Inorg. Chem. **2003**, *42*, 8377–8384

Enhancement of Luminescence Lifetimes of Mononuclear Ruthenium(II)–Terpyridine Complexes by Manipulation of the σ-Donor Strength of Ligands

Marco Duati,[†,‡] Stefania Tasca,[†] Fiona C. Lynch,[†] Holger Bohlen,[†] and Johannes G. Vos*[,†]

National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

Stefano Stagni[§,||] and Michael D. Ward[§]

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, U.K.

Received June 18, 2003

The synthesis and characterization of mixed ligand 2,2′;6′,2″-terpyridine (tpy) ruthenium complexes with 2,6-bis-([1,2,4]triazol-3-yl)pyridine, 2,6-bis(5-phenyl-[1,2,4]triazol-3-yl)pyridine, and 2,6-bis([1,2,3,4]tetrazol-5-yl)pyridine are reported. The species are characterized by HPLC, ^{1}H NMR, UV/vis, and emission spectroscopy. The photophysical properties of the complexes are investigated as a function of temperature over the range 80–320 K. The emission lifetime observed for the fully deprotonated compounds at room temperature is about 80 ns. This increase by 2 orders of magnitude with respect to the parent "$[Ru(tpy)_2]^{2+}$" complex is rationalized by an increase in the energy of the metal based dσ orbital, rather than by manipulation of the π^* orbitals on the ligands. The acid–base and electrochemical properties of the compounds are reported also.

Introduction

Since the tridentate ligand 2,2′;6′,2″-terpyridine, tpy, was first prepared over 70 years ago,[1] the coordination chemistry of tpy based ligands has been widely studied.[2] Areas of research include the application of tpy complexes as protein labels,[3] reagents for enantioselective synthesis,[4] modifiers for porphyrins,[5] catechols,[6] and macrocycles,[7] and in solar energy devices based on modified nanocrystalline TiO_2 surfaces.[8] With the development of supramolecular chemistry there has also been a growing interest in Ru(II) tpy compounds. This interest is based on the realization that, with such complexes, linear multinuclear assemblies can be prepared, which may act as molecular wires and allow for vectorial energy and electron-transfer processes.[2f,9] However,

* Author to whom correspondence should be addressed. E-mail: johannes.vos@dcu.ie. Fax: +353 1 7005503. Tel: +353 1 700 5307.

† Dublin City University.

‡ Present address: Institute of Molecular Chemistry, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV, Amsterdam, The Netherlands.

§ University of Bristol.

|| Present address: Dipartimento di Chimica Fisica ed Inorganica, Università degli studi di Bologna, Viale Risorgimento, 4, Bologna, Italy.

(1) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1932**, 20.

(2) (a) Balzani, V.; Barigelletti, F.; Belser, P.; Bernhard, S.; De Cola, L.; Flamigni, L. *J. Phys. Chem.* **1996**, *100*, 16786. (b) Constable, E. C. *Prog. Inorg. Chem.* **1994**, *42*, 67. (c) Chodorowski-Kimmes, S.; Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **1996**, *37*, 2963. (d) Cargill Thompson, A. M. W. *Coord. Chem. Rev.* **1997**, *160*, 1. (e) Constable, E. C.; Davies, J. E.; Phillips, D.; Raithby, P. R. *Polyhedron* **1998**, *17*, 3989. (f) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S. Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.

(3) Mukkala, M.; Helenius, M.; Hemmila, I.; Kankare, J.; Takalo, H. *Helv. Chim. Acta* **1993**, *76*, 1361.

(4) (a) Chelucci, G. *Synth. Commun.* **1993**, *23*, 1897. (b) Chelucci, G.; Saba, A.; Vignola, D.; Solinas, C. *Tetrahedron* **2001**, *57*, 1099.

(5) (a) Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *Tetrahedron Lett.* **1991**, *32*, 5977. (b) Chambron, J. C.; Collin, J.-P.; Dalbavie, J.-O.; Dietrich-Buchecker, C. O.; Heitz, V.; Odobel, F.; Solladié, N.; Sauvage, J.-P. *Coord. Chem. Rev.* **1998**, *178*, 1299. (c) Collin, J.-P.; Harriman, A.; Heitz, V.; Odobel, F.; Sauvage, J.-P. *Coord. Chem. Rev.* **1996**, *148*, 63. (d) Kimura, M.; Hamakawa, T.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *Inorg. Chem.* **2001**, *40*, 4775. (e) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Ventura, B.; Collin, J.-P.; Sauvage, J.-P.; Williams, J. A. G. *Inorg. Chem.* **1999**, *38*, 661. (f) Collin, J.-P.; Harriman, A.; Heitz, V.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5679.

(6) (a) Whittle, B.; Everest, N. S.; Howard C.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 2025. (b) Storrier, G. D.; Takad, K.; Abruna, H. D. *Inorg. Chem.* **1999**, *38*, 559.

(7) (a) Tsukube, H.; Hamada, T.; Tanaka, T.; Uenishi, J. *Inorg. Chim. Acta* **1993**, *214*, 1. (b) Loiseau, F.; Di Petrio, C.; Serroni, S.; Campagna, S.; Licciardello, A.; Manfredi, A.; Pozzi, G.; Quici, S. *Inorg. Chem.* **2001**, *40*, 6901. (c) Haider, J. M.; Chavarot, M.; Weidner, S.; Sadler, I.; Williams, R. M.; De Cola, L.; Pikramenou, Z. *Inorg. Chem.* **2001**, *40*, 3912.

10.1021/ic034691m CCC: $25.00
Published on Web 10/25/2003

the application of this class of complex, although structurally very attractive, is severely hindered by their very short excited-state lifetimes (<1 ns at room temperature).[10] As a result attention has been focused on the design of novel tpy based Ru(II) complexes exhibiting extended excited-state lifetimes.[2,11−14] The approach taken in previous studies has primarily involved the manipulation of the energy of the emitting triplet metal-to-ligand charge-transfer transition (^{3}MLCT) by, for example, the use of substituents[14] or cyclometalating ligands[15] or by delocalization of the π-system.[16]

In this contribution the synthesis and characterization of a series of Ru(II) tpy compounds incorporating the tridentate ligands 2,6-bis([1,2,4]triazol-3-yl)pyridine (H_2L1), 2,6-bis-(5-phenyl-[1,2,4]triazol-3-yl)pyridine (H_2L2), and 2,6-bis-([1,2,3,4]tetrazol-5-yl)pyridine (H_2L3) (see Figure 1) are reported. The most important observation in this study is that deprotonation of the triazole/tetrazole ligand results in an enhancement of the excited-state lifetime by as much as 2 orders of magnitude with respect to the parent $[Ru(tpy)_2]^{2+}$ complex. This observation is rationalized in terms of an increase of the energy of the deactivating triplet metal centered (^{3}MC) excited state, which is achieved by an increase of the ligand field strength of one of the ligands. This approach complements the studies outlined above which are primarily concerned with the manipulation of the π^* level of the ligands, and the combination of these methods opens the possibility of the design of complexes with novel excited-state properties. Preliminary results on the preparation and characterization of Ru(II) complexes based on H_2L1 were reported in an earlier communication.[17]

Experimental Section

Instrumentation. High-performance liquid chromatography (HPLC) was carried out on a Waters 510 HPLC system using a Waters 990 photodiode array detector equipped with a 20 μL injector loop and a Partisil SCX radial PAK cartridge, using a detection wavelength of 280 nm, a mobile phase of 0.08 M $LiClO_4$ {acetonitrile/water, 80/20 (v/v)}, and a flow rate of 1.8 mL/min. Semipreparative HPLC was performed using an ACS pump, a 1 mL injection loop, a Waters Partisil SCX 10 μm cation exchange column (25 × 100 mm), a mobile phase of 0.1 M ammonium acetate in methanol, and a flow rate of 1.4 mL/min.

