Photophysical and Photochemical Properties of Ruthenium and Osmium Complexes with Substituted Terpyridines

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Ruthenium(II) and osmium(II) complexes with 2,2′:6′,2″-terpyridine (terpy), 4′-(*p*-tolyl)-2,2′:6′,2″-terpyridine (tterpy) and 4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine (tpterpy) have been prepared and characterized. Their electrochemical, photophysical and photochemical properties (room temperature) have been studied. Metal-to-ligand charge-transfer excited-state quenching measurements using various redox active species clearly show that $[Ru(tpterpy)_2]^{2+}$ is a good electron-transfer agent under light irradiation.

The room-temperature emitting character of numerous ruthenium(II) complexes bearing bidentate ligands of the 2,2′-bipyridine (bipy) type is now well established and documented.[1,2] By contrast, the corresponding ruthenium(II) and osmium(II) complexes containing tridentate ligands of the 2,2′:6′,2″-terpyridine (terpy) type have been much less investigated.[3–9] Among others, a possible explanation for this is the delicate synthetic problems attached to terpy derivatives and to their complexes [in particular for osmium(II)].[10] Another reason is that the luminescence properties of both families of ruthenium(II) compounds are drastically different. For instance, it is striking that $[Ru(terpy)_2]^{2+}$, the parent compound of the so universally utilized $[Ru(bipy)_3]^{2+}$ complex, becomes luminescent only at low temperatures.

Some systems containing terpy derivatives have been made so as to render the corresponding ruthenium(II) complexes more compact[8] or with lower lying metal-to-ligand charge-transfer (m.l.c.t.) excited states.[6] However, none of the ruthenium complexes examined turned out to luminesce at room temperature, except for $[Ru(tpterpy)_2]^{2+}$ (tpterpy = 4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine) which was briefly reported as a light emitter in ethanol–methanol with a lifetime of ≈0.2 μs.[6] Intrigued by these results we have repeated the synthesis of $[Ru(tpterpy)_2]^{2+}$ and prepared the new complex $[Os(tpterpy)_2]^{2+}$. We now report some of their photophysical and photochemical properties. For comparison, the less-substituted complexes $[Ru(terpy)_2]^{2+}$, $[Ru(tterpy)_2]^{2+}$ [tterpy = 4′-(*p*-tolyl)-2,2′:6′,2″-terpyridine], $[Os(terpy)_2]^{2+}$ and $[Os(tterpy)_2]^{2+}$ have been studied under identical conditions.

Results and Discussion

Syntheses of Ligands and Complexes.—The synthesis of terpy was first developed by Case and Kasper[11] and has been improved recently by Spahni and Calzaferri.[12] The overall yield of tpterpy can be dramatically improved (38%) using this three-step procedure derived from Kröhnke's method.[13] Various complexes of Ru^{II} and Os^{II} were prepared by procedures derived from literature methods. However, special care was taken in purifying the compounds. All the complexes studied were chromatographed on silica and isolated as their Cl^- or PF_6^- salts.

Table 1 Electrochemical data for complexes of Ru and Os, $E_{\frac{1}{2}}$/V (*vs.* SCE) (±0.002 V)*

Complexes	$M^{III/II}$	$M^{II/I}$	$M^{I/0}$
$[Ru(terpy)_2]^{2+}$	1.30	−1.24	−1.49
$[Ru(tterpy)_2]^{2+}$	1.26	−1.22	−1.46
$[Ru(tpterpy)_2]^{2+}$	1.22	−1.19	−1.42
$[Os(terpy)_2]^{2+}$	0.97	−1.23	−1.52
$[Os(tterpy)_2]^{2+}$	0.93	−1.22	−1.54
$[Os(tpterpy)_2]^{2+}$	0.90	−1.15	−1.40

* In CH_3CN; glassy-carbon or platinum electrode; scan rate = 100 mV s^{-1} (0.1 mol dm^{-3} NBu_4BF_4).

