Stereochemical Control of Donor and Acceptor Groups in a Monomeric Chromophore−Quencher Complex of Ruthenium(II)

Todd J. Rutherford and F. Richard Keene*

Department of Chemistry and Chemical Engineering, School of Molecular Sciences, James Cook University of North Queensland, Townsville, Queensland 4811, Australia

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The chromophore−quencher complex $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(bpy\text{-}PTZ)]^{4+}$, containing one donor (phenothiazine, PTZ) and one acceptor (methyl viologen, MV^{2+}) functionality, has been synthesized and separated into its four geometric isomers. This was achieved through the intermediacy of $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(py)_2]^{4+}$, the two isomers of which were separated and each reacted stereoselectively with bpy-PTZ to produce two distinct isomer pairs of the target molecule. Cation-exchange chromatography allowed separation to realize the four forms. The isomers of the product and of the intermediates were characterized by NMR spectroscopy. This is the first example of the isolation of geometric isomers of a mononuclear system containing a single donor and single acceptor functionality.

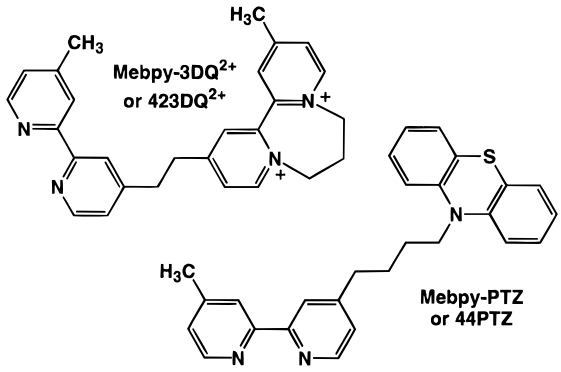
Introduction

Redox charge separation is a fundamental process in the utilization of absorbed light energy, both in natural photobiological processes such as photosynthesis[1,2] and also in artificial systems designed as photochemical molecular devices.[3]

In both contexts, intramolecular electron and/or energy transfer processes which follow light-absorption are undoubtedly influenced by the nature and relationship of the light absorbing centers (chromophores) and the redox-active groups (quenchers). In particular, their spatial relationship may control the directional characteristics of the relay processes and determine reactivity pathways.

Charge separation processes have been studied in a number of model systems,[4−12] including chromophore−quencher complexes involving polypyridyl complexes of the d^6 metal centers Ru^{II}, Os^{II}, and Re^{I}, which are of particular interest because of their particular physical characteristics.[3,13−22]

All natural and artificial systems share a common principle: a chromophore (C) with associated redox-active quenchers which may accept (A) or donate (D) electrons. In the model, the initial D−C−A species absorbs light energy and forms an excited state D−*C−A, which produces the charge-separated species D^+-C-A^- by a series of electron transfer steps. Previous studies on chromophore−quencher complexes have probed the influence of the separation distance of the donor and acceptor groups and the nature of the rigidity and electronic character of the bridging groups. However, the dependence of the electron transfer process on the stereochemical relationship among the components of the complex has not been addressed. In some cases, the systems have been deliberately chosen to avoid this spatial ambiguity,[15,16] while other studies of this type have investigated target compounds which were mixtures of stereoisomers. As a representative example of the latter scenario, it is noted that, in their studies of charge-separated excited states in mononuclear complexes containing ligands with donor− and acceptor−quencher functionalities, Elliott and coworkers have investigated the system $[Ru(44PTZ)_2(423DQ^{2+})]^{4+}$,[17−19] in which there are four possible stereoisomers (geometric).



A similar number of forms exist for $[Ru(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$,

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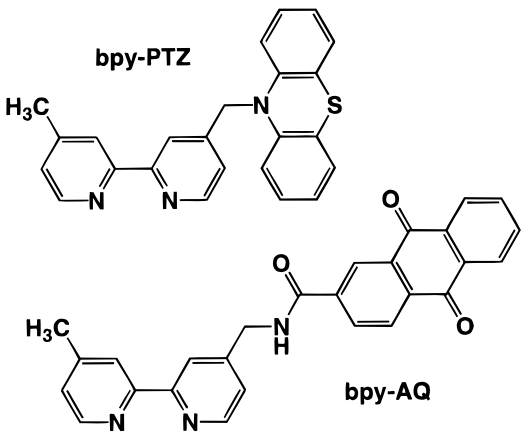
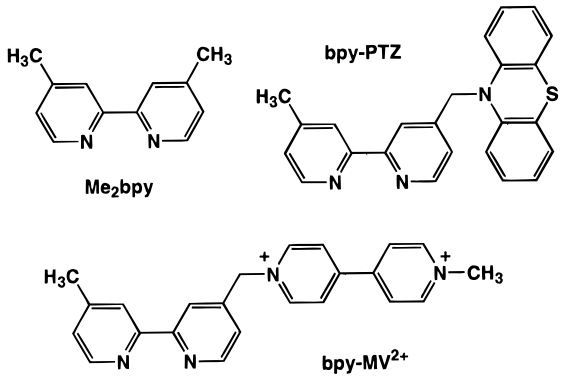
studied by Meyer *et al.*[21]



In both of these studies,[17−19,21] the possible existence of geometric isomers was acknowledged. Indeed in one case[18] it was evoked as a possible explanation for the observations of broadening in the transient absorption spectrum of the charge transfer excited state, and the possible existence of more than one component in its decay.

The spatial dependence of the photophysical behavior is unknown, as we are not aware of any report of the isolation of stereoisomers of a mononuclear species containing a single donor and a single acceptor functionality.



We have recently reported the synthesis of tris(heteroleptic)-ruthenium(II) complexes of bidentate polypyridyl ligands,[23] as well as the stereochemical aspects of such systems.[24,25] As an extension of the above studies, we now report a synthetic and stereochemical study in which we have isolated the four geometric isomers of the system $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(bpy\text{-}PTZ)]^{4+}$ (Figure 1) {Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; bpy-MV^{2+} = 1-[(4′-methyl-2,2′-bipyridin-4-yl)methyl]-1′-methyl-4,4′-bipyridinediium cation (MV^{2+} is an acceptor quencher); bpy-PTZ = 10-[(4′-methyl-2,2′-bipyridin-4-yl)methyl]phenothiazine (PTZ is a donor quencher)}.

