Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information for:

Complexes of a [2]rotaxane ligand with terminal terpyridine groups

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Experimental

General Methods

4-Tolualdehyde, 2-acetylpyridine, N-bromosuccinimide, 2,2´,6´,2´´-terpyridine (terpy), $RuCl_3.xH_2O$, and **DB24C8** were purchased from Aldrich and used as received. $[RuCl_3(terpy)]$,[1] and 1,2-bis(4,4'-bipyridinium)ethane triflate (**1**)[2] were synthesized using literature methods. Solvents were dried using an Innovative Technology Solvent Purification System. ^{1}H NMR spectra were obtained on a Bruker Avance 500 instrument operating at 500 MHz. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. High-resolution mass spectra were recorded in 50/50 $MeCN/H_2O$ on a Micromass LCT Electrospray TOF mass spectrometer. The UV/Vis absorption spectrum of $[Ru(terpy)_2(\mathbf{2}\subset\mathbf{DB24C8})]^{8+}$ was recorded on a Cary 50 spectrometer in acetonitrile (BDH®) at a concentration of 1.0×10^{-5} M.

1. B. P. Sullivan, J. M. Calvert, T. J. Meyer, *Inorg. Chem.* **1980**, *19*, 1404.
2. S. J. Loeb, J. Tiburcio, S. J. Vella and J. A. Wisner, *Org. Biomol. Chem.*, 2006, **4**, 667

Synthesis of 4´-(4-Tolyl)-2,2´,6´,2´´-terpyridine

4-Tolualdehyde (12.6 g, 12.4 mL, 0.105 mol) was dissolved in methanol (40 mL) and cooled to 0°C. To this was added 2-acetylpyridine (25.4 g, 23.5 mL, 0.209 mol) dissolved in methanol (20 mL) and 40% aqueous NaOH (30 mL). The mixture was stirred at -10 °C for 1 h, then allowed to warm to room temperature and stirred overnight. $[NH_4][CH_3CO_2]$ (40.0 g, 0.516 mol) was added to the reaction mixture which was then refluxed for 24 h. The reaction was cooled to room temperature and the methanol evaporated. The product was extracted with $CHCl_3$, and the $CHCl_3$ solution dried over anhydrous $MgSO_4$, filtered and evaporated. The residue was recrystallized from CH_3CN to give an off-white solid. Yield 0.xx g (33 %).

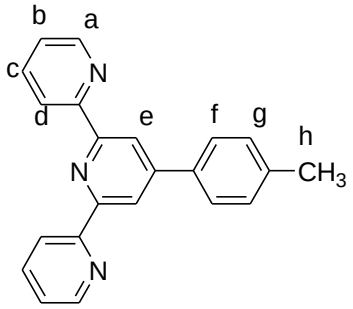

Table S1. ^{1}H NMR spectroscopic data for 4´-(4-tolyl)-2,2´,6´,2´´-terpyridine in CD_3CN.

Proton	δ (ppm)	Multiplicity	# protons	J (Hz)
a	8.73	d	2	5.75
b	7.44	ddd	2	5.75, 7.52, 0.79
c	7.96	ddd	2	7.82, 7.52,1.67
d	8.68	d	2	7.82
e	8.73	s	2	-
f	7.81	d	2	8.07
g	7.40	d	2	8.07
h	2.43	s	3	-

Synthesis of 4´-(4-Bromobenzyl)-2,2´,6´,2´´-terpyridine

4´-(4-Tolyl)-2,2´,6´,2´´-terpyridine (2.00 g, 6.20 mmol) was dissolved in CCl_4 (40 mL). To this solution was added N-bromosuccinimide (1.10 g, 6.20 mmol) and benzoyl peroxide (0.54 g, 2.20 mol). The solution was refluxed overnight and then cooled to room temperature. The reaction was filtered to remove succinamide and the CCl_4 layer washed with $NaHCO_3$(*aq*) (3 x 50 mL) then H_2O (2 x 50 mL), dried with anhydrous $MgSO_4$, filtered and the solution evaporated. The residue was recrystallized from 2:1 EtOH/acetone to give an off-white solid. Yield 0.xx g (35 %).

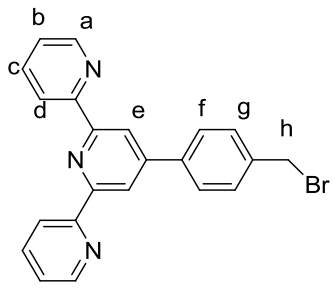

Table S2. ^{1}H NMR spectroscopic data for 4´-(4-bromobenzyl)-2,2´,6´,2´´-terpyridine in CD_3CN.

