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Trifluoromethyl-Substituted 2,2′-Bipyridine Ligands. Synthetic Control of Excited-State Properties of Ruthenium(II) Tris-Chelate Complexes

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The synthesis of the novel bidentate ligands 4,4′-bis(trifluoromethyl)-2,2′-bipyridine (4,4′-BTFMB), 5,5′-bis(trifluoromethyl)-2,2′-bipyridine (5,5′-BTFMB), and 4,4′,5,5′-tetrakis(trifluoromethyl)-2,2′-bipyridine (4,4′,5,5′-TTFMB) is reported. The photophysical and photochemical properties of a series of tris-chelate complexes $[Ru(bpy)_n(BTFMB)_{3-n}]^{2+}$ (n = 0–2; bpy = 2,2′-bipyridine) are described. From spectroscopic and electrochemical measurements, it has been shown that the BTFMB ligand has lower lying π^* levels which not only lead to significant changes in ground- and excited-state redox potentials but also exert relatively large effects on absorption and emission spectral properties. From measurements of emission lifetime and quantum yield at room temperature, the radiative (k_r) and nonradiative (k_{nr}) decay rate constants were obtained. Trends in k_{nr} properties are understandable on the basis of the energy gap law. Possible applications in excited-state redox chemistry are also discussed.

Introduction

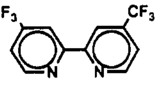
Luminescent d^6 transition-metal complexes are useful as photosensitizers for energy- and electron-transfer reactions. Ru(II) complexes, in particular, have been used most widely in this regard.[1] Since the metals, ligands, and solvent environment can all affect excited-state properties, variations of one or more of these factors can be used to tune the photophysical and photochemical properties.[2,3]

The lowest excited state of $Ru(bpy)_3^{2+}$ is largely metal-to-ligand charge transfer (MLCT) in nature and is best described as $Ru^{III}(bpy)_2(bpy^{\bullet-})$.[3-8] The polarization of this transition has been thoroughly studied by polarized-emission experiments in fluid solution. It was concluded that optical absorption leads to a state in which the transferred electron is intrinsically localized on a single ligand but undergoes rapid intramolecular transfer based on the exciton hopping.[9] Nanosecond transient Raman studies on mixed-ligand derivatives of Ru(II) complexes have also shown that, in most cases, the optical electron is localized on the most easily reduced ligand.[10-12]

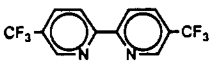
Photophysical studies on the MLCT excited state by a series of lifetime and emission quantum yield measurements have revealed that subsequent nonradiative decay of the excited state can be accounted for by the energy gap law.[8,13,14] The qualitative "energy gap law" for nonradiative decay predicts that ln k_{nr} should decrease linearly with the emission energy.[15]

An additional feature in the excited-state structure for $Ru(bpy)_3^{2+}$ is the existence of low-lying dd states, which can provide an additional decay channel.[16-18] For the use of Ru(II) complexes as photosensitizers, it is desirable to introduce an MLCT state sufficiently low in energy that the dd states are not accessible at room temperature. An approach to the problem of controlling the accessibility of low-lying dd states is to make variations in the ligand.[19] In this sense, it is necessary to synthesize new bpy ligands which have low-lying π^* levels. Studies on intramolecular processes in heterobinuclear (polypyridine)metal complexes have prompted us to synthesize new ligands for maintaining the large span of the energy gap between two complexes.[20] A trifluoromethyl group can be a good candidate for the substituent group because of its σ-accepting power and chemical stabilities.

