Synthesis and Study of a Mixed-ligand Ruthenium(II) Complex in Its Ground and Excited States: Bis(2,2′-bipyridine)(dipyrido[3,2-*a*:2′,3′-*c*]phenazine-N^4N^5)ruthenium(II)

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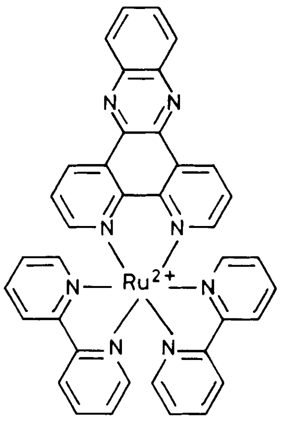
The ruthenium(II) complex $[Ru(bipy)_2(dppz)]^{2+}$ (bipy = 2,2′-bipyridine, dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) was synthesized, characterized, and studied. Its oxidation and first reduction potentials are respectively 1.24 and −1.02 V (*vs.* saturated calomel electrode). The maxima of the metal-to-ligand charge-transfer absorption and emission occur respectively at 448 and 610 nm. These data suggest that $[Ru(bipy)_2(dppz)]^{2+}$ is made up of two electronically independent units, one behaving as a $[Ru(bipy)_3]^{2+}$-like chromophore, the other as a phenazine-like electron acceptor. Excited-state absorption spectra were obtained for $[Ru(bipy)_2(dppz)]^{2+}$ and its parent complex $[Ru(bipy)_3]^{2+}$. Above 500 nm the latter shows only one maximum (at 510 nm), and the former shows two maxima (around 526 and 557 nm), whereas radical anions of both bipyridine and phenazine or dipyridophenazine show two maxima (at 512 and 552 nm for phenazine). In the case of $[Ru(bipy)_2(dppz)]^{2+}$ these results can be interpreted in terms of a light-induced directed charge transfer from the ruthenium to the phenazine part of the dipyridophenazine ligand, and its localization on this ligand moiety. Photochemical properties of $[Ru(bipy)_2(dppz)]^{2+}$ were studied in ethanol. The excited state of the complex is quenched both by an electron acceptor (methylviologen, $k_q = 1.37 \times 10^9$ dm³ mol⁻¹ s⁻¹) and an electron donor (triethanolamine, $k_q = 4.40 \times 10^7$ dm³ mol⁻¹ s⁻¹).

There is a transient charge separation at the molecular level in metal complexes such as $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) which displays a light-induced, metal-to-ligand charge-transfer (m.l.c.t.) excited state.[1,2] While magnetic circular polarized luminescence studies[3] seemed to favour the delocalization of the promoted electron over all three bipyridines, electronic absorption,[4–11] resonance Raman,[11–15] and emission photoselection[16,17] spectroscopies supported its localization on one of the bipyridines, thus suggesting that the light-induced electron transfer was vectorial in nature [equation (1)].[15]

$$[Ru^{II}(bipy)_3]^{2+} \xrightarrow{h\nu} [Ru^{III}(bipy)_2(bipy^{\bullet-})]^{2+} \quad (1)$$

However, as shown by near-i.r. absorption spectroscopy,[18] rapid electron hopping between ligands occurs, leading to a symmetrical charge distribution in the excited state. Thus the excited state of $[Ru(bipy)_3]^{2+}$ has the disadvantage of a lack of directed c.t. character. As pointed out by Meyer and co-workers,[1] basically this problem could be overcome by replacing one bipyridine ligand with stronger electron-accepting groups. Several $[Ru(bipy)_3]^{2+}$ derivatives containing appended mono- or di-pyridinium cations have been synthesized and studied.[1,19–22] Furthermore, a chromophore quencher complex containing both an electron acceptor (a linked viologen) and an electron donor (a linked phenothiazine) has recently been described.[23] Other interesting results were obtained with rhenium(I)[24] or iridium(I)[25] complexes. Our approach to this problem was described in a preliminary communication[26] in which we accounted for some properties of the complex $[Ru(bipy)_2(dppz)]^{2+}$, where dppz is dipyrido[3,2-*a*:2′,3′-*c*]-phenazine. In this paper we will present further evidence for the directed character of the m.l.c.t. state of $[Ru(bipy)_2(dppz)]^{2+}$.



