Photophysical Study of Tolylterpyridine Complexes. Intramolecular Electron Transfer in an Osmium(II) Dyad†

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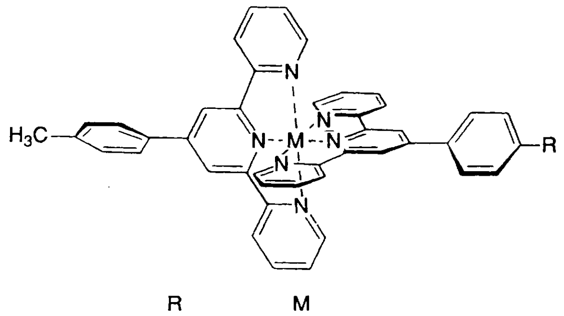
Spectroscopic and photophysical properties of 4′-*p*-tolyl-2,2′:6′,2″-terpyridine (tterpy) complexes of Fe^{II}, Ru^{II} and Os^{II} and of a dyad $[Os^{II}(tterpy)(dmbipy\text{-}pterpy)]^{4+}$ {dmbipy-pterpy = 1-methyl-1′-[4-(2,2′:6′,2″-terpyridin-4-yl)benzyl]-4,4′-bipyridinediium} are described. The luminescence of the osmium(II) complex is the most intense of the three whereas that of the other complexes is hardly or not detectable. The luminescence quantum yields of the osmium(II) and ruthenium(II) complexes (Φ_E = 0.009 and 0.000 01 respectively in ethanol) are much lower than those of the corresponding 2,2′-bipyridine (bipy) complexes (Φ_E = 0.006 and 0.078 respectively in ethanol). This may be explained by the less-rigid structure of terpy complexes rather than by deactivation *via* a low-lying d state. Excited-state spectra and lifetimes of the complexes of Ru^{II} and Os^{II} have been determined by laser flash spectroscopy. Transient absorptions are assigned to triplet metal-to-ligand charge transfer states with appreciable singlet character. The presence of absorption bands in the visible region is interpreted in terms of localization of the excited electron on one of the two equivalent ligands. The excited-state lifetimes of the complexes of Ru^{II} and Os^{II} measured in ethanol at room temperature are 4.5 and 245 ns respectively. The long-lived $^{\bullet}[Os(tterpy)_2]^{2+}$ reacts with an electron acceptor such as 1,1-dimethyl-4,4′-bipyridinium by electron transfer (k_q = 9.2 × 10^8 dm^3 mol^{-1} s^{-1} in water). Comparison of the properties of the dyad with those of $[Os(tterpy)_2]^{2+}$ shows in particular that the steady-state and transient emissions of the dyad chromophore are quenched by the viologen moiety. The quenching most probably involves an intramolecular electron transfer in a preferential direction over a long distance (11.8 Å) and leads to a charge-separated state of lifetime 720 ps. Such properties make terpy dyads excellent candidates for the design of molecular photodiodes.

The number of photophysical and photochemical studies of polypyridine complexes of transition metals has grown impressively, particularly because of the ability of these complexes to undergo electron- or energy-transfer processes. Indeed, they are used as photosensitizers in model systems for photochemical conversion of solar energy,[1] and they are potential candidates as components of molecular electronics devices.[2] Contrary to 2,2′-bipyridine complexes of ruthenium(II), expecially $[Ru(bipy)_3]^{2+}$, which have been extensively studied,[1,3] very few photophysical studies have been devoted to 2,2′:6′,2″-terpyridine (terpy) complexes of transition metals probably because $[Ru(terpy)_2]^{2+}$ analogues are considered as non-luminescent, and because of a very short excited-state lifetime at room temperature.[4] However, these complexes may be interesting for at least two reasons. First, they exhibit an axial symmetry which is preserved upon substitution at the 4′ position of the ligand. Such a structure seems well adapted for constructing linear devices for electron transfer in a preferential direction. Secondly, we have demonstrated recently[5] for a terpyridine complex bearing two identical ligands, $[Ru(cpterpy)_2]^{2+}$ [cpterpy = 4′-(*p*-chlorophenyl)-2,2′:6′,2″-terpyridine], that in the excited state the electron is localized on a single ligand. In other words, distinct oxidizing and reducing sites are present simultaneously within the same excited compound $[Ru^{III}(cpterpy)(cpterpy^{\bullet -})]^{2+}$. An asymmetry results which may be important for the design of supramolecular systems of dyad and triad types[2a,3c] for which long-range intramolecular electron transfer and charge separation are expected.