Electrochemical Data.—The redox potentials of the various complexes of Ru and Os determined by cyclic voltammetry in CH_3CN are reported in Table 1. The electrochemical reactions are consistent with a single metal-based oxidation and a series of ligand-based reductions. The $M^{3+/2+}$ and the formal $M^{2+/+}$ and $M^{+/0}$ couples show characteristic patterns for reversible couples (ΔE_p close to 60 mV, $I_{pc} = I_{pa}$ and I_p proportional to $v^{\frac{1}{2}}$). Replacing one hydrogen atom *para* to a nitrogen atom by a tolyl group (tterpy) or three hydrogen atoms by three phenyl groups (tpterpy) has a clear effect on the redox potentials of the corresponding complexes of Ru and Os (negative shift of 70–80 mV for the $M^{3+/2+}$ couples and positive shift of 70–120 mV for the $M^{+/0}$ couples). Comparison of all these redox potentials indicates that the presence of aromatic substituents leads to stabilization of both high and low oxidation states. The small stabilization of the +3 state can be explained by the weak electron-donor ability of the phenyl group.[14] By contrast, where low oxidation states are involved, *p*-tolyl or phenyl substituents have a significant electron-withdrawing effect. In this case the aromatic group appears to permit a good electron delocalization in the reduced forms of the complexes.

Table 2 Spectroscopic and excited-state properties of complexes of Ru and Os[a]

Complex	Absorption λ_{max}/nm ($10^{-3} \times \varepsilon$/ dm^3 mol^{-1} cm^{-1})	Emission[b] λ_{max}/nm	φ_{em} (±15%)	τ_0/ns (±15%) (298 K)
$[Ru(terpy)_2]^{2+}$	476 (17.7), 309 (70.2), 271 (55.9)	—	—	≤0.1
$[Ru(tterpy)_2]^{2+}$	490 (29.3), 310 (75.8), 284 (68.0)	—	—	0.7
$[Ru(tpterpy)_2]^{2+}$	501 (38.4), 326 (155.4)	650	7.4×10^{-4}	3.8
$[Os(terpy)_2]^{2+}$	657 (3.65), 477 (13.75), 312 (66.25), 271 (38.85), 227 (37.90)	718	0.014	269[c]
$[Os(tterpy)_2]^{2+}$	668 (7.7), 490 (29.75), 315 (83.9), 286 (64.90), 202 (98.60)	736	0.012	236
$[Os(tpterpy)_2]^{2+}$	692 (9.2), 502 (33.05), 336 (96.75), 290 (77.75), 270 (74.8), 245 (71.15), 202 (122.60)	751	0.028	266

[a] In ethanol–methanol (4/1 : v/v). [b] Not corrected. [c] In CH_3CN at 23 ± 2 °C, τ_0 = 269 ns.[7]

Table 3 Quenching of $[*Ru(tpterpy)_2]^{2+}$ by electron acceptors or donors

Quencher	E^0/V *vs.* SCE	E_Q/dm^3 mol^{-1} s^{-1}
tmpd	+0.12	1.7×10^{10}
Benzoquinone	−0.49	1.1×10^{10}
$dmbipy^{2+}$	−0.68	1.0×10^{9}
$[Fe(CN)_6]^{3-}$	+0.22	$>10^{11}$[c]

[a] In ethanol–methanol (4:1, v/v). [b] tmpd = *N,N,N′,N′*-Tetramethyl-*p*-phenyldiamine. [c] Static quenching by ion-pair formation.

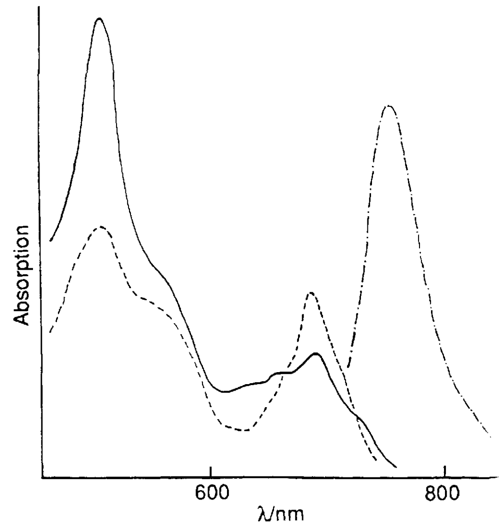

Fig. 1 Visible absorption (——), excitation (- - - -) and emission spectra (— · — · —) (not corrected) of $[Os(tpterpy)_2]^{2+}$ in ethanol–methanol (4:1, v/v)