Experimental

Materials.—Absolute ethanol (Prolabo), triethanolamine (Fluka), 1,10-phenanthroline monohydrate, 2,2′-bipyridine, phenazine, methyl viologen dichloride (1,1′-dimethyl-4,4′-bipyridinium) hydrate (Aldrich), $RuCl_3 \cdot xH_2O$ (Roth), and $[Ru(bipy)_3]Cl_2 \cdot 6H_2O$ (Ventron) were used as received. Acetonitrile (Fluka) was distilled over CaH_2 and *o*-phenylenediamine (Aldrich) was recrystallized several times from water before use.

Physical Measurements and Instrumentation.—U.v.–visible spectra were recorded with a Beckman DB-G spectrophotometer. Room-temperature emission spectra were obtained with a Perkin-Elmer MPF-3 apparatus. Solutions for emission and

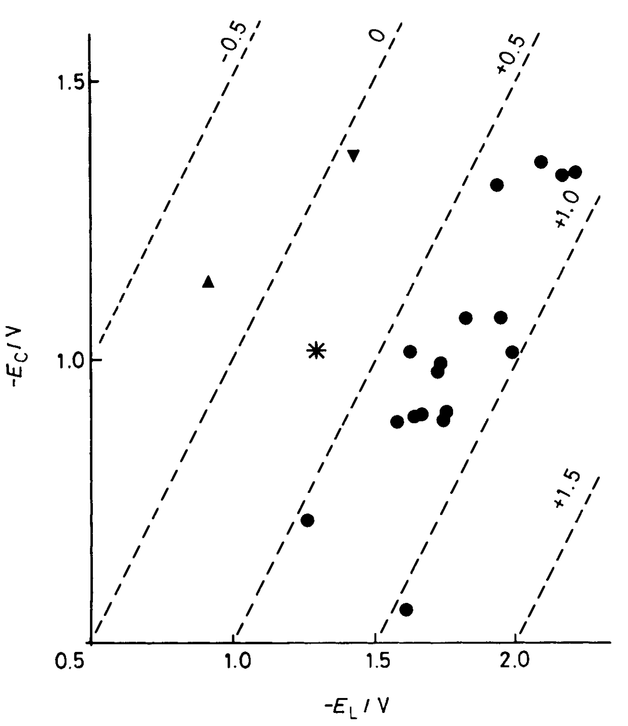


Figure 1. Plot of the reduction potential of ligand L (E_L) *vs.* the first reduction potential of $[Ru(bipy)_2L]^{2+}$ (E_C) (potentials in V *vs.* s.c.e.). Dashed lines show the locus where $E_C - E_L = -0.5, 0, +0.5, +1.0$, and $+1.5$. Odd points are $[Ru(bipy)_2(4,4'\text{-}Cl_2\text{-}bipy)]^{2+}$ (▲), $[Ru(bipy)_2(4,4'\text{-}Bu^t{}_2\text{-}bipy)]^{2+}$ (ref. 29) (▼), and $[Ru(bipy)_2(dppz)]^{2+}$ (✱)

quenching studies were degassed by three freeze–pump–thaw cycles before measurements. Controlled-potential electrolyses of phenazine and dipyridophenazine at *ca.* −1.30 V *vs.* saturated calomel electrode (s.c.e.) were performed using a Tacussel PRT40.1-X potentiostat and a Tacussel IG5-LN integrator. Cyclic voltammograms were obtained with a Bruker E130M potentiogalvanostat, using s.c.e. as the reference electrode. Laser flash spectroscopy was performed using a tunable dye laser (Lambda Physik FL 2000, 450-nm pulses of duration 10 ns and energy 10 mJ) pumped with an excimer laser (Lambda Physik EMG 100, 308-nm pulses of duration 10 ns and energy 150 mJ) as an excitation source. The detection system consisted of a xenon flash lamp, a Jobin Yvon H25 monochromator, a RCA 1P28 photomultiplier, and a Tektronix 7904 oscilloscope. Exciting and monitoring radiations were in a crossed-beam arrangement. The analysis was carried out within the first millimetre of the sample excited by the laser pulse, using quartz cells of path lengths 10 or 20 mm. In order to normalize transient optical densities, the relative laser pulse intensity was monitored by diverting a small fraction of the excimer laser beam onto a photodiode (EG&G, UV 100 BQ) whose output was displayed on a custom-built electronic integrator. The laser intensity was attenuated, particularly when using the excimer beam directly as the excitation source. The values obtained for the excited-state absorption coefficients at 450 nm were 7 900 $dm^3\ mol^{-1}\ cm^{-1}$ for $[Ru(bipy)_2(dppz)]^{2+*}$ and 6 050 $dm^3\ mol^{-1}\ cm^{-1}$ for $[Ru(bipy)_3]^{2+*}$, the latter being consistent with literature data (see refs. 6 and 8).

