Inorg. Chem. **2000,** *39,* 71−75

One-Pot Synthesis and Characterization of a Chromophore−Donor−Acceptor Assembly

Kimberly A. Maxwell, Milan Sykora, Joseph M. DeSimone, and Thomas J. Meyer*

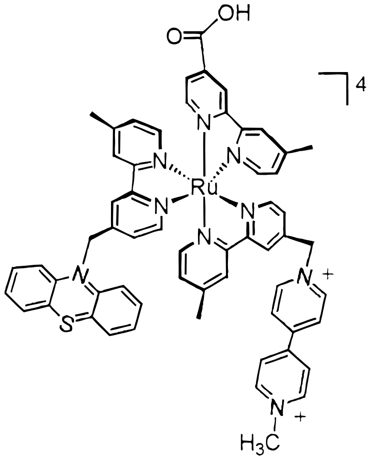
Department of Chemistry, The University of North Carolina at Chapel Hill, CB 3290,
Chapel Hill, North Carolina 27599-3290

Received May 11, 1999

The acid-functionalized tris-heteroleptic chromophore−donor−acceptor assembly $[Ru^{II}(bpyCOOH)(bpyCH_2PTZ)(bpyCH_2MV^{2+})](PF_6)_4]^{4+}$ (**1**) (bpyCOOH = 4′-methyl-2,2′-bipyridine-4-carboxylic acid; $bpyCH_2PTZ$ = 10-((4′-methyl-2,2′-bipyridin-4-yl)methyl)phenothiazine; $bpyCH_2MV^{2+}$ = 1-((4′-methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′-bipyridinediium) was synthesized in a one-pot reaction by careful selection of the order of ligand addition to $RuCl_2(DMSO)_4$ (DMSO = dimethyl sulfoxide). The success of this method was based upon separation and isolation of **1** from mixtures containing ligand-scrambled products by cation exchange chromatography. Metal-to-ligand charge-transfer (MLCT) excitation in acetonitrile at 464 nm was followed by intramolecular electron transfer to give a redox-separated state $[Ru^{II}(bpyCOOH)(bpyCH_2PTZ^{\bullet +})(bpyCH_2MV^{\bullet +})]^{4+}$ with an efficiency of $\eta_{RS} = 0.35 \pm 0.05$.

Introduction

In the preparation of polypyridyl-based molecular assemblies for the study of photoinduced electron and energy transfer, synthetic procedures are required for preparing highly asymmetrical ligand environments. Multiple-step methods have been described for the preparation of tris-heteroleptic complexes of the type $[Ru(bpy')(bpy'')(bpy''')]^{2+}$ in which there are three different ligands in the same coordination environment.[1−3] More recent procedures have appeared based on $RuCl_2(DMSO)_4$ and $Ru(bpy)(CH_3CN)_2Cl_2$ that involve fewer steps and give higher yields.[4] We report here a related procedure in which a one-pot synthesis leads to the preparation of a tris-heteroleptic molecular assembly, containing three different asymmetrical polypyridyl ligands.[5] The complex, **1**, contains an electron-transfer donor ligand, $bpyCH_2PTZ$ 10-((4′-methyl-2,2′-bipyridin-4-yl)methyl)phenothiazine), an acceptor ligand, $bpyCH_2MV^{2+}$ 1-((4′-methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′-bipyridinediium), and a carboxylic acid, bpyCOOH (4′-methyl-2,2′-bipyridine-4-carboxylic acid), which allows attachment of **1** to metal oxide surfaces[6] or amine-derivatized polymers.[7]



1

Experimental Section

Materials. Ethanol (Aaper Alcohol), acetonitrile (Burdick and Jackson), and dimethyl sulfoxide (Fisher Scientific) were used without further purification. All manipulations involving the donor and acceptor ligands and complexes were performed under nitrogen in subdued or red light. 4,4′-Dimethyl-2,2′-bipyridine (dmb, Aldrich) and phenothiazine (PTZ, Aldrich) were recrystallized twice from ethanol. Acetonitrile-d_3, ammonium hexafluorophosphate, sodium toluene-4-sulfonate, 4,4′-bipyridine, *n*-butyllithium (2.5 M in THF), and iodomethane were obtained from Aldrich. THF was freshly distilled from Na/benzophenone before use. *n*-Butyllithium was titrated with *N*-pivaloyl-*o*-benzylaniline.[8] Hydrated ruthenium trichloride was obtained from

---

(1) (a) Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145. (b) Strouse, G. F.; Anderson, P. A.; Schoonover, J. R.; Meyer, T. J.; Keene, F. R. *Inorg. Chem.* **1992**, *31*, 3004. (c) Anderson, P. A.; Strouse, G. F.; Treadway, J. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 3863. (d) Treadway, J. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2267.

