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Absorption spectra, luminescence properties and electrochemical behaviour of ruthenium(II) complexes containing bis(pyridyl)triazole ligands

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Abstract

Four novel complexes of general formula $Ru(L)_2(T)^{2+}$ (**1**, L=bpy, T=trz; **2**, L=bpy, T=trz-Q; **3**, L=biq, T=trz; **4**, L=biq, T=trz-Q; bpy=2,2′-bipyridine, biq=2,2′-biquinoline; trz=4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole; trz-Q=4(4′-*N*,*N*-dimethylamino-phenyl)imino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole) have been synthesized, and their absorption spectra, luminescence properties (both in fluid solution at room temperature and in rigid matrix at 77 K), and electrochemical behaviour have been investigated. The absorption spectra of the complexes show intense absorption bands in the UV region (ϵ in the range 10^4–10^5 M^{-1} cm^{-1}) that are assigned to ligand-centred transitions and moderately intense absorption bands in the visible (ϵ in the range 10^3–10^4 M^{-1} cm^{-1}) that are attributed to metal-to-ligand charge transfer (MLCT) transitions. The absorption bands in the visible of the biq-containing complexes are at lower energies than those of the bpy-containing ones. The four complexes emit from a MLCT excited state both at 77 K and at room temperature, with lifetimes in the range 10^{-5}–10^{-6} s and 10^{-7}–10^{-8} s, respectively. The luminescence lifetimes and quantum yields are practically the same for **1** and **3** and for **2** and **4**, respectively, indicating that the presence of the *N*,*N*-dimethylamino unit on the triazole ligand does not affect the radiative and radiationless rate constants of the chromophores and does not cause an electron-transfer quenching process. On electrochemical oxidation, **1** and **3** exhibit a reversible one-electron wave at +1.22 and +1.37 V versus SCE, respectively, that are assigned to metal-centred oxidations, while **2** and **4** undergo two successive one-electron oxidations at +1.30 and +1.56 V (**2**) and +1.30 and +1.71 V (**4**). By comparison with the redox behaviour of the free ligands, in both **2** and **4** the first process is attributed to oxidation of the *N*,*N*-dimethylamino moiety, and the second one to metal-centred oxidation. Two reversible reduction processes occur in all the complexes at about −1.15 and −1.40 V (**1** and **2**) and at about −0.60 and −0.85 V (**3** and **4**). Such processes are assigned as bpy- and biq-centred reductions, respectively. The positive shift of the metal-centred oxidation on passing from **1** and **3** to **2** and **4** is attributed to electronic 'communication' between the chromophoric metal unit and the electron-donor *N*,*N*-dimethylamino group across the triazole ligand and the conjugate $-N{=}CH-C_6H_4-$bridge, and to an electrostatic term.

Introduction

Ruthenium(II)–polypyridine complexes have been extensively studied over the last ten years because a unique combination of ground and excited state properties makes them most useful in several fields of chemistry [1–12].

In the last few years Ru(II)–polypyridine complexes have also been used extensively to study photoinduced intramolecular energy- and/or electron-transfer processes in supramolecular arrays [10, 12–15], with the aim of obtaining useful insights towards a better understanding of the factors that govern important natural phenomena (e.g. photosynthesis [16]) and the design of artificial photochemical molecular devices [17]. Suitable systems for these studies are the so-called covalently-linked chromophore–quencher species (CQ) based on luminescent metal complexes**. One of the requisites a CQ system has to exhibit is the possibility of comparing its properties to those of its 'reference' complex (C). The more the intrinsic† properties of C

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**The literature on this very recent research topic is already so vast that it cannot be quoted exhaustively. For some reviews, see refs. 10, 12 and 13.

†For intrinsic properties of C we mean the value of the rate constants of the radiative and radiationless decays.