UV/vis spectra were recorded using a Shimadzu UV-3100 spectrophotometer. Emission spectra were obtained on a Perkin-Elmer LS50-B luminescence spectrometer with excitation and emission slit widths set at 10 nm. Luminescence quantum yields were measured using literature methods.[18] In both absorption and emission spectroscopy deprotonation was achieved using diethylamine, and protonation using 60% (w/v) perchloric acid. The ground-state pK_a's were determined by pH titration (in Britton−Robinson buffer: 0.04 M boric acid, 0.04 M acetic acid, 0.04 M phosphoric acid) monitored by UV/vis absorption spectroscopy. The pH was adjusted by adding concentrated NaOH or concentrated H_2SO_4 and measured using a Corning 240 digital pH meter. Emission lifetime measurements were carried out using time-correlated single photon counting (Edinburgh Analytical Instruments) in a T setting, consisting of an nF900 (N_2 filled) flashlamp, J-yA monochromators, a single photon photomultiplier detection system, model S 300 detector, with a Norland N5000 MCA card. The F900 Program (version 5.13) is used for data processing, with the quality of fits determined by examination of the χ^2 and residual plots of the fitted functions. Temperature dependent measurements were carried out using an Oxford Instruments liquid nitrogen cooled cryostat model 39426 with samples being held in a homemade quartz cuvette; ^{1}H NMR spectra were recorded on a Bruker Avance (400 MHz) NMR spectrometer. All measurements were carried out in d_6-DMSO for ligands or d_4-methanol for complexes. Peak positions are relative to residual solvent peaks. Protonation/deprotonation of samples was achieved using NaOD or DCl.

Electrochemical measurements were carried out using a CH Instruments model 660 electrochemical workstation with a scan rate of 100 mV s^{-1} using 0.1 M tetrabutylammonium hexafluorophosphate (TBAP), *N*,*N*-dimethylformamide, a 3-mm diameter Teflon shrouded glassy carbon working electrode, saturated calomel electrode (SCE) reference, and platinum wire auxiliary electrode. The ferrocene/ferrocenium couple was used as an internal reference. Solutions were purged with argon for 15 min prior to reductive measurements. The protonation state of the complexes was controlled using concentrated $NH_{3(aq)}$ or perchloric acid (70%). Spectroelectrochemistry was carried out using an EG&G PAR

(8) (a) Pechy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. J. *Chem. Soc., Chem. Commun.* **1995**, 65. (b) Liang, Y. W.; Schmehl R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 1007. (c) Rice, C. R.; Ward, M. D.; Nazeeruddin, M. K.; Grätzel, M. *New J. Chem.* **2000**, *24*, 651. (d) Islam, A.; Sugihara, H.; Arakawa, H. *J. Photochem. Photobiol. A: Chem.* **2003**, *158*, 131. (e) Bauer, C.; Boschloo, G.; Mukhtar, E.; Hagfeldt, A. *J. Phys. Chem. B* **2002**, *106*, 12693.

(9) (a) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681. (b) Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schneider, A. G.; Springler, B.; Zehnder, M. *Inorg. Chim. Acta* **2000**, *300*, 49. (c) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Collin, J.-P.; Dixon, I. M.; Sauvage, J.-P.; Gareth Williams, J. A. *Coord. Chem. Rev.* **1999**, *190*, 671. (d) Collin, J. P.; Gillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Flamigni, L.; De Cola, L.; Balzani, V. *Coord. Chem. Rev.* **1991**, *111*, 291. (e) Johansson, O.; Borgstrom, M.; Lomoth, R.; Palmblad, M.; Bergquist, J.; Hammarström, L.; Sun, L.; Åkermark, B. *Inorg. Chem.* **2003**, *42*, 2908. (f) Collin, J.-P.; Dietrich-Buchecker, C.; Gavina, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477.

(10) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.

(11) (a) Harriman, A.; Ziessel, R. *Coord. Chem. Rev.* **1998**, *171*, 331. (b) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707. (c) Elghayoury, A.; Harriman, A.; Khatyr, A.; Ziessel, R. *J. Phys. Chem. A* **2000**, *104*, 1512.

(12) Encinas, S.; Flamigni, L.; Barigelletti, F.; Constable, E. C.; Housecroft, C. E.; Schofield, E. R.; Figgemeier, E.; Fenske, D.; Neuburger, M.; Vos, J. G.; Zehnder, M. *Chem. Eur. J.* **2002**, *8*, 137.

(13) Swavey, S.; Fang, Z.; Brewer, K. J. *Inorg. Chem.* **2002**, *41*, 2598.

(14) (a) Constable, E. C.; Cargill Thompson, A. M. W.; Ararmoli, N.; Balzani, V.; Maestri, M. *Polyhedron* **1992**, *11*, 2707. (b) Indelli, M. T.; Bignozzi, C. A.; Scandola, F.; Collin, J.-P. *Inorg. Chem.* **1998**, *37*, 6084. (c) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chem.* **1995**, *34*, 2759. (d) Barigelletti, F.; Flamigni, L.; Guardigli, M.; Juris, A.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1996**, *35*, 136. (e) Fang, Y.-Q.; Taylor, N. J.; Hanan, G. S.; Loiseau, F.; Passalacqua, R.; Campagna, S.; Nierengarten, H.; van Dorsselaer, A. *J. Am. Chem. Soc.* **2002**, *124*, 7912.

(15) (a) Constable, E. C.; Cargill Thompson, A. M. W.; Cherryman J.; Liddiment, T. *Inorg. Chim. Acta* **1995**, *235*, 165. (b) Collin, J.-P.; Beley, M.; Sauvage, J.-P.; Barigelletti, F. *Inorg. Chim. Acta* **1991**, *186*, 91. (c) Beley, M.; Chodorowski, S.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L.; Barigelletti, F. *Inorg. Chem.* **1994**, *33*, 2543.

(16) (a) Hammarström, L.; Barigelletti, F.; Flamigni, L.; Indelli, M. T.; Armaroli, N.; Calogero, G.; Guardigli, M.; Sour, A.; Collin, J.-P.; Sauvage, J.-P. *J. Phys. Chem. A* **1997**, *101*, 9061. (b) Vogler, L. M.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 818.