(2) (a) Ross, H. B.; Boldaji, M.; Rillema, D. P.; Blanton, C. B.; White, R. P. *Inorg. Chem.* **1989**, *28*, 1013. (b) von Zelewsky, A.; Gremaud, G. *Helv. Chim. Acta* **1988**, *71*, 1108. (c) Juris, A.; Campagna, S.; Balzani, V.; Gremaud, G.; von Zelewsky, A. *Inorg. Chem.* **1988**, *27*, 3652. (d) Thummel, R. P.; Lefoulon, F.; Chirayil, S. *Inorg. Chem.* **1987**, *26*, 3072.

(3) Rutherford, T. J.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 2872.

(4) (a) Zakeeruddin, S. M.; Nazeeruddin, Md. K.; Humphry-Baker, R.; Grätzel, M.; Shklover, V. *Inorg. Chem.* **1998**, *37*, 5251. (b) Freedman, D. A.; Evju, J. K.; Pomije, M. K.; Mann, K. R. *Abstr. Pap.*—*Am. Chem. Soc.* **1998**, *216*, INOR 178.

(5) Maxwell, K. A.; DeSimone, J. M.; Meyer, T. J. *Polym. Prepr.* **1998**, *39*, 600.

(6) (a) Trammell, S. A.; Meyer, T. J. *J. Phys. Chem. B* **1999**, *103*, 104. (b) Striplin, D. R.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Phys. Chem. B* **1998**, *102*, 2383. (c) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.

(7) (a) Dupray, L. M.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 6299. (b) Friesen, D. A.; Kajita, T.; Danielson, E.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 2756. (c) Kurimura, Y.; Shinozaki, N.; Ito, F.; Uratani, Y.; Shigehara, K.; Tsuchida, E.; Kaneko, M.; Yamada, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 380.

10.1021/ic990512i CCC: \$19.00

Janssen Chimica. SP-Sephadex C25 resin was purchased from Pharmacia Biotech. Tetra-*n*-butylammonium hexafluorophosphate ([N(*n*-$C_4H_9)_4$](PF_6), recrystallized three times from ethanol) and ferrocene (Fc, sublimed before use) were obtained from Aldrich.

Syntheses. $RuCl_2(DMSO)_4$ was prepared as described by Wilkinson et al.[9] 4′-Methyl-2,2′-bipyridine-4-carboxylic acid (bpyCOOH) and 4′-Methyl-2,2′-bipyridine-4-carbaldehyde (bpyCHO) were synthesized according to published procedures.[10] Chemical analyses were performed by Oneida Research Services, Inc. (Whitesboro, NY).

4-(Hydroxymethyl)-4′-methyl-2,2′-bipyridine (bpyCH$_2$OH). A literature method[11] was used with the following modifications. The volume of the chloroform extract was reduced to ~25 mL, and ~100 mL of hexanes was added. The volume was reduced to ~75 mL by rotary evaporation to precipitate a white solid. The flask was refrigerated at 4 °C for several hours, and the white powder was collected on a fine-porosity frit. The final product was recrystallized from methanol/hexanes (2.0 g, 90%). ^{1}H NMR (chlorform-*d*): 2.42 (3H, s), 3.12 (1H, br s), 4.79 (2H, s), 7.15 (1H, d), 7.30 (1H, d), 8.20 (1H, s), 8.33 (1H, s), 8.51 (1H, d), 8.61 ppm (1H, d).

4-(Bromomethyl)-4′-methyl-2,2′-bipyridine (bpyCH$_2$Br). Slight modifications of a literature method[11] were made. The hydrogen bromide salt was neutralized by dropwise addition to a stirring biphasic solution of CH_2Cl_2 (200 mL)/Na_2CO_3(aq) (100 mL, 0.5 M), extracted into CH_2Cl_2 (3 × 200 mL), and washed with water (3 × 200 mL). The organic extracts were dried over Na_2SO_4, and the solvent was removed by rotary evaporation (<30 °C). The pale pink precipitate was purified by column chromatography to give a white solid (1.1 g, 84%). This ligand was used in subsequent reactions within a week of preparation. ^{1}H NMR (chlorform-*d*): 2.44 (3H, s), 4.80 (2H, s), 7.15 (1H, d), 7.32 (1H, d), 8.21 (1H, s), 8.33 (1H, s), 8.51 (1H, d), 8.61 ppm (1H, d).

1-Methyl-4,4′-bipyridinium Hexafluorophosphate ([MQ$^+$](PF$_6^-$)). The quaternized bipyridinium salt was synthesized as described by Yonemoto et al.[12] with the following modifications. The yellow iodide salt was dissolved in water, and the solution was filtered to remove a dark impurity into an aqueous solution containing excess ammonium hexafluorophosphate to form a pale yellow precipitate. This process was repeated to afford a white precipitate, which was collected on a fine-porosity frit, rinsed with aqueous ammonium hexafluorophosphate (dilute) and ether, and dried under vacuum (1.4 g, 69%). ^{1}H NMR (acetonitrile-*d*$_3$): 4.33 (3H, s), 7.78 (2H, dd), 8.29 (2H, d), 8.70 (2H, d), 8.84 ppm (2H, dd).