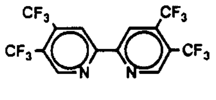
The purposes of this paper are to demonstrate (1) the synthesis of trifluoromethyl-substituted 2,2′-bipyridine ligands and a series of symmetrical and mixed-ligand, tris-chelate complexes of bpy and BTFMB with Ru(II), (2) the systematic changes of redox potentials by appropriate combinations of bpy and BTFMB ligands, and (3) the photophysical and photochemical properties, including lifetimes and emission quantum yields, of the excited states of Ru(II) complexes. The new ligands addressed in this paper are as follows:



4,4′-BTFMB



5,5′-BTFMB



4,4′,5,5′-TTFMB

Experimental Section

General Procedures and Reagents. ^{1}H NMR spectra were recorded on JEOL 270-MHz and 400-MHz NMR spectrometers at ambient temperature. Thin-layer chromatograms were run on Merck Kieselgel

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(1) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.
(2) Krause, R. A. *Struct. Bonding* **1987**, *67*, 1.
(3) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Besler, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(4) (a) Bensasson, R.; Salet, C.; Balzani, V. *J. Am. Chem. Soc.* **1976**, *98*, 3722. (b) DeArmond, M. K.; Myrick, M. L. *Acc. Chem. Res.* **1989**, *22*, 364.
(5) (a) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231. (b) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391. (c) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (d) Krausz, E.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293.
(6) DeArmond, M. K.; Myrick, M. L. *Acc. Chem. Res.* **1989**, *22*, 364.
(7) Krausz, E.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293.
(8) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
(9) Cooley, L. F.; Bergquist, P.; Kelley, D. F. *J. Am. Chem. Soc.* **1990**, *112*, 2612.
(10) McClanahan, S. F.; Dallinger, R. F.; Holler, F. J.; Kincaid, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 4853.
(11) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526.
(12) Chang, Y. J.; Xu, X.; Yabe, T.; Yu, S.-C.; Anderson, D. R.; Orman, L. K.; Hopkins, J. B. *J. Phys. Chem.* **1990**, *94*, 729.
(13) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.
(14) Barqawi, K. R.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 47.
(15) Freed, K. F. *Acc. Chem. Res.* **1978**, *11*, 74.
(16) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803.
(17) Meyer, T. J. *Pure Appl. Chem.* **1990**, *62*, 1003.
(18) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227.
(19) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.
(20) Furue, M.; Hirata, M.; Kinoshita, S.; Kushida, T.; Kamachi, M. *Chem. Lett.* **1990**, 2065.

0020-1669/92/1331-3792$03.00/0

60 F_{254} precoated silica gel plates. Column chromatography was performed on silica gel (Wakogel C200). Perdeuterioacetonitrile for NMR spectra was purchased from Aldrich Chemical Co. Tetrahydrofuran (THF) was distilled from sodium wire under an atmosphere of nitrogen prior use.

Reagents for homocoupling of halopyridines were prepared as described in the literature.[21] $NiBr_2(PPh_3)_2$ was prepared from 1 equiv of $NiBr_2$ and 2 equiv of PPh_3 in refluxing 1-butanol and purified by continuous extraction with 1-butanol in a Soxhlet extractor, followed by heating at 80 °C under reduced pressure. Zinc powder was washed successively with diluted hydrochloric acid, water, ethanol, acetone, and anhydrous ether and dried under reduced pressure. Tetraethylammonium iodide (Et_4NI) was purchased from Tokyo Kasei and dried at 100 °C under reduced pressure.

$RuCl_3 \cdot xH_2O$ was purchased from Mitsuwa's Pure Chemicals.

2-Chloro-4-(trifluoromethyl)pyridine (bp 145 °C), 2-chloro-5-(trifluoromethyl)pyridine (mp 30 °C), and 2-chloro-4,5-bis(trifluoromethyl)pyridine (bp 98 °C/135 mmHg) were kindly supplied by the Central Research Laboratory, Ishihara Sangyo Kaisha, Ltd.

Compounds whose analytical data are given as PF_6 salts have been prepared from chloride salts by treatment with ammonium hexafluorophosphate in water. PF_6 salts were obtained as a precipitate. Purification was carried out by LH-20 Sephadex column chromatography with EtOH as an eluent.