Proton	δ (ppm)	Multiplicity	# protons	J (Hz)
a	8.73	d	2	5.96
b	7.45	ddd	2	4.96, 7.41
c	7.97	ddd	2	7.41, 7.81, 1.62
d	8.69	d	2	7.81
e	8.75	s	2	-
f	7.90	d	2	8.20
g	7.63	d	2	8.20
h	4.69	s	2	-

Synthesis of 2[OTf]$_4$

1[OTf]$_2$ (0.100 g, 0.157 mmol) was dissolved in $MeNO_2$ (10 mL) and 4´-(4-bromobenzyl)-2,2´,6´,2´´-terpyridine (0.189 g, 0.470 mmol) added and the mixture allowed to heat at 60 °C for 3 days. The organic layer was removed and the orange solid dissolved in a two layer solution of $MeNO_2$ and NaOTf(*aq*) and stirred overnight. The colourless layer was separated, dried with anhydrous $MgSO_4$, filtered and the solvent removed by evaporation. The residue was stirred in $CHCl_3$. The resulting white solid was dissolved in CH_3CN, and *iso*-propyl ether allowed to slowly diffuse into the solution producing an off-white solid, yield 0.100g (31%).

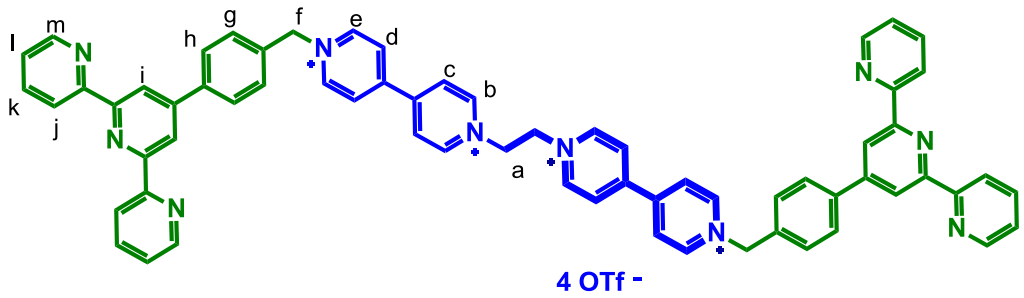

Table S3. ^{1}H NMR spectroscopic data for [**2**][OTf]$_4$ in CD_3CN

Proton	δ (ppm)	Multiplicity	# protons	J (Hz)
a	5.31	s	4	-
b	9.06	m	4	-
c	8.52	d	4	6.82
d	8.49	d	4	6.81
e	9.06	m	4	-
f	5.95	s	4	-
g	7.72	d	4	8.15
h	8.05	d	4	8.15
i	8.77	s	4	-
j	8.72	m	4	-
k	8.00	t	4	5.70, 7.66
l	7.48	t	4	4.79, 6.85
m	8.72	m	4	-

Synthesis of [2⊂DB24C8][OTf]$_4$

DB24C8 (0.702 g, 0.157 mmol) and **1**[OTf]$_2$ (0.100 g, 0.157 mmol) were dissolved in $MeNO_2$ (10 mL) and stirred overnight. 4´-(4-Bromobenzyl)-2,2´,6´,2´´-terpyridine (0.189 g, 0.470 mmol) were dissolved in $MeNO_2$ and the mixture stirred for 7 days. The organic layer was removed and the orange solid dissolved in a two layer solution of $MeNO_2$ and NaOTf(*aq*) which was stirred overnight. The organic layer was separated, dried with anhydrous $MgSO_4$ and the solvent removed by evaporation. The residue was then stirred in toluene. The resulting orange solid was dissolved in CH_3CN and *iso*-propyl ether allowed to slowly diffuse into the solution to produce an orange solid. Yield 0.100 g (31 %). **ESI-MS**: *m/z* [**2⊂DB24C8**]$^{2+}$ calc. 865.2752, found 865.2775.