1-((4′-Methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′-bipyridinediium hexafluorophosphate (bpyCH$_2$MV^{2+}) was synthesized with a few modifications of literature procedures.[3,12] [MQ$^+$](PF_6) (1.02 g, 3.21 mmol) and bpyCH$_2$Br (0.508 g, 1.93 mmol) were heated at reflux under nitrogen in 100 mL of acetonitrile (fresh bottle) for 10 h. The reaction mixture was cooled to 0 °C for 1 h. The pale yellow precipitate that appeared was collected on a fine-porosity frit and dissolved in distilled water. The solution was filtered into an aqueous solution containing excess ammonium hexafluorophosphate. The resulting white powder was filtered off, washed with aqueous ammonium hexafluorophosphate (dilute) and chloroform, and dried under vacuum (0.77 g, 62%). ^{1}H NMR (acetonitrile-*d*$_3$): 2.45 (3H, s), 4.40 (3H, s), 5.94 (2H, s), 7.29 (1H, d), 7.38 (1H, d), 8.28 (1H, s), 8.35 (2H, d), 8.41 (2H, d), 8.51 (2H, s), 8.76 (1H, d) 8.84 (2H, d), 9.02 ppm (2H, d).

10-((4′-Methyl-2,2′-bipyridin-4-yl)methyl)phenothiazine (bpyCH$_2$PTZ) was synthesized by modifying a published procedure.[13] Phenothiazine (0.416 g, 2.09 mmol) was added to a flame-dried flask under nitrogen. Argon-purged THF (40 mL) was added through a cannula, and the temperature was reduced to −78 °C. Freshly titrated *n*-BuLi (1.35 mL, 1.54 M in THF) was added dropwise to the solution over 25 min. BpyCH$_2$Br (0.55 g, 2.09 mmol) was added, and the solution was warmed slowly to room temperature. The mixture was extracted into diethyl ether and washed with water. The organic layer was dried over Na_2SO_4, and the solvent was removed by rotary evaporation. The residue was chromatographed (silica; diethyl ether), and solvent was removed by rotary evaporation to give a white solid (0.56 g, 70%), which was rinsed with hexanes. ^{1}H NMR (acetonitrile-*d*$_3$): 2.46 (3H, s), 5.17 (2H, s), 6.62 (2H, d), 6.86 (2H, t), 6.97 (2H, t), 7.08−7.11 (2H, dd), 7.14 (1H, d), 7.21 (1H, d), 8.22 (1H, s), 8.43 (1H, s), 8.53 ppm (2H, d).

(4′-Methyl-2,2′-bipyridine-4-carboxylic acid)[1-((4′-methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′-bipyridiniium][10-((4′-methyl-2,2′-bipyridin-4-yl)methyl)phenothiazine]ruthenium(II) Hexafluorophosphate [Ru^{II}(bpyCOOH)(bpyCH$_2$PTZ)(bpyCH$_2$MV^{2+})](PF$_6$)$_4$] (1). bpyCH$_2$MV^{2+} (285 mg, 0.442 mmol) and bpyCOOH (95 mg, 0.44 mmol) were added to $RuCl_2(DMSO)_4$ (195 mg, 0.402 mmol) in ethanol (20 mL), and the mixture was heated at reflux for 35 min. A pale brown precipitate formed. The final ligand, bpyCH$_2$PTZ (152 mg, 0.398 mmol), and deionized water (9 mL) were added, and the reaction was monitored by UV−visible spectroscopy. The ratio Abs(290 nm):Abs(254 nm) progressed from 0.77 at 1 h to 0.85 at 5 h and remained at 0.85 for 6 h in acetonitrile. The solution was cooled to room temperature and added to ~500 mL of deionized water containing 20% acetonitrile and buffer (0.01 M NaH_2PO_4 and 0.01 M Na_2HPO_4). The solution was filtered, and the product was separated from the filtrate by cation-exchange chromatography (SP-Sephadex C25, 0.025−0.4 M aqueous sodium toluene-4-sulfonate gradient; 20% acetonitrile containing buffer) based on methods developed by Keene et al.[3,14] The desired product was eluted with a solution 0.1−0.2 M in the sodium salt. Acetonitrile was removed by rotary evaporation, and the complex was precipitated by addition of excess ammonium hexafluorophosphate in water, acidified with dilute HCl, and cooled to 0 °C for 2 h. The product (125 mg, 19%) was filtered off on a fine-porosity frit and rinsed with dilute aqueous ammonium hexafluorophosphate (acidic) and diethyl ether. For photophysical measurements, the product was further chromatographed twice (0.05−0.25 M aqueous sodium toluene-4-sulfonate gradient; 20% acetonitrile containing buffer) to remove possible minute impurities. Anal. Calcd for $RuC_{59}H_{53}N_9P_4F_{24}$: C, 43.45; H, 3.15; N, 7.73. Found: C, 43.17; H, 3.35; N, 7.54. IR (KBr): ν(C=O) at 1733 cm^{-1}.