Charge separation processes have previously been investigated in a system based on the the tridentate ligand tpy (2,2′:6′,2″-terpyridine), $[Ru(tpy\text{-}A)(tpy\text{-}B)]^{2+}$, involving the same quencher groups. In that case there was no stereochemical ambiguity as the two functionalities were attached to the central pyridine ring in the respective tpy moieties, constraining the substituents to a "*trans*" relationship.[15,26]

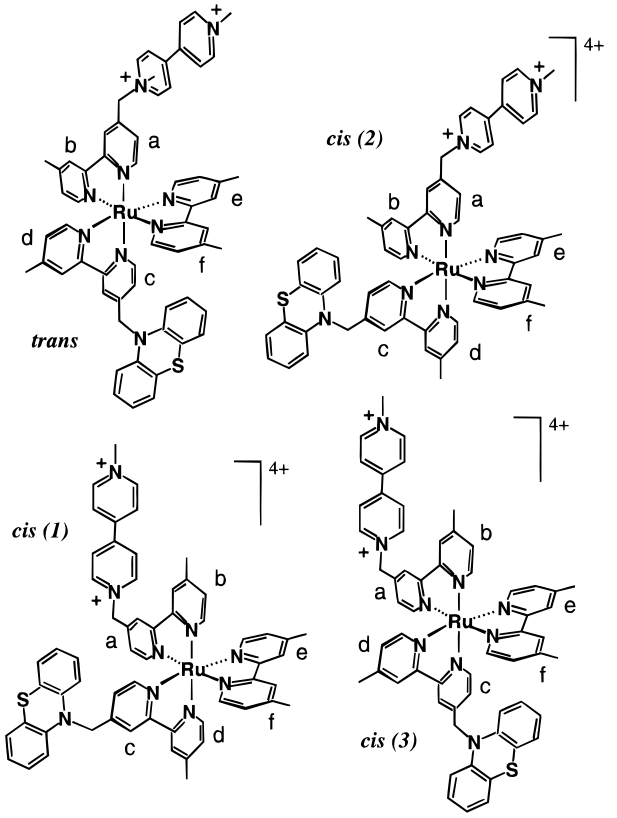


Figure 1. Geometric isomers of $[Ru(Me_2bpy)(bpy\text{-}MQ^{2+})(bpy\text{-}PTZ)]^{4+}$. Ring notation is used in discussion of NMR spectra.

A detailed comparative photophysical study of the four isomers of the present title system is in progress and will be reported subsequently.[27]

Experimental Section

Instrumentation. ^1H,^1H-decoupling, NOE-difference, and COSY experiments were performed on a Bruker Aspect 300 MHz NMR spectrometer (CD_3CN solutions). UV−visible spectra were recorded in acetonitrile solution on a Hewlett Packard HP-89532K spectrophotometer using quartz cells.

All electrochemical experiments were performed under argon in an inert-atmosphere drybox using a Bioanalytical Systems BAS 100A electrochemical analyzer. Measurements were made in acetonitrile/0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ solution using a platinum button working electrode and a Ag/Ag^+ (0.01M $AgClO_4$/0.1 M $[(n\text{-}C_4H_9)_4N]ClO_4$ in acetonitrile) reference electrode (+0.31 V *vs* SCE). Cyclic voltammetry was performed with a sweep rate of 100 mV/s; differential pulse voltammetry was run with a sweep rate of 4 mV/s and a pulse amplitude, width, and period of 50 mV, 60 ms, and 1 s, respectively.

Elemental analyses were performed within the Department of Chemistry and Chemical Engineering at James Cook University of North Queensland and were within acceptable limits (0.4%) after allowance was made in some cases for inclusion of hydration within the crystal. In addition, the characterization of the complexes was achieved unequivocally by a combination of NMR and electrochemical data, as described herein.

Materials. Ruthenium(III) chloride trihydrate (Strem, 99.9%), cesium carbonate (Aldrich, 99.9%), potassium carbonate (Ajax), acetonitrile (Aldrich, 99.9+%), potassium hexafluorophosphate (Aldrich, 99%), sodium toluene-4-sulfonate (Aldrich, 95%), and iodomethane (Ajax) were used without further purification. 4,4′-Dimethyl-2,2′-bipyridine (Adrich, 98%), 4,4′-bipyridine (Aldrich, 98%), and selenium(IV) oxide (Aldrich, 99.9+%), were dried *in vacuo* overnight. Phenothiazine (Fluka) was recrystallized from refluxing

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toluene and then from benzene. Dimethylformamide (M&B), pyridine (Ajax), 2-methoxyethyl ether (Aldrich), and standard laboratory solvents were dried and distilled prior to use. Trimethylamine *N*-oxide dihydrate (TMNO; Fluka) was sublimed under vacuum at 120 °C, yielding the anhydrous form. The complex $[Ru(Me_2bpy)_3](PF_6)_2$ was synthesized according to literature procedures.[28]

Syntheses. 4-Methyl-2,2′-bipyridine-4′-carbaldehyde (bpy-CHO) was synthesized on a 33 mmol scale using a method described by Furue *et al*.,[29] with the following modifications.[30] 2-Methoxyethyl ether was the solvent, and upon isolation of the initial product the residue was dissolved in ethyl acetate (*ca.* 750 mL) and stirred with 0.5 M K_2CO_3 solution (100 mL). The mixture was extracted with 0.2 M sodium bisulfite solution (3 × 300 mL), and the aqueous extracts were adjusted to pH 9 with K_2CO_3 and re-extracted with dichloromethane (3 × 100 mL), with the remaining aqueous layer being continually extracted with dichloromethane overnight. The organic extracts were combined and dried (Na_2SO_4), and the solvent was evaporated, giving a white solid. Physical data were identical to those described by Furue *et al.*[29] Yield: 42%.

4-(Hydroxymethyl)-4′-methyl-2,2′-bipyridine (bpy-CH_2OH)[27] and 4-(bromomethyl)-4′-methyl-2,2′-bipyridine dihydrobromide (bpy-CH_2Br·2HBr)[31] were prepared as described in the literature.

10-[(4′-Methyl-2,2′-bipyridin-4-yl)methyl]phenothiazine (bpy-PTZ). Phenothiazine (398 mg, 1.99 mmol) and Cs_2CO_3 (970 mg, 2.985 mmol) were dissolved in a degassed (N_2) solution of DMF (30 mL) and the mixture stirred for 0.5 h. Bpy-CH_2Br·2HBr (280 mg, 0.66 mmol) and Cs_2CO_3 (845 mg, 2.6 mmol) were then added, and the reaction mixture was stirred for 48 h in subdued light. The DMF was removed under vacuum and the residue purified by vacuum column chromatography[32] (silica; diethyl ether), yielding white-cream crystals. Physical data were identical to those described by Meyer *et al*.[31] using an alternative synthetic procedure. Yield: 127 mg, 50%.