Syntheses.—Melting points were taken using a Leitz microscope and are uncorrected. Proton n.m.r. spectra were recorded at 200 MHz with a WP 200 SY Bruker spectrometer, chemical shifts being given *vs.* $SiMe_4$ and coupling constants in Hz. Microanalyses were performed by the Service de Microanalyse of the Institut de Chimie de Strasbourg.

1,10-*Phenanthroline*-5,6-*dione*. Unlike the literature[27] procedure, this compound was prepared in one step. 1,10-Phenanthroline monohydrate (25 g, 0.126 mol) in 20% oleum (125 cm^3) was heated to 110—115 °C and 72% HNO_3 (33 cm^3) was added. The reaction mixture was then refluxed to 143 °C and 72% HNO_3 (66 cm^3) was added over 0.5 h. At the end of the addition the temperature had dropped to 115 °C. After stirring for 1.5 h the reaction mixture was cooled to room temperature, poured onto ice, and neutralized with 30% NaOH. The beige precipitate was removed by filtration and thoroughly washed with water. After drying it yielded crude 5-nitro-1,10-phenanthroline (18.7 g). The filtrate, containing the desired product, was extracted with CH_2Cl_2. The crude extract (7.9 g) was recrystallized from methanol and yielded pure 1,10-phenanthroline-5,6-dione (5.26 g, 20%), m.p. 251 °C (lit.,[27] m.p. 258 °C); $\delta_H(CDCl_3)$ 9.12 (2 H, dd, J = 1.82, 4.66), 8.51 (2 H, dd, J = 1.87, 7.91), and 7.59 (2 H, dd, J = 4.68, 7.86 Hz).

Dipyrido[3,2-a:2′,3′-c]*phenazine*. This was synthesized according to ref. 28, m.p. 254–255 °C (lit.,[28] m.p. 250 °C); $\delta_H[(CD_3)_2SO]$ 9.46 (2 H, d, J = 7.58), 9.19 (2 H, dd, J = 1.41, 4.35), 8.34 (2 H, dd, J = 3.52, 5.98, 6.46, 3.80), 8.04 (2 H, dd, J = 3.40, 6.52), and 7.92 (2 H, dd, J = 4.42, 8.10 Hz).

Bis(2,2′-*bipyridine*)(*dipyrido*[3,2-a:2′,3′-c]*phenazine*)-*ruthenium*(II) *tetrafluoroborate*. The procedure described here was a slight modification of ref. 29. A mixture of $[Ru(bipy)_2]Cl_2\cdot 2H_2O$[30] (1.54 g, 2.97 mmol) and dipyridophenazine (0.93 g, 3.19 mmol) in methanol–water (1:2, v/v; 380 cm^3) was refluxed for 4.5 h. The deep red solution was concentrated to 10%, diluted with water (140 cm^3), boiled for 10 min, cooled in an ice-bath, and filtered. The tetrafluoroborate salt of the complex was precipitated by addition of 10% $NaBF_4$ (30 cm^3) to the filtrate. The crude product was recrystallized from ethanol (2.14 g, 80%). Samples for laser-flash spectroscopy were recrystallized twice (Found: C, 51.10; H, 3.10; N, 12.30. $C_{38}H_{26}B_2F_8Ru\cdot 1.5H_2O$ requires C, 50.90; H, 3.25; N, 12.35%). $\delta_H(CD_3CN)$ 9.69 (2 H, dd, J = 8.2, 1.5), 8.57 (4 H, t, J = 7.64), 8.50 (2 H, dd, J = 3.46, 6.60), 8.21—8.10 (6 H, overlapping multiplets), 8.04 (2 H, td, J = 1.6, 9.2), 7.91 (2 H, dd, J = 5.40, 8.22), 7.88 (2 H, d, J = 5.64), 7.76 (2 H, d, J = 5.58), 7.49 (2 H, ddd, J = 5.7, 1.5), and 7.29 (2 H, ddd, J = 5.70, 1.5 Hz).