Measurements. ^{1}H NMR spectra were obtained on a Bruker Aspect 3000 (WM 250 MHz) spectrometer in acetonitrile-*d*$_3$, 99.6 atom % D. A Bruker AX500 NMR spectrometer with a 30° pulse, relaxation delay of 1 s, and 256 scans was used to generate the ^{1}H NMR spectrum of the chromophore−donor−acceptor assembly in acetonitrile-*d*$_3$ (99.95 atom % D).

Electrochemical measurements were performed by using an EG&G PAR model 273 potentiostat. Measurements were made in nitrogen-purged acetonitrile 0.1 M in [N(*n*-$C_4H_9)_4$](PF_6) in a three-compartment cell. A platinum coil counter electrode, a platinum disk working electrode (polished with 0.3 μm alumina), and an Ag/AgNO$_3$ (0.01 M in acetonitrile) reference electrode (+0.31 V vs SSCE; calibrated with Fc$^{+/0}$) were used. Voltammograms were generated at a sweep rate of 100 mV/s. The $E_{1/2}$ values were calculated as the average of the oxidative and reductive peak potentials, $(E_{p,a} + E_{p,c})/2$.

UV−visible spectra (acetonitrile solutions) were recorded on a Hewlett-Packard HP-8452A diode array spectrophotometer with quartz cells. The infrared spectrum of **1** was obtained by using a Mattson Galaxy 5000 series FT-IR spectrometer at 2 cm^{-1} resolution, averaging 25 scans (forward and reverse mirror velocity at 0.32 cm/s at 10 000 Hz). Photophysical measurements (continuous wave and time-resolved) were conducted as described previously.[15] Solutions were purged with argon for 50 min prior to measurement.

Transient absorbance measurements were performed by using a Surelite II-10 (Continuum) Nd:YAG-OPO laser system as an excitation source. The excitation wavelength was 464 nm, and the power of the

---

(8) Suffert, J. *J. Org. Chem.* **1989**, *54*, 509.

(9) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

(10) Peek, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, G. J.; Meyer, T. J.; Erickson, B. W. *Int. J. Pept. Protein Res.* **1991**, *38*, 114.

(11) Furue, M.; Yoshidzumi, T.; Kinoshita, S.; Kushida, T.; Nozakura, S.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1632.

(12) Yonemoto, E. H.; Riley, R. L.; Kim, Y. I.; Atherton, S. J.; Schmehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081.

(13) Della Ciana, L.; Hamachi, I.; Meyer, T. J. *J. Org. Chem.* **1989**, *54*, 1731.

(14) Rutherford, T. J.; Reitsma, D. A.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1994**, 3659.

(15) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7448.

beam (defocused to ~3 cm^2) at the sample was 1.2 mJ/(pulse cm^2). The pulse width was 5−7 ns (fwhm). The excitation beam from the laser irradiated the sample perpendicularly to the optical axis of an Applied Photophysics laser kinetic spectrometer consisting of a 250 W pulsed Xe lamp, f3.4 monochromator, and Hammamatsu R446 PMT. The output from the PMT was coupled to a LeCroy 7200A oscilloscope interfaced with an IBM PC. Electronic synchronization and control of the experiment were achieved by electronics of local design. Kinetic traces (average of 50) decaying to >5 lifetimes of the transient observed were acquired and averaged at each wavelength. The average decay curves were fit to a first-order kinetic model by using SigmaPlot (Jandel Scientific, Inc.). Spectrophotometric grade acetonitrile (Burdick and Jackson) was used for all spectroscopic measurements.

The quantum yield for formation of the redox-separated state (η_{RS}) was measured relative to $Ru(bpy)_3^{2+}$ (chloride salt used) in H_2O under otherwise identical conditions and calculated using the eq 1, where

$$\frac{\eta_{RS}}{\eta_{Rb3}} = A_c \frac{\Delta OD_{RS}/\Delta\epsilon_{RS}}{\Delta OD_{Rb3}/\Delta\epsilon_{Rb3}} \qquad (1)$$