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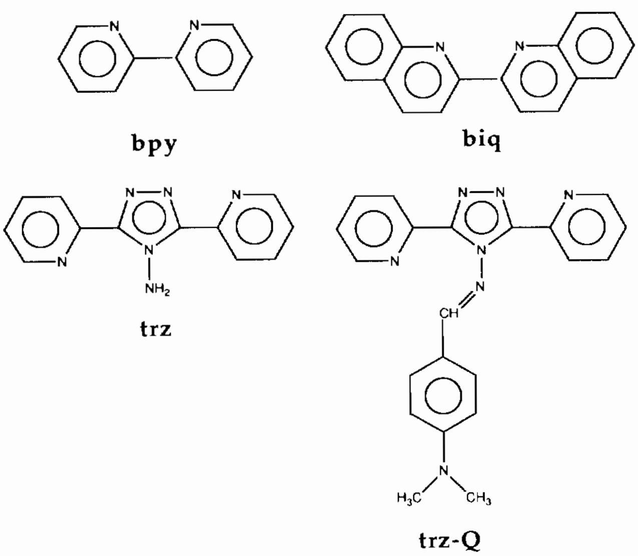

Fig. 1. Structural formulas of the ligands.

are unaffected by the presence of the quencher in CQ, the more the results obtained are reliable [13, 18]. Because the coupling between C and Q is bridge-dependent, the nature and function of the connectors between C and Q play a fundamental role in designing useful CQ systems.

Here we present the synthesis, absorption spectra, luminescence properties and electrochemical behavior of four novel Ru(II)–polypyridine complexes of general formula $Ru(L)_2(trz)^{2+}$ (chromophore complexes, C_s) and $Ru(L)_2(trz\text{-}Q)^{2+}$ (chromophore-quencher complexes, CQ_s) (L = bpy or biq; bpy = 2,2′-bipyridine; biq = 2,2′-biquinoline; trz = 4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole; trz-Q = 4(4′-*N*,*N*-dimethylaminophenyl)imino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole; see Fig. 1). Two of the complexes carry a potential excited-state quencher Q, a *N*,*N*-dimethylamino electron-donor group, connected with the triazole ligand by a conjugate $-N{=}CH-C_6H_4-$ bridge.

Experimental

Materials and methods

All the reactants and solvents used were of the best commercial grade. IR spectra were performed on a Perkin-Elmer FTIR spectrometer using KBr pellets and nujol as solvent. ^1H NMR spectra were obtained with a 80 MHz Bruker spectrometer. For the absorption spectra a Kontron Uvikon 860 spectrophotometer was employed. Luminescence spectra were performed with a Perkin-Elmer LS-5B fluorimeter, equipped with a Hamamatsu R928 phototube; the luminescence spectra were corrected for photomultiplier response by using a standard lamp. Luminescence lifetimes were measured with an Edinburgh 199 single photon counting spectrometer. Luminescence quantum yields were measured by the optically diluted method [19] using $Ru(bpy)_3{}^{2+}$ in aerated aqueous solution as a reference ($\Phi = 0.028$ [20]).

Electrochemical measurements were carried out in deaerated acetonitrile solution at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode used was either a Pt microelectrode or a hanging mercury-drop electrode. The counter electrode was a Pt wire, and the reference electrode was an SCE (saturated calomel electrode) separated with a fine glass frit. Tetraethylammonium perchlorate (polarographic grade) was used as supporting electrolyte. Cyclic voltammograms were usually obtained at a scan rate of 100 mV s^{-1}. Differential-pulse voltammetry was performed with a scan rate of 20 mV s^{-1}, a pulse height of 50 mV, and a duration of 50 ms. For reversible processes, half-wave potentials (versus SCE) were calculated as an average of the cathodic and anodic peaks. The criteria for reversibility were the separation between cathodic and anodic peaks (~ 60 mV for monoelectronic processes), the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate.

When necessary, the solution were deaerated by bubbling nitrogen.

Experimental errors are as follows: absorption maxima, ± 2 nm; emission maxima, ± 4 nm, emission lifetimes, 10%; emission quantum yields, 20%; redox potentials, 20 mV.

