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Assemblies of luminescent ruthenium(II)– and osmium(II)–polypyridyl complexes based on hydrogen bonding

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Contents

Abstract

The spectroscopic properties of complexes denoted as $Ru(^tBu_2bpy)_2(bpy\text{-}X)^{2+}$ (Ru–X) and $Os(^tBu_2bpy)_2(bpy\text{-}Y)^{2+}$ (Os–Y) are reported (bpy is 2,2′-bipyridine and $^tBu_2bpy$ is 4,4′-bis-(*tert*-butyl)-2,2′-bpy). X and Y are pairs of functional groups containing bases known to be capable of hydrogen bonding; X/Y = adenine/thymine (A/T) form double hydrogen bonds, and cytosine/guanine (C/G) can form triple hydrogen bonds. The association processes for the Ru–X/Os–Y couples bearing complementary base pairs in dichloromethane have been investigated by using ^1H NMR or luminescence spectroscopy. The adenine/thymine couple is responsible for a low association constant for the Ru–A·T–Os associate, $K_A \sim 10^2\ M^{-1}$, and mixtures of Ru–A and Os–T complexes do not give significant amounts of associate in solution at the highest concentrations used for spectroscopic studies ($\sim 10^{-4}$ M). By contrast, the hydrogen bonding interaction for the couple Ru–C/Os–G results in $K_A \geqslant 5 \times 10^3\ M^{-1}$ in dichloromethane at 22 °C, as evaluated by using luminescence results before and after addition of ethanol. The photoinduced Ru→Os energy transfer within the Ru–C·G–Os associate (exothermicity ca. 0.3 eV) could be monitored with the use of time-resolved luminescence spectroscopy and was found to occur with a rate constant $k_{en} = 9.3 \times 10^7\ s^{-1}$. © 1998 Elsevier Science S.A.

Keywords: Hydrogen-bonding; Energy-transfer

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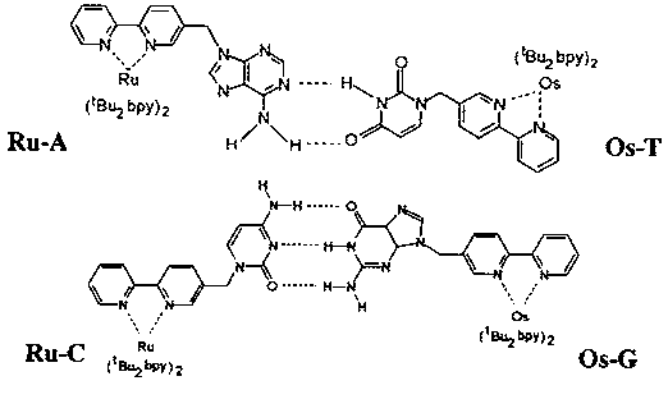
1. Introduction

The study of multicomponent complexes containing luminescent and electroactive metal–polypyridyl units is of particular interest for attempts to prepare molecules that can perform light-triggered useful functions [1,2]. In such supermolecules, the components are linked by suitable bridging ligands which make it possible to control to a certain degree both the structural properties (spatial arrangement of the chromophores, metal–metal separations) and the intercomponent electronic interaction [3,4].

A limitation in the approach based on the use of covalent bonding for assembling the component complexes is the difficulty in developing suitable bridging ligands, and alternative approaches could be based on self-assembly processes [5]. For instance, it should be possible to design complicated multicomponent architectures if the single components bear complementary parts and can then self-assemble in some way by use of non-covalent interactions [5–11]. Thus, hydrogen bonding between appropriate groups attached to mononuclear units may represent an attractive means for the development of large, multinuclear assemblies [5–21]. Within this strategy we have selected the well-known adenine/thymine (A/T) and cytosine/guanine (C/G) complementary units for driving the assembly of the Ru(II)– and Os(II)–tris-bpy complexes (bpy is 2,2′-bipyridine) [22]. For the former couple, a two-point hydrogen bonding interaction might be expected and in the latter couple a stronger three-point interaction is likely to occur. In all cases the appended groups capable of hydrogen bonding were attached to the 5 position of the bpy ligand by a single methylene group [23].

In order to allow effective hydrogen bonding interactions it is necessary to employ very low polarity solvents. Given that most Ru(II)– and Os(II)–polypyridyl complexes are dicationic species [24–27] and therefore not highly soluble in apolar solvents, we have prepared Ru(II) and Os(II) complexes whose ancillary ligands are 4,4′-bis-(*tert*-butyl)-2,2′-bpy (hereafter abbreviated as $^tBu_2$bpy) [23]. Chart I provides a schematic illustration of the interaction patterns expected for the investigated cases.



