Electronic Supplementary Information for:

Controlling the ON/OFF threading of a terpyridine containing [2]pseudorotaxane ligand via changes in coordination geometry

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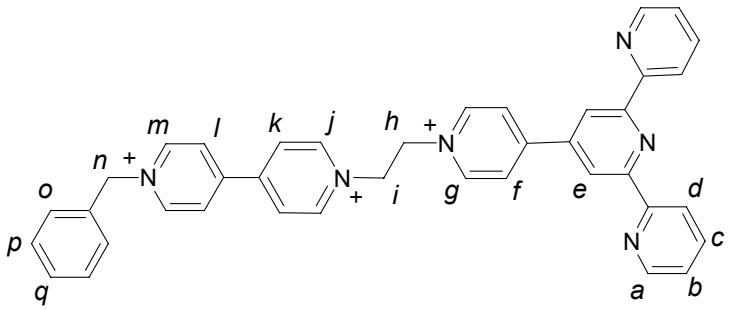
General Methods: Dibenzo-24-crown-8, was obtained from Aldrich and used as received. MeCN was dried using an Innovative Technologies Solvent Purification System. 1-Bromo-2-(4,4'-dipyridinium)ethane tetrafluorborate,[1] 4'-(4"-pyridyl)-2,2':6',2"-terpyridine,[2] 24-crown-8[3] and dinaphtho-24-crown-8[3] were synthesized using literature methods. Thin layer chromatography (TLC) was preformed on Merck Silica gel 60 F_{254} plates and viewed under UV light. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230 - 400 mesh). ^{1}H NMR spectra were obtained on a Bruker Avance 500 instrument operating at 500.1 MHz (using deuterated solvent as the lock and residual solvent or tetramethylsilane as the internal reference). Conventional 2-D NMR (^{1}H-^{1}H COSY and NOESY) were used to assign all peaks. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. Mass spectra were recorded in a 1:1 MeCN/H_2O solution on a Micromass LCT electrospray mass spectrometer.

Preparation of Ligand [1][BF_4]$_3$: One equivalent of 4-(4-pyridyl)-pyridinium-ethyl-4'-4(4-pyridinium)-2,2':6',2"-terpyridine tetrafluoroborate and five equivalents of benzylbromide were dissolved in MeCN and stirred at room temperature for 72 h. The solution was filtered and the solid washed with excess of $CHCl_3$ to remove any excess benzylbromide. The solid was combined with saturated aqueous $NaBF_4$ solution and stirred for 1 h and then filtered to yield [**1**][BF_4]$_3$ (20%). HR ESI-MS: m/*z* calculated for {[**1**][BF_4]}$^+$ 759.2825, found 759.2817. ^{1}H NMR (500 MHz, d^3-MeCN)

^{1}H NMR (500 MHz, d^3-MeCN)

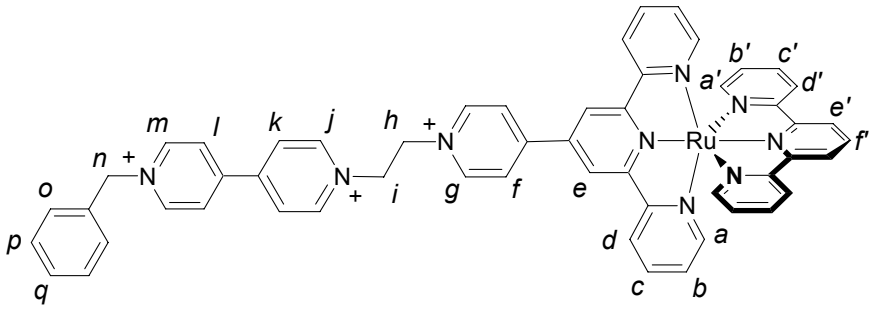
Proton	δ(ppm)	Multiplicity	# of Protons	Coupling Constant (Hz)
a	8.77	m	2	---
b	7.54	ddd	2	---
c	8.06	ddd	2	$^3J_{cb} \approx {}^3J_{cd} = 7.6$, $^4J_{ca} \approx 0$
d	8.77	m	2	$^3J_{dc} = 7.9$
e	8.92	s	2	---
f	8.58	d	2	$^3J_{fg} = 6.8$
g	8.83	d	2	$^3J_{gf} = 6.8$
h	5.26	m	2	---
i	5.26	m	2	---
j	9.01	d	2	$^3J_{jk} = 6.8$
k	8.42	d	2	$^3J_{kj} = 6.8$
l	8.47	d	2	$^3J_{lm} = 6.8$
m	8.91	d	2	$^3J_{ml} = 6.8$
n	5.85	s	2	---
o	7.54	s	2	---
p	7.54	s	2	---
q	7.54	s	1	---



Preparation of Complex [Ru(terpy)(1)][BF$_4$]$_5$: A solution of **1**[BF$_4$]$_3$ (0.052 g, 0.118 mmol) and (terpy)RuCl$_3$ (0.100 g, 0.118 mmol) were dissolved in 1:1 a EtOH/H$_2$O solution and refluxed for 12 h to give a deep red solution. The reaction mixture was cooled to room temperature and filtered through a Celite pad washing with EtOH until the eluent was colourless. The filtrate was then reduced to half the volume and the addition of NaBF$_4$ produced a red precipitate of [Ru(terpy)(**1**)][BF$_4$]$_5$ (0.080 g, 50%). HR ESI-MS: m/*z* calculated for {[Ru(terpy)(**1**)][BF$_4$]$_3$}$^{2+}$, 590.6425; found, 590.6448.