R	M
CH_3	Fe, Ru, Os
$dmbipy^{2+}$	Os

In recent communications, Sauvage and co-workers[6] have described the synthesis and some electro- and photo-chemical properties of ruthenium(II) and osmium(II) dyads. In the present work we have studied spectroscopic and photophysical properties of tolylterpyridine complexes of d^6 Group 8 metals, *i.e.* Fe^{II}, Ru^{II} and Os^{II}. In particular, we have determined by laser flash spectroscopy the lifetimes and spectra of the excited states and find that $[Os(tterpy)_2]^{2+}$ (tterpy = 4′-*p*-tolyl-2,2′:6′,2″-terpyridine) is an interesting chromophore for constructing and studying supramolecular systems of the dyad type. We have therefore examined the dyad $[Os^{II}(tterpy)(dmbipy\text{-}pterpy)]^{4+}$ {dmbipy-pterpy = 1-methyl-1′-[4-(2,2′;6′,2″-terpyridin-4′-yl)benzyl]-4,4′-bipyridinediium} containing this chromophore covalently linked to methyl viologen (1,1′-dimethyl-4,4′-bipyridinium, $dmbipy^{2+}$) and consider the possibility of a photoinduced intramolecular electron transfer.

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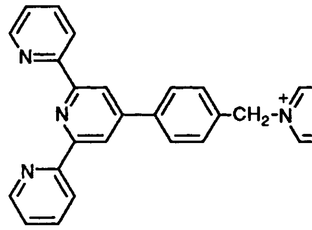
† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

Table 1 Spectroscopic and excited-state properties of tolylterpyridine complexes of Fe^{II}, Ru^{II}, Os^{II} and of the osmium(II) dyad at room temperature

Compound	Solvent	λ_{max}^{abs}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})^a	λ_{max}^{em} ^{b}/nm	φ_E ^{c}	τ^d/ns
$[Fe(tterpy)_2]^{2+}$	C_2H_5OH	567 (2.76), 320 (7.0), 285 (6.7)	—	0	—
$[Ru(tterpy)_2]^{2+}$	C_2H_5OH	488 (2.64), 307 (6.65), 283 (5.69)	650	0.000 01	4.5
$[Os(tterpy)_2]^{2+}$	C_2H_5OH	668 (0.59), 642 (0.5), 615 (sh) (0.43), 491 (2.22), 315 (6.24), 286 (4.81)	732	0.009	245
	CH_3CN	668 (0.57), 642 (0.5), 615 (sh) (0.43), 490 (2.16), 314 (6.08), 286 (4.96)	733	0.008	240
Os(tterpy)(dmbipy-pterpy)	CH_3CN	668 (0.54), 642 (0.47), 615 (sh) (0.4), 490 (2.24), 315 (5.7), 285 (6.3)	748	0.000 9	0.72

^{a} Absorption maximum. ^{b} Uncorrected emission maximum. ^{c} Emission quantum yield. ^{d} Excited-state lifetime.



dmbipy-pterpy

Experimental

Methyl viologen dichloride (Sigma) and $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ (Alfa) were used as received. The other complexes and the dyad $[Os^{II}(tterpy)(dmbipy\text{-}pterpy)][PF_6]_4$ were supplied by J. P. Sauvage and J. P. Collin (Université Louis Pasteur, Strasbourg).[6] Absolute ethanol (Merck pro analysi) was dehydrated by distillation when necessary, or used as received. Acetonitrile (Merck Uvasol for spectroscopy) was dried by distillation over 4 Å molecular sieves activated by heating to 350 °C overnight and was stored under argon. Water was freshly double distilled over alkaline potassium permanganate. Sample concentrations were in the $(1\text{–}5) \times 10^{-5}$ mol dm^{-3} range. Solutions were deaerated either by bubbling with argon or by vacuum degassing with successive freeze–pump–thaw cycles.

