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# Synthesis, Characterization, and Photophysical Studies of New Bichromophoric Ruthenium(II) Complexes

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The photophysical properties of a series of prepared ruthenium tris(bipyridine) complexes, covalently linked to aromatic species, of type [Ru(bpy)$_2$-(4-methyl-4′-(arylaminocarbonyl)-2,2′-bipyridine)]$^{2+}$ ([Ru(bpy)$_2$(mbpy-L)]$^{2+}$, where bpy = 2,2′-bipyridine; mbpy = 4-methyl-4′-carbonyl-2,2′-bipyridine; and L = 2-aminonaphthyl (naph), 9-aminoanthryl (anth), 1-aminopyrenyl (pyr), or 9-aminoacridinyl (acrd)) were studied by electronic absorption spectroscopy and steady state and time resolved luminescence spectroscopies. The absorption spectra of the MLCT electronic transition of the complexes are similar, which is in agreement with a practically constant redox potential of Ru(III/II) close to 1.28 V versus Ag/AgCl. However, the luminescence spectra of the new complexes are red shifted compared to Ru(bpy)$_3^{2+}$, and this effect is ascribed to solvation and inductive effects of the amide group which enhance the symmetry breakdown among the three bipyridyl ligands. The energy stabilization of the $^3$MLCT state is in the range 2.1–8.4 kJ/mol. The triplet–triplet energy transfer between the Ru complex and the aromatic species linked by an amide spacer is a slow process with rate constants of $2.6 \times 10^4$, $3.6 \times 10^4$, and $4.9 \times 10^4$ s$^{-1}$ for anthracene, acridine, and pyrene as acceptors in methanol, respectively. The energy transfer rate constant increases with decreasing polarity of the solvent. In dichloromethane, the rate constants for anthracene, acridine, and pyrene acceptors are $2.6 \times 10^5$, $1.5 \times 10^5$, and $2.9 \times 10^5$ s$^{-1}$, respectively. The low efficiency of energy transfer is due to the small difference in triplet energy between donor and acceptor species, weak electronic coupling, and unfavorable Franck–Condon factors, despite the short separation distance between donor and acceptor species in an amide bridge.

## Introduction

Considerable progress has been made in learning how to control photoinduced electron and energy transfer processes within model compounds.[1] These model compounds with donor and acceptor spaced by rigid or flexible molecular groups allow a detailed investigation of the factors that control the efficiency of the photoinduced process. Bichromophoric complexes consisting of a Ru(bpy)$_3^{2+}$ and a second chromophore/quencher covalently attached to one of the bipyridine ligands have been widely used to elucidate the mechanisms of energy[2−4] and electron transfer[5−7] processes. The breadth of interest in polypyridyl transition metal complexes for such applications arises, in part, because they exhibit a wide range of photophysical and electrochemical properties.[8,9] The lowest electronic excited state of the tris(bipyridine) Ru complex, which is based on a metal-to-ligand charge transfer (MLCT) transition, is able to transfer energy to the aromatic acceptor by a Dexter type mechanism.[10−12]

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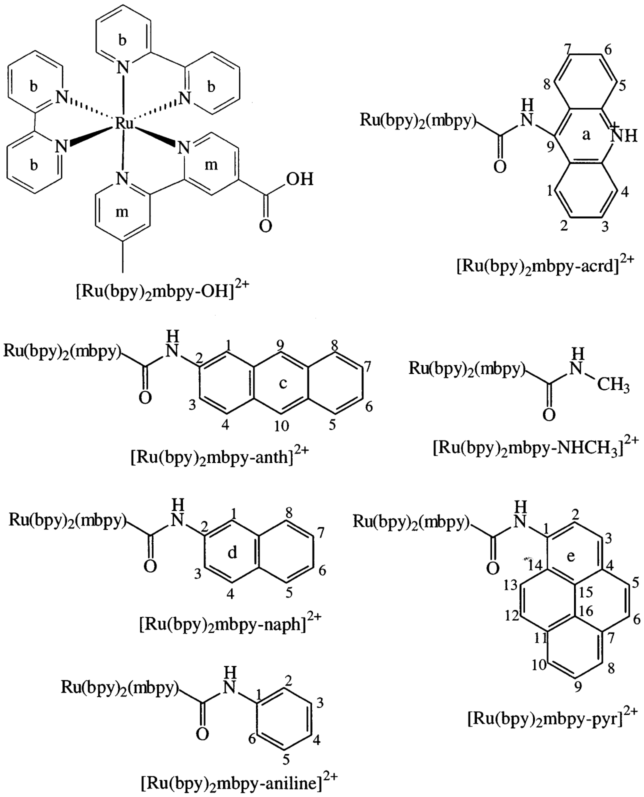
**Scheme 1.** Model compounds.



On the other hand, the MLCT electronic excited state is a long lived and luminescent species, allowing easy measurement of excited state kinetics by using conventional time resolved emission techniques. The properties of these excited states can be varied systematically by varying the ligands.[8,9,13,14] The photophysical properties of a series of ruthenium tris(bipyridine) complexes in which one of the bipyridines is covalently linked to an aromatic chromophore are reported. The molecular structure of the new complexes of the type [Ru(bpy)$_2$-(4-methyl-4′-(arylaminocarbonyl)-2,2′-bipyridine)]$^{2+}$ ([Ru(bpy)$_2$(mbpy-L)]$^{2+}$), where bpy = 2,2′-bipyridine; mbpy = 4-methyl-4′-carbonyl-2,2′-bipyridine; and L = 2-aminonaphthyl (naph), 9-aminoanthryl (anth), 1-aminopyrenyl (pyr), or 9-aminoacridinyl (acrd), are shown in Chart 1. The choice of the aromatic group was dictated primarily by the energy level of their lowest lying triplet state.[15] These complexes were studied in three solvents of different polarities: acetonitrile (CH$_3$CN), methanol (CH$_3$OH), and dichloromethane (CH$_2$Cl$_2$).