In this report we discuss the spectroscopic properties of the mononuclear complexes in dichloromethane (static dielectric constant, $\epsilon = 9.1$) and we compare the extent of the association processes for the couples Ru–A/Os–T and Ru–C/G–Os. In the former case, titration of Os–T with Ru–A was performed and the shift in the position of the signal of the thymine NH proton was used to obtain estimates for the association constant K_A [28]:

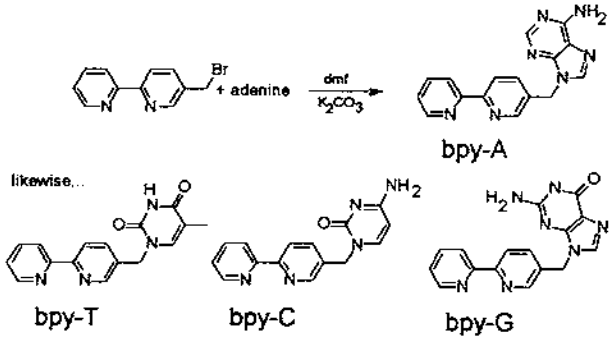
$$X + Y \rightleftharpoons X \cdot Y \tag{1a}$$

$$K_A = \frac{[X \cdot Y]}{[X][Y]} \tag{1b}$$

In the latter case (see below) we were able to obtain an estimate for the association constant by using a simple approach based on the steady state luminescence intensity of Ru–C. In addition, observation of the Ru-based time-resolved luminescence allowed an evaluation of the rate constant for the Ru→Os excitation energy transfer within the Ru–C · G–Os associate.

2. Experimental

The ligands functionalized with the nucleotide bases have been prepared following the method described in earlier reports [23,28]. Alkylation of the nucleotide bases with 5-bromomethyl-bipyridine afforded the substituted ligands bpy-X with X = A and T, Chart II. Subsequent reaction of bpy-A with $[Ru(^tBu_2bpy)_2Cl_2]$ and of bpy-T with $[Os(^tBu_2bpy)_2Cl_2]$ gave the functionalized mononuclear complexes $[Ru(^tBu_2bpy)_2(bpy\text{-}A)](PF_6)_2$ (Ru–A) and $[Os(^tBu_2bpy)_2(bpy\text{-}T)](PF_6)_2$ (Os-T). A similar synthetic path afforded the ligands bpy-C and bpy-G (see below) and the complexes $[Ru(^tBu_2bpy)_2(bpy\text{-}C)](PF_6)_2$ (Ru–C) and $[Os(^tBu_2bpy\text{-}G)](PF_6)_2$ (Os–G). Purification of the complexes was by chromatography on alumina (Brockmann activity III) with dichloromethane containing between 2 and 5% MeOH. Characterization was by elemental analysis, electron impact (EI) mass spectroscopy and ^1H NMR spectroscopy.



The association process for the Ru–A/Os–T couple was investigated via ^{1}H NMR spectroscopy by observing the signal of the thymine NH proton of Os–T, both in CD_2Cl_2 and CD_3CN [28]. The change in proton chemical shift at the employed concentration X_0 and Y_0 [for $(Os–T)_0$ and $(Ru–A)_0$, respectively, with the latter being varied] was analysed with reference to Eqs. (1a) and (1b) and following the approach described by Wilcox [29].

The ground state absorption spectra were measured with a Perkin-Elmer lambda 5 spectrophotometer using 1 cm or 0.5 cm cells, for dilute ($\sim 10^{-5}$ M) or concentrated ($\sim 10^{-4}$ M) solutions, respectively. Luminescence spectra were obtained from a Spex Flurolog II spectrofluorimeter. Uncorrected luminescence band maxima are used throughout the text. In order to determine luminescence quantum yields we employed corrected luminescence spectra on an energy scale (cm^{-1}). The corrected spectra were obtained either by using a correction curve provided by the firm or by employing a calibrated 45 W quartz–halogen tungsten filament lamp by Optronic Laboratories as a standard for the correction of the phototube response. Luminescence quantum yields Φ were computed by using dilute samples ($\sim 10^{-5}$ M) following the method described by Demas and Crosby [30] and with reference to $[Ru(bpy)_3]Cl_2$ ($\Phi = 2.8 \times 10^{-2}$ in air-equilibrated water) [31]. Further details are reported elsewhere [32]. The uncertainty in the band maxima was 2 nm and that in the luminescence quantum yields was within 20%.