Spectroscopic Properties.—In Table 2 are collected some absorption and emission properties of ruthenium and osmium complexes. The six complexes studied exhibit intense and broad absorption bands in the range 470–690 nm. From previous investigations of complexes of Ru and Os these bands correspond to d–π* m.l.c.t. transitions.[6] The UV region of the absorption spectra shows several strong bands with absorption coefficients in the order of 10^5 dm^3 mol^{-1} cm^{-1}. They can be assigned to ligand-centred π–π* transitions.[6] The positions of the m.l.c.t. band maximum exhibits a red shift for the complexes of Ru and Os as the number of aromatic groups in the ligand increases. The three osmium complexes luminesce at room temperature with emission band maxima shifted to lower energy as substitution in the ligands increases.

Although the complexes Ru and Os of display analogous electrochemical and spectral properties, the luminescent behaviour of the two series is dramatically different. Contrary to the ruthenium complexes all the osmium(II) compounds strongly luminesce at room temperature in fluid solution. This can be explained by the fact that the ligand-field strength is expected to increase by a factor of 1.45 and 1.75 on passing from metal ions in the first transition series to metals in the second and third transition series respectively.[15] The nature of the metal centre is thus directly related to the separation of the m.l.c.t. and the d–d states. Only $[Ru(tpterpy)_2]^{2+}$ shows an emission band easily detectable at 650 nm. The absorption, excitation and emission spectra of $[Os(tpterpy)_2]^{2+}$ are presented in Fig. 1.

In contrast, $[Ru(terpy)_2]^{2+}$ and $[Ru(tterpy)_3]^{2+}$ have no emission under the same conditions. For $[Ru(tpterpy)_2]^{2+}$ the emission quantum yield is however ≈70 times weaker than that of $[*Ru(bipy)_3]^{2+}$ and the excited-state lifetime is two orders of magnitude shorter.[1] Very probably, the energy level of the m.l.c.t. state is significantly decreased by the presence of three phenyl rings at the back of each terpy chelate in $[Ru(tpterpy)_2]^{2+}$. The resulting increase in the barrier between the m.l.c.t. and the d–d states will thus lead to enhancement of the m.l.c.t. excited-state lifetime as compared to systems bearing less phenyl groups. This hypothesis is corroborated by the absorption spectra of the various compounds studied. The m.l.c.t. band of $[Ru(tpterpy)_2]^{2+}$ is indeed shifted to the red by comparison to the other compounds. If the observation made earlier by Crosby *et al.*[6] that $[Ru(tpterpy)_2]^{2+}$ does emit light at room temperature in fluid solution is correct, then the quantitative data reported by these authors are different from ours. The short lifetime of $[*Ru(tpterpy)_2]^{2+}$ (3.8 ns) is more in agreement with the low emission quantum yield.

Excited-state Electron-transfer Properties of Ruthenium Complexes.—In order to test the potential use of $[Ru(tpterpy)_2]^{2+}$ as a redox photocatalyst, the ability of its m.l.c.t. excited state to undergo electron transfer has been studied. Several electron-donor and -acceptor reagents have been tested as quenchers and some quenching rate constants are given in Table 3. It is noteworthy that some electron-transfer reactions are extremely efficient, in analogy with $[Ru(bipy)_3]^{2+}$.[1,2]

The complex $[Ru(tpterpy)_2]^{2+}$ was also shown to be usable in the classical system consisting of a redox photoactive species, triethanolamine as electron donor and 1,1′-dimethyl-4,4′-bipyridinium ($dmbipy^{2+}$) as electron acceptor.[16] Visible light irradiation (cut-off filter at λ >420 nm) led to generation of the highly coloured species $dmbipy^{\bullet+}$. If $[Ru(tpterpy)_2]^{2+}$ is absent from the system, no formation of $dmbipy^{\bullet+}$ is observed. For comparison, the same experiment was carried out using $[Ru(tterpy)_2]^{2+}$ instead of $[Ru(tpterpy)_2]^{2+}$. In this case, formation of $dmbipy^{\bullet+}$ is not observed.