The systems investigated here resemble the studies reported for model compounds in which Ru(II) diimine complexes (1,10 phenanthroline or 2,2′-bipyridine) contain covalently bound arenes and heterocycles spaced by single C−C and C−N bonds and also extended ethyl group and large flexible links.[16−26] There are several advantages to the amide bond in bichromophoric compounds. The coupling chemistry is quantitative, and the complexes are easily characterized by NMR. Amino derivatives of a variety of chromophores and quenchers are available, and amide linkages have been used in preparation of modified peptides.[27,28] The role of peptides in mediating long-range electronic interaction in the excited state has important physical, chemical, and biological implications.[29] Furthermore, the amide linkage used in our complexes has an important role in nonradiative decay pathways of the electronic excited state of the Ru complexes.

## Experimental Section

**Equipment.** Absorption spectra of dilute solutions (1 × $10^{-5}$ M) were measured with a Hitachi U-2000 spectrophotometer, and the steady state emission and excitation spectra were recorded using a CD-900 Edinburgh spectrofluorimeter. Emission quantum yields were calculated relative to [Ru(bpy)$_3$]$^{2+}$ in CH$_3$CN with $\Phi_{em} = 0.062$. $^1$H and $^{13}$C NMR spectra were obtained in the designated solvents on a Bruker (400 MHz) spectrometer. Luminescence decay were measured by single photon counting in a CD-900 Edinburgh spectrometer. The decays were analyzed with monoexponential or biexponential functions using the standard data treatment software. Oxygen was removed from the samples by repeated freeze−pump−thaw cycles. Electrochemical data were obtained by cyclic voltammetry with a BAS 100W. The experiments were performed in argon deaerated CH$_3$CN solutions, with Pt-bead working, Au-wire auxiliary, and Ag/AgCl reference electrodes in a single compartment cell. The concentration of the supporting electrolyte (tetra-*n*-butylammonium perchlorate, TBAP) was maintained at 0.1 M. All the potentials reported in this study were quoted versus the Ag/AgCl electrode, which under the given experimental conditions gave a value of 0.37 V for the ferrocene/ferrocenium couple.

**Materials.** Acetonitrile, 9-aminoacridine, 2-aminoanthracene, 2-aminonaphthalene, 1-aminopyrene, tetrafluoroboric acid, 1,3-diisopropilcarbodiimide (DIC), 4,4′-dimethyl-2,2′-bipyridine, selenium dioxide, 1-hydroxybenzotriazole hydrate (HOBT), and *N*-methylmorpholine (NMM) were obtained from Aldrich Co. Hydrochloric acid, dichloromethane, ethanol, ammonium hydroxide,

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sodium hydroxide, and methanol were obtained from Mallinckrodt. Sulfuric acid, trifluoracetic acid (HTFA), silver nitrate, and methylamine were obtained from Merck. These reagents, as well as ammonium carbonate (Reagen), ruthenium trisbipyridine chloride (G. Frederick Smith Chemical Co. (GFS)), and cobalt nitrate (Carlo Erba), were all used as received. Acetone (Mallinckrodt) was treated with sodium sulfate and then distilled and stored with 4 Å molecular sieves. Dimethylformamide (DMF, Merck) was distilled under reduced pressure at 75 °C and dried with 4 Å molecular sieves. Ether (Synth) was treated with sodium and then distilled twice before use.

**Synthesis. 4′-Methyl-2,2′-bipyridine-4-carboxylic acid (m-OH).** This compound was prepared by the method described by McCafferty and co-workers.[27]

**$[Ru(bpy)_2mbpy\text{-}OH](BF_4)_2$ and $[Ru(bpy)_2mbpy\text{-}NHCH_3](BF_4)_2$.** These compounds were prepared by following the method of Peek and co-workers.[30]

**$[Ru(bpy)_2mbpy\text{-}acrd](BF_4)_2$.** The active ester was prepared by the reaction of 0.100 g of $[Ru(bpy)_2mbpy\text{-}OH](BF_4)_2$, 30 $\mu$L of DIC, and 0.022 g of HOBT in 250 $\mu$L of DMF. After 15 min, 0.066 g of 9-aminoacridrine and 20 $\mu$L of NMM were added, and the coupling reaction mixture was allowed to proceed for 3 h, under stirring at room temperature. At the end of the reaction, a small amount of water was added, and the reaction mixture was filtered to remove an excess of organic starting materials. The solvent was removed by rotary evaporation. The resulting slurry was dissolved in a minimum amount of water and loaded on a Bio-Gel P2 (45−90 $\mu$m, from Bio-Rad laboratories) column. The elution was performed by washing the column with water. The collected fractions were concentrated, and its purity level was evaluated by HPLC ($\mu$-Bondapak C18, Waters Associates, 10 $\mu$m, 3.9 mm × 30 cm). The first and major orange band containing the desired complex was dried by rotary evaporation, dissolved in a minimum amount of ethanol, and precipitated by adding a few drops of concentrated $HBF_4$ followed by anhydrous ethyl ether. The precipitate was filtered off, washed with an excess of anhydrous ether, and dried under vacuum (0.106 g, 87% yield). Spectral data. $^1H$ NMR ($(CD_3)_2SO$): $\delta$ 2.31 (3H, m4′-$CH_3$), 6.82−6.86 (2H, a2, a7), 6.97−7.00 (2H, a4, a5), 7.03−7.09 (2H, a1, a8), 7.14−7.20 (5H, m5′, b5), 7.29−7.33 (2H, m5, m6′), 7.53−7.60 (5H, b6, m6), 7.74−7.86 (6H, a3, a6, b4), 8.21−8.33 (5H, b3, m3′) and 8.70 (1H, m3). $^{13}C$ NMR: $\delta$ 16.79 (m4′-$CH_3$), 118.51 (a1′, a8′), 120.45 (a2, a7), 123.24 (a4 and a5), 125.27 (a1, a8), 126.49 (m5′), 126.73 (b5), 126.91 (m5), 128.03 (m6′), 129.81 (b6), 130.32 (m6), 130.93 (a3, a6), 140.40 (b4), 140.63 (a4′, a5′), 146.02 (m4′), 153.43 (b3), 153.94 (m3′), 154.18 (m3), 157.83 (a9), 157.96 (m2′), 158.02 (m2), 159.63 (b2), 160.98 (m4) 165.13 (m4-CO). Anal. Calcd: %C 55.24; %H 3.61; %N 11.45. Found: %C 55.30; %H 3.77; %N 11.52.