Syntheses

trz-Q

0.200 g of 4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole (Aldrich product) were added to a previously refluxed solution of 4-(dimethylamino)benzaldehyde (0.125 g, 0.839 mmol) in methanol (20 ml). The mixture was maintained at 40 °C under stirring for 30 min and then cooled to room temperature. The yellow solid that precipitated was purified by several recrystallizations (yield 88%).

$[Ru(bpy)_2(trz)](PF_6)_2$ (1)

$Ru(bpy)_2Cl_2$ [21] (0.100 g, 0.206 mmol) and trz (0.110 g) were stirred and refluxed in EtOH (20 ml) for 2 h and then rotary-evaporated *in vacuo*. The resulting material was washed several times with diethyl ether and then dissolved in the smallest possible amount of MeOH. Solid KPF_6 was added to the solution until the precipitation was complete. After filtration a red–orange product was recovered which was further purified by several recrystallizations (yield 75%).

[Ru(bpy)$_2$(trz-Q)](PF$_6$)$_2$ (2)

The procedure was identical with that described for **1**. The final product was an orange–yellow solid (yield 72%).

[Ru(biq)$_2$(trz)](PF$_6$)$_2$ (3)

The procedure was identical with that described for **1**, using Ru(biq)$_2$Cl$_2$ [22] as starting material. After several recrystallizations a dark purple solid was recovered (yield 76%).

[Ru(biq)$_2$(trz-Q)](PF$_6$)$_2$ (4)

The procedure was identical with that described for **1**. The final product was a dark red solid (yield 80%).

Elemental analyses, IR spectra and NMR spectra were in agreement with the expectations.

Results

All the complexes are stable in the solvents used for at least 24 h, as showed by the constancy of their absorption spectra.

The absorption spectra of the complexes (see Figs. 2 and 3) show intense absorptions in the UV region (ϵ in the range 10^4–10^5 M^{-1} cm^{-1}) and moderately intense absorptions in the visible region (ϵ in the range 10^3–10^4 M^{-1} cm^{-1}). In each case, the absorption bands in the visible of the biq-containing complexes are at lower energies than those of the bpy-containing ones. Data on absorption spectra of the complexes are listed in the Table 1, in which also absorption data on trz and trz-Q are reported. For the sake of comparison, the absorption spectra of the free ligands are also shown in Fig. 4.

On electrochemical oxidation, **1** and **3** exhibit a reversible one-electron wave at +1.22 and +1.37 V versus SCE, respectively, while **2** and **4** undergo to two successive reversible one-electron oxidation processes at +1.30 and +1.56 V (**2**) and at +1.30 and +1.71 V (**4**). The reduction pattern exhibited by all the complexes is similar, showing two reversible one-electron processes. For **1** and **2** the reduction waves occur at more negative potentials than for **3** and **4**. As far as the free ligands are concerned, while no oxidation process is shown by the differential pulse voltammogram of trz upto +1.80 V, trz-Q exhibits a reversible oxidation at +1.24 V. Table 2 collects the electrochemical data of the new complexes, along with the data of the free ligands.

All four complexes exhibit luminescence both in fluid solution at room temperature and in rigid matrix at 77 K, where for **1** and **2** the spectra display a vibrational progression of about 1300 cm^{-1}. The luminescence spectra of **1** and **3** are shown in Figs. 2 and 3. The luminescence lifetimes are in the range 10^{-8}–10^{-7} s at room temperature and 10^{-6}–10^{-5} s at 77 K. The luminescence quantum yields are practically the same for **1** and **2**, as are the relative luminescence intensity for **3** and **4**. The quantum yield values of **3** and **4** could not be measured because it was impossible to obtain reliable corrected spectra owing to the red limit of our equipment. Data on luminescence properties are gathered in Table 1.

As far as the free ligands are concerned, no luminescence has been detected for trz both at 77 K and room temperature. On the contrary, trz-Q exhibits an emission at approximately 500 nm, probably due to an intraligand charge-transfer (from the dimethylamino moiety to the −N=C− group) excited state; such an emission is completely quenched in the complexes.