Preparation of Compounds. 4,4'-Bis(trifluoromethyl)-2,2'-bipyridine (4,4'-BTFMB). The ligand was prepared by modifying the method of Iyoda and co-workers.[21] To a 100-mL three-necked flask, equipped with a magnetic stir bar, a gas inlet adaptor, and a rubber septum, were added $NiBr_2(PPh_3)_2$ (2.23 g; 3 mmol), zinc powder (0.981 g; 15 mmol), and Et_4NI (2.01 g; 10 mmol) under argon pressure. Dry and O_2-free THF (20 mL) was added by syringe through septum. The reaction mixture was stirred at room temperature for 30 min. An argon-purged solution of 2-chloro-4-(trifluoromethyl)pyridine (1.82 g; 10 mmol) in THF (10 mL) was added by syringe, and the mixture was heated at 50 °C for 24 h. The reaction mixture was poured into 2 M aqueous ammonia (100 mL), and precipitates were filtered off. The filtrate was extracted with $CHCl_3$ (2 × 100 mL). The organic layer was washed with water (2 × 50 mL), dried with $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel using $CHCl_3$ as an eluent to give 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (0.59 g; 40.1%): mp 81.5–82 °C; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 7.58$ (d, 2 H), 8.73 (s, 2 H), 8.88 (d, 2 H). Anal. Found: C, 49.54; H, 2.10; N, 9.59. Calcd for $C_{12}H_6F_6N_2$: C, 49.33; H, 2.07; N, 9.59.

5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (5,5'-BTFMB). The compound was prepared by the method described for 4,4'-BTFMB (20.3% yield): mp 108.5–110 °C; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 8.10$ (d, 2 H), 8.63 (d, 2 H), 8.97 (s, 2 H). Anal. Found: C, 49.45; H, 1.98; N, 9.56. Calcd for $C_{12}H_6F_6N_2$: C, 49.33; H, 2.07; N, 9.59.

4,4',5,5'-Tetrakis(trifluoromethyl)-2,2'-bipyridine (4,4',5,5'-TTFMB). The compound was prepared by the method described for 4,4'-BTFMB (3.2% yield): mp 133.5–134 °C; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 9.00$ (s, 2 H), 9.22 (s, 2 H). Anal. Found: C, 39.36; H, 0.98; N, 6.61. Calcd for $C_{14}H_4F_{12}N_2$: C, 39.27; H, 0.94; N, 6.54.

$Ru(4,4'\text{-}BTFMB)_2Cl_2$ and **$Ru(5,5'\text{-}BTFMB)_2Cl_2$** were prepared by using the literature method for $Ru(bpy)_2Cl_2$.[22]

$[Ru(4,4'\text{-}BTFMB)_3]Cl_2$ and $[Ru(4,4'\text{-}BTFMB)_2(bpy)]Cl_2$. To approximately 100 mg of $Ru(4,4'\text{-}BTFMB)_2Cl_2$ was added the 2- or 3-fold excess of 2,2'-bipyridine or 4,4'-BTFMB needed to prepare the appropriate complex. The solids were dissolved in 50 mL of methanol, and the solution was heated at reflux until the absorption at 550 nm disappeared. The reaction mixture was condensed to a few milliliters and subjected to Sephadex LH20 chromatography to afford the desired complex. Anal. for $[Ru(4,4'\text{-}BTFMB)_3](PF_6)_2$. Found: C, 33.39; H, 1.73; N, 6.48. Calcd for $RuC_{36}H_{18}F_{30}N_6P_2 \cdot 1.8H_2O$: C, 33.26; H, 1.54; N, 6.46. Anal. for $[Ru(4,4'\text{-}BTFMB)_2(bpy)]Cl_2$. Found: C, 41.95; H, 3.01; N, 8.59. Calcd for $RuC_{34}H_{20}Cl_2F_{12}N_6 \cdot 3.5H_2O$: C, 41.86; H, 2.79; N, 8.61.

$[Ru(4,4'\text{-}BTFMB)(bpy)_2]Cl_2$. The complex was prepared from $Ru(bpy)_2Cl_2$ and 4,4'-BTFMB. Anal. Found: C, 46.20; H, 3.60; N, 10.15. Calcd for $RuC_{32}H_{22}Cl_2F_6N_6 \cdot 3H_2O$: C, 46.28; H, 3.40; N, 10.12.