In order to minimize geometric and inner filter effects while running luminescence experiments for samples exhibiting absorbance values larger than 0.1, off-center illumination of the sample was employed [33]. In this case we used a home-made cell holder which allowed a right angle arrangement with ~ 1.5 mm optical path. For this geometric set up, titration of the luminescence intensity (I) vs. absorbance values at the excitation wavelength (A) was performed according to $I_{corr} = I_{obs} \times \text{antilog}(A \times f_{corr})$ [33]; for the experimental conditions employed the geometric factor f_{corr} was 0.32. Lifetimes were measured with an IBH single-photon counting equipment whose lamp was filled by N_2 ($\lambda_{exc} = 337$ nm); the time resolution of the instrument was 0.25 ns and the uncertainty in lifetimes was within 7%.

3. Results and discussion

Table 1 lists room temperature absorption band maxima, luminescence band maxima, quantum yields and lifetimes for Ru–A, Ru–C, Os–T, and Os–G.

For comparison purposes spectroscopic data for $[Re(bpy\text{-}T)(CO)_3Cl]$ (Re–T) [28] and $[Ru(bpy\text{-}C)(CN)_4]^{2-}$ [34] are also reported. These latter complexes were designed for checking possible effects related to electrostatic interactions because Re–T (to be coupled with Ru–A) is neutral and the tetracyano complex (to be coupled with Os–G) is a dianion. Unfortunately, in the first case K_A was low, i.e. $\sim 20\ M^{-1}$ [28], and in the second case the tetracyano complex was found to be soluble in water/MeOH but not in dichloromethane. [Similarly, in a previous study dealing with the interaction of a thymine residue, attached to a Ru(II)-2,2′:6′,2″-terpyridine chromophore, with 2′,3′-isopropyliden-adenosine, a value of K_A of ca.

Table 1
Spectroscopic and photophysical data[a]

	Absorption			Luminescence		
	λ (ϵ) [nm ($M^{-1}cm^{-1}$)]			λ^{b}_{max} (nm)	Φ^{c}	τ (ns)
Ru–Ad[d]	288 (78700)	458 (13400)		626	4.8×10^{-2}	500
Os–T[d]	292 (66000)	491 (10200)	586 (3000)	750	2.9×10^{-3}	500
Ru–C	288 (93900)	459 (14900		626	3.6×10^{-2}	400
Os–G	291 (89700)	484 (11600)	590 (3000)	744	2.9×10^{-3}	42
Re–T[d]	295 (18000)	390 (2800)		614	3.0×10^{-3}	30
$Ru(bpy\text{-}C)(CN)_4^{2-}$[e]				624	3.0×10^{-3}	53

[a] Room temperature air-equilibrated CH_2Cl_2 solvent unless otherwise stated.
[b] Uncorrected band maxima.
[c] From corrected spectra.
[d] Ref. [28].
[e] Water/MeOH (1:1 v/v) solvent.

$30\ M^{-1}$ was reported, see ref. [35]]. This circumstance prevented us from checking a possible competition between association processes driven by hydrogen bonding and by electrostatic interactions; in water/MeOH solvent it was actually found that an associative process took place between $[Ru(bpy\text{-}C)(CN)_4]^{2-}$ and Os–G [34].

The association constant for the Ru–A/Os–T couple, as estimated with ^1H NMR titration experiments, was very low; the values for K_A obtained were 123 and $60\ M^{-1}$ in CD_2Cl_2 and CD_3CN solvents, respectively [28]. These figures indicate that the amount of associate that can be obtained in $\sim10^{-4}$ M solutions of the two partners is too low to be observed spectroscopically.

On the contrary, for the Ru–C/Os–G couple some useful information can be obtained from the spectroscopic behavior, as illustrated below for a representative example of a mixture containing 1.1×10^{-4} and 1.0×10^{-4} M of Ru–C and Os–G, respectively.

Fig. 1 compares absorption and luminescence spectra ($\lambda_{exc}=458$ nm, so as to produce a 1.3:1 ratio of Ru- and Os-based excited states) obtained from a CH_2Cl_2 solution before (a) and after (b) addition of drops of EtOH. From this figure one sees that the Ru-based luminescence intensity is significantly larger for case (b) than for case (a). This shows that (i) quenching of the Ru-based luminescence intensity at 626 nm takes place in case (a) and that (ii) addition of EtOH, case (b), results in an increase of the Ru-based luminescence, consistent with disruption of the hydrogen bonds by EtOH.