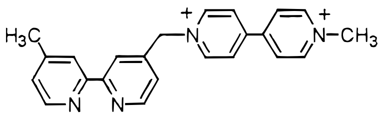
ΔOD_{RS} and ΔOD_{Rb3} are the transient signal changes for RS and $^*Ru(bpy)_3^{2+}$, respectively, obtained by extrapolation of the exponential kinetic fits to $t = 0$ at the monitoring wavelength. The changes in molar extinction coefficients $\Delta\epsilon_{RS}$ and $\Delta\epsilon_{Rb3}$ are defined as $\Delta\epsilon_{RS} = \epsilon_{PTZ^+} + \epsilon_{MV^+} - \epsilon_{PTZ} - \epsilon_{MV^{2+}}$ and $\Delta\epsilon_{Rb3} = \epsilon_{*Ru(bpy)_3^{2+}} - \epsilon_{Ru(bpy)_3^{2+}}$. The individual extinction coefficients (in M^{-1} cm^{-1}) are literature values.[16] A_c is a correction for the difference in the ground-state absorbance between the molecular assembly (A_{RC}) and $Ru(bpy)_3^{2+}$, (A_{Rb3}) at the excitation wavelength:

$$A_c = \frac{1 - 10^{-A_{Rb3}}}{1 - 10^{-A_{RC}}} \qquad (2)$$

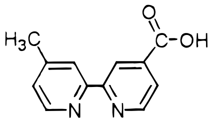
The value of η_{RS} reported is an average of independent measurements at eight different wavelengths between 500 and 530 nm. The value of η_{Rb3} was assumed to be 1.

Results and Discussion

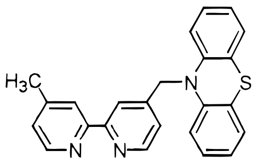
Tris-heteroleptic polypyridyl complexes of Ru(II) have been reported as the products of a general, multistep method, which yields well-defined complexes containing three different ligands.[1−3] The method is time consuming, and the reactions must be optimized carefully to obtain substantial yields (overall yields are ~2−20%).[1,3] We report here a facile alternative based on methods for the preparation of bis-heteroleptic complexes by Elliott et al.,[17] a tris-heteroleptic complex by Thummel et al.,[2d] and the chromatographic separation techniques of Keene et al.[3,14] With three different ligand combinations, 10 possible complexes can result. The tris-heteroleptic complex containing one each of the different ligands was isolated on the basis of ligand charge differences. In this case, the product complex contains bipyridine ligands that have three different charge types during chromatography since bpyCOOH (pK_a ~ 3.0 in H_2O)[18] exists as $bpyCOO^-$ during the separation procedure. The isolation of the tris-heteroleptic product from the many complexes that form due to ligand scrambling was accomplished by chromatography with increasing gradients of sodium *p*-toluenesulfonate in 4:1 water/acetonitrile. The resulting tris-heteroleptic complex has eight possible positional isomers due to the asymmetrical nature of the ligands. Since no significant difference in photophysical properties of the isomers is expected,[19] the separation of these isomers was not attempted.



$bpyCH_2MV^{2+}$



bpyCOOH



$bpyCH_2PTZ$

The synthetic procedure utilizes $RuCl_2(DMSO)_4$ as a precursor with successive additions of the electron transfer donor, $bpyCH_2PTZ$, the acceptor, $bpyCH_2MV^{2+}$, and bpyCOOH. The order of addition is important. With the more basic ligand $bpyCH_2PTZ$ added initially, the tris complex, $[Ru^{II}(bpyCH_2PTZ)_3]^{2+}$, forms immediately as evidenced by the appearance of its characteristic red color ($\lambda_{max} = 464$ nm). With the initial addition of bpyCOOH or $bpyCH_2MV^{2+}$, no red color characteristic of tris complex formation results. The final assembly ($\lambda_{max} \sim 460$ nm (broad), $\epsilon = 11\,600$ M^{-1} cm^{-1}) was obtained by allowing 1.1 equiv of $bpyCH_2MV^{2+}$ and 1.1 equiv of bpyCOOH to react with $RuCl_2(DMSO)_4$ for 35 min, followed by addition of $bpyCH_2PTZ$. It was necessary to monitor the reaction by UV−vis spectroscopy (5−6 h) to establish when formation of **1** was maximized. The absorbance ratio [290 nm ($\pi \rightarrow \pi_1^*$]:[254 nm ($d\pi \rightarrow \pi_2^*$ and $\pi \rightarrow \pi^*(MV^{2+})$)], was monitored during the course of the 5−6 h reaction. When the reaction was allowed to proceed for ~12 h, $[Ru^{II}(bpyCH_2PTZ)_3]^{2+}$ formed as the dominant product and the yield of **1** fell to zero because of ligand scrambling.

Six fractions were isolated during ion-exchange chromatography (at least two additional fractions remained on the column) by elution with increasing gradients of aqueous sodium *p*-toluenesulfonate in the following sequence: (1) 0.025 M, (2) 0.05−0.1 M, (3) 0.1−0.2 M, (4) 0.2−0.25 M, (5) 0.2−0.3 M, (6) 0.3−0.4 M. Individual fractions were collected by precipitation with excess ammonium hexafluorophosphate. The [290 nm]:[254 nm] absorbance ratios for the separated fractions were (1) 0.73, (2) 1.4, (3) 0.98, (4) 0.83, (5) 0.95, and (6) 1.3.