1-Methyl-4,4′-bipyridinium iodide (MQ^+I^-) was synthesized (yield, 70%) as described by Yonemoto *et al*.[33]

1-[(4′-Methyl-2,2′-bipyridin-4-yl)methyl]-1′-methyl-4,4′-bipyridinediium hexafluorophosphate [(bpy-MV^{2+})$(PF_6)_2$] was synthesized using methods similar to those used by Yonemoto *et al*.[33] bpy-CH_2-Br·2HBr (1.2 g, 2.8 mmol) was dissolved in H_2O (15 mL) and excess K_2CO_3 added with stirring to liberate the free base, which was extracted with $CHCl_3$ (3 × 30 mL) and dried under vacuum. Yield: 0.75 g. A portion (250 mg, 1.07 mmol) was dissolved in acetonitrile (50 mL), the solution degassed for 20 min, MQ^+I^- (365 mg, 2.14 mmol) added, and the mixture refluxed for 28 h in subdued light. Acetonitrile was removed under vacuum, the residue dissolved in a minimum amount of water, the solution filtered, and the product precipitated by the addition of a saturated solution of KPF_6. After the suspension was cooled overnight at 4 °C, the product was filtered, washed with H_2O, $CHCl_3$, and Et_2O, and air-dried. Physical data were in agreement with those described for the same product obtained by Yonemoto *et al*.[33]

Dicarbonyl(4,4′-dimethyl-2,2′-bipyridine)bis(trifluoromethanesulfonato)ruthenium(II) [Ru$(Me_2bpy)(CO)_2(CF_3SO_3)_2$] was synthesized by the literature procedure.[23]

Dicarbonyl(4,4′-dimethyl-2,2′-bipyridine)[1-((4′-methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′-bipyridinediium]ruthenium(II) Hexafluorophosphate [Ru(Me_2bpy)(bpy-MV^{2+})$(CO)_2](PF_6)_4$, I]. The ligand bpy-MV^{2+} (321 mg, 0.5 mmol) was dissolved in absolute ethanol (30 mL) and the solution degassed with N_2 for 20 min. [Ru(Me_2bpy)-$(CO)_2(CF_3SO_3)_2$] (300 mg, 0.468 mmol) was added and the reaction refluxed for 90 min, during which time the mixture turned a blue color. The reaction mixture was cooled, the solvent removed under vacuum, the residue dissolved in hot water, KPF_6 added to the filtered solution and the mixture stored at 4 °C overnight. The precipitate was collected by filtration. Fractional recrystallization from ethanol allowed the isolation of one geometric isomer. Alternatively, purification could be achieved by cation-exchange chromatography (SP-Sephadex C25): the ligand was eluted using 0.2 M NaCl/10% acetone and the complex with 0.5 M NaCl/10% acetone. The complex was precipitated with KPF_6 and collected by filtration. This latter method retained the original isomer ratio. Yield: 405 mg, 68%. IR: $\bar{\nu}_{CO}$ 2084 and 2034 cm^{-1}.

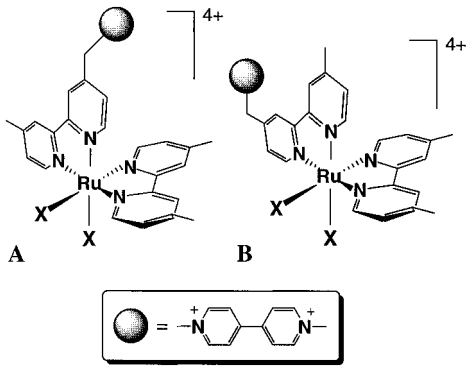

Figure 2. Geometric isomers of [Ru(Me_2bpy)(bpy-MQ^{2+})(monodentate)$_2$]$^{4+}$: **I**, X = CO; **II**, X = py.

(4,4′-Dimethyl-2,2′-bipyridine)[1-((4′-methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′-bipyridinediium]bis(pyridine)ruthenium(II) Hexafluorophosphate [[Ru(Me_2bpy)(bpy-MV^{2+})$(py)_2](PF_6)_4$, II]. Pyridine (200 mg, 2.5 mmol) was added to 2-methoxyethanol (10 mL) and the mixture degassed (N_2) for 20 min. [Ru(Me_2bpy)(bpy-MV^{2+})-$(CO)_2](PF_6)_4$ (500 mg, 0.39 mmol) was added and the mixture heated to 50 °C. TMNO (68 mg, 0.905 mmol) was dissolved in 2-methoxyethanol (*ca.* 30 mL) and added dropwise over 2−3 h. The mixture was stirred at 60 °C in subdued light for 8 h, then diluted with water, and purified by cation exchange chromatography (SP-Sepahdex C25; 0.5 M NaCl eluent). The product was precipitated by the addition of a saturated solution of KPF_6. Yield: 140 mg, 27%.

The two geometric isomers (**A** and **B**, Figure 2) were separated by cation-exchange chromatography (SP-Sephadex C25; 0.25 M sodium toluene-4-sulfonate eluent), and the products were precipitated by the addition of a saturated solution of KPF_6. The two isomers were collected and separately dissolved in a minimum volume of acetone, and distilled water was added followed by a saturated solution of KPF_6. In each case the product was filtered, washed with water and ether, and air-dried.

(4,4′-Dimethyl-2,2′-bipyridine){1-[(4′-methyl-2,2′-bipyridin-4-yl)methyl]-1′-methyl-4,4′-bipyridinediium}{10-[(4′-methyl-2,2′-bipyridin-4-yl)methyl]phenothiazine}ruthenium(II) Hexafluorophosphate [[Ru(Me_2bpy)(bpy-MV^{2+})(bpy-PTZ)]$(PF_6)_4$, III]. bpy-PTZ (21 mg, 0.0543 mmol) was added to ethylene glycol (15 mL, containing 10% H_2O) and the mixture degassed with N_2 for 20 min. **A** (or **B**) [Ru(Me_2bpy)(bpy-MV^{2+})$(py)_2](PF_6)_4$ (25 mg, 0.0181 mmol) was added and the mixture heated at 110−120 °C in subdued light for 3.5 h. The solution was added to water (*ca.* 50 mL) and the excess bpy-PTZ removed by filtration. The product was purified by cation-exchange chromatography (SP-Sephadex C25, 0.3 M sodium toluene-4-sulfonate eluent) and precipitated by addition of a saturated solution of KPF_6. The single geometric isomers **A** and **B** yielded the two geometric forms *trans/cis(2)* and *cis(1)/cis(3)*, respectively (see Figure 3). Total yield: 20 mg, 70%.