$[Ru(5,5'\text{-}BTFMB)_2(bpy)]Cl_2$ and $[Ru(5,5'\text{-}BTFMB)(bpy)_2]Cl_2$. These complexes were prepared by the method described for 4,4'-BTFMB derivatives. Anal. for $[Ru(5,5'\text{-}BTFMB)_2(bpy)](PF_6)_2$. Found: C, 36.04; H, 1.87; N, 7.32. Calcd for $RuC_{34}H_{20}F_{24}N_6P_2$: C, 36.09; H, 1.78; N, 7.43. Anal. for $[Ru(5,5'\text{-}BTFMB)(bpy)_2](PF_6)_2$. Found: C, 37.70; H, 2.30; N, 8.30. Calcd for $RuC_{32}H_{22}F_{18}N_6P_2 \cdot H_2O$: C, 37.92; H, 2.39; N, 8.29.

$[Ru(5,5'\text{-}BTFMB)_3]Cl_2$. The complex was prepared from $Ru(DMSO)_4Cl_2$ and 5,5'-BTFMB by using a literature method.[23] Anal. for $[Ru(5,5'\text{-}BTFMB)_3](PF_6)_2$. Found: C, 31.65; H, 1.69; N, 6.48. Calcd for $RuC_{36}H_{18}F_{30}N_6P_2 \cdot 1.5H_2O$: C, 33.26; H, 1.52; N, 6.46.

Physical Measurements. Spectrograde solvents for spectroscopic measurements were purchased from Nakarai Chemicals. Static absorption and luminescence measurements were performed using a Shimadzu UV-2100 spectrometer and an RF-502A spectrofluorimeter, respectively. Room-temperature luminescence quantum yields, Φ, were measured with $Ru(bpy)_3^{2+}$ in dearated water as a reference.[24] Samples for luminescence measurements were deoxygenated by purging with argon gas. Luminescence lifetimes were measured by the time-correlated single-photon-counting method, as described elsewhere.[25] The luminescence lifetimes for the complexes at room temperature are listed in Table III. Electrochemical measurements were performed as described elsewhere.[26]

Results and Discussion

Synthesis. Introduction of ring substituents into bpy ligands offers the possibility of tuning the optical properties of transition-metal complexes. 2,2'-Bipyridine and 4,4'-dimethyl-2,2'-bipyridine are versatile and inexpensive sources of bipyridine derivatives. There have been many reports on the synthesis of bipyridine derivatives.[27,28] However, we can find only few examples of bpy derivatives containing electron-attracting substituents such as NO_2[27] and CN[29] groups. The tris-chelate complex of $4,4'\text{-}(NO_2)_2bpy$ with Ru(II) shows a low quantum yield for luminescence (0.001) in alcoholic media at ambient temperature.[27] 2-Chloropyridines containing the trifluoromethyl group have attracted our attention as starting materials. Various methods are available for aryl–aryl carbon bond formation. Direct coupling of aryl halides by zerovalent nickel reagents has been accomplished in high yields under mild conditions.[21,30] We have employed this method for the synthesis of trifluoromethyl-substituted bpy. Details on the procedure and synthesis were described in the Experimental Section.

BTFMB and 4,4',5,5'-TTFMB ligands can react readily with $Re(CO)_5Cl$ to give the corresponding $bpy\text{–}Re(CO)_3Cl$ complexes in quantitative yields.[31] Attempts to prepare a Ru(II) complex containing the 4,4',5,5'-TTFMB ligand have been unsuccessful.

Electronic Spectra. In Figures 1 and 2 are presented absorption spectra for $Ru(bpy)_n(4,4'\text{-}BTFMB)_{3-n}$ and $Ru(bpy)_n(5,5'\text{-}BTFMB)_{3-n}$ (n = 0–2) in methanol, respectively. Absorption maxima and molar extinction coefficients are listed in Table I. The assignments for the absorptions are based on the spectrum

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(21) Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80.

(22) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

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

(24) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

(25) Kinoshita, S.; Kushida, T. *Anal. Instrum.* **1985**, *14*, 503.