^{1}H NMR (500 MHz, MeCN-d_3):

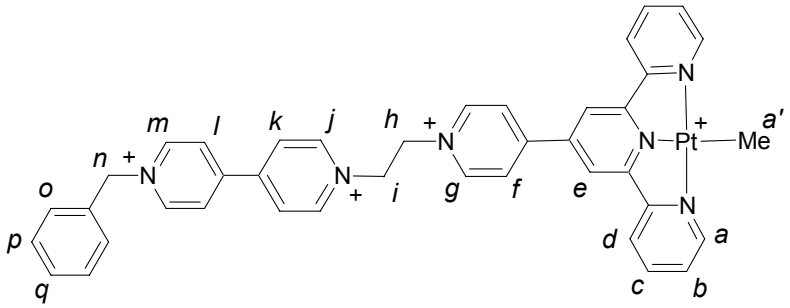
Proton	δ(ppm)	Multiplicity	# of Protons	Coupling Constant (Hz)
a	7.38	m	2	---
b	7.26	ddd	2	$^3J_{ba} \approx {}^3J_{bc} = 5.8$, $^4J_{bd} \approx 1.3$
c	8.01	ddd	2	$^3J_{cb} \approx {}^3J_{cd} = 7.5$, $^4J_{ca} \approx 1.2$
d	8.91	d	2	$^3J_{dc} = 7.1$
e	9.2	s	2	---
f	8.75	d	2	$^3J_{fg} = 7.5$
g	9.12	m	2	$^3J_{gf} = 6.7$
h	5.4	m	2	---
i	5.4	m	2	---
j	9.12	d	2	---
k	8.54	d	2	---
l	8.54	d	2	---
m	9.02	d	2	$^3J_{ml} = 6.9$
n	5.87	s	2	---
o	7.54	s	2	---
p	7.54	s	2	---
q	7.5 4	s	1	---
a'	7.38	d	2	---
b'	7.17	ddd	2	$^3J_{b'a'} \approx {}^3J_{b'c'} = 5.7$, $^4J_{b'd'} = 1.1$
c'	7.54	ddd	2	$^3J_{c'b'} \approx {}^3J_{c'd'} = 7.8$ $^4J_{c'a'} = 1.3$
d'	8.58	d	2	$^3J_{d'c'} = 7.1$
e'	8.79	d	2	$^3J_{e'f'} = 8.1$
f'	8.51	t	1	$^3J_{f'e'} = 8.1$



Preparation of Complex [PtMe(1)][BF_4]$_4$: A solution of *trans*-[PtMeCl(Me_2S)$_2$] (0.025 g, 0.070 mmol) in MeOH (5 mL) was added dropwise over 5 min to a solution of [Ag][BF_4] (0.014 g, 0.070 mmol) in MeOH (10 mL) and the resulting solution was stirred at room temperature for 1 h. **1**[BF_4]$_3$ (0.059 g, 0.070 mmol) was then added and the solution refluxed at 50 °C for 24 h. The solution was cooled and filtered through Celite to remove AgCl(*s*). The filtrate was evaporated and then dissolved in $CHCl_3$ (2 mL). Upon standing at room temperature a precipitate formed and [PtMe(**1**)][BF_4]$_4$ collected by vacuum filtration as an orange solid (0.030 g, 38%).

^{1}H NMR (500MHz, MeCN-d_3)

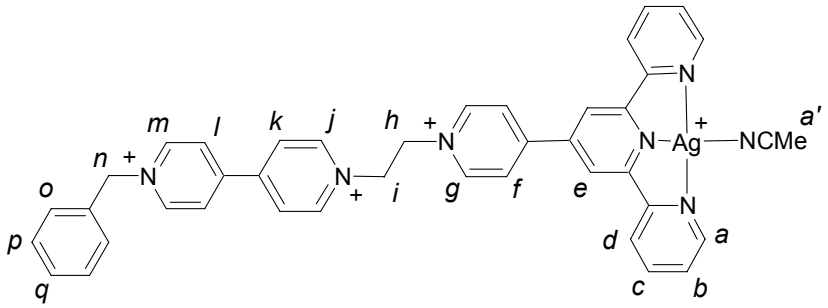
Proton	δ(ppm)	Multiplicity	# of Protons	Coupling Constant (Hz)
a	8.61	d	2	---
b	7.78	ddd	2	$^3J_{ba} \approx {}^3J_{bc} = 6.2$, $^4J_{bd} \approx 1.3$
c	8.32	ddd	2	---
d	8.39	d	2	$^3J_{dc} = 7.9$
e	8.65	s	2	---
f	8.42	m	2	$^3J_{fg} = 6.9$
g	8.92	m	2	---
h	5.2	m	2	---
i	5.2	m	2	---
j	8.92	m	2	---
k	8.34	d	2	---
l	8.37	d	2	---
m	8.57	d	2	$^3J_{ml} = 6.8$
n	5.76	s	2	---
o	7.44	s	2	---
p	7.44	s	2	---
q	7.44	s	1	---
a'	1.31	s	3	$^2J_{a'Pt} = 62$