Electronic absorption and uncorrected emission spectra were recorded on a Beckman Acta MIV spectrophotometer and a Jobin Yvon JY3CI spectrofluorimeter, respectively. Emission quantum yields for argon-degassed solutions of the complexes and the dyad were determined relative to an aqueous solution of $[Ru(bipy)_3]^{2+}$ using $\Phi_E = 0.042$.[7] Laser flash spectroscopy was performed using 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 Hamamatsu R955 photomultiplier, and a Tektronix 7904 oscilloscope or a Gould 4072 storage oscilloscope. The excitation and monitoring sources were in a crossed-beam arrangement. 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 onto a photodiode (EG & G, UV 100BQ) whose output was displayed on a custom-built electronic integrator. Some of the experimemts were carried out with a pulsed Nd:YAG laser (Quantel: $\lambda = 353$ nm, 100 mJ, pulse width 3 ns) as an excitation source. For both set-ups the laser intensities were attenuated to avoid biphotonic effects. Picosecond experiments were carried out with a time-resolved picosecond fluorescence set-up (Nd:YAG laser from B. M. Industries, $\lambda = 353$ nm, 1.2 mJ, pulse width 30 ps) as previously described.[8] The measurements were performed at room temperature.

Results

Ground-state Absorption.—The spectral properties of tolylterpyridine complexes of Fe^{II}, Ru^{II} and Os^{II} and those of the dyad $[Os^{II}(tterpy)(dmbipy\text{-}pterpy)]^{4+}$ are summarized in Table 1. The absorption of $[Ru(tterpy)_2]^{2+}$ in ethanol presents a visible band at 488 nm shifted by 1980 and 650 cm^{-1} relative to the metal-to-ligand charge transfer (m.l.c.t.) bands of $[Ru(bipy)_3]^{2+}$ and $[Ru(terpy)_2]^{2+}$ respectively. This visible band with a molar absorption coefficient twice that of $[Ru(bipy)_3]^{2+}$ is assigned to a m.l.c.t. transition by analogy with the results for the last two compounds. The absorption spectrum of $[Fe(tterpy)_2]^{2+}$ presents also a single visible band which we assign to a ^{1}m.l.c.t. transition by analogy with $[Fe(bipy)_3]^{2+}$.[9] This broad band is dissymmetric with a maximum at 567 nm ($\varepsilon = 27\,600$ dm^3 mol^{-1} cm^{-1}). The absorption spectrum of $[Os(tterpy)_2]^{2+}$ in acetonitrile is similar to that of osmium(II) diimine complexes[10,11] and of $[Os(terpy)_2]^{2+}$,[11,12] but is more complex than that of the corresponding iron(II) and ruthenium(II) compounds in the m.l.c.t. spectral region. For the bipy series with Fe^{II}, Ru^{II} and Os^{II} it has been shown that the spin–orbit interaction is responsible for the complexity of the $[Os(bipy)_3]^{2+}$ absorption spectrum.[13] The spin–orbit coupling constant increases with the atomic number of the metal (410, 990 and 3000 cm^{-1} for Fe^{II}, Ru^{II} and Os^{II} respectively[14]). As a result, a significant mixing of singlet and triplet states occurs and singlet–triplet transitions become allowed. By analogy with this compound, we assign the visible band at lower energy of $[Os(tterpy)_2]^{2+}$ ($\lambda_{max} = 668$ nm) to a $S_0 \longrightarrow {}^3$m.l.c.t. transition and the more intense band ($\lambda_{max} = 490$ nm) to a $S_0 \longrightarrow {}^1$m.l.c.t. transition. In the UV range, the tolylterpyridine complexes of Fe^{II}, Ru^{II} and Os^{II} have similar absorption spectra. The observed bands are associated with $\pi \longrightarrow \pi^*$ transitions centred on the ligands ($\lambda_{max} = 286$ and 314 nm).

The absorption spectrum of the dyad $[Os^{II}(tterpy)(dmbipy\text{-}pterpy)]^{4+}$ is similar to that of $[Os(tterpy)_2]^{2+}$ (Table 1). At 285 nm a more intense peak due to the presence of methyl viologen in the dyad is observed. Clearly the absorption spectrum of the dyad corresponds to the sum of the contributions of $[Os(tterpy)_2]^{2+}$ and dmbipy^{2+}. We did not detect the presence of new bands which could indicate an interaction between these two components linked covalently. Consequently, the photosensitizer and electron-acceptor sites of the dyad are not electronically coupled in the ground state. In other words, the dyad is a supermolecule. This result is in good agreement with electrochemical data[6] showing that the dyad exhibits the same redox potentials as those of $[Os(tterpy)_2]^{2+}$ [+0.90, −1.20 and −1.45 V *vs.* saturated calomel electrode (SCE) for Os^{III}–Os^{II}, Os^{II}–Os^{I} and Os^{I}–Os^{0} respectively] and a reduction wave (−0.35 V *vs.* SCE) corresponding to the viologen moiety.