Conclusion

The ruthenium and osmium complexes of variously substituted terpyridine ligands described in the present paper constitute a homogeneous series of compounds with analogous redox and absorption spectroscopic properties. A continuous variation is observed for both families of complexes, depending on the substitution degree on the terpyridine ligands. The energy of the m.l.c.t. absorption band decreases with increasing number of aromatic nuclei present at the periphery of the molecule. Since the luminescence properties are strongly dependent on the respective energy levels of the d–π* (m.l.c.t.) and d–d states, $[\mathrm{Ru(tpterpy)_2}]^{2+}$ has a noticeably different behaviour to $[\mathrm{Ru(terpy)_2}]^{2+}$ and $[\mathrm{Ru(tterpy)_2}]^{2+}$.

Experimental

Chemicals.—The chemicals used were of reagent-grade quality and were used without purification. Acetonitrile, methanol and ethanol (Merck, spectroscopic quality) were used as received. The compounds $RuCl_3$ and $OsCl_3$ were obtained from Johnson Matthey and from Aldrich respectively. Tetrabutylammonium tetrafluoroborate (Fluka, puriss) was dried overnight under vacuum prior to use.

Preparation of Ligands and Complexes.—2,2′:6′,2″-Terpyridine and 4′-(*p*-tolyl)-2,2′:6′,2″-terpyridine were prepared according to the literature procedure.[12] 4,4′,4″-Triphenyl-2,2′:6′,2″-terpyridine was prepared following Kröhnke's synthesis.[13] 4-Phenylpyridine and benzaldehyde were condensed in the presence of sodium ethoxide to yield 3-phenyl-1-(4-phenylpyridine)prop-2-enone. This chalcone was then treated with 1-(4-phenylpyridinecarbonylmethyl)pyridinium iodide in the presence of ammonium acetate in acetic acid under reflux for 4 h to afford tpterpy in 30% yield, m.p. = 258–259 °C (lit.,[11] 257–258 °C); $\delta_H(CD_2Cl_2)$ 9.00 (2 H, dd, *J* 1.8 and 0.7), 8.82 (2 H, s), 8.77 (2 H, dd, 5.0 and 0.7), 7.90 (6 H, m), 7.63 (2 H, dd, 4.2 and 1.8 Hz) and 7.54 (9 H, m); *m*/*z* 461 ($C_{33}H_{23}N_3$ requires 461.6) (Found: C, 85.70; H, 5.10; N, 8.95. Calc. for $C_{33}H_{23}N_3$: C, 85.85; H, 5.00; N, 9.10%). The complexes $[\mathrm{Ru(terpy)_2}]\mathrm{Cl_2}$,[17] $[\mathrm{Ru(tterpy)_2}][\mathrm{PF_6}]_2$,[18] $[\mathrm{Os(terpy)_2}]\mathrm{Cl_2}$[19] and $[\mathrm{Os(tterpy)_2}][\mathrm{PF_6}]_2$[20] were prepared according to literature methods.

$[\mathrm{Ru(tpterpy)_2}][\mathrm{PF_6}]_2$. The complex $[\mathrm{Ru(dmso)_4}]\mathrm{Cl_2}$ (dmso = dimethyl sulphoxide) (52 mg, 0.1 mmol) and tpterpy (100 mg, 0.21 mmol) in ethanol (20 cm^3) were heated under reflux for 4 h under argon. After cooling, an aqueous solution of NH_4PF_6 (0.2 g in 20 cm^3) was slowly added. The precipitate formed was filtered off and the complex was further purified by chromatography on silica, using previously described conditions.[20] Yield: 68% (90 mg); $\delta_H(CD_3CN)$ 9.2 (4 H, s), 8.97 (4 H, d, *J* 1.3), 8.33 (4 H, dd, *J* 4 and 0.8 Hz), 7.81 (18 H, m) and 7.53 (16 H, m). Fast-atom bombardment (FAB) mass spectrum (3-nitrobenzyl alcohol matrix); *m*/*z* 1169.2, $[\mathrm{Ru(tpterpy)_2(PF_6)}]^+$ requires 1169.3.

