈: to a solution of 2[OTf]₃ (0.080 g, 0.05 mmol) dissolved in 1 : 1 MeOH/MeCN solution was added solid Fe(H₂O)₆[BF₄]₂ (0.0087 g, 0.025 mmol) and the mixture was stirred at room temperature for 2 h to give a deep blue solution. The solvent was removed and the resulting solid was purified by column chromatography (6 : 2 : 2-MeOH/2MNH₄Cl/MeNO₂). The fractions containing the product were evaporated under reduced pressure and redissolved in H₂O. Following salt metathesis with NaOTf and collection by vacuum filtration the compound was isolated as a deep blue solid (0.074 g, 83%). δ_{H} (500 MHz, CD₃CN): 9.48 (d, 2H, 6.7 Hz, H_j), 9.42 (d, 2H,

6.6 Hz, H_j), 9.22 (s, 2H, H_c), 8.99 (d, 2H, 6.7 Hz, H_i), 8.90 (d, 2H, 6.7 Hz, H_m), 8.87 (d, 2H, 8 Hz, H_d), 8.24 (d, 2H, 6.6 Hz, H_k), 8.17 (d, 2H, 6.7 Hz, H_i), 8.02 (ddd, 2H, 6.8 Hz, H_c), 7.61 (d, 2H, 8.4 Hz, H_p), 7.50 (d, 2H, 8.4 Hz, H_o), 7.19 (ddd, 2H, 7.0 Hz, H_b), 7.20 (d, 2H, 5.2 Hz, H_a), 6.82 (m, 2H, H_i), 6.52 (m, 2H, H_u), 5.83 (s, 2H, H_n), 5.73 (m, 4H, H_h and H_j), 4.19–4.09 (m, 24H, H_v, H_w and H_x), 1.35 (s, 9H, H_q); UV-vis (MeCN), λ_{\max}/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 277 (13.5×10^4), 328 (2.5×10^4), 604 (2.6×10^4). HRESI, m/z : calc. for C₇₁H₇₃N₆O₂₀F₁₂S₄Fe [M-2-OTf]⁺, 1741.2920; found, 1741.2882.

⁷[OTf]₈: 81%; δ_{H} (500 MHz, CD₃CN): 9.53 (d, 2H, 6.7 Hz, H_g), 9.45 (d, 2H, 6.6 Hz, H_j), 8.83 (d, 2H, 6.7 Hz, H_i), 8.68 (s, 2H, H_c), 8.60 (m, 4H, H_d and H_m), 8.24 (d, 2H, 6.6 Hz, H_k), 8.03 (ddd, 2H, 7.6 Hz, H_c), 7.71 (d, 2H, 6.7 Hz, H_i), 7.67 (d, 2H, 8.4 Hz, H_p), 7.55 (d, 2H, 8.4 Hz, H_o), 7.48 (m, 4H, H_s), 7.28 (ddd, 2H, 6.1 Hz, H_b), 7.17 (s, 4H, H_u), 7.01 (d, 2H, 5.5 Hz, H_a), 6.68 (m, 4H, H_i), 5.81 (m, 4H, H_h and H_j), 5.67 (s, 2H, H_n), 4.34–4.20 (m, 24H, H_v, H_w and H_x), 1.39 (s, 9H, H_q); UV-vis (MeCN), λ_{\max}/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 230 (28.7×10^4), 322 (3.3×10^4), 606 (3.3×10^4). HRESI, m/z : calc. for C₇₉H₇₇N₆O₂₀F₁₂S₄Fe [M-3-OTf]⁺, 1841.3233; found, 1841.3170.

⁸[OTf]₈: 88%; δ_{H} (500 MHz, CD₃CN): 9.56 (s, 2H, H_c), 9.48 (d, 2H, 6.4 Hz, H_g), 9.41 (d, 2H, 6.4 Hz, H_j), 9.21 (d, 2H, 6.4 Hz, H_i), 9.09 (d, 2H, 6.5 Hz, H_m), 8.86 (d, 2H, 8 Hz, H_d), 8.63 (d, 2H, 6.4 Hz, H_k), 8.55 (s, 2H, 6.5 Hz, H_i), 7.99 (ddd, 2H, 7.6 Hz, H_c), 7.58 (d, 2H, 8.4 Hz, H_p), 7.50 (d, 2H, 8.4 Hz, H_o), 7.28 (d, 2H, 5.4 Hz, H_a), 7.17 (ddd, 2H, 6.6 Hz, H_b), 5.85 (s, 2H, H_n), 5.57 (m, 4H, H_h and H_j), 3.61 (s, 32H, H_v), 1.34 (s, 9H, H_q); UV-vis (MeCN), λ_{\max}/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 278 (19.7×10^4), 348 (2.0×10^4), 603 (1.9×10^4). HRESI, m/z : calc. for C₆₃H₇₃N₆O₂₀F₁₂S₄Fe [M-4-OTf]⁺, 1645.2920; found, 1645.2844.

⁹[OTf]₈: 79%; δ_{H} (500 MHz, CD₃CN): 9.46 (s, 2H, H_c), 9.20 (d, 2H, 6.7 Hz, H_g), 9.14 (d, 2H, 6.9 Hz, H_j), 9.05 (m, 4H, H_i and H_m), 8.75 (d, 2H, 8 Hz, H_d), 8.59 (d, 2H, 6.9 Hz, H_k), 8.52 (d, 2H, 6.8 Hz, H_i), 7.95 (ddd, 2H, 7.7 Hz, H_c), 7.55 (d, 2H, 8.4 Hz, H_p), 7.46 (d, 2H, 8.4 Hz, H_o), 7.22 (d, 2H, 5.3 Hz, H_a), 7.13 (d, 2H, 6.1 Hz, H_b), 5.84 (s, 2H, H_n), 5.42 (m, 4H, H_h and H_j), 1.31 (s, 9H, H_q); UV-vis (MeCN), λ_{\max}/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 279 (9.3×10^4), 333 (2.8×10^4), 603 (2.4×10^4). HRESI, m/z : calc. for C₄₇H₄₁N₆O₁₂F₁₂S₄Fe [M-5-OTf]⁺, 1293.0823; found, 1293.0876.

X-ray crystallography

Single crystals of **3** suitable for X-ray analysis were grown by slow diffusion of isopropyl ether into an MeCN solution of the compound. Crystals were mounted in a cryoloop with paratone oil. Data were collected on a Bruker APEX CCD single crystal diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Although the data was not of particularly good quality, a satisfactory structural solution was possible with some restraints as outlined. Crystal data: C₇₇H₇₇ClF₆N₆O_{15.5}S₂, $M = 1548.02$, monoclinic, $P2_1/c$ (no. 14), $a = 27.432(4)$, $b = 19.886(3)$, $c = 14.4704(19) \text{ \AA}$, $\beta = 100.981(18)^\circ$, $V = 7749.3(18) \text{ \AA}^3$, $Z = 4$, $D_c = 1.327 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.186 \text{ mm}^{-1}$, $T = 173.0(1) \text{ K}$, yellow plates; 6076 independent measured reflections, F^2 refinement, $R_1 = 0.1096$, $wR_2 = 0.3278$, goodness-of-fit = 0.913, 976 parameters, 68 restraints.

CCDC reference number 215956.

See <http://www.rsc.org/suppdata/dt/b3/b308553h/> for crystallographic data in CIF or other electronic format.

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