Emission.—The uncorrected emission maximum λ_{max} and the emission quantum yields φ_E of tolylterpyridine complexes and of the osmium dyad are presented in Table 1. No emission was observed for $[Fe(tterpy)_2]^{2+}$, at room temperature and even at 77 K, whatever the excitation wavelength. This result is not surprising because excited states of iron(II) polypyridine complexes relax principally by non-radiative processes and have very short lifetimes.[1] The $[Ru(tterpy)_2]^{2+}$ complex presents a very weak emission with a maximum at 650 nm in

Table 2 Spectroscopic and photophysical properties of $[M(bipy)_3]^{2+}$ and $[M(tterpy)_2]^{2+}$ (M = Fe, Ru or Os) complexes in ethanol[a] at room temperature[b]

	Fe				Ru				Os			
Ligand	λ^{abs}_{max}/nm	λ^{em}_{max}/nm	φ_E	τ/ns	λ^{abs}_{max}/nm	λ^{em}_{max}/nm	φ_E	τ/ns	λ^{abs}_{max}/nm	λ^{em}_{max}/nm	φ_E	τ/ns
bipy	521	—	0	0.81[c]	445	610	0.078	1330	640	715	0.006	66
tterpy	567	—	0	—	488	650	0.000 01	4.5	668	732	0.009	245

[a] Unless otherwise stated. [b] For explanation of the symbols see footnotes to Table 1. [c] In water.[15]

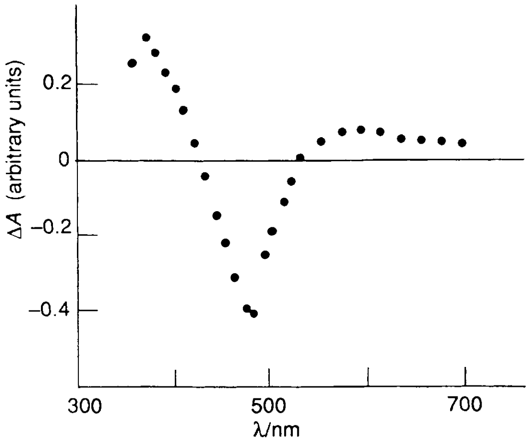


Fig. 1 Differential excited-state absorption spectrum of $[Ru(tterpy)_2]^{2+}$ in ethanol, observed immediately after the laser pulse

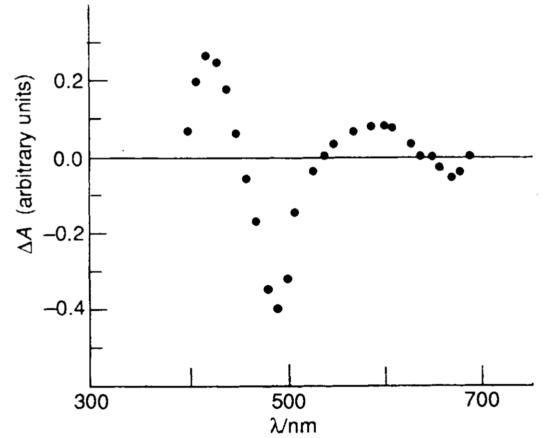


Fig. 2 Differential excited-state absorption spectrum of $[Os(tterpy)_2]^{2+}$ in acetonitrile, observed immediately after the laser pulse

ethanol. The emission quantum yield is 7800 times weaker than that of $[Ru(bipy)_3]^{2+}$ (Table 2). For $[Os(tterpy)]^{2+}$ excitation at 314, 490 or 668 nm gives the same emission spectrum at room temperature. This spectrum is characterized by a single broad band with a maximum at 732 nm in ethanol (Table 1). The observed emission is much more intense ($\varphi_E = 9 \times 10^{-3}$ in ethanol) than that of $[Ru(tterpy)_2]^{2+}$ ($\varphi_E = 10^{-5}$, $\lambda_{max} = 650$ nm in ethanol) and is shifted to the red, like the corresponding absorptions. By analogy with $[Os(terpy)_2]^{2+}$ and osmium(II) diimine complexes, the $[Os(tterpy)_2]^{2+}$ emission is assigned to a m.l.c.t. state.