$[\mathrm{Os(tpterpy)_2}][\mathrm{PF_6}]_2$. Osmium trichloride (40 mg, 0.11 mmol) and tpterpy (100 mg, 0.21 mmol) were heated in refluxing ethylene glycol (10 cm^3) for 24 h under argon. After cooling and addition of aqueous NH_4PF_6 (0.1 g in 100 cm^3) a brown precipitate was obtained. It was filtered off, washed successively with water (200 cm^3), toluene (100 cm^3) and diethyl ether (100 cm^3) and dried under vacuum. The compound was then purified by column chromatography on silica with CH_3CN–aqueous KNO_3 as eluent. Yield: 79% (120 mg); $\delta_H(CD_3CN)$ 9.25 (4 H, s), 8.93 (4 H, dd), 8.30 (4 H, dd), 7.8 (12 H, m), 7.55 (14 H, m) and 7.42 (8 H, m). FAB mass spectrum (3-nitrobenzyl alcohol matrix); *m*/*z* 1259.3, $[\mathrm{Os(tpterpy)_2(PF_6)}]^+$ requires 1258.3.

Physical Measurements.—The ^1H NMR spectra were recorded on a Bruker WP 200 SY spectrometer with tetramethylsilane as a reference, mass spectra using VG ZAB-HF and Thomson THN 208 mass spectrometers, ultraviolet–visible spectra on a Kontron (Uvicon 860) apparatus and emission spectra with a Shimazu RF 450 fluorimeter. The cyclic voltammetry equipment has been described previously.[18] The temperature was 22 °C and the potentials were measured *versus* a saturated calomel electrode (SCE).

Lifetime Measurements.—The time-resolved fluorescence measurements were carried out using a time-correlated single-photon counting method. The solutions were excited by low-energy laser pulses delivered by a cavity-dumped RbG dye laser (Spectra Physics 344–375) synchronously pumped by a CW mode-locked (80 MHz) argon-ion laser (Spectra Physics 2030). The excitation was performed with a repetition rate of 80 kHz at 590 nm (20 nJ, 20 ps) and for the ruthenium samples also at 295 nm after frequency doubling of the laser pulses with a ADA temperature-matched non-linear crystal. The emission was observed at right angles through a monochromator (Zeiss MM 12) and was detected at 650 nm with a RTC XP 2020 photomultiplier for the ruthenium derivatives, or at 760 nm with a RTC 2254B tube (response extended to the red) for the osmium compounds. To avoid fluorescence depolarization effects, a polarizer set at the magic angle was inserted between the sample and the monochromator. The full width and half maximum of the instrumental response was typically 300 ps. For $[\mathrm{Ru(tterpy)_2}]^{2+}$ showing a fast decay and for $[\mathrm{Ru(terpy)_2}]^{2+}$ whose emission could not be measured with this set-up, streak camera detection was used in conjunction with a CV Nd:YAG laser, mode-locked, Q-switched and cavity dumped at 500 Hz repetition rate. Following excitation by the frequency-doubled pulses (532 nm, 300 μJ), the fluorescence decays were registered at right angles through a Corning CS-260 filter, with the camera operating in the repetitive mode (ARP-KR10K) and equipped with an image intensifier and a photodiode detector. The resolution was limited by the laser pulse width (100 ps).

Acknowledgements

We thank the Centre National de la Richerche Scientifique for financial support and Johnson Matthey for a generous loan of ruthenium chloride.

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Received 18*th March* 1991; *Paper* 1/01298C