(17) Duati, M.; Fanni, S.; Vos, J. G. *Inorg. Chem. Commun.* **2000**, *3*, 68.

(18) Demas, J. N.; Crosby G. A. *J. Phys. Chem.* **1971**, *75*, 991.

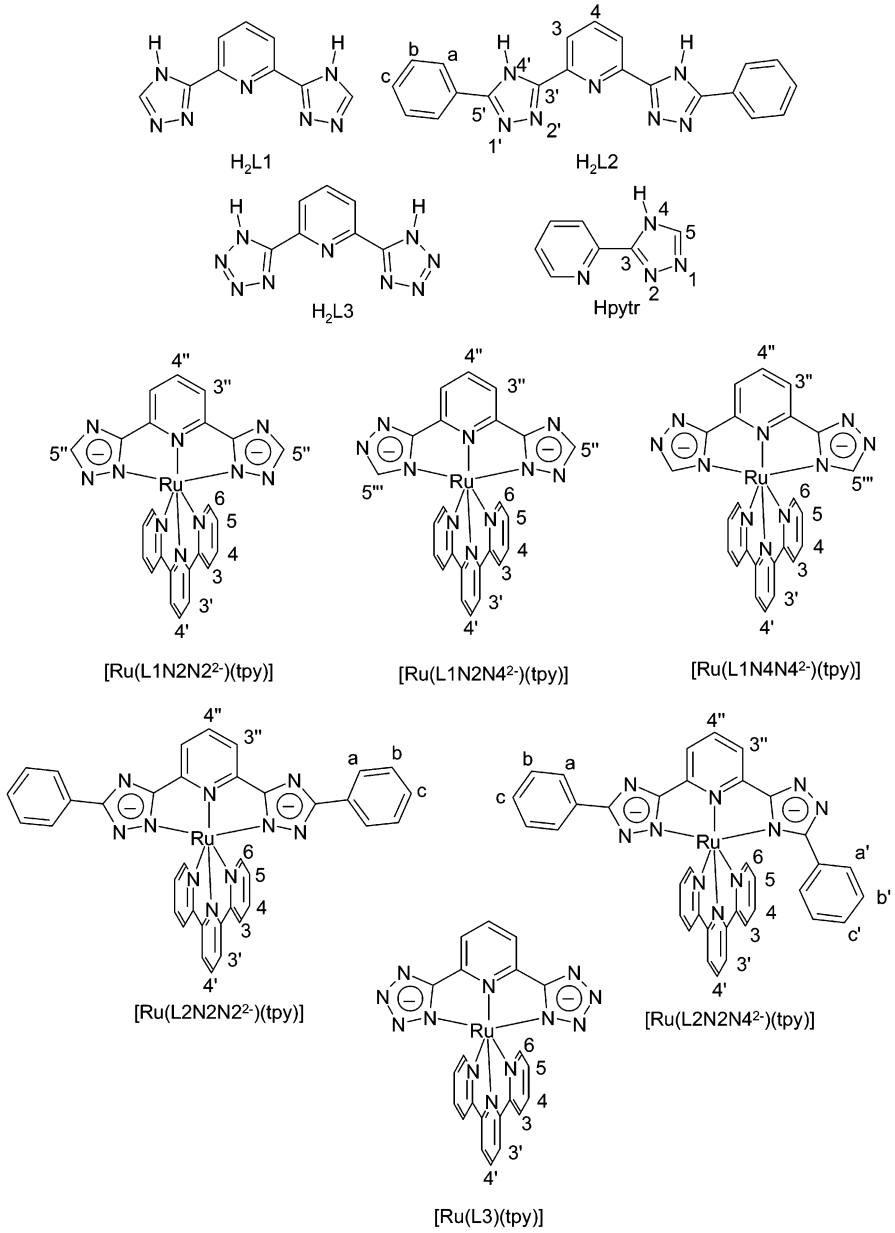

Figure 1. Structures of ligands and complexes.

model 362 scanning potentiostat and a Shimadzu 3100 UV/NIR spectrometer, together with a homemade Pyrex OTTLE cell (1 mm), a platinum/rhodium gauze working electrode, a pseudo Ag/AgCl reference electrode, and a platinum wire counter electrode. The electrolyte used was 0.1 M TBAP in acetonitrile.

Mass spectra were obtained using a Bruker-Esquire LC-00050 electrospray ionization mass spectrometer at positive polarity with cap-exit voltage of 167 V. Spectra were recorded in the scan range 50−2200 *m*/*z* with an acquisition time of between 300 and 900 μs and a potential of between 30 and 70 V. Each spectrum was recorded by summation of 20 scans. Elemental analysis has been carried out at the Micro-analytical Laboratory at University College Dublin.

Synthetic Methods. [Ru(tpy)Cl_3] was prepared as reported before.[9] The ligands 2,6-bis([1,2,4]triazol-3-yl)pyridine, H_2L1, and 2,6-bis([1,2,3,4]tetrazol-5-yl)pyridine, H_2L3, were prepared by literature procedures.[19,20]

The new ligand 2,6-bis(5-phenyl-[1,2,4]triazol-3-yl)pyridine (H_2L2) was prepared using the method reported for H_2L1, by changing in the last step of the reaction benzoyl chloride for formic acid. Yield: 80%. MS: found 366, 388 *m*/*z* (calcd for H_3L^+ 366, H_2LNa^+ 388). ^{1}H NMR (d_6-DMSO): 7.54 (t), 2H; 7.58 (dd), 4H; 8.20 (d), 4H; 8.30 (single broad peak, multiplet), 3H.

Synthesis of H[Ru(2,6-bis([1,2,4]triazol-3-yl)pyridine)(2,2′:6′,2”-terpyridine)]$_2$·(PF_6)·4H_2O [Ru(L1)(tpy)]. [Ru(tpy)Cl_3] (1 g, 2.2 mmol) was heated at reflux for 2 h in water containing 0.095 g, 2.3 mmol, of NaOH and a few drops of *N*-ethylmorpholine in the presence of a stoichiometric amount of H_2L1 (0.5 g, 2.2 mmol). The dark green reaction mixture was concentrated and acidified to pH 2 with HCl, and an excess of NH_4PF_6 was added. Purification by column chromatography on alumina (acetonitrile/methanol 50:

(19) Sugiyarto, K. H.; Craig, D. C.; Rae A. D.; Goodwin H. A. *Aust. J. Chem.* **1993**, *46*, 1269.
(20) Finnegan, W. G.; Henry, R. A.; Lofquist, R. *J. Am. Chem. Soc.* **1958**, *80*, 3908.

50) yielded a mixture of three isomers. The product obtained was recrystallized from acetone/water. Yield: 30% (0.42 g) Elemental anal. Calcd for $H[Ru(L1)(tpy)]_2[PF_6]\cdot 4H_2O$ ($C_{48}H_{41}N_{20}O_4PF_6Ru_2$) C, 44.03; H, 3.16; N, 21.40. Found: C, 43.70; H, 2.60; N, 21.03. Mass spectrometry, EI-MS, $[Ru(HL1)(tpy)]^+$: found 547.0, theoretical 547.0.