**$[Ru(bpy)_2mbpy\text{-}anth](BF_4)_2$.** Preparation of this complex is similar to that for $[Ru(bpy)_2mbpy\text{-}acrd](BF_4)_2$ species, except the use of 2-aminoanthracene instead of the 9-aminoacridine compound (0.100 g, 82% yield). Spectral data. $^1H$ NMR ($(CD_3)_2CO$): $\delta$ 2.53 (3H, m4′-$CH_3$), 7.25−7.28 (1H, c1), 7.34−7.39 (5H, m5′, b5), 7.40−7.43 (2H, m5, c3), 7.63−7.65 (1H, m6′), 7.76−7.82 (6H, b6, c9, c6), 7.97−7.98 (1H, c7), 8.03−8.08 (6H, m6, c10, b4), 8.44 (1H, c8), 8.52−8.55 (7H, c5, d4, m3′, b3), 8.57 (1H, m3). $^{13}C$ NMR: $\delta$ 21.11 (m4′-$CH_3$), 121.85 (c1), 123.07 (m5′), 124.41 (b5), 125.60 (m5), 125.80 (c3), 126.38 (m6′), 127.78 (b6), 127.82 (c9), 127.99 (c6), 128.97 (c7), 129.02 (m6), 137.97 (c10), 138.02 (c4′), 138.12 (b4), 138.60 (c8), 145.66 (c5), 150.71 (c5′), 150.87 (c4), 151.55 (c8′), 151.63 (c1′), 151.69 (m4′), 151.74 (m3′), 151.95 (b3), 152.90 (m3), 155.95 (m2′), 156.88 (m2), 157.11 (b2), 157.62 (m4), 163.97 (c2), and 164.68 (m4-CO). Anal. Calcd: %C 56.58; %H 3.61; %N 10.04. Found: %C 56.51; %H 3.57; %N 9.98.

**$[Ru(bpy)_2mbpy\text{-}pyr](BF_4)_2$.** Procedures used were the same as those used for the preparation of $[Ru(bpy)_2mbpy\text{-}acrd](BF_4)_2$, except the use of 1-aminopyrene in substitution of the 9-aminoacridine compound (0.095 g, 76% yield). Spectral data. $^{13}C$ NMR ($(CD_3)_2CO$): $\delta$ 21.29 (m4′-$CH_3$), 122.79 (e2), 122.95 (e14), 123.57 (e13), 124.00 (m5′), 124.25 (e8), 125.35 (b5), 125.49 (e6), 125.81 (e10), 126.45 (e4), 126.73 (m5), 126.92 (e15), 127.05 (e12), 127.30 (m6′), 128.69 (e9), 128.52 (e16), 128.73 (b6), 128.93 (e3), 129.96 (m6), 138.90 (b4), 139.05 (m4′), 139.51 (e5), 145.80 (e11), 146.70 (e7), 151.63 (e1), 151.77 (m3′), 152.62 (b3), 153.82 (m3), 156.94 (m2′), 157.98 (m2), 158.05 (b2), 159.47 (m4), and 164.90 (m4-CO). Anal. Calcd: %C 57.62; %H 3.53; %N 9.80. Found: %C 57.67; %H 3.59; %N 9.83.

**$[Ru(bpy)_2mbpy\text{-}naph](BF_4)_2$.** This compound was prepared following the same procedures used for $[Ru(bpy)_2mbpy\text{-}acrd](BF_4)_2$ substituting 2-aminonaphthalene by 9-aminoacridine (0.098 g, 85% yield). Spectral data. NMR $^{13}C$ ($(CD_3)_2CO$): $\delta$ 21.10 (m4′-$CH_3$), 122.80 (m5′), 124.53 (b5), 126.38 (d1), 126.45 (d3), 126.57 (d6), 126.67 (d8), 126.78 (m5), 127.08 (m6′), 127.21 (d7), 127.33 (d5), 128.81 (b6), 129.60 (d4′), 139.01 (m6), 139.11 (b4), 151.84 (d4), 151.90 (d1′), 152.53 (m4′), 152.85 (b3), 153.85 (m3′), 156.93 (m3), 156.99 (d10), 157.23 (d2), 157.85 (m2′), 157.96 (m2), 158.08 (b2), 159.54 (m4), 164.82 (d1), and 167.19 (m4-CO). Anal. Calcd: %C 54.45; %H 3.59; %N 10.58. Found: %C 54.52; %H 3.64; %N 10.66.