The two isomeric mixtures were each separated by cation-exchange chromatography (SP-Sephadex C25; 0.25 M sodium toluene-4-sulfonate/5% acetone eluent) and the separated isomers [*trans* and *cis(2)*, *cis(1)* and *cis(3)*] precipitated by the addition of KPF_6. The products were twice reprecipitated and collected as described above.

Bis(4,4′-Dimethyl-2,2′-bipyridine){1-[(4′-methyl-2,2′-bipyridin-4-yl)methyl]-1′-methyl-4,4′-bipyridinediium}ruthenium(II) Hexafluorophosphate [[Ru$(Me_2bpy)_2$(bpy-MV^{2+})]$(PF_6)_4$, IV]. bpy-MV^{2+} (55 mg, 0.086 mmol) was added to 50% aqueous ethanol (10 mL) and the solution degassed for 20 min with N_2. [Ru$(Me_2bpy)_2Cl_2$]·H_2O (25 mg, 0.045 mmol) was added and the mixture refluxed for 1.5 h. The product was purified by cation-exchange chromatography (SP-Sephadex C-25; 0.3 M sodium toluene-4-sulfonate eluent) and precipitated by the addition of a saturated solution of KPF_6. The product was then reprecipitated as described above. Yield: 42 mg, 70%.

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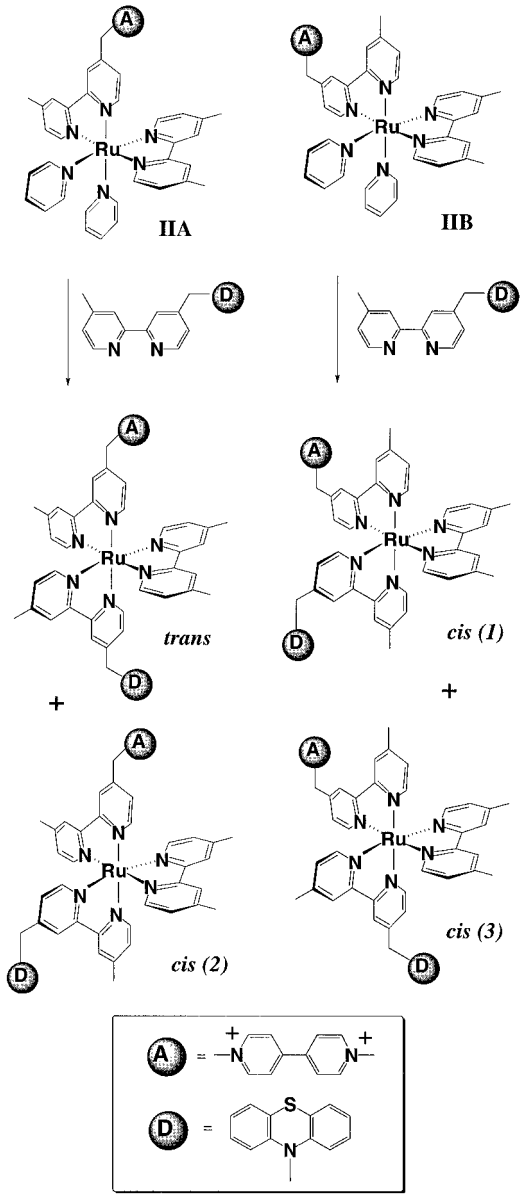

Figure 3. Stereochemistry of the conversion **II** → **III**.

Bis(4,4′-Dimethyl-2,2′-bipyridine){10-[(4′-methyl-2,2′-bipyridin-4-yl)methyl]phenothiazine}ruthenium(II) Hexafluorophosphate [[Ru(Me$_2$bpy)$_2$(bpy-PTZ)](PF$_6$)$_2$, V]. The reaction was performed under conditions similar to those used for Ru(Me$_2$bpy)$_2$(bpy-MV^{2+})(PF$_6$)$_4$, but using bpy-PTZ instead of bpy-MV^{2+}. Yield: 75%.

Results and Discussion

Syntheses. The ligand bpy-MV^{2+} was prepared by a slight modification of literature procedures, and bpy-PTZ was obtained by reaction of the PTZ anion with bpy-CH$_2$Br in DMF solution for 48 h.

The synthetic strategy for the target complex, [Ru(Me$_2$bpy)(bpy-MV^{2+})(bpy-PTZ)]$^{4+}$ (**III**), required that the ligands bpy-PTZ and bpy-MV^{2+} be added sequentially to the [Ru(Me$_2$bpy)(CO)$_2$(CF$_3$SO$_3$)$_2$] precursor. However, the PTZ functionalization is sensitive to oxidation by TMNO, which is used in the decarbonylation procedure in the final stages of the synthetic scheme. Accordingly, bpy-MV^{2+} was added first: [Ru(Me$_2$bpy)(bpy-MV^{2+})(CO)$_2$]$^{4+}$ (**I**) was prepared by the reaction of [Ru(Me$_2$bpy)(CO)$_2$(CF$_3$SO$_3$)$_2$] with bpy-MV^{2+} in refluxing ethanol.

The presence of the unsymmetrically-substituted bpy-MV^{2+} may induce stereoisomerism in its complexes: in the synthetic scheme, **I** is the first complex in which geometric isomerism is observed and can therefore be controlled. Figure 2 shows the two possible geometric forms: **IA** contains the MV^{2+} substituent in a *cis/trans* orientation with respect to the carbonyl ligands whereas in **IB** it has a *cis/cis* orientation.

The stereochemical predetermination and structural identification of one of the precursors greatly simplifies the stereochemical characterization of the target complex. The separation of the two geometric forms **I** is possible by fractional recrystallization from ethanol, with **IB** being the less soluble form. However, the stereochemical control of the reaction sequence at this point was not pursued for a number of reasons, as the more soluble form **IA** always contained traces of **IB**, and to retain stereochemical integrity the subsequent decarbonylation reactions of **I** must be undertaken at low temperatures, leading to low yields.[24,25] In addition, the lack of visible absorption by **I** renders the separation of the geometric isomers by chromatography more difficult.