In Table 1 are presented characterization data for each isolated product. The ^1H NMR spectra are complicated because of the asymmetrical nature of the ligands and the existence of positional isomers for the complexes; however, the ^1H NMR spectra in the region between 4.2 and 6.2 ppm shown in Table 1 support the assignments of the eluted fractions. The integrated intensities of the methyl resonance of the quaternized amine of $bpyCH_2MV^{2+}$ (4.42 ppm) and the methylene resonances for $bpyCH_2PTZ$ (5.30 ppm) and $bpyCH_2MV^{2+}$ (5.98 ppm) provided a useful comparison for the various fractions. The ratio for **1** is 3:2:2, for $[Ru^{II}(bpyCH_2PTZ)_2(bpyCH_2MV)]^{4+}$ it is 3:4:2, and

---

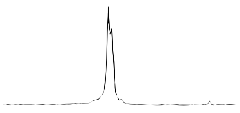
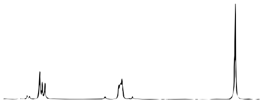
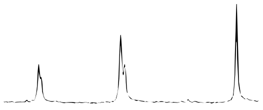
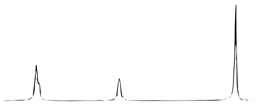
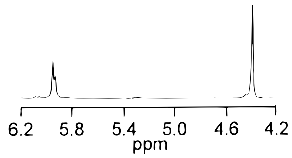
[16] (a) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617. (b) Hester, R. E.; Williams, K. P. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 852. (c) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

[17] (a) Elliott, C. M.; Freitag, R. A.; Blaney, D. D. *J. Am. Chem. Soc.* **1985**, *107*, 4647. (b) Larson, S. L.; Elliott, C. M.; Kelley, D. F. *J. Phys. Chem.* **1995**, *99*, 6530.

[18] Lay, P. A.; Sasse, W. H. F. *Inorg. Chem.* **1984**, *23*, 4125.

[19] Treadway, J. A.; Chen, P. Y.; Rutherford, T. J.; Keene, F. R.; Meyer, T. J. *J. Phys. Chem. A* **1997**, *101*, 6824.

Table 1. Characterization of Products by ^{1}H NMR (250 MHz, CD_3CN) and Cyclic Voltammetry (0.1 M TBAH in CH_3CN)

		^{1}H NMR Spectra	$E_{1/2}$ Values (V vs. SSCE)					
Fraction	Product[a]	(6.2-4.2 ppm)	$Ru^{III/II}$	$PTZ^{+/0}$	$MV^{2+/+}$	$MV^{+/0}$	$bpy^{0/-}$	$bpy^{0/-}$
1	$[Ru(b\text{-}PTZ)_3]^{2+}$		1.32	+0.81			-1.38	
2	$[Ru(b\text{-}MV^{2+})(b\text{-}COOH)_2]^{4+}$		1.34		-0.34	-0.78		
3	$[Ru(b\text{-}MV^{2+})(b\text{-}PTZ)(b\text{-}COOH)]^{4+}$		1.31	+0.81	-0.34	-0.75	-1.38	
4	$[Ru(b\text{-}MV^{2+})(b\text{-}PTZ)_2]^{4+}$		1.28	+0.82	-0.34	-0.74	-1.36	-1.53
5	$[Ru(b\text{-}MV^{2+})_2(b\text{-}PTZ)]^{6+}$		1.28	+0.81	-0.34	-0.74	-1.35	-1.53
6	$[Ru(b\text{-}MV^{2+})_3]^{8+}$		1.32		-0.34	-0.75	-1.39	

[a] b-COOH is bpyCOOH, b-PTZ is $bpyCH_2PTZ$, b-MV^{2+} is $bpyCH_2MV^{2+}$

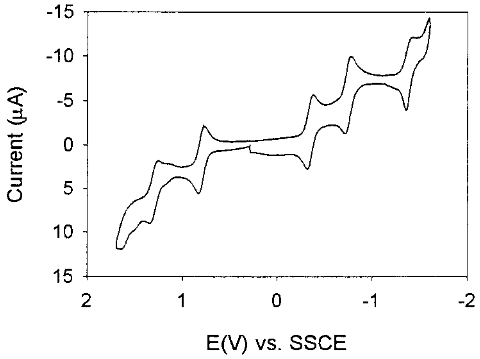


Figure 1. Cyclic voltammogram of $[Ru^{II}(bpyCOOH)(bpyCH_2PTZ)(bpyCH_2MV^{2+})](PF_6)_4$ at 100 mV/s in CH_3CN, 0.1 M TBAH.

for $[Ru^{II}(bpyCH_2PTZ)(bpyCH_2MV^{2+})_2]^{6+}$ it is 3:1:2. Integrations of the total resonances in the aromatic region yielded consistent results.