**$[Ru(bpy)_2mbpy\text{-}aniline](BF_4)_2$.** This compound was prepared following the same procedures used for $[Ru(bpy)_2mbpy\text{-}acrd](BF_4)_2$ substituting aniline by the 9-aminoacridine ligand (0.093 g, 85% yield). Spectral data. NMR $^1H$ ($(CD_3)_2CO$): $\delta$ 2.60 (3H, m4′-$CH_3$), 7.46−7.48 (1H, m5′), 7.56−7.59 (4H, b5), 7.85−7.89 (3H, f3, m5, m6′), 8.01−8.05 (4H, b6), 8.08−8.12 (1H, f4), 8.17−8.22 (5H, m6, b4), 8.26−8.27 (2H, f2), 8.82−8.84 (b3, m3′), and 9.10 (1H, m3). NMR $^{13}C$: 21.11 (m4′-$CH_3$), 123.80 (m5′), 125.43 (b5), 126.38 (f3), 126.78 (m5), 127.08 (m6′), 128.81 (b6), 129.60 (f4), 139.01 (m6), 139.11 (b4), 151.84 (f2), 152.53 (m4′), 152.85 (b3), 153.85 (m3′), 156.93 (m3), 157.85 (m2′), 157.96 (m2), 158.08 (b2), 159.54 (m4), 164.27 (f1), and 165.69 (m4-CO). Anal. Calcd: %C 52.08; %H 3.57; %N 11.19. Found: %C 52.01; %H 3.48; %N 11.12.

## Results and Discussions

The electronic spectra of the title complexes present a very similar characteristic to that for $[Ru(bpy)_3]^{2+}$ species.[8,9] In the visible region, the spectrum is dominated by MLCT bands arising from $\pi^*(bpy) \leftarrow d\pi(Ru^{II})$ transitions, and in the UV region, there is a strong ligand-based $\pi^* \leftarrow \pi$ band. The $\lambda_{max}$ values observed for the MLCT transitions of these new compounds (Table 1) are practically in the same wavelength position, but with a small red shift of about 5 nm in relation to the MLCT absorption band of the $[Ru(bpy)_3]^{2+}$ (ca. 450 nm). This points out that the pendant aromatic compounds do not disturb significantly the central Ru−bpy chromophore unit.

Figure 1 shows the excitation spectra for the ruthenium complexes and for the respective pendant aromatic ligand free of coordination, with emission collected at the maximum of the emission spectrum of the aromatic compounds. The

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**Table 1.** Redox Potentials for the Ru(II) Complexes in 0.1 M $[N(n\text{-}C_4H_9)_4](ClO_4)-CH_3CN$ Solution at 298 K and Wavelength Maximum of the MLCT Absorption Band[a]

| complex | $E_{1/2}$ (V) oxidation | $E_{1/2}$ (V) reduction | $\lambda_{max}$ (nm) |
|---|---|---|---|
| $[Ru(bpy)_3]^{2+}$ | 1.25 | −1.10; −1.31; −1.53 | 450 |
| $[Ru(bpy)_2mbpy\text{-}OH]^{2+}$ | 1.29 | −1.15; −1.39; −1.61 | 452 |
| $[Ru(bpy)_2mbpy\text{-}NHCH_3]^{2+}$ | 1.28 | −1.20; −1.36; −1.54 | 454 |
| $[Ru(bpy)_2mbpy\text{-}aniline]^{2+}$ | 1.29 | −1.23; −1.50; −1.66 | 459 |
| $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$ *b* | 1.29 | −1.15; −1.38; −1.54 | 457 |
| $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$ | 1.28 | −1.21; −1.40; −1.63 | 454 |
| $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$ | 1.28 | −1.23; −1.38; −1.61 | 453 |
| $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$ | 1.29 | −1.17; −1.50; −1.73 | 455 |

[a] All the potentials are referenced against a Ag/AgCl electrode with $E_{1/2} = 0.37$ V for the Fc/Fc$^+$ couple. $\lambda_{abs}$ (nm) is the maximum of the absorption spectrum of the complex in methanol. [b] This complex has a low reduction potential of −0.87 V related to the reduction process of the acrd group.

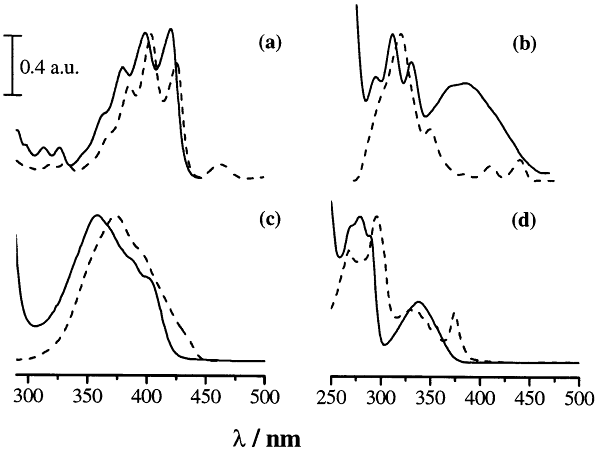

**Figure 1.** Excitation spectra in $CH_3OH$ ($1 \times 10^{-5}$ M) at 293 K by recording emission signal at (a) 460 nm (—) 9-aminoacridine and (---) $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$; (b) 500 nm (—) 2-aminoanthracene and (---) $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$; (c) 455 nm (—) 1-aminopyrene and (---) $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$, and (d) 400 nm (—) 2-aminonaphthalene and (---) $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$.

excitation spectra for the complexes clearly show the presence of the pendant aromatic groups. These results corroborate the bichromophoric nature of the systems, indicating the interconversion among excited states, which give rise to the emission of the complex (MLCT) and of the organic chromophores linked through the amide bridges. Actually, the excitation spectra of the $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$ complex with emission at 400 nm (Figure 1a) is similar to that of 9-aminoacridine. The spectrum for the $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$ complex with emission at 500 nm (Figure 1b) presents the transitions of the aromatic group (2-amidoanthracene). For this complex, the wide band centered at 400 nm present in the free aromatic disappears giving rise to a structured band of low intensity. The spectra for the bichromophric compounds $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$ (Figure 1c) and $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$ (Figure 1d), with emission at the respective organic chromophores, also exhibited the contributions characteristic of the excitation transitions of the aromatic moieties. When the emission was centered in the MLCT band of the compounds, the excitation spectra observed had the same characteristic profile of that of $[Ru(bpy)_3]^{2+}$.