To avoid the problem of the sensitivity of the the PTZ grouping in the decarbonylation process, an extra step was introduced into the previously reported synthetic scheme,[23] involving the decarbonylation of **I** with TMNO and substitution with pyridine. The conditions were varied from those described by Anderson *et al.*[23] as it was observed that any excess TMNO also led to slow decomposition of the bpy-MV^{2+} ligand. The reaction was performed in 2-methoxyethanol, and a solution of TMNO in 2-methoxyethanol was added dropwise over several hours while the reaction mixture was heated at *ca.* 60−70 °C for a total of 7−8 h. These conditions allowed the formation of [Ru(Me$_2$bpy)(bpy-MV^{2+})(py)$_2$]$^{4+}$ (**II**) in *ca.* 30% yield.

The complex **II** proved a very useful precursor to **III**. The two geometric isomers were easily distinguished by NMR spectroscopy; the complex was colored (due to MLCT absorptions in the visible spectral region) facilitating chromatographic separation procedures; and the reaction of **II** with a third bidentate polypyridyl ligand is known to proceed with stereochemical retention of configuration at high temperatures.[34] The two geometric isomers, **IIA** and **IIB** (Figure 2), were separated by cation-exchange chromatography (approximately equal proportions) and characterized by NMR spectroscopy (see below). The separation of the two geometric forms is thought to result from their differential association with the toluene-4-sulfonate anion of the eluent.[25,35]

The stereochemical consequences of the reactions of **IIA** and **IIB** with bpy-PTZ are shown in Figure 3. In ethylene glycol/10% water at 120 °C (subdued light), the substitution of pyridine reaction occurs with retention of the stereochemical integrity of the metal center,[31] so that **IIA** yields a *trans*-**III** + *cis(2)*-**III** mixture and **IIB** produces *cis(1)*-**III** + *cis(3)*-**III**. The two pairs of isomeric mixtures of [Ru(Me$_2$bpy)(bpy-MV^{2+})(bpy-PTZ)]$^{4+}$ were separated by cation-exchange chromatography on SP-Sephadex C25 with sodium toluene-4-sulfonate as the eluent. Interestingly, the separation of *cis(1)* and *cis(3)* was significantly more efficient than the separation of the *trans* and *cis(2)* forms: this observation and the order of elution are consistent with previous studies involving the separation of the geometric forms of [Ru(Me$_2$bpy)(pmb)$_2$]$^{2+}$ (pmb = 4-methyl-4-neopentyl-2,2′-bipyridine).[25] In that earlier work the *s-cis* [corresponding to *cis(1)*-**III** in the present case] and *u-cis* mixtures [corresponding to *cis(2)*- + *cis(3)*-**III** in the present case] were more easily separated than *trans* and *u-cis* mixtures, and the chromatographic elution order was *u-cis* > *s-cis* > *trans*, which is analogous to the orders observed in the present separations (*viz.* *cis (3)* > *cis(1)* and *cis(2)* > *trans*).[25]

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Table 1. Electrochememical Data (Acetonitrile Solution) for Complexes Used in This Study and Related Species

complex (as PF_6^- salts)	$E_{1/2}$ values (vs SSCE)					
	$Ru^{III/II}$	$PTZ^{0/+}$	$MV^{+/0}$	$MV^{2+/+}$	$pp^{0/-1}$	$pp^{0/-1}$
$[Ru(bpy)_3]^{2+}$	+1.29				−1.33	−1.52
$[Ru(Me_2bpy)_3]^{2+}$	+1.09				−1.44	−1.62
$[Ru(Me_2bpy)(bpy\text{-}MV)(py)_2]^{4+}$	+1.23		−0.35	−0.74	−1.39	−1.63
$[Ru(Me_2bpy)_2(bpy\text{-}MV)]^{4+}$	+1.21		−0.33	−0.73	−1.39	−1.62
$[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{2+}$	+1.19	+0.79			−1.40	−1.59
$[Ru(Me_2bpy)(bpy\text{-}MV)(bpy\text{-}PTZ)]^{4+}$	+1.22	+0.80	−0.34	−0.74	−1.37	−1.57

Table 2. Chemical Shifts (ppm) for the Two Geometric Isomers of $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(py)_2]^{4+}$ and $[Ru(Me_2bpy)_2(py)_2]^{2+}$ [a]

	MV^{2+}				bpy-MV^{2+}								Me_2bpy							
	H2′	H3′	H3	H2	H6	H5	H3	H3′	H5′	H6′	CH_2	CH_3	H6	H5	H3	H3′	H5′	H6′	CH_3(c)	CH_3(d)
$[Ru(Me_2bpy)_2(py)_2]^{2+}$													8.68	7.57	8.19	8.10	7.18	7.67	2.42	2.57
IIA[b]	8.90	8.42	8.35	8.83	7.96	7.31	8.20	8.20	7.61	8.71	5.86	2.56	8.68	7.59	8.20	8.10	7.19	7.66	2.42	2.56
IIB[b]	9.10	8.49	8.39	8.90	8.93	7.70	8.30	8.13	7.22	7.69	6.01	2.41	8.68	7.59	8.20	8.13	7.15	7.69	2.41	2.57

[a] All spectra were recorded in CD_3CN. Pyridine chemical shifts are equivalent in the above compounds: H2, H6 = 8.23 ppm (d, 5 Hz); H3, H5 = 7.26 ppm (dd, 5, 8 Hz); H4 = 7.81 ppm (t, 8 Hz). H6 and H5 are doublets with J = 5 Hz. H2, H2′, H3, and H3′ are doublets with J = 7 Hz. N^+-CH_3 = 4.40−4.38 ppm (s). [b] $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(py)_2]^{4+}$.

Electrochemistry. The cyclic voltammetry of complexes involved in this study are given in Table 1, and the data provide valuable information regarding their electronic nature and also an electronic means of characterization. Cyclic voltammetry (acetonitrile/0.1 M $[(n\text{-}C_4H_9)_4]PF_6$ solution) indicated that $Ru^{III/II}$ redox couples ranged from $E_{1/2}$ = +1.09 V to +1.29 V, showing a small variation in that couple for the complexes—as expected from the small varations in the ligand environment. As observed by Lever *et al.*,[36,37] the electronic environment of any ligand is relatively unaffected by the other ligands present, which is apparent in the small variations in the $pp^{0/-1}$ redox potentials, and to a much lesser extent in the redox potentials of the MV^{2+} and PTZ substituents.