Separation of the three coordination isomers (**[Ru(L1N2N2)(tpy)]**, **[Ru(L1N2N4)(tpy)]**, and **[Ru(L1N4N4)(tpy)]**) (See Figure 1) was achieved by a combination of column chromatography and semipreparative HPLC. On alumina a first fraction containing the N2N2 and N2N4 isomers was obtained using 100% acetonitrile as eluent. Subsequent elution with 100% methanol yielded the pure N4N4 fraction, identified by ^{1}H NMR spectroscopy. Semipreparative HPLC was then utilized for the separation of the two isomers in fraction 1 as outlined above. The three isomers were obtained with a purity of 95% or better.

Synthesis of [Ru(H-2,6-bis(5-phenyl-[1,2,4]triazol-3-yl)pyridine)(2,2′:6′,2″-terpyridine)](PF$_6$)·H$_2$O, [Ru(L2)(tpy)]. The complex was prepared following the **[Ru(L1)(tpy)]** method using 1 equiv of the H_2L2. A first-stage purification by column chromatography on alumina (acetonitrile/methanol 50:50) gave a 25% yield. Elemental anal. Calcd for $[Ru(HL2)(tpy)]_2(PF_6)\cdot H_2O$, $C_{36}H_{27}N_{10}OPF_6Ru$: C, 50.17; H, 3.16; N, 16.26. Found: C, 50.19; H, 3.41; N, 15.81. Mass spectrometry, EI-MS, $[Ru(HL2)(tpy)]^+$: found 699.0, theoretical 699.0. The ^{1}H NMR spectrum of the product obtained showed the presence of two isomers, which were separated on neutral alumina; 100% acetonitrile was used as mobile phase to isolate the first fraction containing the N2N2 isomer and 100% methanol in the isolation of the second fraction containing the N2N4 isomer.

Synthesis of [Ru(2,6-bis([1,2,3,4]tetrazol-5-yl)pyridine)(2,2′:6′,2″-terpyridine)]·H$_2$O, [Ru(L3)(tpy)]. $[Ru(tpy)Cl_3]$ (1 g, 2.2 mmol) and a stoichiometric amount of H_2L3 (0.5 g, 2.2 mmol) were heated at reflux for 2 h in 20 mL of ethylene glycol, containing a few drops of *N*-ethylmorpholine. A brown solid was obtained upon the addition of H_2O. The complex was recrystallized from DMF/water (1:1). Yield: 55% (0.66 g). Elemental anal. Calcd for $[Ru(L3)(tpy)]\cdot(H_2O)$, $C_{22}H_{16}N_{12}ORu$: C, 46.73; H, 2.85; N, 29.72. Found: C, 46.50; H, 2.60; N, 29.03.

Results and Discussion

Synthesis and Purification. One disadvantage of the use of the terdentate ligand, H_2L1, is the formation of three coordination isomers by virtue of the inequivalence of the N2 and N4 positions of the 1,2,4-triazole moieties. In previous studies of $Ru(bpy)_2$ based (bpy = 2,2′-bipyridyl) complexes involving bidentate 1,2,4-triazole based ligands, coordination isomers have been observed. It was found that substitution of the 1,2,4-triazole ligands in the C5 (See Figure 1) position with methyl or phenyl groups imparted excellent control over the coordination mode by restricting the formation of the N4 isomer.[21] In the present contribution two approaches are taken to overcome the isomer problem. In the first, the effect of the introduction of steric hindrance on the number of isomers obtained is studied with the preparation of the new complex based on the ligand H_2L2. In a second approach, the tetrazole unit is introduced in place of the triazole, (i.e., H_2L3), with the symmetrical nature of this tetrazole ring resulting in the formation of a single coordination isomer. Initial attempts to prepare heteroleptic complexes using $[Ru(H_2L)Cl_3]$ type precursors proved to be unsuccessful; however, reaction of the ligands H_2L1, H_2L2, and H_2L3 with $[Ru(tpy)Cl_3]$ resulted in the formation of the desired products. The range of solvent systems available for the reactions was limited by the low solubility of the ligands. For the ligands H_2L1 and H_2L2 a basic aqueous solution was employed containing *N*-ethyl morpholine as a reducing agent, while for H_2L3 ethylene glycol proved to be the most suitable solvent.

For the H_2L1 based complex, elemental analysis suggests that the complex crystallized in a semiprotonation state so that the compound in the solid state is best described as $H[Ru(L1)(tpy)]_2^+$. Although this is initially surprising, a recent study has shown that semiprotonation of such compounds is observed when triazole-containing ruthenium polypyridyl complexes are isolated from mixed organic/aqueous solutions.[21] The X-ray data for the $Ru(bpy)_2$ complex of 2-(1′H-[1,2,4]triazol-3′-yl)pyrazine (Hpztr) indicated the presence of two molecular units bridged by a proton, as confirmed by the presence of 3 rather than the expected 2 or 4 PF_6^- counterions, per 2 molecular units that would be expected for fully deprotonated and fully protonated compounds, respectively. This indicates that in the solid state the molecular formula of this compound is best described as $H[(Ru(bpy)_2(pztr)]_2(PF_6)_3\cdot H_2O$, similar to that suggested for the H_2L1 complex reported here. For the H_2L2 based complex elemental analysis is consistent with the structure $[Ru(HL2)(tpy)]^+$, where one of the triazoles in each ruthenium unit is fully protonated, while in the H_2L3 based complex both tetrazole rings are fully deprotonated.

Regardless of the solid-state protonation state of the materials obtained, interest in this study lies in the photophysical and electrochemical properties of the totally deprotonated species. To ensure full deprotonation of the compounds all measurements were carried out in basic solutions as outlined in the Experimental Section. Unless otherwise stated the compounds are referred to as [Ru(L)(tpy)], indicating that they are fully deprotonated.

HPLC and ^{1}H NMR spectroscopy confirm the presence of three species in the crude product obtained on complexation of H_2L1 with the $[Ru(tpy)Cl_3]$ precursor. These species were identified as coordination isomers in which L1 is coordinated via N2 or N4 of the triazole ring. Separation of the species [**Ru(L1N2N2)(tpy)]**, **[Ru(L1N2N4)(tpy)]**, and **[Ru(L1N4N4)(tpy)]** (for structures see Figure 1) was achieved by chromatographic methods as outlined in the experimental part. HPLC analysis of the isomers obtained in this manner indicates an isomeric purity of 95% or better (see Figure S1, Supporting Information). Isomer ratios were estimated by ^{1}H NMR spectroscopy (see below). The major isomer, **[Ru(L1N2N4)(tpy)]** (~65%), has a retention time of 7.3 min. The second isomer (~20%) is assigned to the symmetrical isomer, **[Ru(L1N4N4)(tpy)]**, and appears in the HPLC trace as a broad peak with retention time of 20.2 min.

(21) Browne, W. R.; Hesek, D.; Gallagher, J. F.; O'Connor, C. M.; Killeen, J. S.; Aoki, F.; Ishida, H.; Inoue, Y.; Villani, C.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **2003**, 2597.