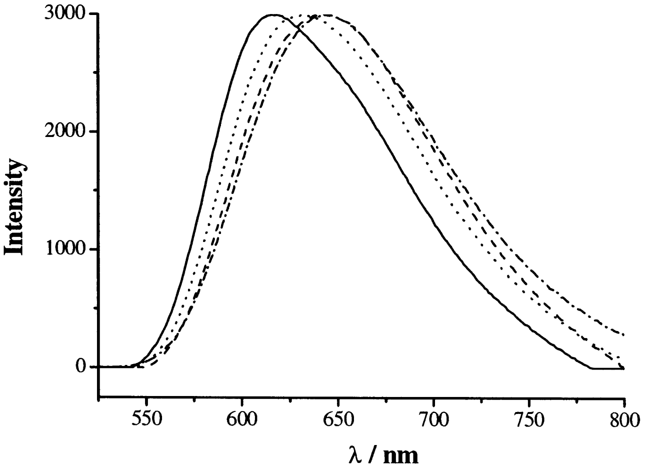

**Figure 2.** Emission spectra following excitation at 450 nm for the complexes in methanol ($5 \times 10^{-5}$ M) at 293 K. The spectra presented from left to right are for the following: (—) $[Ru(bpy)_3]^{2+}$, (---) $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$, (— —) $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$, and (- — -) $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$.

The formal reduction potentials ($E_{1/2}$) for the title complexes, obtained by cyclic voltammetry in 0.1 M TBAP acetonitrile solution, are reported in Table 1. The $E_{1/2}$ values obtained are close to that for the $[Ru(bpy)_3]^{2+}$ species.[8,9] For all of the complexes, the first polypyridyl-based reductions were observed from −1.1 to −1.7 V, and the $Ru^{III/II}$ couples from +1.25 to +1.29 V. These small changes observed for the Ru(III/II) redox potentials are consistent with the spectroscopic results for the optical MLCT transition.

Figure 2 illustrates the luminescence spectra carried out with excitation of the complexes at 450 nm, corresponding approximately to the absorption maximum of the MLCT bands of the complexes. The complexes are luminescent, exhibiting broad and structureless emission bands, which are characteristic of the $^3$MLCT state. Considering the emission spectrum of the $[Ru(bpy)_3]^{2+}$ species as a reference, the spectra of the title complexes are red shifted. This fact may be ascribed to a specific effect of the amide bridge in the bipyridine-arylcarboxamide, which lowers the electronic energy of the localized $^3$MLCT electronic state and breaks the symmetry among three bipyridyl ligands. By comparing the energy of the $E_{0-0}$ of the MLCT transition of the complexes, calculated from the crossing between the normalized absorption and emission spectra, with that of $[Ru(bpy)_3]^{2+}$ species, the energy stabilization of the new complexes in the $^3$MLCT state lies in the range 2.1−8.4 kJ/mol.

It should be mentioned that the complex $[Ru(bpy)_2mbpy\text{-}NHCH_3]^{2+}$ was first studied by Meyer and co-workers,[31,32] and it was established by time-resolved Raman spectroscopy that the excited electron density is localized principally on the mbpy-$NHCH_3$ ligand. Its electrochemical characterization yielded half-wave potentials (vs SSCE) of 1.27 V for Ru(III/II), and −1.28 and −1.51 V, for the first and second

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**Table 2.** Lifetime, Quantum Yield and Wavelength of Emission Maximum at 293 K in Different Solvents. Acetonitrile ($CH_3CN$), Methanol ($CH_3OH$), and Dichloromethane ($CH_2Cl_2$)[a]

| | $CH_3CN$ | | $CH_3OH$ | | $CH_2Cl_2$ | |
|---|---|---|---|---|---|---|
| complex | $\tau$ (ns) | $\Phi_{em}$ ($\lambda_{max}$, nm) | $\tau$ (ns) | $\Phi_{em}$ ($\lambda_{max}$, nm) | $\tau$ (ns) | $\Phi_{em}$ ($\lambda_{max}$, nm) |
| $[Ru(bpy)_3]^{2+}$ | 836 | 0.061 (621) | 813 | 0.045 (616) | 485 | 0.091 (609) |
| $[Ru(bpy)_2mbpy\text{-}OH]^{2+}$ | 1080 | 0.048 (627) | 919 | 0.045 (622) | 554 | 0.046 (651) |
| $[Ru(bpy)_2mbpy\text{-}NHCH_3]^{2+}$ | 1105 | 0.076 (632) | 789 | 0.048 (623) | 638 | 0.112 (618) |
| $[Ru(bpy)_2mbpy\text{-}aniline]^{2+}$ | 1320 | 0.073 (657) | 867 | 0.039 (656) | 732 | 0.112 (642) |
| $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$ | 1255 | 0.064 (652) | 910 | 0.029 (639) | 707 | 0.101 (645) |
| $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$ | 1296 | 0.077 (640) | 918 | 0.029 (640) | 655 | 0.085 (633) |
| $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$ [b] | 983 | 0.071 (630) | 900 | 0.034 (637) | 645 | 0.093 (636) |
| $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$ | 1321 | 0.078 (662) | 941 | 0.034 (659) | 792 | 0.124 (645) |

[a] Emission band maxima are in nm (±2). Emission quantum yields, ±10%. Lifetimes (±5%) measured at the emission maximum following excitation of the complexes at 450 nm. [b] The luminescence decay of $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$ is biexponential in $CH_3CN$ and in $CH_2Cl_2$ with a long-lived component of $46 \pm 2$ and $2.3 \pm 0.2$ $\mu$s, respectively.