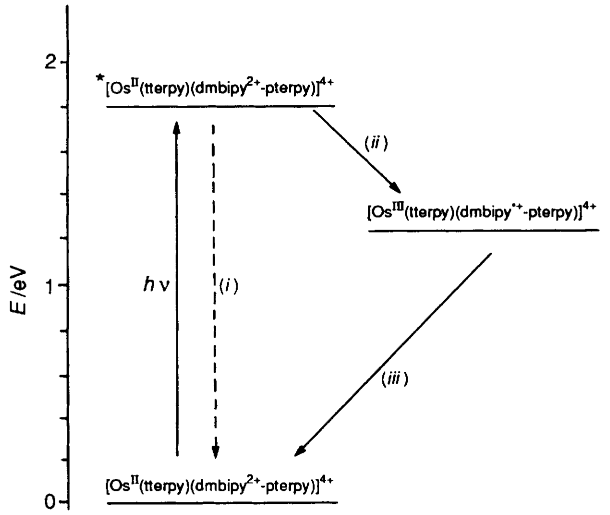
The emission spectrum of the dyad $[Os^{II}(tterpy)(dmbipy\text{-}pterpy)]^{4+}$ is similar to that of $[Os(tterpy)_2]^{2+}$ when the dyad is excited at 490 or 668 nm. It presents a maximum at 748 nm shifted to the red by about 270 cm^{-1} as compared to the corresponding complex $[Os(tterpy)_2]^{2+}$ (Table 1). However, the emission quantum yield of the dyad measured in acetonitrile is about ten times lower, in good agreement with previous results.[6b] Clearly, the emission of the osmium(II) chromophore is quenched in the presence of the $dmbipy^{2+}$ subunit.

Excited State.—As expected, neither transient absorption nor transient emission is observed between 300 and 700 nm by laser flash spectroscopy of $[Fe(tterpy)_2]^{2+}$ solutions on the nanosecond time-scale. However, in the case of $[Ru(tterpy)_2]^{2+}$ and $[Os(tterpy)_2]^{2+}$ we have observed the excited state of these complexes by emission and absorption. The absorption spectrum of the excited state of $[Ru(tterpy)_2]^{2+}$ in ethanol (Fig. 1) is similar, for $\lambda < 550$ nm, to that of $[Ru(terpy)_2]^{2+}$ observed in water by picosecond spectroscopy.[4a] It presents a maximum at 380 nm and a minimum at 490 nm corresponding to the depopulation of the ground state. However, beyond 550 nm, a new band is observed with a maximum at 590 nm and a shoulder at about 670 nm. This transient absorption has a lifetime of 4.5 ns at all wavelengths, identical to the emission lifetime observed at 650 nm. By analogy with $[Ru(terpy)_2]^{2+}$ we assign the transient absorption and the emission to the triplet m.l.c.t. state. The absorption spectrum of $^*[Os(tterpy)_2]^{2+}$ in acetonitrile presents two maxima at 420 and 590 nm as well as two bleaching bands at 490 and 670 nm (Fig. 2). Beyond 700 nm, absorption signals are perturbed by transient emission. The absorption and bleaching signals at 590 and 490 nm respectively, follow first-order kinetics with the same lifetime of 245 ns in ethanol. This result shows that the repopulation of the ground state occurs at the same rate as that of decay of the excited state. The transient emission of $^*[Os(tterpy)_2]^{2+}$ also has a lifetime of 245 ns, which indicates that the transient absorption and emission are due to the same excited state. Moreover, this excited state is quenched by oxygen with a rate constant $k_q(O_2) = 2.2 \times 10^9$ dm^3 mol^{-1} s^{-1} which is similar to the diffusion rate constant in ethanol $k_{diff} = 5.5 \times 10^9$ dm^3 mol^{-1} s^{-1} (ref. 16). This quenching indicates that the excited state has largely triplet character, but as a consequence of the much greater effect of spin–orbit coupling in osmium(II) complexes transient absorption and emission of $^*[Os(tterpy)]^{2+}$ are due to triplet m.l.c.t. states with substantial singlet character. The lifetime of this excited state is long enough to induce photoredox reactions. In particular, it reacts with methyl viologen by an electron-transfer process (1). The rate constant of reaction (1),

$$^*[Os(tterpy)_2]^{2+} + dmbipy^{2+} \longrightarrow [Os(tterpy)_2]^{3+} + dmbipy^{\bullet +} \quad (1)$$