The above complexes exhibit electrochemical characteristics expected for complexes of the respective formulations and are in agreement with those previously reported for related species containing these ligands.[17,21,26,33] It is also noted that all redox couples were quasi-reversible with ΔE_p values between 87 and 126 mV. Cyclic voltammetry was performed on the geometric isomers of $[Ru(Me_2bpy)(bpy\text{-}MV)(py)_2]^{4+}$ (**II**) and $[Ru(Me_2bpy)(bpy\text{-}MV)(bpy\text{-}PTZ)]^{4+}$ (**III**) and no significant differences were observed between the stereoisomeric forms. The cyclic voltammogram for the target complex **III** is provided as Supporting Information (Figure S1).

Electronic Spectroscopy. As anticipated, the electronic absorption spectra of the complexes listed in Table 1 are closely similar, being dominated in the visible region by ^{1}MLCT transitions, $d\pi(Ru^{II}) \rightarrow \pi^*$(bpy), and in the UV region by bpy-ligand $\pi \rightarrow \pi^*$transitions and those arising from the PTZ and MV^{2+} substituents.[14] No differences were observed between the spectra of stereoisomers of the same complex.

^{1}H NMR Studies. The geometric isomers of $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(CO)_2]^{4+}$ (**I**), $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(py)_2]^{4+}$ (**II**), and the target species $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(bpy\text{-}PTZ)]^{4+}$ (**III**) were assigned by ^{1}H NMR spectroscopy. Chemical shifts were determined by ^{1}H COSY, selective decoupling and NOE experiments, and their assignments based on the relative degree of diamagnetic anisotropic interactions between the adjacent ligands, coupling constant values, and comparisons with structurally similar complexes $[Ru(Me_2bpy)_3]^{2+}$, $[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{2+}$, and $[Ru(Me_2bpy)_2(bpy\text{-}MV^{2+})]^{4+}$. The NMR data for all of these complexes are discussed below.

$[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(CO)_2]^{4+}$ (I). The geometric isomers **IA** and **IB** were not separated. Both possess C_1 point group symmetry so that the ^{1}H NMR spectrum of the mixture will consist of resonances due to 42 distinct protons (21 from each isomer, allowing for free rotation about the methylene group). Nevertheless, the two isomers were easily identified in the spectrum due to the different relative degrees of diamagnetic anisotropic interactions arising from the carbonyl and polypyridyl ligands:[25] isomers **IA** and **IB** were most clearly distinguished by the methylene proton (H4) resonance, which was observed at 5.93 ppm and 6.11 ppm, respectively. These shifts are explained by the reduced anisotropic interactions between the methylene-substituted pyridyl ring and carbonyl ligands in **IB** relative to its interaction with the Me_2bpy ligand in **IA**.

$[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(py)_2]^{4+}$ (II). The separated geometric isomers **IIA** and **IIB** both possess C_1 point group symmetry, so that their ^{1}H NMR spectra were each composed of 24 proton resonances, the assignments of which are given in Table 2. The atom- and ring-numbering sequences used are shown in Figure 4. These two isomeric forms exhibited well-dispersed proton resonances (shown in Figure 5) resulting from the different relative degrees of anisotropic interaction between the bidentate (bpy-based) and the pyridine ligands. The assignment of **IIA** and **IIB** to the two NMR spectra shown in parts A and B, respectively, of Figure 5 was based on the differential anisotropic interactions.

In isomer **IIA**, ring a is situated over the plane of the adjacent Me_2bpy ligand, whereas in **IIB** ring a is orientated over the plane of the monodentate pyridine ligand (Figure 2). The consequent anisotropic interactions result in the ring a protons (H6, H5, and H3) being more shielded in **IIA** relative to **IIB** (see Table 2). This shielding influence is clearly observed in the methylene resonances of **IIA** compared to **IIB** (5.86 ppm and 6.01 ppm, respectively). The relative differences in the anisotropic interactions are most significant in the H6 protons, which are manifested as increased induced chemical shift differences; for example, the difference in chemical shifts of H6 (ring a) in **IIA** and **IIB** is approximately 1 ppm, compared with a difference of 0.2 ppm in the chemical shifts of H3 (ring a).

$[Ru(Me_2bpy)_3]^{2+}$. Because of the D_3 symmetry of this complex, a spectrum composed of one AX coupling system and one singlet resonance is observed in the aromatic region. The protons H6, H5, H3, and H4 were assigned to the resonances at 7.48 ppm, 7.17 ppm, 8.31 ppm, and 2.48 ppm, respectively, on the basis of coupling constant values and NOE experiments.

$[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{2+}$ (V). With C_1 point group symmetry, this complex has a ^{1}H NMR spectrum consisting of 29

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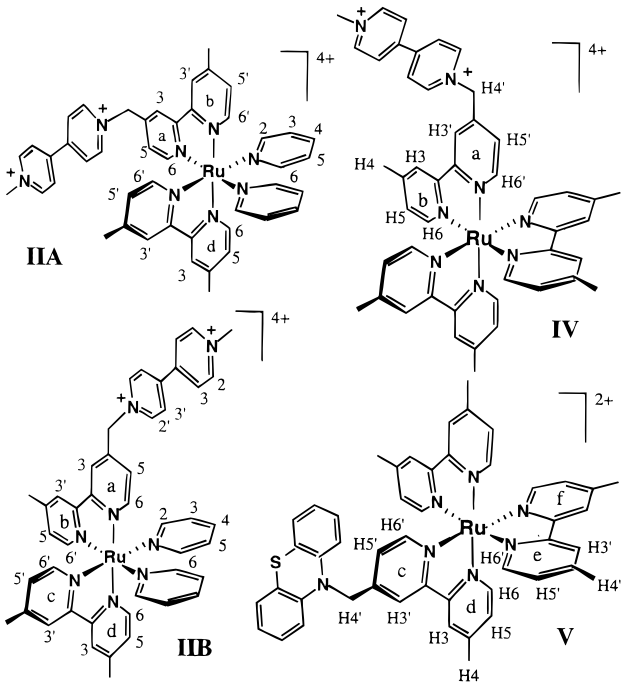

Figure 4. Atom- and ring-numbering sequences used in NMR discussion for the geometric isomers of $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(py)_2]^{4+}$ (**IIA** and **IIB**) and for the complexes $[Ru(Me_2bpy)_2(bpy\text{-}MV^{2+})]^{4+}$ (**IV**) and $[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{2+}$ (**V**).