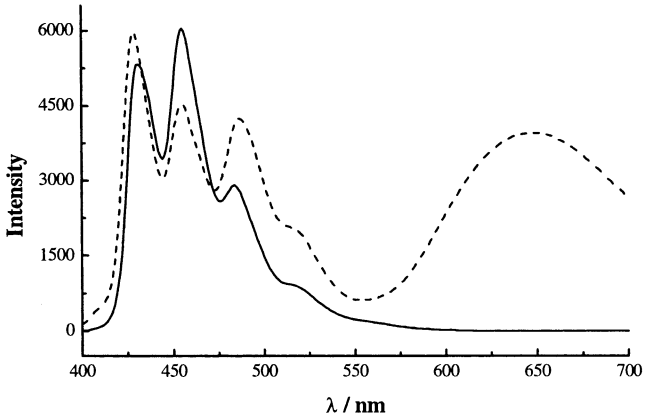

**Figure 3.** Emission spectra following excitation at 380 nm for (—) 9-aminoacridine and (---) $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$ in methanol ($5 \times 10^{-5}$ M) at 293 K.

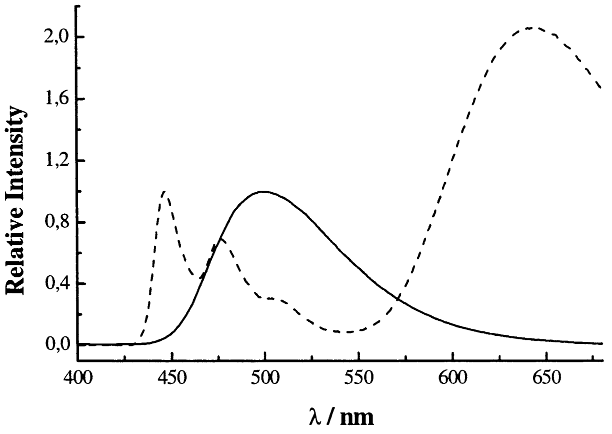

**Figure 4.** Emission spectra following excitation at 350 nm for (—) 2-aminoanthracene and (---) $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$ in methanol ($5 \times 10^{-5}$ M) at 293 K.

ligand-based reductions. The MLCT absorption band was observed at 456 nm, and the emission at 645 nm, with a luminescence quantum yield of 0.087 and a lifetime of 1380 ns.[31,32] These values of redox potentials are in agreement with the reported values in Table 1. The spectroscopy properties of complex $[Ru(bpy)_2mbpy\text{-}NHCH_3]^{2+}$ (see Tables 1 and 2), but with a different counterion ($BF_4$), approach those reported by Meyer and co-workers.[31,32]

The results of the emission experiments, when the excitation is accomplished at the region of fluorescence of the aromatic chromophores, provide clear evidence of the bichromophore nature of the complexes. For example, the emission spectrum of the $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$ complex (Figure 3) presents the characteristic fluorescence spectrum of 9-aminoacridine. The structured emission around 400−550 nm is due to the acridine moiety, and the broad band with maximum at 646 nm is the luminescence from the $^3$MLCT state.

The emission spectrum of the complex $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$, reported in Figure 4, shows the presence of the two chromophores, but when it is compared with the emission spectrum of the 2-aminoanthracene alone, there is a clear difference regarding the emission of the aromatic group. In polar solvent, 2-aminoanthracene has emission from a twisted intramolecular charge transfer (TICT) state,[33] and therefore, its emission spectrum shows a broad band of lower energy than the fluorescence spectra of anthracene. When the aromatic is covalently bound to the bpy ligand by an amide bridge, the TICT process is absent, and as a result, the emission of the 2-amidoanthracene appears in the region 425−525 nm as a structured band. The emission spectra of $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$ and $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$, with excitation of the aromatic group, also present the characteristic bands of the organic compounds (1-aminopyrenyl, 2-aminonaphthyl) linked to the Ru complex.

The lifetimes, luminescence quantum yield, and wavelength of emission maximum ($\lambda_{max}$) of the complexes are listed in Table 2. The parameters concerning the $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2mbpy\text{-}OH]^{2+}$, $[Ru(bpy)_2mbpy\text{-}NHCH_3]^{2+}$, and $[Ru(bpy)_2mbpy\text{-}aniline]^{2+}$ species were included for comparative purposes. At a first glance, the bathochromic shift in $\lambda_{max}$ reported for the all complexes with bpy derived ligands, when compared with the spectrum for the $[Ru(bpy)_3]^{2+}$ precursor, contrasts with the long luminescence lifetime which could be inconsistent with the energy gap law.[34] However, as demonstrated by Meyer et al.,[35] ligand modification with chemical groups with extended $\pi$ systems allows a greater delocalization of the excited electron that reduces the adjustments in local bond displacements and modulates the vibrational overlap. As a result, the nonra-