Discussion

The spectroscopic and electrochemical properties of transition metal complexes can be discussed with the assumption that the ground as well as the excited and redox states involved in the processes are described in a sufficiently approximate way by localized molecular orbital configurations [3, 23, 24]. Within such an assumption, the various spectroscopic transitions can be classified as metal-centred (MC), ligand-centred (LC), or charge transfer (either metal-to-ligand, MLCT, or ligand-to-metal, LMCT) [23]. In the same way, the oxidation and reduction processes are classified as metal- or ligand-centred [3].

Electrochemistry

The oxidation behaviour of **1** and **3** (Table 2) is similar to that of other Ru(II)–polypyridine complexes [9]. The one-electron oxidation exhibited by both the complexes is assigned to a metal-centred process.The positive shift of the oxidation on passing from **1** to **3** is rationalized when one considers the differences in σ-donor and π-acceptor ability between bpy and biq [25].

The trz-Q free ligand undergoes one-electron oxidation at +1.24 V, that involves the *N*,*N*-dimethylamino group (see comparison with trz, Table 2). Therefore, the two oxidation processes occurring in **2** and **4** (see Table 2) are indeed expected. For both complexes, the first oxidation is attributed to oxidation of the *N*,*N*-dimethylamino moiety, and the second to a metal-centred process. Such an assignment is based on the fact that: (i) the first oxidation of the complexes occurs at the same potential; (ii) the difference in potential energy between the second oxidations of the two com-