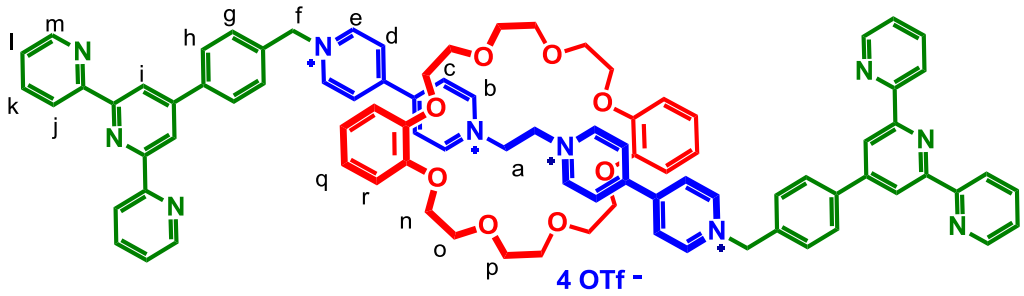

Table S4. ^{1}H NMR spectroscopic data for [**2⊂DB24C8**][OTf]$_4$ in CD_3CN.

Proton	δ (ppm)	Multiplicity	# protons	J (Hz)
a	5.60	s	4	-
b	9.31	d	4	6.61
c	8.19	d	4	6.62
d	8.15	d	4	6.63
e	9.01	d	4	6.64
f	5.95	s	4	-
g	8.08	d	4	8.16
h	7.75	d	4	8.14
i	8.79	s	4	-
j	8.72	m	4	-
k	7.99	t	4	6.83, 8.66
l	7.47	t	4	5.32, 6.67
m	8.72	m	4	-
q	6.66	m	4	-
r	6.48	m	4	-
n-p	4.00-4.04	m	24	-

Synthesis of [(Ru(terpy))$_2$(2⊂DB24C8)][OTf]$_8$

To a solution of [**2⊂DB24C8**][OTf]$_4$ (0.030 g, 0.0148 mmol) dissolved in 1:1 EtOH/H_2O solution was added solid [$RuCl_3$(terpy)] (0.013 g, 0.0246 mmol) and the mixture was brought to reflux for 24 h to give a deep red solution. The reaction mixture was cooled to room temperature, filtered through a Celite pad and then washed with EtOH until the eluent was colourless. The filtrate was then reduced to half the original volume and NaOTf added which produced a red precipitate. The red solid was dissolved in CH_3CN and *iso*-propyl ether slowly diffused to give a red solid in quantitative yield. **ESI-MS**: *m/z* [Ru(terpy)$_2$(**2⊂DB24C8**)]$^{3+}$ calc. 949.2006, found 949.2072. UV/Vis (MeCN): λ_{max}/nm (ε/L mol^{-1} cm^{-1}) 485 (11 896).

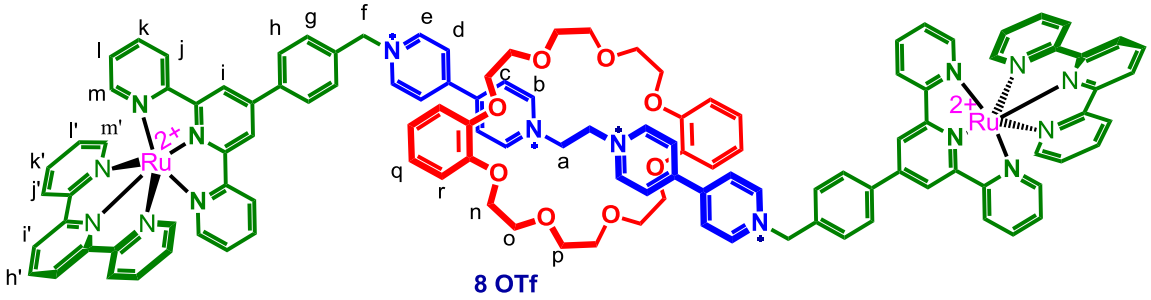

Table S5. ^{1}H NMR spectroscopic data for [(Ru(terpy))$_2$(**2⊂DB24C8**)][OTf]$_8$ in CD_3CN.

Proton	δ (ppm)	Multiplicity	# protons	J (Hz)
a	5.64	s	4	-
b	9.36	d	4	6.11
c	8.31	m	4	-
d	8.31	m	4	-
e	9.14	d	4	6.23
f	6.05	s	4	-
g	7.94	m	4	-
h	8.37	d	4	7.95
i	9.05	s	4	-
j	8.50	d	4	8.09
k	7.91	m	4	-
l	7.16	m	4	-
m	7.41	d	4	5.18
q	6.70	m	4	-
r	6.51	m	4	-
n-p	4.03-4.07	m	24	-
m'	7.35	d	4	5.34
l'	7.16	m	4	-
k'	7.91	m	4	-
j'	8.68	d	4	8.01
i'	8.76	d	4	8.14
h'	8.41	t	2	8.05, 8.23