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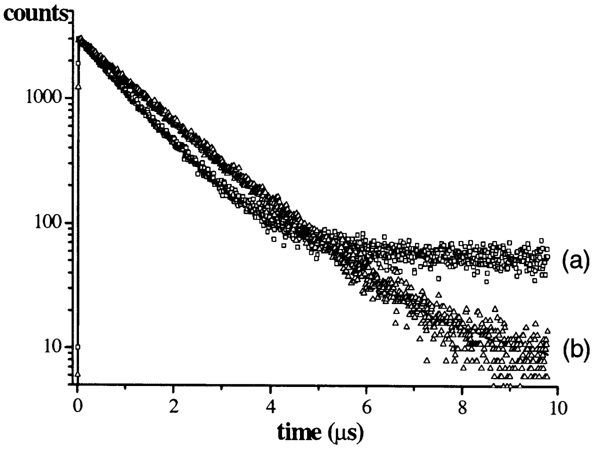

**Figure 5.** Luminescence decays of $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$ (a) and $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$ (b) in acetonitrile at 298 K. Lifetimes are reported in Table 2.

diative decay rate constant decreases, and the lifetime of the $^3$MLCT increases. Note that the nonradiative pathways are the transitions to the ground state directly or by thermal population and decay from the dd state. The lifetimes of $[Ru(bpy)_2mbpy\text{-}anilene]^{2+}$ and $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$ increase by a factor of about 1.6 with respect to the lifetime of $[Ru(bpy)_3]^{2+}$ in acetonitrile. The same trend was observed with other similar complexes.[35,36] For instance, lifetimes of 1350 ns for $[Ru(dmb)_2(vbpy)]$, 1150 ns for $[Ru(dmb)_2(bbpe)]$, and 950 ns for $[Ru(dmb)_3]$ at 298 K in acetonitrile, where dmb, vbpy, and bbpe are 4,4'-dimethyl-2,2'-bipyridine, 4-(4'-methyl)-2,2'-bipyridyl-ethene, and *trans*-1,2-bis-(4-(4'-methyl)-2,2'-bipyridyl)ethene, respectively, are reported in the literature.[35]

The complex $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$ is of particular interest since the triplet energy of the naphthalene is much higher than the triplet energy of the $[Ru(bpy)_3]^{2+}$ complex, which precludes an energy transfer from the metal complex to the peripheral naphthalene. Taking $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$ as a reference for the luminescence quantum yield and lifetime of the $^3$MLCT, comparison with the properties of the donor/acceptor system in which the triplet energy of the aromatic acceptor is similar or lower than the Ru complex would give an idea about the extent of the energy transfer process. In fact, $\tau$ and $\Phi_{em}$ are reduced in the case of $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$, $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$, and $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$complexes, suggesting a deactivation by energy transfer. However, the differences in both parameters are not very pronounced which would indicate that the process of energy transfer is not very efficient.

Contrasting with the other systems, the $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$complex has a very long-lived component in acetonitrile with a decay time of 46 ± 2 $\mu$s, although its weight fraction is low (less than 4%). In dichloromethane, the decay times are 0.64 and 2.3 $\mu$s, and in methanol, the decay is a single exponential with lifetime of 0.9 $\mu$s. This fact is illustrated in Figure 5 where the decay of $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$ is compared with that for the $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$ complex. The unusual decay behavior observed for the ruthenium complexes having a peripheral pyrene linked to metal ligand by a short or medium size bridge has already been documented in early studies reported in the literature.[17−24] The long excited state lifetime that was observed varied from a few to a hundred microseconds. The fact has been explained on the basis of the assumption of close lying triplet states of the Ru(II) complex and pyrene. The triplet state of pyrene would serve as a reservoir of a long-lived excited state and, by energy transfer to the Ru complex, would produce delayed luminescence. In the case of $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$, the emission of the $^3$MLCT state increases in energy when compared with the other complex with an extended $\pi$ system of the aromatic (see the emission maxima reported in Table 2) species. This effect is enhanced in acetonitrile where there is a long-lived component in the luminescence decay. A possible explanation for this fact would be a mixing of the nearly isoenergetic $^3$MLCT and $T_1$ (pyrene) states originating and upper level with charge transfer character and a lower excited state level with mainly $T_1$ character of the aromatic pyrene. This assumption would require a favorable geometry, with bridge aromatic systems being coplanar to support a weak orbital interaction.

**Table 3.** Rate Constants of Energy Transfer in Bichromophoric Compounds

| | $k_{et}$ (s$^{-1}$) | | |
|---|---|---|---|
| complex | $CH_3CN$ | $CH_3OH$ | $CH_2Cl_2$ |
| $[Ru(bpy)_2mbpy\text{-}anth]^{2+}$ | $1.5 \times 10^4$ | $2.6 \times 10^4$ | $2.6 \times 10^5$ |
| $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$ | $4.0 \times 10^4$ | $3.6 \times 10^4$ | $1.5 \times 10^5$ |
| $[Ru(bpy)_2mbpy\text{-}pyr]^{2+}$ | $2.6 \times 10^5$ | $4.9 \times 10^4$ | $2.9 \times 10^5$ |

A kinetic modeling of this type of donor−acceptor system should consider the reversibility in the energy transfer process if the energy gap between donor and acceptor is small. The excitation of the Ru complex forms the $^3$MLCT state in a nonequilibrium condition which may relax exponentially to an equilibrated triplet state with a rate parameter given by the sum of the forward ($k_{et}$) and back ($k_{-et}$) energy transfer rate constants. Considering the measured lifetime (fast component) of the donor−acceptor system ($\tau$) and the lifetime of the reference compound ($\tau_0$), the following relation may be written in the exponential regime of decay:

$$\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \le k_{et} + k_{-et} \qquad (1)$$

In the situation where $k_{et} > k_{-et}$, the difference of the inverse of lifetimes given by eq 1 would give a good estimation of $k_{et}$.