Table 1. ^{1}H NMR Spectroscopic Data (ppm) for Basic d_4-Methanol Solutions of Ligands and Their Ruthenium Complexes

	H^3 (d)	H^4 (dd)	H^5 (dd)	H^6 (d)	$H^{3'}$ (d)	$H^{4'}$ (t)	$H^{3''}$ (d)	$H^{4''}$ (t)	$H^{5''}$ (s)	$H^{5'''}$ (s)	H^a (d)	H^b (dd)	H^c (t)	$H^{a'}$ (d)	$H^{b'}$ (dd)	$H^{c'}$ (t)
tpy	8.70	8.00	7.50	8.70	8.55	8.10										
H_2L1[a]							8.15	8.15		8.35						
H_2L2[a]							8.30	8.30			8.20	7.58	7.54			
H_2L3[a]							8.15	8.15								
[Ru(L1N2N2)(tpy)]	8.43	7.75	7.10	7.33	8.63	8.08	8.30	8.27	7.60							
[Ru(L1N2N4)(tpy)]	8.40	7.73	7.07	7.26	8.60	8.08	8.22	8.17	7.59	6.80						
[Ru(L1N4N4)(tpy)]	8.30	7.69	7.05	7.21	8.57	8.08	8.10	8.10		6.96						
[Ru(L2N2N2)(tpy)]	8.37	7.75	7.17	7.44	8.34	7.55	8.20	8.29			6.19	6.76	6.98			
[Ru(L2N2N4)(tpy)]	8.34	7.70	7.12	7.38	8.01	7.90	8.22	8.19			6.36	6.86	6.98	7.61	7.12	7.17
[Ru(L3)(tpy)]	8.80	8.00	7.30	7.38	9.00	8.35	8.45	8.35								
$[Ru(tpy)_2]^{2+}$	8.82	8.08	7.34	7.72	9.09	8.59										

[a] Basic d_6-DMSO.

In the third isomer (∼ 15%) the triazoles are N2N2 bound, and this species elutes from the column with a retention time of 3.3 min.

It was anticipated that in complexes based on H_2L2, the presence of two phenyl substituents at the 5-position would, for steric reasons, result in the formation of the N2N2 isomer as the main product (See Figure 1) as observed for the analogous complexes based on bidentate ligands (e.g., 2-(5′-methyl-1′H-[1,2,4]triazol-3′-yl)pyridine).[22,23] However, HPLC analysis of the material obtained indicates the presence of two compounds. One with a retention time of 2 min (55%) was identified by ^{1}H NMR as the N2N2 isomer while the second species, which elutes after 3 min, is assigned to the N2N4 (45%) isomer. As expected HPLC analysis shows that reaction of H_2L3 with $[Ru(tpy)Cl_3]$ yields a single species.

^{1}H NMR Spectroscopy. The ^{1}H NMR data obtained for the complexes are given in Table 1. Peak assignments are made from ^{1}H COSY NMR spectra and by comparison with related complexes.[24,25] On the basis of the resonance obtained for the different species a number of conclusions may be drawn about the coordination mode of the triazole rings in the different isomers. Some typical spectra are shown in Figures 2 and S2 (Supporting Information). The differences observed for the **[Ru(L1)(tpy)]** isomers are best highlighted as shown in Figure S2 rather than by showing the spectra of the isomers individually. The isomer ratio of the products obtained is determined by integration of the H^6 resonances. Figure 2 shows that the protons most sensitive to changes in the ligand conformations are H^6 of tpy and H^5 of the triazole rings (for numbering see Figure 1). This is explained by diamagnetic anisotropic interaction of these protons with the aromatic rings of the other ligand in the complex. For example, for $[Ru(bpy)_2(pytr)]^+$, where Hpytr is 2-(1′H-[1,2,4]-triazol-3′-yl)pyridine, the triazole H^5 proton is found at 8.35 ppm when the ligand is coordinated via N4 and at 8.68 ppm for N2 coordination.[26] Therefore, it can be concluded that this H^5 resonance shifted furthest downfield is associated

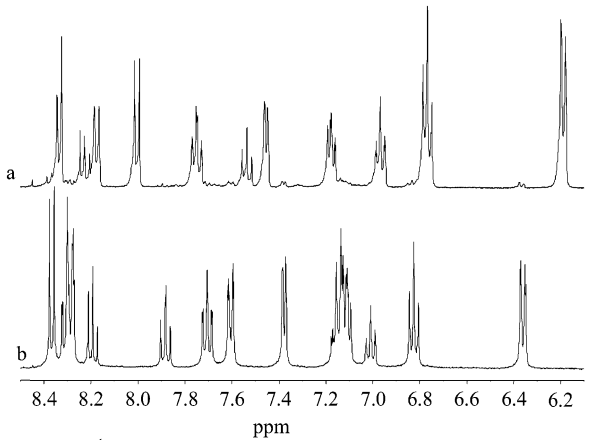

Figure 2. ^{1}H NMR (400 MHz) spectra of (a) [Ru(L2N2N2)(tpy)] and (b) [Ru(L2N2N4)(tpy)] in basic CD_3OD.

with N2 coordination of the triazole ring. On the basis of this model the triazole H^5 proton of the N2 bond species ($H^{5''}$) is found at about 7.60 ppm, while in the N4 coordinated species $H^{5''}$ is observed at 6.96 ppm. The H^6 protons of the tpy ring are found between 7.2 and 7.4 ppm. For the N2N2 isomer a value of 7.33 ppm is obtained while the H^6 protons in the N2N4 and N4N4 isomers are assigned to resonances found at 7.26 and 7.21 ppm, respectively. Table 1 shows that, for one of the two isomers obtained for **[Ru(L2)(tpy)]**, 11 resonances are observed (six from the tpy ligand and five associated with L2), while for the second isomer 14 resonances are observed. The ^{1}H NMR spectrum of the first of the isomers (See Figure 2a) contains a single set of three phenyl protons. H^a, H^b, and H^c are observed at 6.19, 6.76, and 6.98 ppm, respectively, suggesting that both phenyl rings are equivalent and hence the coordination mode of both of the 1,2,4-triazole rings is identical. Considering that N4N4 coordination would be sterically unfavorable, it is most likely that this isomer is coordinated via the N2 nitrogens of the triazole rings (i.e., **[Ru(L2N2N2)(tpy)]**). The presence of two sets of signals for each phenyl ring, at 6.36 and 7.61, 6.86 and 7.12, and 6.98 and 7.17 ppm (Figure 2b), indicates that the coordination mode of the two triazole rings is different and identifies this species as the asymmetric **[Ru(L2N2N4)(tpy)]**. The ^{1}H NMR spectrum of the H_2L3

(22) Hage, R.; Turkenburg, J. P.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Acta Crystallogr., Sect. C* **1989**, *45*, 381.
(23) Hage, R.; Haasnoot, J. G.; Reedijk J.; Wang, R.; Ryan, E. M.; Vos, J. G.; Spek, A. L.; Duisenberg, A. J. M. *Inorg. Chim. Acta* **1990**, *174*, 77.
(24) Hage, R.; Prins, R.; Haasnoot, J. G.; Reedijk, J.; Vos J. G. *J. Chem. Soc., Dalton Trans.* **1987**, 1389.
(25) Constable, E. C.; Cargill Thompson, A. M. W.; Tocher, D. A.; Daniels, M. A. M. *New J. Chem.* **1992**, *16*, 855.
(26) Buchanan, B. E.; Wang, R.; Vos, J. G.; Hage, R.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 3263.