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

(27) (a) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thomson, A. J.; Glasper, J. L.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1293. (b) Anderson, S.; Constable, E. C.; Seddon, K. R.; Turp, J. E.; Baggott, J. E.; Pilling, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2247. (c) Ghosh, P. K.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 5543. (d) Furue, M.; Sumi, K.; Nozakura, S. *Chem. Lett.* **1981**, 1349. (e) Furue, M.; Yoshidzumi, T.; Kinoshita, S.; Kushida, T.; Nozakura, S.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1632. (f) Elliott, C. M.; Freitag, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, 156. Furue, M.; Kuroda, N.; Nozakura, S. *Chem. Lett.* **1986**, 1209. (g) Launikonis, A.; Lay, P. A.; Mau, A. W.-H.; Sargeson, A. M.; Sasse, W. H. F. *Aust. J. Chem.* **1986**, *39*, 1053.

(28) (a) Della Ciana, L.; Hamachi, I.; Meyer, T. J. *J. Org. Chem.* **1989**, *54*, 1731. (b) Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745. (c) Wenkert, D.; Woodward, R. B. *J. Org. Chem.* **1983**, *48*, 283. (d) Jones, R. A.; Boney, B. D.; Sasse, W. H. F.; Wade, K. O. *J. Chem. Soc. B* **1967**, 106.

(29) Baxter, P. N. W.; Connor, J. A. *J. Organomet. Chem.* **1988**, *355*,

(30) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.

(31) Unpublished results.

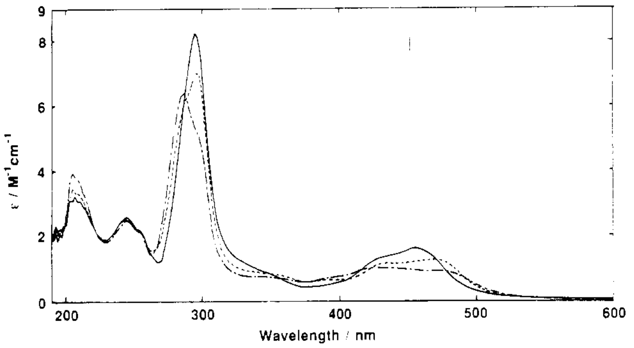

Figure 1. Absorption spectra of $[Ru(4,4'\text{-}BTFMB)_3]^{2+}$ (—), $[Ru(4,4'\text{-}BTFMB)_2(bpy)]^{2+}$ (- - -), and $[Ru(4,4'\text{-}BTFMB)(bpy)_2]^{2+}$ (– • –) in methanol.

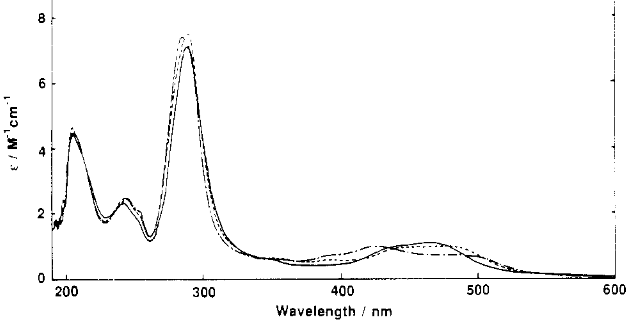

Figure 2. Absorption spectra of $[Ru(5,5'\text{-}BTFMB)_3]^{2+}$ (—), $[Ru(5,5'\text{-}BTFMB)_2(bpy)]^{2+}$ (- - -), and $[Ru(5,5'\text{-}BTFMB)(bpy)_2]^{2+}$ (– • –) in methanol.