Although the $[Ru(bpy)_2mbpy\text{-}NHCH_3]^{2+}$, $[Ru(bpy)_2mbpy\text{-}aniline]^{2+}$, and $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$ complexes were synthesized for the purpose of serving as a reference standard, only the last complex could be taken as a reference compound. Taking the value of $[Ru(bpy)_2mbpy\text{-}naph]^{2+}$ lifetime as a reference, we can estimate $k_{et}$ in different solvents for the $[Ru(bpy)_2mbpy\text{-}L]^{2+}$ systems, L = anth, acrd, pyr. The results obtained are reported in Table 3. The values calculated show that triplet−triplet energy transfers between the Ru(II) donor and the aromatic acceptors linked by the

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amide spacer are slow processes in most of the situations. However, when the polarity of the solvent is reduced, there is an increase in the energy transfer rate. In dichloromethane, the rate constants are 5- to 10-fold greater than in acetonitrile. This fact agrees with energy transfer involving a high polar excited state like the $^3$MLCT, for which solvent reorganization energy is part of the activation barrier of the process. The luminescence quenching of $[Ru(bpy)_3]^{2+}$ by a series of organic aromatics in acetonitrile indicated that solvent reorganization energy is about 23.0 ± 2.1 kJ/mol.[12] In a less polar solvent like dichloromethane, the activation barrier due to solvent reorganization is reduced, and therefore, the energy transfer rate constant increases.

In principle, the energy transfer process could be quantified by the difference in luminescence quantum yield between the reference compound ($\phi_0$) and the bichromophoric system ($\phi$). In a reversible bichromophoric energy transfer system, the following equation holds:

$$\left(\frac{\phi_0}{\phi} - 1\right)\tau_0^{-1} = \frac{k_{et}}{1 + \tau_a k_{-et}} \qquad (2)$$

where $\tau_a$ is the triplet lifetime of the aromatic acceptor. The application of eq 2 is possible whether the difference in luminescence quantum yields is outside the intrinsic error of measurement, which is better fulfilled in the data obtained in $CH_2Cl_2$ (see Table 2). In this solvent, using eq 1 and considering $\tau_a k_{-et} \ll 1$, the values of $k_{et}$ of $[Ru(bpy)_2mbpy\text{-}L]^{2+}$ systems, L = anth, acrd, pyr, are, respectively, 5.8, 2.9, and $4.2 \times 10^5$ s$^{-1}$. These values are on the same order of the previous values of $k_{et}$ estimated from the lifetimes in $CH_2Cl_2$ (see Table 3).

The low efficiency of energy transfer would be expected from the small difference in triplet energy between donor and acceptor, which is about 4.18 kJ/mol for pyrene, 12.5 kJ/mol for acridine, and about 20.9 kJ/mol for anthracene, in acetonitrile and assuming the $^3$MLCT energy of $[Ru(bpy)_3]^{2+}$ as 204.8−209.0 kJ/mol.[12,15,20] As cited before, the triplet energy of the functionalized Ru(II) is reduced by 2.1−8.4 kJ/mol in the model compounds. However, the triplet energy levels of the aromatics are also changed with the introduction of a substituent in the aromatic compound. In general, an inductive substituent causes a small-to-moderate red shift for an n−$\pi$* transition and a moderate blue shift for a $\pi$−$\pi$* transition. Considering these two facts related to the donor $^3$MLCT and acceptor $\pi$−$\pi$* triplet levels in the complexes studied, the systems investigated would approach an isoenergetic condition of triplet states, as in the case of the complex with pyrene, and a weak favorable (exothermic) condition as in the case of acridine and anthracene acceptors.

The weak overlap of the frontier orbitals in the presence of an amide bridge reduces the electronic coupling between donor and acceptor species. The coupling is dictated by the geometry attained by ligand−bridge−aromatic, which is enhanced when the $\pi$ systems are coplanar. In the case of more flexible bridges, a contribution from electron exchange by collisional/through solvent interaction involving the neighboring Ru(II) ligand and the acceptor may be the reason for the fast rate of T−T energy transfer that has been observed.[16,17] Besides, the system described by Boyde et al.[16] has three anthracene acceptors in the same molecular frame, and therefore a higher probability of energy transfer. An additional argument that should affect and reduce the energy transfer rate is the unfavorable Franck−Condon factors related to the low frequency conformational change of the amide bridge (torsional motion) necessary for the donor and acceptor $\pi$ systems approaching a coplanar alignment.

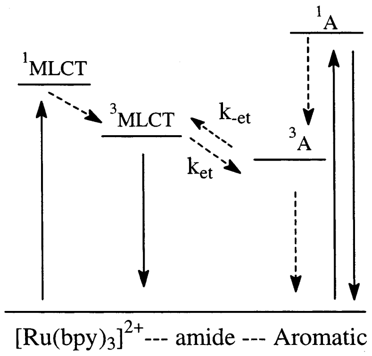

**Figure 6.** Jabłoński diagram of the bichromophoric systems with nearly isoenergetic triplet states.

Considering the results obtained, a diagram of the possible electronic energy and of the interconversion between different states of these bichromophoric complexes is given in Figure 6. It is supposed that the energy transfer of the excited singlet state of the aromatic to the $^1$MLCT state is an inefficient process. In the case of $[Ru(bpy)_2mbpy\text{-}acrd]^{2+}$, the lifetime of the fluorescence decay of the acridine chromophore in the complex is practically equal to the lifetime of the free 9-aminoacridine in the same solvent ($\tau$ = 15 ns). This indicates that the singlet−singlet energy transfer does not occur to a great extent. Therefore, the observed luminescence of the $^3$MLCT when the complex is excited in the UV region (400 nm) may result from prompt MLCT excitation due to residual absorption, but a possible back energy transfer between the close lying triplet state of the aromatic and of the Ru complex is not excluded.

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**Supporting Information Available:** Listings of equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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