Table 2. Absorption, Emission, and Electrochemical Data

	abs 298 K[a]		emission 298 K[a]			emission 77 K[b]		electrochem[c]	
	λ (nm)[d]	ϵ (M^{-1} cm^{-1})	λ (nm)[e]	τ (ns)[f]	ϕ_{em}	λ (nm)[e]	τ (μs)	E_{red} (V)	E_{ox} (V)
$[Ru(tpy)_2]^{2+}$ [g]	474	10400	629	0.25	$<5 \times 10^{-6}$	598	8.9	−1.67	0.92
[Ru(L1N2N2)(tpy)]	480	9800	702	77	5×10^{-4}	670	4.1	(−1.38)	0.50
[Ru(L1N2N4)(tpy)]	480	8700	698	62	5×10^{-4}	662	4.2	(−1.38)	0.49
[Ru(L1N4N4)(tpy)]	479	9900	692	70	5×10^{-4}	660	4.2	(−1.35)	0.47
[Ru(L2N2N2)(tpy)]	486	13500	694	52	2.5×10^{-4}	648	7	(−1.36)	0.50
[Ru(L2N2N4)(tpy)]	485	12800	701	24	1.0×10^{-4}	660	5.5	(−1.35)	0.60
[Ru(L3)(tpy)]	474	9500	680	42	7.0×10^{-4}	615	8.4	−1.53	0.89

[a] Ethanol. [b] Methanol/ethanol (1:4). [c] 0.1 M TBAP/DMF, V vs Fc^+/Fc; (values) indicate irreversible reductions. [d] λ_{max} of the lowest energy absorption maximum. [e] λ_{max} of highest energy emission feature. [f] ±7%. [g] From ref 14c.

complex confirms that a single isomer is formed, in agreement with HPLC data, vide supra.

Electronic Spectroscopy. The UV/vis absorption and emission data of the complexes are listed in Table 2. In basic ethanol the complexes show strong ^{1}MLCT bands at ∼390 and 480 nm similar to the values observed for $[Ru(tpy)_2]^{2+}$. Features at ∼275 and ∼309 nm are assigned to the ligand based $\pi-\pi^*$ transitions. The nature of two shoulders at 626 and 579 nm is at present not understood and is under further investigation

Figure 3 shows the effect of pH in Britton−Robson buffer on the UV/vis and emission spectra of **[Ru(L1N2N4)(tpy)]**. Two sets of isosbestic points are observed at 467 and 405 nm and at 453 and 397 nm, indicating that two distinct protonation steps occur. On increasing the acidity of the solution from pH 8 to 1 the ^{1}MLCT maximum shifts from 470 to 442 nm. This increase in energy can be explained by successive protonation of the two triazole rings and the formation of **$[Ru(HL1)(tpy)]^+$** and **$[Ru(H_2L1)(tpy)]^{2+}$**, respectively. The changes in λ_{max} are explained by a decrease in the σ-donor capacity of the protonated triazole ligand and are in agreement with changes observed for $[Ru(bpy)_2(pytr)]^+$.[26] The pK_a values obtained are given in Table 3. The short excited-state lifetime of the protonated complexes (<1 ns) prevents the establishment of an acid/base equilibrium in the excited state. As a result excited-state pK_a values were not determined. The N2 and N4 isomers of $[Ru(bpy)_2(pytr)]^+$ have pK_a values of 4.07 and 5.95, respectively,[27] illustrating that the N2 atom acts as a stronger σ-donor than N4. A similar trend for the tpy based triazole complexes is observed, but the difference between the isomers is much less pronounced. The results obtained in this study suggest that in the tpy complexes the coordination mode of the triazole rings affects the pK_a much less, probably because of the presence of two triazolate moieties, which show substantial interaction as demonstrated by the two-step protonation process. For the H_2L2 complex very similar pK_a values are obtained, indicating that phenyl groups do not affect the acid−base properties of the triazole rings significantly. No acid/base chemistry was observed for **[Ru(L3)(tpy)]** above pH 0.5.

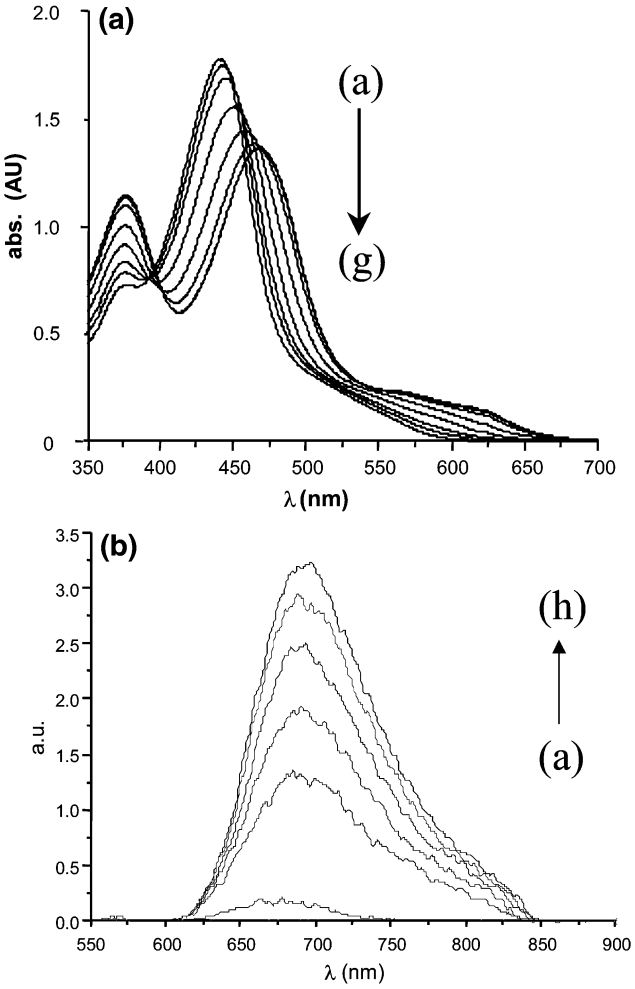

Figure 3. (a) UV−vis absorption spectrum of [Ru(L1N2N4)(tpy)] in Britton−Robinson buffer at pH (a) 2.08, (b) 2.46, (c) 3.23, (d) 4.19, (e) 5.21, (f) 5.72, and (g) 8.88. (b) Emission spectrum of [Ru(L1N2N4)(tpy)] in Britton−Robinson buffer at pH (a) 3.51, (b) 5.21, (c) 5.51, (d) 5.93, (e) 6.61, (f) 8.88.