Table I. Absorption Data

	MLCT		ligand π–π^*	
compd[a]	λ_{max}, nm	ϵ, $M^{-1}\ cm^{-1}$	λ_{max}, nm	$10^{-4}\epsilon$, $M^{-1}\ cm^{-1}$
$Ru(4,4'\text{-}BTFMB)(bpy)_2$	432.5 472.0	1.02×10^4 9.29×10^3	286.5	6.37
$Ru(4,4'\text{-}BTFMB)_2(bpy)$	438.5 470.0	1.15×10^4 1.26×10^4	296.0	6.99
$Ru(4,4'\text{-}BTFMB)_3$	430.0 455.5	1.31×10^4 1.60×10^4	294.5	8.23
$Ru(5,5'\text{-}BTFMB)(bpy)_2$	425.5 486.5	9.87×10^3 6.97×10^3	285.0	7.44
$Ru(5,5'\text{-}BTFMB)_2(bpy)$	454.0 476.0	9.44×10^3 9.74×10^3	289.0	7.51
$Ru(5,5'\text{-}BTFMB)_3$	440.0 467.0	9.61×10^3 1.09×10^4	288.5	7.13

[a] PF_6 salt.

Table II. Redox Potentials[a]

compd[b]	E_0^{ox}	E_0^{red}	E_0^{red}	E_0^{red}
$Ru(bpy)_3$	+1.27	−1.31	−1.50	−1.77
$Ru(4,4'\text{-}BTFMB)(bpy)_2$	+1.44	−0.89	−1.38	−1.59
$Ru(4,4'\text{-}BTFMB)_2(bpy)$	+1.63	−0.83	−1.02	−1.51
$Ru(4,4'\text{-}BTFMB)_3$	+1.75	−0.77	−0.93	−1.16
$Ru(5,5'\text{-}BTFMB)(bpy)_2$	+1.43	−0.83	−1.43	−1.74[c]
$Ru(5,5'\text{-}BTFMB)_2(bpy)$	+1.65	−0.77	−0.92	−1.42[c]
$Ru(5,5'\text{-}BTFMB)_3$	+1.75	−0.71	−0.86	−1.03

[a] All redox potentials, V vs SCE, were measured in acetonitrile, 0.1 M Bu_4NClO_4; scan rate 100 mV/s. [b] PF_6 salt. [c] Irreversible wave.

Table III. Luminescence Data and Related Quantities

compd[a]	λ_{em}-(max), nm	10^{-2}-Φem	τ_0,[b] ns	$10^{-4}k_r$,[c] s^{-1}	k_{nr},[c] s^{-1}
$Ru(bpy)_3$	605	5.3	720	7.4	1.3×10^6
$Ru(4,4'\text{-}BTFMB)(bpy)_2$	677	0.53	253	2.1	3.9×10^6
$Ru(4,4'\text{-}BTFMB)_2(bpy)$	653	2.3	370	6.2	2.6×10^6
$Ru(4,4'\text{-}BTFMB)_3$	619	6.4	1050	6.1	8.9×10^5
$Ru(5,5'\text{-}BTFMB)(bpy)_2$	700	0.044	42	1.1	2.4×10^7
$Ru(5,5'\text{-}BTFMB)_2(bpy)$	670	0.30	94.5	3.1	1.1×10^7
$Ru(5,5'\text{-}BTFMB)_3$	652	0.62	125	5.0	8.0×10^6

[a] PF_6 salt. [b] N_2 degassed; excited at 457.9 nm. [c] Calculated from $k_r = \Phi_{em}/\tau_0$ and $k_{nr} = (1 - \Phi_{em})/\tau_0$.

of $Ru(bpy)_3^{2+}$.[32] The high-energy absorptions in the 240–290-nm region are generally assigned to $\pi \rightarrow \pi^*$ transitions. The low-energy absorptions in the 380–500-nm region are assignable to $d\pi \rightarrow \pi^*$ transitions. The π^* levels of bpy and BTFMB are at different energies. The electrochemical measurements reveal that the first reduction process is BTFMB based (vide infra). The band located at low energy can be assigned to a $d\pi(Ru) \rightarrow \pi^*$(BTFMB) transition. Thus, mixed-chelated complexes are expected to give rise to different $d\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions characteristic of ligands coordinated to the metal center. As the number of bpy ligands increases, the low-energy transition shifts to the red. It is possible to understand the electronic origins of the shifts based on the $Ru^{III/II}$ redox potentials. The MLCT transition involves electronic excitation from donor orbitals [$d\pi(Ru)$] to acceptor orbitals π^*(ligand). In mixed-chelated complexes, the lowest energy transition can be assigned to the ligand containing the lowest π^* level (BTFMB). As can be inferred from the $E_{1/2}$ values for the $Ru^{III/II}$ couples, there is a corresponding decrease in the reductive ability of Ru^{II} [$d\pi(Ru)$ level] with the decrease of the number of bpy ligands.