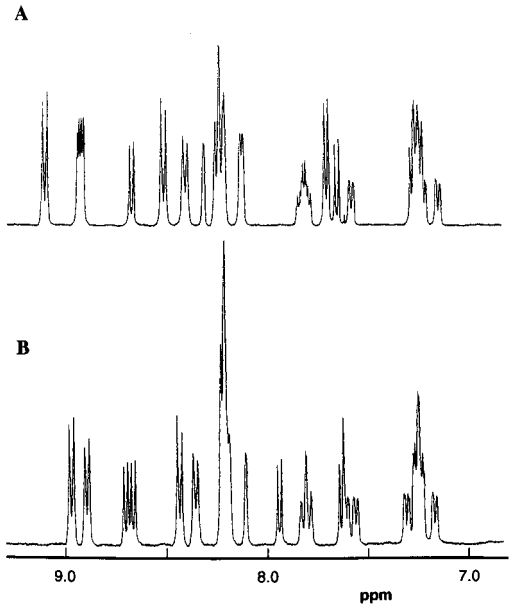

Figure 5. ^{1}H spectra (300 MHz; CD_3CN solvent) of the geometric isomers of $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(py)_2]^{4+}$ (**II**).

proton resonances, some of which are equivalent due to the similarity of the magnetic environments of the "base" Me_2bpy polypyridyl ligands. The atom- and ring-numbering sequences used are shown in Figure 4. The methylene proton resonance of bpy-PTZ at 5.27 ppm exhibited NOE effects to protons at 6.75 ppm (PTZ substituent), 7.28 ppm (H5′ on the PTZ-substituted ring or ring c), and 8.48 ppm (H3′ of the PTZ-substituted ring or ring c). Selective decoupling and NOE experiments enabled the complete assignment of chemical shifts in the bpy-PTZ ligand. The remaining chemical shifts were assigned to the two Me_2bpy ligands, which showed minor variations compared with protons in the $[Ru(Me_2bpy)_3]^{2+}$ complex (discussed above) with one significant exception: a resonance (d, $J = 5$Hz) at 7.32 ppm which was determined to originate from a H6 proton (>1 ppm upfield compared to other H6 and H6′ proton resonances). Models suggest that the most probable H6 proton experiencing the increased anisotropic interactions (shielding influence) is the H6 proton associated with the pyridyl ring (ring e) orientated over the plane of the PTZ-substituted pyridyl ring (ring c).

$[Ru(Me_2bpy)_2(bpy\text{-}MV^{2+})]^{4+}$ (IV). The C_1 symmetry results in a ^{1}H NMR spectrum showing 29 proton resonances. The atom- and ring-numbering sequences used are shown in Figure 4. The methylene resonance at 5.96 ppm (deshielded relative to the resonance of the methylene bridge in the analogous bpy-PTZ species due to inductive influences) showed NOE effects to the proton at 9.06 ppm (H3, MV^{2+} substituent), 7.33 ppm (H5′, MV^{2+}-substituted ring or ring a), and 8.44 ppm (H3′, MV^{2+}-substituted ring or ring a). ^{1}H COSY spectra confirmed coupling between the protons resonating at 7.33 ppm and 7.76 ppm. The H6′ (ring a) and H6 (ring b) protons of bpy-MV^{2+} are deshielded by 0.2 and 0.05 ppm, respectively, relative to the H6/H6′ proton resonances of the Me_2bpy ligand.

In the above two tris(bidentate) polypyridyl complexes, attention is drawn to two significant results: the shielding influence in the H6 protons orientated over the plane of the PTZ-substituted pyridyl ring and the relative deshielding influence experienced by the H6/H6′ protons on the bpy-MV^{2+} ligand. By comparison of isomers **IIA** and **IIB**, a small deshielding influence is experienced in the H6 protons orientated over the plane of the MV^{2+}-substituted pyridyl rings of the bpy ligands.

$[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(bpy\text{-}PTZ)]^{4+}$ (III). A complete assignment of all chemical shifts for the four isomers of **III** was not possible due to the equivalence of several proton resonances, and this might only be addressed by subsequent measurement at higher frequency or with the aid of pulse-relay NMR experiments. However, chemical shift data was used in conjunction with the known stereochemical possibilities (Figure 1) to make the isomeric assignments discussed below. The ^{1}H NMR assignments for the four isomeric forms [*trans*, *cis(1)*, *cis(2)*, and *cis(3)*] were simplified by the predetermination of the stereochemistry of the precursor complex **II**, thus reducing the number of isomeric options to two [*trans/cis(2)* or *cis(1)/cis(3)*] as previously described (Figure 3). The assignment of the ^{1}H NMR spectra between each of these pairs was achieved by comparisons of the chemical shifts with structurally similar complexes [such as $[Ru(Me_2bpy)_2(bpy\text{-}MV^{2+})]^{4+}$ and $[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{2+}$] and the relative degree of diamagnetic anisotropic interactions between the ligands within the particular stereochemistry.

These assignments were further confirmed by comparison of the chromatographic elution order for the four isomeric forms with previous studies involving the separation and characterization of the three isomeric forms of $[Ru(Me_2bpy)(pmb)_2]^{2+}$.[25] The ring-numbering sequences used for the various isomers are shown in Figure 1.

For the *cis(3)* isomer, the ^{1}H NMR spectrum consisted of 27 proton resonances and is shown in Figure 6C. The two singlet resonances at 5.93 ppm and 5.29 ppm are assigned to the methylene resonances H4′ (bpy-MV^{2+}) and H4′ (bpy-PTZ), respectively, based on NOE experiments and comparisons with $[Ru(Me_2bpy)_2(bpy\text{-}MV^{2+})]^{4+}$ and $[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{2+}$. ^{1}H COSY, NOE, and selective decoupling experiments confirmed connectivity between the methylene resonance H4′ (bpy-MV^{2+}) and H3′ of ring a (8.42 ppm), H5′ of ring a (7.33 ppm), and H6′ of ring a (7.66 ppm). Similarily, connectivity between the upfield methylene resonance H4′ (bpy-PTZ) and H3′ of ring c (8.48 ppm), H5′ of ring c (7.30 ppm) and H6′ of ring c (7.54 ppm), was established. Further chemical shift assigments were