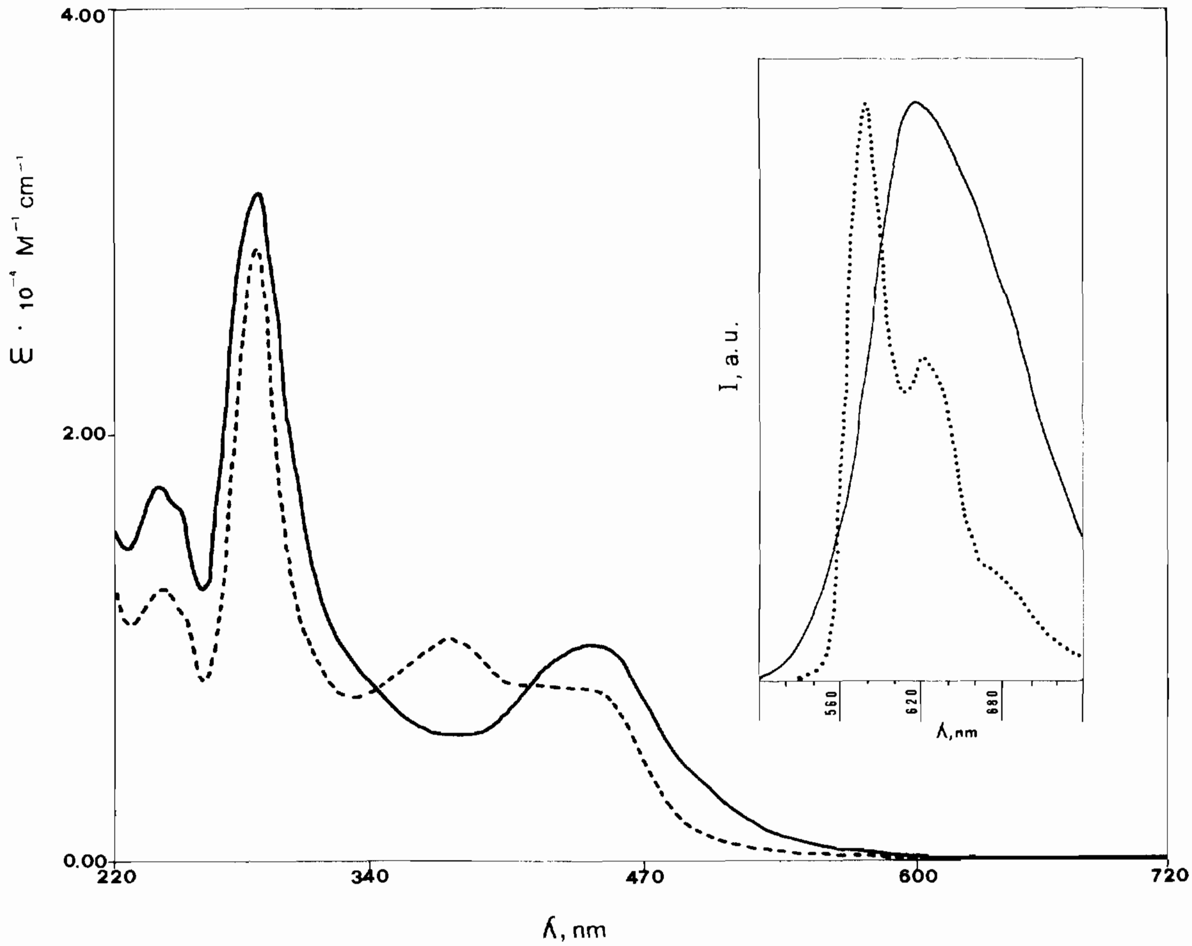

Fig. 2. Absorption spectra of **1** (solid line) and **2** (dashed line) in acetonitrile solution at room temperature. The inset shows the luminescence spectra of **1** in acetonitrile fluid solution at room temperature (solid line) and in methanol/ethanol 4:1 vol./vol. at 77 K (dashed line).

plexes (about 150 mV, see Table 2) is the same as the difference in potential energy between the metal-centred oxidation processes of **1** and **3**. The positive shift of the metal-centred oxidations of **2** and **4** compared to **1** and **3**, respectively (340 mV in both cases) is attributed to electronic 'communication' across the triazole ligand and the conjugated bridge and to an electrostatic term, that origins from the fact that the metal-centred oxidation in **2** and **4** occurs adjacent to a greater positive charge than in **1** and **3**.

The reduction waves of **1–4** (Table 2) can be assigned to successive reductions of the two bpy or biq that are present in the complexes. Triazole ligands are known [26] to be more difficult to reduce than polypyridine-like ligands. This assignment is also supported by the differences between the potential of the two reduction waves (about 200 mV, see Table 2), typical of interligand interactions between bpy or biq ligands in Ru(II)–polypyridine complexes [25], and by the reduction properties of the free triazole ligands (Table 2).

Absorption spectra

In the electronic absorption spectra (Table 1, Figs. 2 and 3) one can distinguish two main regions. Below 400 nm there are intense absorption bands mainly due to ligand-centred (LC) transitions. Comparison with other bpy- and biq-containing Ru(II) complexes [9] and free ligand absorption spectra (Fig. 4) leads us to assign the absorption band at about 282 nm of **1** and **2** to the bpy ligands, the broad absorption band at about 360 nm of **2** to the trz-Q ligand (this band is probably due to an intraligand charge transfer, ILCT, transition from the dimethylamino donor to the C=N group), and the absorption feature at about 265 nm and the narrow bands at 360 and 380 nm of **3** and **4** to the biq ligands. The increased absorption of **4** compared to **3** in the region 300–400 nm is attributed to overlap of biq and trz-Q LC and ILCT transitions.

For $\lambda > 400$ nm, the spectra are dominated by moderately intense bands that can be assigned to MLCT transitions. In particular, for **1** and **2**, the absorption band at 455 nm is assigned to a Ru → bpy CT transition,