Results and Discussion

Synthesis.—Dipyrido[3,2-*a*:2′,3′-*c*]phenazine was synthesized from *o*-phenylenediamine and 1,10-phenanthroline-5,6-dione.[28] The latter compound is usually obtained by sulphonitration of the reduction product of 5-nitro-1,10-phenanthroline by sodium tetrahydroborate.[28] In their preparation of 5-nitro-1,10-phenanthroline, Smith and Cagle[27] obtained less than 1% of the dione. We obtained this dione in 20% yield, probably because of the slightly lower temperature and stronger oleum.

Electrochemical and Spectroscopic Properties.—The electrochemical and spectroscopic data are shown in Table 1. Dipyridophenazine is more easily reduced than bipyridine by 1 V, due to the lower energy π^* orbital of the phenazine moiety. Thus the π-accepting site in dipyridophenazine is localized on the phenazine portion of the molecule. Comparison of the first reduction potentials [$E_{\frac{1}{2}}$(red)] of $[Ru(bipy)_3]^{2+}$ and $[Ru(bipy)_2(dppz)]^{2+}$ shows that this site is a better electron acceptor than the bound 2,2′-bipyridine groups by *ca.* 0.30 V. However, the phenazine site is only slightly coupled electronically to the ruthenium ion as shown both by the low potential displacement between the free and the co-ordinated dipyridophenazine ligand {*ca.* 0.30 V; as shown in Figure 1, this displacement lies between +0.5 and +0.1 V for most of the complexes of the $[Ru(bipy)_2L]^{2+}$ family, where L is a stronger π acceptor than

Table 1. Electrochemical and spectroscopic data

Compound	Oxidation[a]	Reduction[a]				Absorption $\lambda_{max.}$/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})	Emission $\lambda_{max.}$/nm (φ_{em})
		1	2	3	4		
Phenazine	1.91[b]	−1.14[c] −0.70[d]				400 (sh), 362 (1.32), 248 (12.4), 241 (sh), 211 (2.75)[e]	
Dipyridophenazine	1.80[f]	−1.18[c]	−1.80[c]			378 (1.29), 367 (1.05), 360 (1.19), 351 (0.86), 343 (0.75), 335 (sh), 315 (sh), 295 (sh), 270 (6.07), 242 (3.13), 212 (2.77)[d]	
$[Ru(bipy)_2(dppz)]^{2+}$		−0.86[c] −0.77[d]	−1.30[c]	−1.51[c]	−2.02[c]	448 (1.57), 366 (1.55), 357 (1.56), 352 (sh), 342 (sh), 315 (sh), 284 (9.36), 255 (4.18), 212 (5.00)[d]	610 (0.021)[d]
	1.24	−1.02	−1.44	−1.67	−2.07		
$[Ru(bipy)_3]^{2+}$	1.29	−1.33	−1.52	−1.76	−2.40	452 (1.45), 345 (sh), 323 (sh), 285 (8.71), 250 (2.51), 238 (2.95), 208 (sh), 185 (8.91)	607[g] (0.042)

[a] Unless otherwise noted, redox potentials are quoted *vs.* s.c.e. in MeCN at room temperature. Supporting electrolyte: NEt_4ClO_4. [b] R. N. Adams, 'Electrochemistry at Solid Electrodes,' Marcel Dekker, New York, 1969. [c] In dimethylformamide. [d] In EtOH. [e] In MeOH; 'U.V. Atlas of Organic Compounds,' vol. 1, Butterworths, London, Verlag Chemie, Weinheim, 1966. [f] Estimated. [g] In water.