$k_q(dmbipy^{2+}) = 9.2 \times 10^8$ dm^3 mol^{-1} s^{-1}, was determined by laser flash spectroscopy of aqueous solutions of $[Os(tterpy)_2]^{2+}$ in the presence of different concentrations of $dmbipy^{2+}$, from 1.6×10^{-3} to 1.3×10^{-2} mol dm^{-3}. By spectrofluorimetry in deaerated aqueous solutions and according to the Stern–Volmer treatment with $k_0 = 9 \times 10^6$ s^{-1}, a value of $k_{q(SV)} = 9.6 \times 10^8$ dm^3 mol^{-1} s^{-1} is obtained, in good agreement with the previous value and with the literature value 5×10^8 dm^3 mol^{-1} s^{-1} measured in acetonitrile.[6b]

In the case of the dyad $[OS^{II}(tterpy)(dmbipy\text{-}pterpy)]^{4+}$, where the methyl viologen is covalently linked to the $[Os(tterpy)_2]^{2+}$ complex, a nanosecond laser flash spectroscopy



Scheme 1 Simplifed energy-level diagram for the deactivation of the dyad excited state [(*i*) luminescence, (*ii*) electron transfer, (*iii*) charge recombination]. The excited state and the charge-separated state lie at about 1.8 and 1.25 eV respectively above the ground state

study has shown that the decay of the excited state is very rapid, faster than the time resolution of the apparatus (3 ns). The quenching of the excited state is thus very efficient. A measurement carried out by picosecond fluorescence spectroscopy shows that the decay of the luminescent state is monoexponential with a 720 ps lifetime, at room temperature.

Discussion

As can be seen from Table 1, changing the metal gives rise to important changes in the spectroscopic and photophysical properties. Concerning the absorption and emission maxima, the perturbation by the metal is similar to that observed for the corresponding series of bipyridine complexes (Table 2). The excited-state lifetime of $[Ru(tterpy)_2]^{2+}$ is as short as that of $[Ru(terpy)_2]^{2+}$ analogues[4a,5a] and much shorter than that of $[Ru(bipy)_3]^{2+}$ (Table 2). Similarly the luminescence quantum yield at room temperature is much lower (Table 2). It follows that an efficient non-radiative deactivation channel exists. A possible explanation would be deactivation *via* a low-lying d state, as has been proposed to describe the behaviour of $[Ru(dpterpy)_2]^{2+}$ (dpterpy = 6,6″-diphenyl-2,2′:6′,2″-terpyridine).[4b] It is indeed adequate for explaining the total absence of luminescence of the iron(II) complexes (Table 2), as was recently confirmed by molecular orbital calculations.[5a] However, this theoretical study has also shown that in the ruthenium(II) and even more so in the osmium(II) complexes the d states lie far above the m.l.c.t. state and can be neglected.[5a] Consequently, the deactivation channel is not due to a coupling with d states but most probably to the structure of the terpyridine complexes which is less rigid than that of $[Ru(bipy)_3]^{2+}$. The involvement of deactivation channels by internal conversion due to intramolecular movements and hence to the non-rigidity of the structures is well established for organic molecules.[17] Figs. 1 and 2 show that the absorption spectrum of the excited state of $[Os(tterpy)_2]^{2+}$ is similar to that of $*[Ru(tterpy)_2]^{2+}$, however it is different from that of $*[Os(bipy)_3]^{2+}$ for wavelengths higher than 500 nm. Thus, we observe a new band at 590 nm, as in the case of $*[Ru(tterpy)_2]^{2+}$. Such a band has been observed recently in the absorption spectra of $*[Ru(bipy)_3]^{2+}$ (refs. 18 and 19) and $[Ru(bipy)_2(dppz)]^{2+}$ (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) (ref. 19) as well as in those of $*[Ru(mopterpy)_2]^{2+}$ [mopterpy = 4′-(*p*-methoxyphenyl)-2,2′:6′,2″-terpyridine] and $*[Ru(cpterpy)_2]^{2+}$.[5] For the latter compounds it has been clearly shown that these new bands are similar to the absorption bands of the free ligand anions mopterpy$^{•-}$ and cpterpy$^{•-}$ respectively, and that consequently the excited electron is localized on only one of the two equivalent ligands. By analogy with these complexes, the existence of a visible band with the same energy in the absorption spectra of the excited states of $[Ru(tterpy)_2]^{2+}$ and $[Os(tterpy)_2]^{2+}$ is a strong indication for the electron to be localized on one of the two ligands rather than delocalized on the two ligands.