Electrochemistry. Formal oxidation and reduction potentials vs SCE were obtained from cyclic voltammograms recorded at a glassy-carbon electrode in acetonitrile containing 0.1 M tetrabutylammonium perchlorate. These are listed in Table II. Scan rates were 100 mV/s. $E_{1/2}$ values were obtained from an average of anodic and cathodic peak potentials [$E_{1/2} = (E_{pa} + E_{pc})/2$]. The difference in potential between anodic and cathodic peak currents varied from 50 to 100 mV. By analogy with the (polypyridine)ruthenium electrochemical data, the assignment of these one-electron couples is straightforward. As the number of BTFMB ligands increases, the potential of the $Ru^{III/II}$ couple also increases. The sequence of reduction steps is best interpreted as the stepwise reduction of each ligand π^* system. The strong σ-attracting CF_3 substituent is responsible for the shifts of 0.5–0.7 V in the reduction and oxidation potentials of $Ru(BTFMB)_3^{2+}$ vs $Ru(bpy)_3^{2+}$.

Photophysical Properties. Room-temperature luminescence spectra were obtained in methanol. Emission maxima for the series of complexes are summarized in Table III. Concomitant with the red shift in the visible spectrum is a red shift in the emission spectrum of approximately the same energy. From electrochemical measurements, the BTFMB ligand has a lower π^* level than the bpy ligand. The lowest lying, emitting charge-transfer states in the mixed chelates $Ru(bpy)_n(BTFMB)_{3-n}$ (n = 0–2) are based on the $Ru^{III}(BTFMB^{\bullet-})$ chromophore. The linear correlation of the emission energy (E_{em}, eV) with the difference between the first reduction and first oxidation potentials can be used to rationalize the MLCT nature of the emissive state.

Excited-state lifetimes, determined by a time-correlated single-photon-counting method, are given in Table III. Lifetimes (τ_0) in methanol span the range 42–1050 ns, depending upon the number of BTFMB ligands and the position of the CF_3 substituent. Even though several of the complexes are mixed chelates containing different chromophoric ligands, all complexes examined show single-exponential decay.

Quantum yields for luminescence were deduced by comparison to $Ru(bpy)_3^{2+}$, having a known quantum yield of 0.042 at λ_{ex} = 436 nm.[24]

Rate constants for radiative (k_r) and nonradiative (k_{nr}) decay can be obtained from a combination of lifetime (τ_0) and emission

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(32) Ferguson, J.; Herren, F.; Krausz, E. R.; Maeder, M.; Vrbancich, J. *Coord. Chem. Rev.* **1985**, *64*, 21.

quantum yield (Φ_{em}) measurements, as shown in $1/\tau_0 = k_r + k_{nr}$ and $\Phi_{em} = k_r\tau_0$. Kinetic values are summarized in Table III.

On the basis of electrochemical data and trends in emission energies, it can be concluded that in the mixed chelate Ru(bpy)$_n$(BTFMB)$_{3-n}$ (n = 0–2) the lowest lying emitting charge-transfer states are based on the Ru^{III}(BTFMB)$^{\bullet-}$ chromophore. This is the expected result since, from electrochemical measurements, the relative ordering of the π^* levels in the free and complexed chelates is π^*(BTFMB) < π^*(bpy). In the nonradiative process, which dominates excited-state decay for these complexes, the important feature microscopically is the loss of energy into the surrounding molecular vibrations. There is no requirement for thermal activation to cross a barrier or to improve vibrational overlap.