In Figure 1 is shown a cyclic voltammogram of assembly **1** in acetonitrile 0.1 M in $[N(n\text{-}C_4H_9)_4](PF_6)$. The expected $Ru^{III/II}$ wave appears at $E_{1/2} = 1.31$ V, the $PTZ^{+/0}$ wave appears at 0.81 V, the $MV^{2+/+}$ wave appears at -0.34 V, the $MV^{+/0}$ wave appears at -0.75 V, and the first bpy reduction wave appears at -1.38 V vs SSCE.

With these waves assigned, waves for the various fractions in Table 1 are consistent with the proposed assignments, as are the relative peak heights of the $PTZ^{+/0}$, $MV^{2+/+}$, and $MV^{+/0}$ waves. Comparison of integrated wave forms for the oxidized and reduced waves of **1** yields the ratio ~1:1:1. This ratio shifts to ~2:1:1 for $[Ru^{II}(bpyCH_2PTZ)_2(bpyCH_2MV)]^{4+}$ and to ~1:2:2 for $[Ru^{II}(bpyCH_2PTZ)(bpyCH_2MV^{2+})_2]^{6+}$.

MLCT emission from **1** is >99% quenched with $\Phi_{em} \sim 0.0001$ at $\lambda_{em}(\max) \sim 672$ nm compared to the emission from the model $[Ru^{II}(dmb)_2(bpyCOOH)](PF_6)_2$ (dmb is 4,4′-dimethyl-2,2′-bipyridine, $\Phi_{em} \sim 0.026$).[20] The extent of quenching is consistent with the expected rapid electron-transfer quenching of the MLCT excited state.

The evidence for intramolecular electron transfer was demonstrated by laser flash photolysis. The transient absorption difference spectrum generated by laser flash excitation at 464 nm (Abs ~ 0.50) in acetonitrile at 1.2 mJ/(pulse cm^2) is shown in Figure 2. The expected features for $MV^{\bullet +}$ at 397 and 607 nm[16a] and for $PTZ^{\bullet +}$ at 513 nm[16b] are present in the spectrum. The intermediate redox-separated (RS) state that appears was formed during the 5−7 ns laser flash. Transient absorption changes following the flash were independent of monitoring wavelength from 400 to 700 nm with $k_{ET} = 6.3\ (\pm 0.1) \times 10^6$ s^{-1} ($\tau = 160$ ns). This rate constant for back electron transfer, Scheme 1, reflects an average value for the series of eight possible positional isomers. In previous work on $[Ru^{II}(dmb)(bpyCH_2PTZ)(bpyCH_2MV^{2+})]^{4+}$, the four positional isomers

---

(20) (a) To ensure complete protonation, a few drops of a dilute solution of sulfuric acid were added to the sample (purged with Ar for 50 min). For emission from these solutions, $\Phi_{em} = 0.026$. Application of emission spectral fitting to the spectrum gave $E_0 = 14\,423 \pm 2.8$ cm^{-1}, $S_M = 0.684 \pm 0.0037$ cm^{-1}, $\Delta\bar{\nu}_{1/2} = 1930 \pm 5.8$ cm^{-1}, and $\hbar\omega = 1494 \pm 3.4$ cm^{-1}. The fit deviation was 6.6. E_0 is the $\nu^* = 0 \rightarrow \nu = 0$ energy gap, S_M the electronic−vibrational coupling constant (Huang−Rhys factor), $\Delta\bar{\nu}_{1/2}$ the full width at half maximum (bandwidth), and $\hbar\omega$ the quantum spacing for the acceptor mode in the average-mode approximation.[19b−d] (b) Claude, J. P.; Meyer, T. J. *J. Phys. Chem.* **1995**, *99*, 51. (c) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (d) Claude, J. P. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1995.

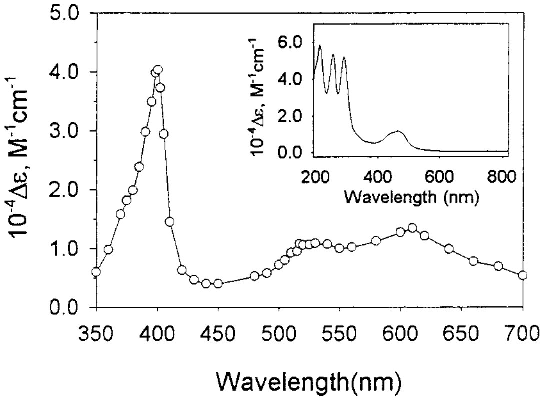
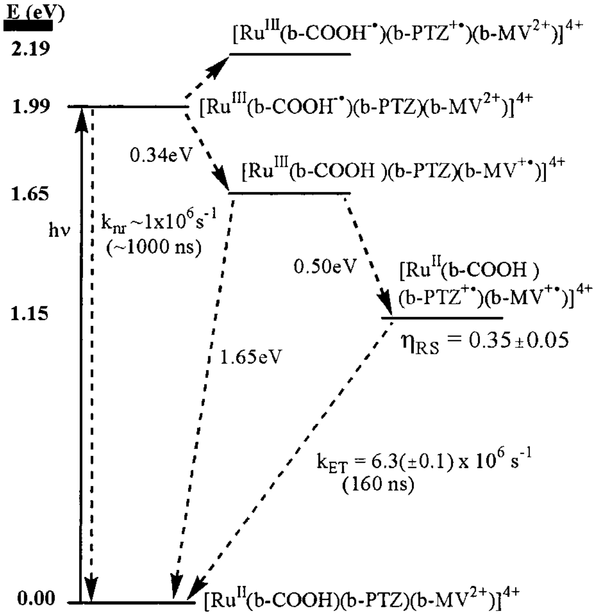