bipyridine itself (from data in refs. 2, 29, and 31—34)} and by the absence of a red shift in the m.l.c.t. absorption of $[Ru(bipy)_2(dppz)]^{2+}$, as in $[Ru(dppz)_3]^{2+}$.[35] Additionally, the oxidation potential of $[Ru(bipy)_2(dppz)]^{2+}$ is very close to that of $[Ru(bipy)_3]^{2+}$. Thus, as evidenced by Barigelletti *et al.*,[31] $[Ru(bipy)_2(dppz)]^{2+}$ does not follow the linear correlation between the maximum of the absorption energy and $\Delta E = E_{\frac{1}{2}}(\text{ox}) - E_{\frac{1}{2}}(\text{red})$ that was established for many comparable complexes in the $[Ru(bipy)_2L]^{2+}$ family. As a consequence, the orbital involved in the light-induced charge transfer (optical orbital)[36—38] and the orbital involved in the first electrochemical reduction step (redox orbital)[36—38] are separated, both in space and energy, within the complex $[Ru(bipy)_2(dppz)]^{2+}$; the optical orbital lies on the bipyridine moieties and the redox orbital on the phenazine portion of the molecule. This is in strong contrast with $[Ru(bipy)_3]^{2+}$ for which the redox and optical orbitals are very similar in nature.[37] Emission studies support these observations. Unlike other complexes containing appended accepting groups,[21] $[Ru(bipy)_2(dppz)]^{2+}$ is luminescent at room temperature. The emission maxima occur at the same energy for $[Ru(bipy)_2(dppz)]^{2+}$ and $[Ru(bipy)_3]^{2+}$. Thus in a result parallel to the absorbance data, $[Ru(bipy)_2(dppz)]^{2+}$ does not follow the linear correlation between the maximum of the emission energy and ΔE.[31] As a consequence, the emission of $[Ru(bipy)_2(dppz)]^{2+}$ originates from an excited state localized on the bipyridine moieties, and not on the phenazine portion of the complex. However, unlike $[Ru(dppz)_3]^{2+}$,[35] which exhibits the same photophysical characteristics as $[Ru(bipy)_3]^{2+}$, both the lifetime (270 ns) and emission quantum yield (0.02) of $[Ru(bipy)_2(dppz)]^{2+}$ in ethanol are roughly half those of $[Ru(bipy)_3]^{2+}$ in water. Another intriguing result is that unlike $[Ru(bipy)_3]^{2+}$ the emission of $[Ru(bipy)_2(dppz)]^{2+}$ is quenched in acidic or neutral water and is low in strongly basic solution. The emission originates from a triplet state of the complex, since it is quenched by oxygen ($k_q = 8 \times 10^8$ dm^3 mol^{-1} s^{-1}). To summarize, the strong π-accepting phenazine site in $[Ru(bipy)_2(dppz)]^{2+}$ is only slightly electronically coupled to the ruthenium.