As shown in Table III, comparison of the luminescent lifetime (τ_0) and the emission energy ($E_{em} = 1/\lambda_{em}$) indicates that as E_{em} decrease, τ_0 decreases. The effect is due to an increase of the nonradiative decay rate (k_{nr}). The energy gap law predicts that radiationless decay rates depend on the energies of the emitting state, namely the lower the energy of an emitting state, the more strongly it couples with ground state and the larger k_{nr}. Meyer and co-workers have demonstrated the applicability of the energy gap law in accounting for variations in k_{nr} of a series of polypyridyl Ru(II) and Os(II) complexes.[33] It would be reasonable to assume that the present variations in k_{nr} are being controlled by the energy gap law.

Excited-State Redox Properties—Reductive Quenching. The search for new photosensitizers to be used in solar energy conversion processes is an important area of investigation. Many redox systems for the photochemical dissociation of water into hydrogen and oxygen have been developed by using Ru(bpy)$_3^{2+}$ as a photosensitizer.[1,3] In the present photophysical characterization of new members of the (polypyridine)ruthenium family, the range in which light can be absorbed can be tuned systematically by the choice of BTFMB ligands. The lifetime (746 ns) of excited Ru(4,4'-BTFMB)$_3^{2+}$ in water is somewhat longer and the redox potentials of the various excited and ground states are almost 0.5 V more positive than those of Ru(bpy)$_3^{2+}$. The small red shifts of the same energy (~200 cm^{-1} = 0.02 eV) in the visible and emission spectra of Ru(BTFMB)$_3^{2+}$ were observed to be similar to those of Ru(bpy)$_3^{2+}$. It is quite likely that these complexes have the same excited emission energy, namely 2.1 eV. The excited-state redox potentials can be estimated by calculating the difference between the ground-state potential and the excited-state emission energy. The formal redox potentials of Ru(4,4'-BTFMB)$_3^{2+*/+}$ and Ru(4,4'-BTFMB)$_3^{3+/2+*}$ couples are 1.3 and −0.35 V vs SCE, respectively. We noted the similarity of the redox potentials of Ru(4,4'-BTFMB)$_3^{2+*/+}$ and Ru(bpy)$_3^{3+/2+}$ couples. There are several known reductants for Ru(bpy)$_3^{3+}$, e.g. triethanolamine (TEOA), ethylenediaminetetraacetic acid (EDTA), oxalate ion ($C_2O_4^{2-}$), hydroxyethanethiol, cysteine, and ascorbate ion. These donors can be expected to quench Ru(4,4'-BTFMB)$_3^{2+*}$, yielding Ru(4,4'-BTFMB)$_3^{+}$, which can reduce methylviologen (MV^{2+}). As a preliminary result, we find that visible-light irradiation (λ > 400 nm) of aqueous solutions containing Ru(4,4'-BTFMB)$_3^{2+}$, MV^{2+}, and TEOA yields MV^{+} under nitrogen. Steady-state emission techniques were used to ascertain the fate of excited Ru(4,4'-BTFMB)$_3^{2+}$. The rate constant for quenching for *Ru(4,4'-BTFMB)$_3^{2+}$ by TEOA is 7.2×10^6 M^{-1} s^{-1}, while MV^{2+} does not quench detectably.

Ru(bpz)$_3^{2+}$ has been known as a photosensitizer to reduce methylviologen in the reductive cycle.[34,35] This must take place under neutral conditions because remarkable self-quenching due to the protonated bpz ligand occurs under acidic conditions.[36]

Because of the chemical stability of the trifluoromethyl group, Ru(4,4'-BTFMB)$_3^{2+}$ can be perceived as an attractive photosensitizer. The charge-transfer excited state of this species also has a redox couple Ru(4,4'-BTFMB)$_3^{2+*/+}$, whose potential is estimated to be ca. +1.3 V, which is thermodynamically sufficient to oxidize water at pH 7. Further studies using Ru(BTFMB)$_3^{2+}$ as a photocatalyst are underway.

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(33) (a) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (b) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91*, 91. Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383. (d) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (e) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. (f) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

(34) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7128.

(35) Neshvad, G.; Hoffman, M. Z. *J. Phys. Chem.* **1989**, *93*, 2445.

(36) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170.