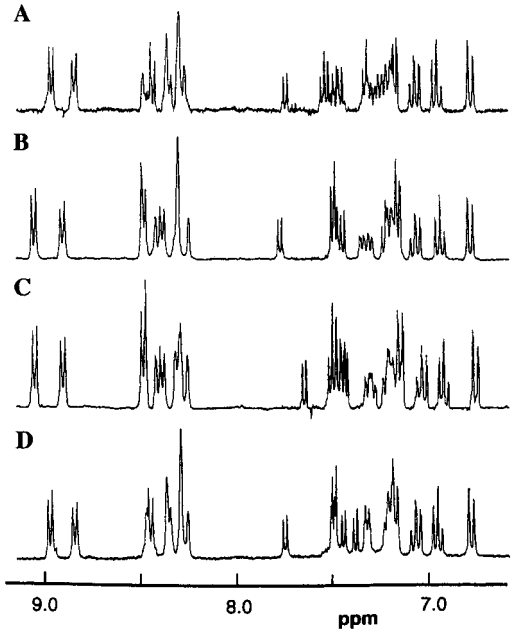

Figure 6. ^{1}H spectra (300 MHz; CD_3CN solvent) of the geometric isomers of $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(bpy\text{-}PTZ)]^{4+}$ (**III**): (A) *cis(2);* (B) *cis(1)*; (C) *cis(3);* (D) *trans*.

possible but had little significance with respect to the stereoisomer assignment.

The stereochemistry of the *cis(3)* isomer (see Figure 1) suggests that the MV^{2+}-substituted pyridyl ring (ring a) is orientated over the plane of the PTZ-substituted pyridyl ring (ring c). As previously discussed for the $[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{2+}$ complex, this relative orientation results in an upfield shift in the proton H6 (ring a) associated with the MV^{2+}-substituted pyridyl ring. This upfield influence of approximately 0.1 ppm is observed for H6′ (7.66 ppm, ring a) relative to the H6′ (ring a) protons in the other isomeric forms and the $[Ru(Me_2bpy)_2(bpy\text{-}MV^{2+})]^{4+}$ complex.

In the *cis(1)* isomer, some overlapping of signals may be expected in the ^{1}H NMR spectrum as a result of its "pseudo-C_2" symmetry in this isomeric form. The spectrum is shown in Figure 6B. The two singlet resonances at 5.93 ppm and 5.29 ppm were assigned to the methylene resonances H4′ (bpy-MV^{2+}) and H4′ (bpy-PTZ), respectively, on the basis of arguments similar to those discussed above. By methods similar to those described for the *cis(3)* isomer, the H6′, H5′, and H3′ protons on ring a were assigned to resonances at 7.79, 7.38, and 8.42 ppm and those on ring c to resonances at 7.52, 7.34, and 8.48 ppm, respectively.

The stereochemistry of the *cis(1)* form (see Figure 1) indicates that a pyridyl ring (ring f) of the Me_2bpy ligand is orientated over the plane of the PTZ-substituted pyridyl ring (ring c). This accounts for the H6′ (ring f) resonance upfield at 7.24 ppm relative to H6 protons on the other methyl-substituted pyridyl rings, for reasons discussed above. This resonance is slightly shielded relative to the equivalent H6 resonance in the $[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{2+}$ complex (7.32 ppm), presumably due to a trans influence from the MV^{2+}-substituted pyridyl ring.

The ^{1}H NMR spectrum of the *cis(2)* isomer is shown in Figure 6A and reveals 27 proton resonances, with overlap of several proton resonances resulting from the C_1 symmetry. By anology with the isomers discussed above, the two methylene singlet resonances at 5.93 ppm and 5.29 ppm may be assigned to H4′ (bpy-MV^{2+}) and H4′ (bpy-PTZ), respectively, enabling the assignment of H6′, H5′, and H3′ protons on ring a to resonances at 7.73, 7.30, and 8.39 ppm and on ring c to resonances at 7.53, 7.28, and 8.48 ppm, respectively.

The stereochemistry of this isomeric form indicates that the pyridyl ring of the Me_2bpy (ring f) is orientated over the plane of the PTZ-substituted pyridyl ring (see Figure 1). For reasons discussed above, the H6′ (Me_2bpy) proton in this geometry is shifted upfield to 7.32 ppm, which is in good agreement with the H6′ (Me_2bpy) proton (at 7.32 ppm), which has a similar geometry in the $[Ru(Me_2bpy)_2(bpy\text{-}PTZ)]^{4+}$ complex.

For the *trans* isomer, the ^{1}H NMR spectrum is shown in Figure 6D; similar to observations for *cis(1)*, a number of overlapping resonances are observed due to its "pseudo-$\mathbf{C}_2$" symmetry. As discussed above, the two methylene singlet resonances at 5.93 ppm (H4′, bpy-MV^{2+}) and 5.29 ppm (H4′, bpy-PTZ) enabled the assignment of H6′, H5′, and H3′ protons on ring a to resonances at 7.75, 7.32, and 8.37 ppm, and on ring c to resonances at 7.48, 7.32, and 8.47 ppm, respectively. As shown in Figure 1, the H6 proton on ring b is orientated over the plane of the PTZ-substituted pyridyl ring. This H6 proton resonance is thus observed upfield (relative to remaining H6/H6′ protons) at 7.36 ppm, by comparison with the H6′ (ring f) in the *cis(2)* isomer where it is shifted downfield by approximately 0.05 ppm. This may be rationalized using the NMR spectrum of $[Ru(Me_2bpy)_2(bpy\text{-}MV)]^{4+}$, which shows a deshielding influence (approximately 0.05 ppm) of H6 (methyl-substituted ring of the bpy-MV^{2+} ligand) relative to the H6/H6′ protons on the Me_2bpy ligands.

Conclusions

Our ability to synthesize and control the stereochemistry of complexes with a variety of ligand types has enabled us to isolate the stereoisomers of a mononuclear chromophore−quencher species of the type D−C−A. Importantly, this will now enable us to probe the influence that the spatial relationship of the donor and acceptor groups have on intramolecular electron transfer processes. Initial photophysical studies suggest that differences are observed between the four geometric forms of the complex $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(bpy\text{-}PTZ)]^{4+}$. Details of our current comparative photophysical study of the four isomers of the present title system will be reported subsequently,[27] and an investigation of analogues in which the linkages between the bpy ligating group and the MV^{2+} and PTZ functionalities are extended from the methylene group to larger alkyl chains is in progress.

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Supporting Information Available: Cyclic voltammogram of $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(bpy\text{-}PTZ)]^{4+}$ (1 page). Ordering information is given on any current masthead page.

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