Excited State Absorption Spectroscopy.—Further characterization of the excited state of $[Ru(bipy)_2(dppz)]^{2+}$ was the determination of its transient absorption spectrum in the range 370—610 nm. This spectrum appeared during the laser pulse (10 ns, 450 nm), then decayed with a first-order rate constant which was the same as the rate constant of luminescence (3.7×10^6 s^{-1}). This is probably accidental. Such spectra were obtained by several authors for $[Ru(bipy)_3]^{2+}$,[4—11] however most limited their study below 500 nm. Also, using the same experimental conditions as in the case of $[Ru(bipy)_2(dppz)]^{2+}$, we determined the transient absorption spectrum of $[Ru(bipy)_3]^{2+}$, in the range 350—560 nm. Differential excited-state absorption spectra and normalized transient absorption spectra are shown in Figure 2(*a*) and (*b*). Both spectra show a maximum around 430 nm and a strong peak at 375 nm for $[Ru(bipy)_3]^{2+}$ which is shifted to 385 nm for $[Ru(bipy)_2(dppz)]^{2+}$. Above 500 nm, however, the two spectra show significant differences. In the range of λ examined, the data obtained for $[Ru(bipy)_3]^{2+}$ (one band, $\varepsilon^* = 2\,050$ dm^3 mol^{-1} cm^{-1} at 510 nm) are roughly consistent with those published by Braterman *et al.*[5] ($\varepsilon^*_{max.} = 3\,000$ dm^3 mol^{-1} cm^{-1} at 540 nm). This band was assigned to a bound bipyridine anion radical. Indeed, the spectrum of the chemically generated anion radical of bipyridine[39] shows similar absorption patterns; however, there are two maxima instead of one, at 527 and 558 nm respectively. This difference is probably not significant, since the species compared (supposedly co-ordinated bipyridine transient anion radical and free bipyridine anion radical) are certainly not the same from the electronic viewpoint. In contrast to $[Ru(bipy)_3]^{2+}$, the transient absorption spectrum of $[Ru(bipy)_2(dppz)]^{2+}$ shows two maxima respectively at 526 and 557 nm ($\varepsilon^* = 5\,000$ dm^3 mol^{-1} cm^{-1}), which may imply that both excited states are different in nature. This was supported by additional data, that is the determination of the absorption spectra of the anion radicals of phenazine and dipyridophenazine generated by controlled electrolysis. The spectrum of reduced phenazine was the same as that obtained by γ-irradiation in 2-methyltetrahydrofuran.[40] Above 500 nm, the radical anion of phenazine shows a wide band with two maxima (512 and 552 nm), whereas in the case of the radical anion of dipyridophenazine there is only one maximum (572 nm); however the shoulder at 540 nm clearly corresponds to the first maximum in the case of the radical anion of phenazine.

The differences (in terms of the number of absorption maxima) between the excited-state spectra of $[Ru(bipy)_3]^{2+}$ and $[Ru(bipy)_2(dppz)]^{2+}$ allow some conjectures about the localization of the promoted electron in the excited state of $[Ru(bipy)_2(dppz)]^{2+}$. It was shown above that unlike bipyridine in $[Ru(bipy)_3]^{2+}$, the phenazine portion of dipyridophenazine was only slightly perturbed by the metal core in $[Ru(bipy)_2(dppz)]^{2+}$. Since the spectra of the phenazine or dipyridophenazine anion radicals basically match that of the excited state of $[Ru(bipy)_2(dppz)]^{2+}$, the latter is probably due to a co-ordinated transient dipyridophenazine anion radical, in