All complexes are luminescent (λ_{max} ∼700 nm) in deaerated basic ethanol at 298 and 77 K (Table 2). At 298 K the luminescence lifetimes are between 20 and 80 ns. The presence of negatively charged ligands results in a destabilization of the ground state and hence a decrease in energy of the ^{3}MLCT based luminescence in comparison with $[Ru(tpy)_2]^{2+}$. However, despite the reduction in the energy gap,[10] the emission lifetimes of the heteroleptic complexes are 2 orders of magnitude greater than the parent complex

(27) Buchanan, B. E.; Vos, J. G.; Kaneko, M.; Van der Putten, W. J. M.; Kelly, J. M.; Hage, R.; de Graaff, R. A. G.; Prins, R.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1990**, 2425.

Table 3. pK_a Values of Complexes[a]

	pK_{a1}	pK_{a2}
[Ru(L1N2N2)(tpy)]	2.2	5.2
[Ru(L1N2N4)(tpy)]	2.7	5.2
[Ru(L1N4N4)(tpy)]	2.8	5.8
[Ru(L2N2N2)(tpy)]	2.1	5.3
[Ru(L2N2N4)(tpy)]	2.6	6.7

[a] Values are + 0.1.

Table 4. Parameters from the Temperature Dependent Lifetime Data in Basic Butyronitrile/Ethanol (4:1) Solutions

	k_0 (s^{-1})	A_1 (s^{-1})	ΔE_1 (cm^{-1})	A_2 (s^{-1})	ΔE_2 (cm^{-1})
$[Ru(tpy)_2]^{2+}$ [a]	0.9×10^5	1.9×10^{13}	1500		
[Ru(L1N2N2)(tpy)]	2.2×10^5	2.0×10^{12}	2730	2.6×10^7	520
[Ru(L1N2N4)(tpy)]	2.2×10^6	2.0×10^{12}	2700	2.2×10^7	439
[Ru(L1N4N4)(tpy)]	1.2×10^6	1.9×10^{12}	2750	2.6×10^7	540
[Ru(L2N2N2)(tpy)]	1.5×10^5	5.0×10^{12}	2850	9.0×10^8	700
[Ru(L2N2N4)(tpy)]	2.0×10^5	2.0×10^{12}	2650	1.0×10^9	350
[Ru(L3)(tpy)]	1.2×10^6	1.4×10^{13}	2450	6.5×10^7	450

[a] From ref 14c.

$[Ru(tpy)_2]^{2+}$. It is, therefore, clear that the use of the triazole or tetrazole moieties dramatically extends the lifetime of the ^{3}MLCT excited states of Ru(tpy) complexes. Interestingly protonation of one or both rings results in an almost total quenching of the emission and an increase in the emission energy (Figure 3b). The increase in the energy is explained by a stabilization of the ground state since the protonated ligands are weaker σ-donors than their deprotonated analogues.

The increase in lifetime observed upon deprotonation of the azole ligands can be explained by considering an averaged ligand field model. The effect of strong σ-donor ligands is to raise the ligand field stabilization energy; this will result in an increase of the Ru(e_g) energy and consequently an increase in the ^{3}MLCT−^{3}MC energy gap. To investigate this assumption, the energy gap between the ^{3}MLCT and ^{3}MC excited states was estimated from the temperature dependence of the emission properties of the deprotonated compounds over the range 80−320 K. In all cases the emission decay was monoexponential. The temperature dependence of the luminescence lifetime above the solvent melting temperature was analyzed using the following equation:[28]

$$\frac{1}{\tau} = k_0 + A_1 e^{(-\Delta E_1/RT)} + A_2 e^{(-\Delta E_2/RT)}$$

where k_0 is the low temperature limiting rate constant, and A_1 and ΔE_1 are the preexponential factor and the energy barrier for activated surface crossing to the higher-energy metal centered (^{3}MC) state, through which deactivation of the luminescent ^{3}MLCT state can occur. The second activated process with parameters A_2 and ΔE_2 can, in agreement with earlier studies, be interpreted as population of another MLCT level.[16a] The parameters obtained from this analysis are shown in Table 4. Comparison of the ΔE_1 values obtained for the polyazo complexes with those reported for the parent $[Ru(tpy)_2]^{2+}$ complex support our earlier assumption that the increase in the emission lifetimes for the deprotonated complexes are related to an increase in the energy gap between the emitting ^{3}MLCT state and the deactivating ^{3}MC level as shown in Figure 4. The prefactors obtained for the process ($\sim 1-14 \times 10^{12}$ s^{-1}) indicate that deactivation of the ^{3}MLCT via the ^{3}MC state is a thermally activated process.[28] The data also indicate that the introduction of the phenyl grouping has no significant effect on the ^{3}MLCT−^{3}MC energy gap, while as expected this energy gap is slightly reduced for the weaker σ-donor tetrazole ligand. The prefactors obtained indicate that interaction between ^{3}MLCT and ^{3}MC states is similar for all deprotonated polyazo compounds.

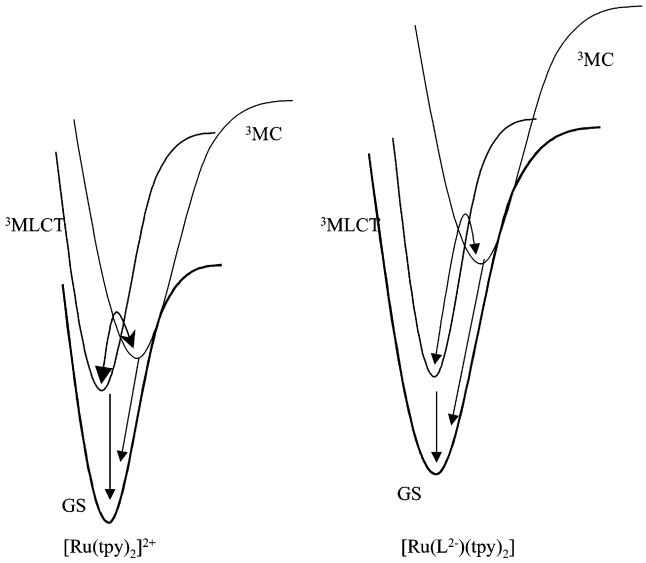

Figure 4. Excited-state electronic structure of tpy based complexes (where L^{2-} is a doubly deprotonated ligand).