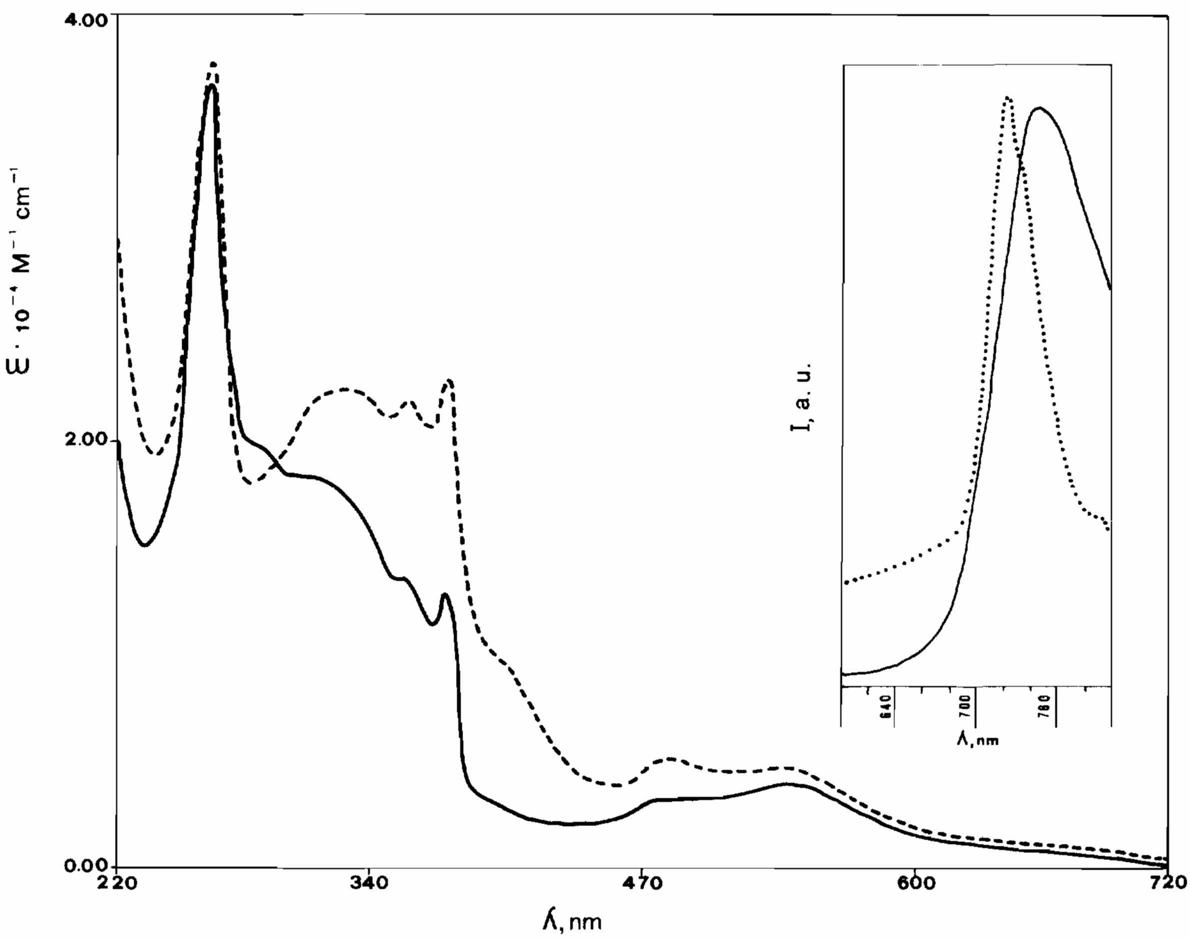

Fig. 3. Absorption spectra of 3 (solid line) and 4 (dashed line) in acetonitrile solution at room temperature. The inset shows the luminescence spectra of 3 in acetonitrile fluid solution at room temperature (solid line) and in methanol/ethanol 4:1 vol./vol. at 77 K (dashed line).