Figure 2. Transient absorption difference spectrum for [Ru^{II}(bpy-COOH)(bpyCH$_2$PTZ)(bpyCH$_2$MV^{2+})](PF$_6$)$_4$ in CH$_3$CN observed at room temperature upon flash excitation with λ_{exc} = 464 nm, 1.2 mJ/(pulse cm^2). The inset shows the ground-state absorption spectrum of the complex in CH$_3$CN.

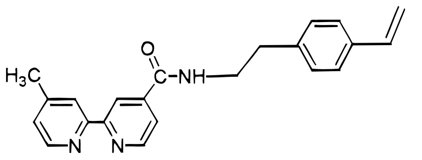
Scheme 1[a]



[a] In acetonitrile; b-COOH is bpyCOOH, b-PTZ is bpyCH$_2$PTZ, and b-MV^{2+} is bpyCH$_2$MV^{2+}.

were separated by cation exchange chromatography with the rate constants somewhat isomer dependent in acetonitrile with k_{ET} = 7.7 × 10^6 s^{-1} (trans), 4.5 × 10^6 s^{-1} (cis 1), 8.7 × 10^6 s^{-1} (cis 2), and 6.3 × 10^6 s^{-1} (cis 3).[19]

The sequence of events that occurs following MLCT excitation is illustrated in Scheme 1.[21] The value of k_{nr} in the scheme was calculated from the lifetime (τ = 935 ns) and quantum yield (Φ_{em} = 0.066) for the model complex [Ru^{II}(dmb)$_2$(bpy-CONHEt′)](PF$_6$)$_2$ by using the relationship $k_{nr} = (1 - \Phi)/\tau$.



bpyCONHEt'

The quantum yield for formation of the redox-separated state was determined as η_{RS} = 0.35 ± 0.05. This is different from η_{RS} = 0.20−0.25 observed for the related [Ru^{II}(dmb)(bpy-CH$_2$PTZ)(bpyCH$_2$MV^{2+})]$^{4+}$ (**2**) complex studied by Treadway et al.[19] The origin of this difference can be explained by referring to Scheme 1.

Electron-transfer quenching of the initial MLCT state in both complexes is dominated by initial electron transfer to −MV^{2+}, which is known to be rapid in [Ru^{II}(bpy)$_2$(bpyCH$_2$MV^{2+})](PF$_6$)$_4$.[22] This reaction is favored by −0.34 eV in **1** and by −0.6 eV in **2**. (Competitive quenching by electron transfer from −PTZ is unfavorable by +0.20 eV.) Subsequent electron transfer from −PTZ to Ru(III) is favorable by −0.50 eV in **1** and by −0.40 eV in **2**. This electron-transfer step is in competition with back electron transfer from −MV$^{\bullet+}$ to Ru(III), which is favorable by −1.65 eV in **1** and by −1.54 eV in **2** and most likely lies in an inverted region. It is presumably the combination of small increases in driving force for both the back electron transfer (which decreases k_{et} in the inverted region) and competing forward electron transfer (which increases k_{et} in the normal region) that increases the efficiency of RS state formation in **1** compared to **2**.

Acknowledgment. We thank the National Science Foundation for support of this research under grant CHE-9705724.

Supporting Information Available: The 500 MHz ^{1}H NMR spectrum of **1** in acetonitrile-d_3 and a display of the positional isomers of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990512I

---

(21) Energies for the states in Scheme 1 were obtained by using the reduction potentials for the PTZ$^{+/0}$ and MV$^{2+/+}$ couples of **1** and the results of emission spectral fitting of [Ru^{II}(dmb)$_2$(bpyCOOH)](PF$_6$)$_2$.[19] On the basis of the emission spectral fitting parameters, $\Delta G^{\circ}_{ES} = E_0 + (\Delta\bar{\nu}_{1/2})^2/(16k_BT \ln 2)$ = 1.99 eV with E_0 = 14 423 cm^{-1} and $\Delta\bar{\nu}_{1/2}$ = 1930 cm^{-1}.

(22) Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786.