Table S6. A comparison of the ^{1}H NMR chemical shifts for dumbbell $\mathbf{2}^{4+}$, [2]rotaxane ligand $[\mathbf{2}\subset\mathbf{DB24C8}]^{4+}$ and complex $[(Ru(terpy)_2)(\mathbf{2}\subset\mathbf{DB24C8})]^{8+}$.

protons	$[2]^{4+}$	$[2\subset DB24C8]^{4+}$	$[(Ru(terpy)_2)(2\subset DB24C8)]^{8+}$
a	5.31	5.60(+0.29)	5.64(+0.04)
b	9.06	9.31(+0.25)	9.36(+0.05)
c	8.52	8.19(-0.33)	8.31(+0.12)
d	8.49	8.15(-0.34)	8.31(+0.16)
e	9.06	9.01(-0.05)	9.14(+0.13)
f	5.95	5.95(0.00)	6.05(+0.10)
g	7.72	7.47(-0.25)	7.94(+0.47)
h	8.05	7.75(-0.30)	8.37(+0.62)
i	8.77	8.79(+0.02)	9.05(+0.26)
j	8.72	8.72(0.00)	8.50(-0.22)
k	8.00	7.99(-0.01)	7.91(-0.08)
l	7.48	8.08(+0.60)	7.16(-0.92)
m	8.72	8.72(0.00)	7.41(-1.31)

Synthesis of $[Zn(H_2O)_3(2\subset DB24C8)][OTf]_8$

To $[\mathbf{2}\subset\mathbf{DB24C8}][OTf]_4$ (0.030 g, 0.0148 mmol) dissolved in 1 mL of CH_3CN was added $[Zn(H_2O)_6][OTf]_2$ (11 mg, 0.0311 mmol) and the mixture stirred at room temperature for 12 h. To this orange solution was added *iso*-propyl ether by slow diffuse to give an orange solid in quantitative yield.

Single Crystal X-ray Diffraction

Crystals were frozen in paratone oil inside a cryoloop. Reflection data were integrated from frame data obtained from hemisphere scans on a Bruker APEX diffractometer using MoK_α radiation and a CCD detector. Decay was monitored using 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined using full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined using a riding model. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL program library[1] and figures drawn with DIAMOND software.[2]

Crystals of the Ru(II) complex had formula $[(Ru(terpy))_2(\mathbf{2}\subset\mathbf{DB24C8})][OTf]_6[Cl]_2.(MeNO_2)_4$ and were weakly diffracting. The unit cell contains an estimated 4 molecules of nitromethane which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[3] The cation has a crystallographic imposed centre of symmetry. Three of the four anions in the asymmetric unit were input as triflate ($CF_3SO_3^-$), the other as chloride (Cl^-). Two of the anion sites were disordered (50:50) between triflate and chloride ion. The source of chloride ions was presumed to be the eluent mixture used for column chromatography as one of the components was $NH_4Cl(aq)$. SADI, SIMU and DELU commands were used to restrain one of the triflate ions as a rigid group. SIMU and DELU commands were also used to restrain displacement parameters to be approximately equal for the disordered triflate and chloride anion pairs. Four ISOR commands were necessary to restrain F10 and F11 (triflate ion), N8 (terpyridine) and C46 (axle) to have approximate isotropic behaviour. AFIX 66 commands were used to restrain the three pyridine rings of the unsubstituted terpy ligand to be idealized hexagons with C-C and C-N bonds equal to 1.39 A.

Crystals of the Zn(II) complex were very weakly diffracting with essentially no diffraction at high angle. The crystals had formula $[(Zn(H_2O)_3)_2(\mathbf{2}\subset\mathbf{DB24C8})][(Zn(H_2O)(BF_4))_2(\mathbf{2}\subset\mathbf{DB24C8})][OTf]_7(MeNO_2)_3$. The source of BF_4^- anion is presumed to be an impurity in axle salt $\mathbf{1}[X]_2$ which was originally synthesized as X = BF_4^- but converted to X = $CF_3SO_3^-$ to match the Zn(II) anion; $CF_3SO_3^-$. SADI, SIMU and DELU commands were used to restrain all seven triflate ($CF_3SO_3^-$) ions and the single tetrafluoroborate (BF_4^-) ion as rigid groups. AFIX 66 commands were used to restrain all the aromatic rings in the complex to be idealized hexagons with C-C and C-N bonds equal to 1.39 A.

1. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
2. DIAMOND 3.2 - CRYSTAL IMPACT, Postfach 1251, D-53002, Bonn, Germany 2009.
3. PLATON/SQUEEZE, P. v. d. Sluis and A. L. Spek, *Acta Cryst.*, 1990, **A46**, 194.