TABLE 1. Spectroscopic and photophysical data[a]

	Absorption		Luminescence				
	λ_{max} (nm)[c]	(ϵ (M^{-1} cm^{-1}))	298 K			77 K[b]	
			λ_{max} (nm)	τ (ns)	Φ	λ_{max} (nm)	τ (μs)
$Ru(bpy)_2(trz)^{2+}$ (1)	445	(10400)	638	90	8×10^{-3}	588	4.38
$Ru(bpy)_2(trz\text{-}Q)^{2+}$ (2)	445	(8000)	638	85	7×10^{-3}	586	4.86
$Ru(biq)_2(trz)^{2+}$ (3)	540	(4000)	764	229	100[d]	728	2.16
$Ru(biq)_2(trz\text{-}Q)^{2+}$ (4)	540	(4500)	764	231	100[d]	728	2.20
trz	296	(32000)					
trz-Q	360	(36000)					

[a] Acetonitrile aerated solutions, unless otherwise noted. [b] Methanol/ethanol 4:1 (vol./vol.) rigid matrix. [c] Lowest energy maximum. [d] Relative intensities, see text.

whereas the lowest absorption band of 3 and 4 at about 540 nm is assigned to a Ru→biq CT transition, red-shifted compared to the Ru→bpy bands of 1 and 2, in accordance with the electrochemical results. The long tail towards the red exhibited by the absorption spectra of 3 and 4 is typical of biq-containing complexes and can be attributed to inter-chromophoric couplings [25], as described by De Armond and coworkers [27, 28].

It is interesting to note that the Ru→bpy and Ru→biq absorption bands are not significantly perturbed by the presence of the *N,N*-dimethylamino electron donor, as

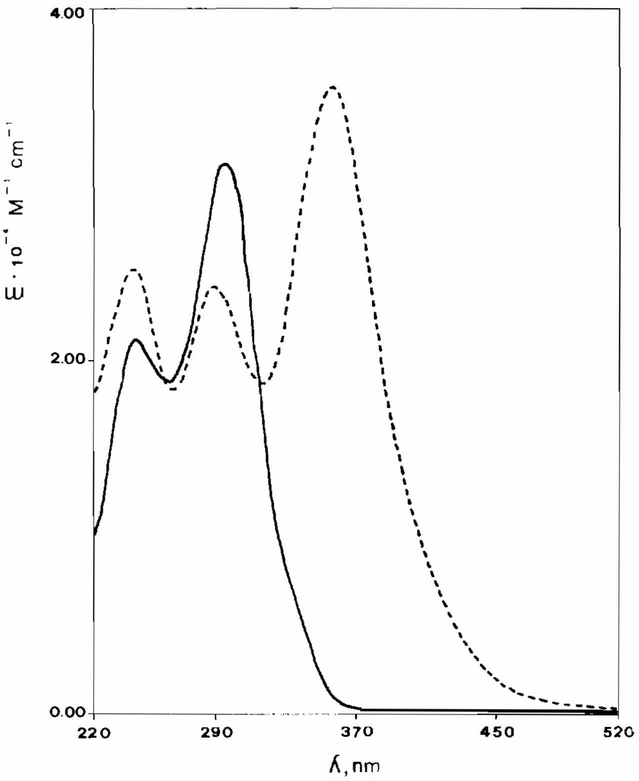

Fig. 4. Absorption spectra of trz (solid line) and trz-Q (dashed line) free ligands in acetonitrile solution at room temperature.

TABLE 2. Electrochemical data[a]

Compound	$E_{1/2}$			
	Oxidation		Reduction	
$Ru(bpy)_2(trz)^{2+}$ (**1**)		+1.22	−1.17	−1.38
$Ru(bpy)_2(trz\text{-}Q)^{2+}$ (**2**)	+1.56;	+1.30	−1.15	−1.41
$Ru(biq)_2(trz)^{2+}$ (**3**)		+1.37	−0.60	−0.88
$Ru(biq)_2(trz\text{-}Q)^{2+}$ (**4**)	+1.71	+1.30	−0.59	−0.85
trz		> +1.80	< −1.80	
trz-Q		+1.24	−1.65[b]	

[a]Acetonitrile solution, room temperature; $E_{1/2}$ values vs. SCE. [b]Irreversible wave, the reported figure refers to the E_{peak} value.

demonstrated by the constancy of their energies in the bpy- and biq-containing complex series.