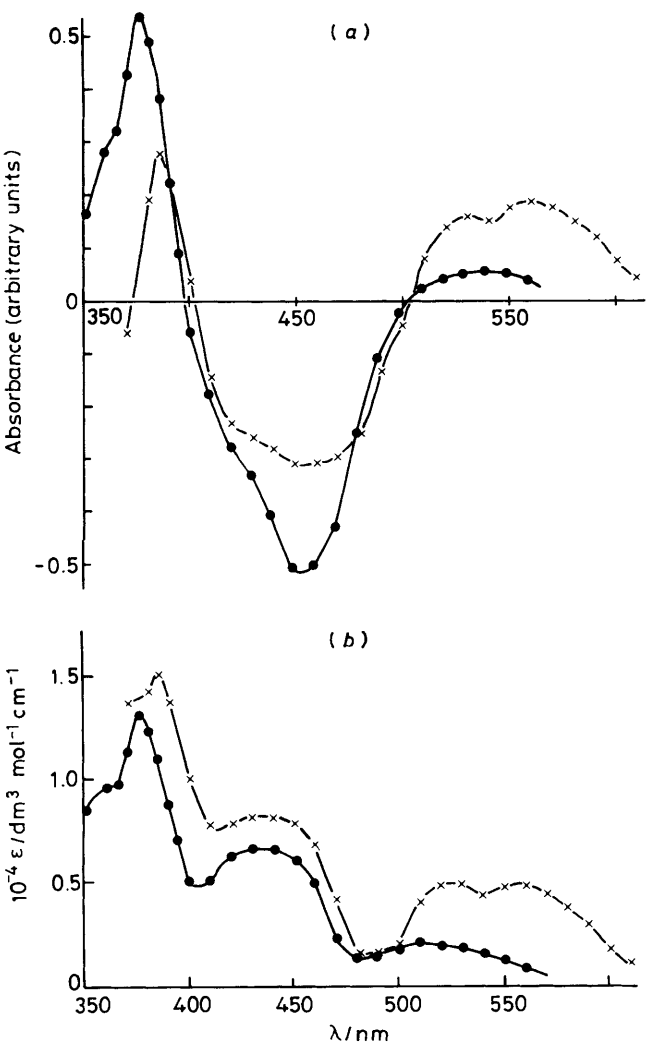


Figure 2. Differential (*a*) and normalized (*b*) excited-state absorption spectra for $[Ru(bipy)_3]^{2+}$ (●) and $[Ru(bipy)_2(dppz)]^{2+}$ (×) in ethanol. Excitation at 450 nm

which the electron is localized on the phenazine portion of the molecule.

The data presented above were interpreted only in terms of an electron transfer from the ruthenium to the phenazine part of the complex. Raman resonance data for mixed-ligand ruthenium complexes showed that the excited electron is localized on the stronger π acceptor.[41] Despite this fact, it may also be suggested that the observed transient absorption spectrum of $[Ru(bipy)_2(dppz)]^{2+}$ is due to both co-ordinated bipyridine and dipyridophenazine anion radicals;* this would be in agreement with the $[Ru(bipy)_3]^{2+}$-like emission of the complex in ethanol. Another interpretation of the data may be energy transfer from the Ru→bipy m.l.c.t. excited state generating the phenazine triplet state.* This is suggested by the fact that the latter shows a low-energy transient absorption band in ethanol at 504 nm[42] which however does not account for the maximum at 560 nm in the transient absorption spectrum of $[Ru(bipy)_2(dppz)]^{2+}$.

Photochemistry.—The $[Ru(bipy)_3]^{2+}$ complex ion has been extensively studied as a photosensitizer for the reduction of water into hydrogen, using a sacrificial electron donor, an electron relay, and a redox catalyst.[43–48] Several other ruthenium di-imine complexes were examined for the same purpose.[49,50] Two catalytic cycles could be evidenced.[50] In the oxidative cycle the excited state of $[Ru(bipy)_3]^{2+}$ is quenched by an electron acceptor, whereas in the reductive cycle it is quenched by an electron donor.

Table 2. Quenching data[a] for $[Ru(bipy)_2(dppz)]^{2+}$

Quencher	*E*/V *vs.* n.h.e.)	K_{SV}/dm^3 mol^{-1}	k_q/dm^3 mol^{-1} s^{-1}
Methyl viologen	-0.44^b	600	1.37×10^9
Triethanolamine	0.82^c	12	4.40×10^7

[a] In ethanol. [b] S. Hunig and J. Gross, *Tetrahedron Lett.*, 1968, **21**, 2599. [c] K. Kalyanasundaram, J. Kiwi, and M. Grätzel, *Helv. Chim. Acta*, 1978, **61**, 2720.

The excited state of $[Ru(bipy)_3]^{2+}$ was shown to decay in most cases *via* oxidative quenching. An interesting property of the reductive cycle is that there is no energy-wasting recombination of separated charges, since the donor is irreversibly oxidized.[50,51] With a view to a study of the possibilities of $[Ru(bipy)_2(dppz)]^{2+}$ as a photosensitizer for the water-splitting reaction, we studied the quenching of its excited state by methyl viologen (electron acceptor) and triethanolamine (electron donor) in ethanol, using flash photolysis and Stern–Volmer quenching experiments. As shown in Table 2, the excited state of $[Ru(bipy)_2(dppz)]^{2+}$ is quenched much more efficiently by methylviologen than by triethanolamine. Reaction with methylviologen was shown to proceed *via* electron transfer by simultaneously monitoring the decay of the luminescence and the increase at the same rate of the absorbance at 602 nm of the cation radical of methyl viologen.[52] As shown by steady-state irradiation experiments, reductive quenching of $[Ru(bipy)_2(dppz)]^{2+}$ by triethanolamine eventually led to an irreversible transformation of the complex.

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