The electronic localization property which implies an asymmetry in the m.l.c.t. excited state may be of importance in long-range electron-transfer processes. For that purpose, terpyridine complexes are choice elements in the design of supramolecular systems of the dyad and/or triad type. Among the complexes studied, $[Os(tterpy)_2]^{2+}$ emerges as the best candidate because of its peculiar photophysical properties. First, contrary to $[Ru(tterpy)_2]^{2+}$ and $[Fe(tterpy)_2]^{2+}$, it is sufficiently luminescent and secondly its lifetime (245 ns, Table 1) is long enough to allow photochemical processes. This complex does in fact react efficiently with dmbipy^{2+} by an intermolecular electron-transfer reaction (1).

It is interesting to examine the spectroscopic and photophysical properties of the $[Os^{II}(tterpy)(dmbipy\text{-}pterpy)]^{4+}$ dyad. Comparison of the ground-state absorption spectrum of the dyad to that of the free $[Os(tterpy)_2]^{2+}$ complex (Table 1) as well as the electrochemical data[6] show that the chromophore and the electron-acceptor sites are not electronically coupled. Moreover, the emission quantum yield and the excited-state lifetime of the dyad are strongly diminished (Table 1). Clearly, the quenching of the excited state of the dyad photoactive site is due to the presence of the dmbipy^{2+} moiety. From an energetic point of view, quenching by an energy-transfer process is unlikely: the triplet energy of osmium(II) terpyridine complexes (≈ 1.8 eV[12]) is much lower than that of dmbipy^{2+} (3.1 eV[20]). In addition, with the low dyad concentrations used in the present experiments, the diminution of φ_E and τ cannot be explained by the occurrence of an intermolecular electron-transfer process. Consequently, the quenching of the excited state of this semi-rigid dyad most probably involves an intramolecular electron transfer from the osmium(II) chromophore to the viologen moiety leading to a charge-separated state $[Os^{III}(tterpy)(dmbipy^{•+}\text{-}pterpy)]^{4+}$ of lifetime 720 ps (Scheme 1). This lifetime corresponds to a charge recombination leading again to the dyad ground state. If this process is the only one that occurs in the dyad deactivation we can estimate the rate constant for the intramolecular electron-transfer reaction to be $k_{ET} = 1.4 \times 10^9\ s^{-1}$. This result indicates that the driving force of the reaction is high, even for an electron transfer over a long distance (11.8 Å between the metal centre and the first nitrogen of the viologen moiety). The free-energy change for the electron-transfer reaction from the m.l.c.t. states of a complex to a viologen electron acceptor may be expressed in terms of donor and acceptor redox potentials.[21] From electrochemical data for the dyad[6] and the triplet energy of the complex, we can get an estimate of $\Delta G = -0.55$ eV for the driving force, if the Coulomb interactions in the charge-separated state are neglected.

In conclusion, the tolylterpyridine complex of Os^{II} for which the excited-state lifetime is relatively long (Tables 1 and 2) appears especially attractive for photochemical reactivity and for the elaboration of linear supramolecular systems. For, in the dyad system $[Os^{II}(tterpy)(dmbipy\text{-}pterpy)]^{4+}$ where the acceptor is methyl viologen, we have observed a long-range intramolecular electron transfer along the symmetry axis, leading to a charge-separated state with a lifetime of 720 ps. Finally, we would like to point out that in the osmium(II) dyad a perturbation by light has induced an asymmetry in the excited state, long-range electron transfer in a preferential direction and full charge separation. These properties are characteristic of photodiodes. In other words, such a supramolecular system may be considered as a first step towards the realization of a molecular photodiode.

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