Luminescence properties

All the complexes exhibit a luminescence band in the visible both at room temperature and at 77 K. Such an emission originates from Ru→bpy and Ru→biq CT excited states for the bpy- and biq-containing complexes, respectively. This assignment is in full agreement with literature data [9] and redox results.

The luminescence lifetimes of **1** and **2** at room temperature are much shorter than those of other Ru→bpy CT excited states which emit at about 640 nm [9]. Furthermore, the energy gap law [29–31] is not obeyed for the complexes examined. This apparently puzzling behavior can be rationalized by taking into account that an important pathway for radiationless decay of Ru(II)–polypyridine MLCT excited states is activated surface crossing to a low-lying MC excited state that promotes fast radiationless decay to the ground state and/or photoreaction [6–9]. The energy gap between the emitting MLCT excited state and the MC level is, as a consequence, a key factor in determining luminescence lifetimes. The triazole ligands are weaker ligand-field ligands than bpy [26] and the MC level in **1** and **2** can lie very close to the MLCT level, leading to efficient deactivation via surface crossing to MC and short luminescence lifetime. The replacement of bpy with biq further decreases the ligand field experienced by the metal, but is also very effective in lowering the MLCT level. This could lead to a larger energy gap between MLCT and MC levels, with an increase in luminescence lifetime.

On passing from room temperature to 77 K, a blue shift of MLCT emission, due to the absence of the solvent reorganization process [7, 9] can be observed (Figs. 2 and 3). As noted previously [25] the Ru→biq CT bands exhibit a smaller blue shift with respect to that of the Ru→bpy bands (Table 1, Figs. 2 and 3), because of the lower charge-transfer nature of the Ru→biq transition. As far as the luminescence lifetimes are concerned, the values at 77 K (Table 1) are in agreement with the energy gap law, as expected because the activated surface crossing pathway to the MC level cannot operate.

The luminescence efficiencies of **1** and **3** are the same as those of **2** and **4**, respectively (Table 1): this indicates that in **2** and **4** no luminescence quenching occurs by electron transfer from the *N*,*N*-dimethylamino donor to the (formally) Ru(III) ion, that is present in the MLCT excited state (eqn. (1)). Actually, by using eqn. (2)* to calculate the driving force of the

$$^*[(L^{\cdot -})(L)Ru^{3+}(trz\text{-}Q)]^{2+} \longrightarrow [(L^{\cdot -})(L)Ru^{2+}(trz\text{-}Q^{+})]^{2+} \qquad (1)$$

$$\Delta E = E_{ox} - {}^*E_{red} \qquad (2)$$

electron-transfer quenching processes, positive values of 0.32 V for **2**, and 0.28 V for **4**, are found for ΔE.

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*In eqn. (2), E_{ox} represents the $E_{(1/2)}$ value of the oxidation potential of the quencher, that is +1.30 V in both **2** and **4**, and $^*E_{red}$ is $[E_{(1/2)red}+E_{00}]$, where $E_{(1/2)red}$ is the first reduction potential of the complex and E_{00} is the energy of the excited state, estimated to be the maximum of the 77 K emission band. In a first approximation, the work term due to the Coulombic interaction between the electron and positive hole in the charge-separated state [10, 13, 18] is neglected.

So, electron-transfer quenching is an endoergonic process in both cases, and therefore cannot be efficient.

Conclusions

The four novel complexes studied in this paper exhibit quite interesting properties. The absorption and luminescence properties of the chromophoric units are practically unperturbed by the presence, in two of the complexes, of an electron-donor moiety. The electrochemical results point out that a noticeable electronic communication occurs between the chromophoric metal units and the *N*,*N*-dimethylamino 'potential' quencher across the triazole ligand and the conjugate $-N=CH-C_6H_4-$ connector. This indicates that such a connector could be efficiently used in designing covalently linked chromophore–quencher complexes suitable for photoinduced intramolecular electron- and/or energy-transfer studies.

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