Hence, for the deprotonated complex, while the ground state to ^{3}MLCT excited state energy gap is reduced, the increase in the natural radiative and nonradiative deactivation rates for the ^{3}MLCT-GS transition has much less effect than the reduction in the deactivation rate via the ^{3}MC excited state. Protonation reduces the σ-donor properties of the triazole ligands and hence decreases the energy gap between the ^{3}MLCT and ^{3}MC states. This results in faster deactivation via the ^{3}MC and hence a significant lowering in quantum yield and lifetime. This is in agreement with results obtained for analogous complexes such as $[Ru(bpy)_2(Hpytr)]^{2+}$, which are photolabile in the protonated state, but photostable when deprotonated.[29] Scandola and co-workers have invoked a similar explanation for the strongly reduced emitting properties of protonated $[(bpy)_2Ru(CN)_2]$.[30]

Redox Properties and Spectroelectrochemistry. The oxidation and reduction potentials of the complexes are given in Table 2. Comparison with other (tpy) based Ru(II)

(28) (a) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *J. Phys. Chem.* **1987**, *91*, 1095. (b) Barigelletti, F.; Belser, P.; von Zelewsky, A.; Juris, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3680.
(29) Fanni, S.; Keyes, T. E.; O'Connor, C. M.; Hughes, H.; Wang, R.; Vos, J. G. *Coord. Chem. Rev.* **2000**, *208*, 77.
(30) Davila, J.; Bignozzi, C. A.; Scandola, F. *J. Phys. Chem.* **1989**, *93*, 1373.

complexes[14c,31] suggests that the first reduction process, observed for these mixed ligand complexes at about −1.40 V, is assigned as being tpy based. This is not unexpected since tpy π^* levels are lower than those of the triazole and tetrazole based ligands. The metal based oxidation potentials of the deprotonated complexes are significantly lower than that observed for $[Ru(tpy)_2]^{2+}$. This is in agreement with the spectroscopic data and can be explained by the stronger σ-donor properties of the triazole and tetrazole based ligands. The ground state of the mixed ligand complexes is destabilized with respect to the homoleptic tpy complex by 400 mV, in agreement with the results obtained for the analogous bpy type complexes.[22] Protonation of the azole ring leads to an increase in the oxidation potentials of the complexes (to ~0.8 V), again due to the reduction of the σ-donor properties of the ligands.

The nature of the redox processes was further investigated using spectroelectrochemical techniques. Oxidation of [Ru(L1)(tpy)] and [Ru(L3)(tpy))] is reversible, with a better than 95% regeneration of the Ru(II) state. In the Ru(III) state the MLCT transitions with maxima around 460 nm are depleted as observed for other Ru−tpy complexes,[32] with simultaneous appearance of transitions at 770 and 840 nm, assigned as $(L1)^{2-}$ or $(L3)^{2-}$ to Ru(III) type LMCT processes, as observed for other polyazo containing ruthenium polypyridyl complexes.[33] In contrast to electrochemical oxidation, reduction at the first reduction potential of [Ru(L1)(tpy)] is irreversible. Electrochemical reduction of [Ru(L3)(tpy)] was found to be reversible. The spectrum of the reduced species is similar to that obtained for $[Ru(tpy)_2]^+$ with the appearance of two strong absorption bands at 340 and 525 nm. Both bands are assigned as a $\pi-\pi^*$ transition of the tpy radical anion.[34−36] A band which grows in at 850 nm can be tentatively assigned to a ligand-to-metal charge-transfer process (LMCT), from $(L3)^{2-}$ to the metal center. The close similarity between the spectra of $[Ru(tpy)_2]^+$ and $[Ru(L3)(tpy)]^-$ supports the assignment of the first reduction process as being tpy based.

Summary

The inclusion of a strong σ-donor moiety into the terpyridine based Ru(II) complex has two major effects. The increased electron density on the metal center results in a significant destabilization of the ground-state energy (see Figure 4). This results in a lowering of the metal based oxidation potential (and hence raising the HOMO energy[37]) by as much as 450 mV relative to the parent $[Ru(tpy)_2]^{2+}$ complex. An additional effect is the increase in back-bonding to the tpy ligand (t_{2g}-π_{tpy}^*) resulting in a lowering in the tpy based LUMO energy by 290 mV.[37] Overall a lowering in the HOMO−LUMO energy gap is observed as a lowering in the energy of the ^{3}MLCT emission. The reduction in the energy gap is not, however, accompanied by the expected reduction in the emission lifetime and quantum yield.[10] An additional effect of the introduction of a string σ-donor ligand is to increase the crystal field splitting energy (t_{2g}-e_g) and hence raise the energy of the ^{3}MC state. The emission properties of $[Ru(tpy)_2]^{2+}$ are dominated by thermal population of the ^{3}MC state. By raising the energy of the ^{3}MC and hence removing the dominant excited state decay pathway, the emission lifetime and quantum yield are greatly extended. Protonation of the triazole ring results in a dramatic decrease in its σ-donor strength and hence increases the HOMO−LUMO energy gap and lowers the energy of the ^{3}MC state. As a result, the emission energy is increased and lifetime decreased.

Conclusions

The sub-nanosecond excited-state lifetime of normal tpy complexes is widely accepted as being due to the small energy gap between the emitting ^{3}MLCT state and the deactivating ^{3}MC level. This is a severe limitation to the application of tpy based compounds as molecular wires and other such molecular assemblies.[9] As discussed above, efforts to improve the luminescence properties of this class of complexes is more usually directed at *lowering of the energy of the emitting ^{3}MLCT state*. This can for example be achieved by a delocalization of the emitting state[38] or substitution of the 4′ positions of the ligand using electron donating or electron accepting substituents.[9,26] In contrast, the approach taken in the present study is to *raise the energy of the ^{3}MC level* by manipulation of the metal based dσ antibonding orbital. The two methods to achieve Ru(II)(tpy) type complexes with long excited-state lifetimes are therefore complementary, and a combination of both strategies may lead to a further increase in excited-state lifetimes. A point of interest is also that the emitting properties of the compound are determined by the protonation state of the azo rings. This opens the possibility of the application of such compounds as proton driven molecular switches. Finally, preliminary experiments have shown that the emitting properties of the polyazo complexes are strongly solvent dependent, and a detailed investigation on the solvatochromic properties of the compounds is at present underway.

Acknowledgment. The authors wish to thank the Enterprise Ireland European Community under the TMR Scheme (Grant 96CT-0076) and the Human Potential Programme (Grant No. HPRT-CT-2002-00185) for supporting this work. Dr. Wesley Browne is thanked for useful discussions.

Supporting Information Available: Figures S1 (HPLC chromatograms) and S2 (^{1}H NMR spectrum). This material is available free of charge via the Internet at http://pubs.acs.org.

IC034691M

(31) Wolfbauer, G.; Bond, A. M.; Deacon, G. B.; Howitt, J.; MacFarlane, D. R.; Spiccia, L. *J. Electrochem. Soc.* **2001**, *148*, E97.
(32) Hecker, C. R.; Fanwick, P. E.; McMillin D. R. *Inorg. Chem.* **1991**, *30*, 659.
(33) Hage, R.; Haasnoot, J. G.; Nieuwenhuis, H. A.; Reedijk, J.; de Ridder, D. J. A.; Vos, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9245.
(34) König, E.; Kremer, S, *Chem. Phys. Lett.* **1970**, *5*, 87.
(35) Berger, R. M.; McMillin, D. R. *Inorg. Chem.* **1988**, *27*, 4245.
(36) Vogler, L. M.; Scott, B.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 898.
(37) HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital.
(38) Ceroni, P.; Credi, A.; Balzani, V.; Campagna, S.; Hanan, G. S.; Arana, C. R.; Lehn, J.-M. *Eur. J. Inorg. Chem.* **1999**, *9*, 1409.