Preparation of Complex [Ag(MeCN)(1)][BF_4]$_4$: A solution of **1**[BF_4]$_3$ (0.025 g, 0.030 mmol) dissolved in MeCN (5 mL) and [Ag][BF_4] (0.007 g, 0.037 mmol) added with stirring. After 1 h at room temperaturethe greenish solution was filtered and *iso*propyl ether added. The resulting off-white solid was collected by vacuum filtration (0.010 g, 30%).

^{1}H NMR (500MHz, MeCN-d_3)

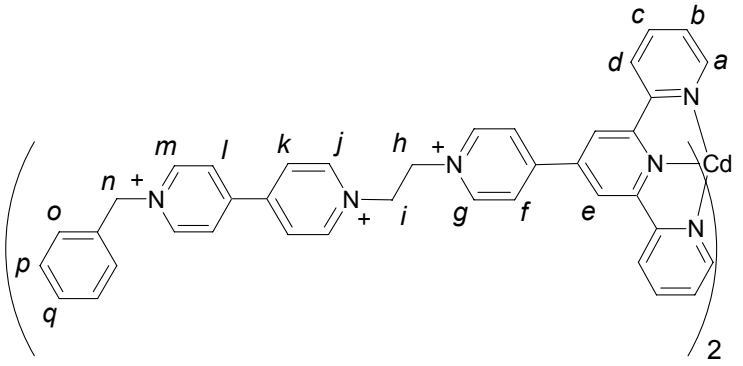
Proton	δ(ppm)	Multiplicity	# of Protons	Coupling Constant (Hz)
a	8.71	d	2	$^3J_{ab}$ 4.6
b	7.55	ddd	2	$^3J_{ba} \approx {}^3J_{bc} = 6$, $^4J_{bd} \approx 1.9$
c	8.02	ddd	2	$^3J_{cb} \approx {}^3J_{cd} = 7.8$, $^4J_{ca} \approx 1.7$
d	8.35	d	2	$^3J_{dc} = 7.9$
e	8.72	s	2	---
f	8.55	m	2	$^3J_{fg} = 6.7$
g	8.88	d	2	$^3J_{gf} = 6.7$
h	5.2	m	2	---
i	5.2	m	2	---
j	8.90	d	2	$^3J_{jk} = 6.8$
k	8.35	d	2	$^3J_{kj} = 6.8$
l	8.40	d	2	$^3J_{lm} = 6.8$
m	8.83	d	2	$^3J_{ml} = 6.8$
n	5.75	s	2	---
o	7.44	s	2	---
p	7.44	s	2	---
q	7.44	s	1	---
a'	2.0	s	3	---



Preparation of Complex $[Cd(1)_2][BF_4]_8$: $[Cd(H_2O)_6][BF_4]_2$ (0.10 g, 0.025 mmol)) and $\mathbf{1}[BF_4]_3$ (0.42 g, 0.050 mmol) were combined in 1:1 MeOH/MeCN solution (1 mL) and stirred for 1 h at room temperature. The addition of diethyl ether induced precipitation of the complex which was collected by vacuum filtration as an off-white solid (0.030 g, 60%).

^{1}H NMR (500MHz, MeCN-d_3)

Proton	δ(ppm)	Multiplicity	# of Protons	Coupling Constant (Hz)
a	8.66	d	2	---
b	7.64	ddd	2	$^3J_{ba} \approx {}^3J_{bc} = 5.9$, $^4J_{bd} \approx 1.7$
c	8.13	ddd	2	$^3J_{cb} \approx {}^3J_{cd} = 7.5$, $^4J_{ca} \approx 0$
d	8.64	d	2	---
e	8.68	s	2	---
f	8.54	m	2	---
g	9.02	m	2	---
h	5.3	s	2	---
i	5.3	s	2	---
j	9.0	m	2	---
k	8.54	m	2	---
l	8.54	d	2	$^3J_{lm} = 6.8$
m	8.98	m	2	---
n	5.8	s	2	---
o	7.5	s	2	---
p	7.5	s	2	---
q	7.5	s	1	---



References

1. G. J. E. Davidson and S. J. Loeb, *Dalton Trans*., 2003, 4319.
2. E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 2947.
3. (a) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017. (b) D. N. Reinhoudt, F. De Jong and H. P. M. Tomassen, *Tetrahedron Lett.*, 1979, **22**, 2067.