From the spectral changes reported in Fig. 1 and by entirely ascribing the residual Ru-based luminescence intensity of case (a) to the unassociated Ru–C complex, one obtains $\frac{[Ru\text{–}C]_0}{[Ru\text{–}C]}=1.44$. Given that $[Ru\text{–}C]_0=1.1\times10^{-4}$ M and $[Os\text{–}G]_0=1.0\times10^{-4}$ M, on the basis of Eqs. (1a) and (1b) one estimates the concentration of the involved species, [Ru–C], [Os–G] and [Ru–C·G–Os]. It is thus

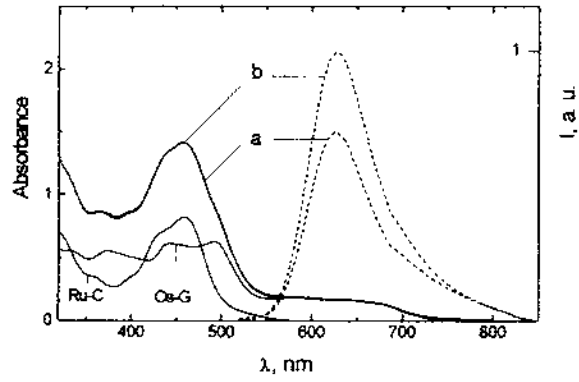


Fig. 1. Absorption (——) and luminescence (· · ·) spectra of a representative mixture of Ru-C/Os-G in CH_2Cl_2 before (a) and after (b) addition of EtOH. The absorption spectra of the mixture overlap with the sum of the component spectra. Measurements performed with 0.5 cm optical cells (see experimental section).

possible to evaluate an association constant $K_A \geq 5 \times 10^3\ M^{-1}$ at 22 °C for formation of the Ru–C·G–Os associate.

Fig. 2 shows time-resolved luminescence results obtained from the same cases illustrated in Fig. 1, as monitored at 626 nm, where the contribution of the Os-based luminescence intensity is negligible, Table 1.

The decay follows a dual exponential law in case (a), $I(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$, *with* $\tau_1 = 10.5$ ns, $\tau_2 = 290$ ns, *and* $B_1/B_2 = 0.7$; *and a single exponential law in case (b),* $I(t) = B \exp(-t/\tau)$, *with* $\tau = 270$ ns. Note that the time resolved luminescence decay of a 1.0×10^{-5} M solution of Ru–C in neat CH_2Cl_2 occurs with $\tau = 400$ ns, Table 1.

From the luminescence band maxima of Table 1, the Ru→Os energy transfer step may be estimated to be exoergonic by ca. −0.3 eV and both the steady state and

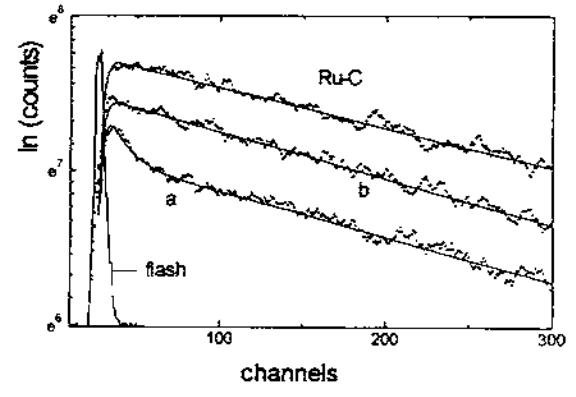


Fig. 2. Luminescence decay of a Ru-C/Os-G mixture in CH_2Cl_2 before (a) and after (b) addition of EtOH. The decay of Ru-C is shown for comparison purposes. Channel width 1.03 ns.

time-resolved luminescence results show that quenching of the Ru-based luminescence of Ru–C by Os–G takes place in neat CH_2Cl_2. In particular, the time-resolved data in neat CH_2Cl_2 [case (a)] indicate that such a quenching is due to both (i) a diffusional process, resulting in $\tau_2 = 290$ ns, and (ii) a second, much more efficient process, resulting in $\tau_1 = 10.5$ ns. The former process is ascribed to diffusional quenching and, according to $\tau_0/\tau_2 = 1 + k_q\tau_0[\text{Os–G}]$, is consistent with a second order quenching constant of $k_q = 1.4 \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$. We ascribe the latter process as Ru→Os energy transfer taking place within the Ru–C·G–Os associate because addition of EtOH [case (b)], which is expected to cause disruption of the hydrogen bonds, results in the disappearance of the shorter-lived component of the luminescence decay, Fig. 2.

The rate constant for the energy transfer occurring within the Ru–C:G–Os associate is evaluated to be $k_{en} = 9.3 \times 10^7\ \text{s}^{-1}$ by using Eq. (2) [on the basis of $1/\tau_0 = k_r + k_{nr}$ and $1/\tau = k_r + k_{nr} + k_{en}$ where r and nr stand for radiative and non-radiative processes, respectively] with $\tau_1 = 10.5$ ns [the shorter-lived component observed in case (a)], and $\tau_0 = 400$ ns, i.e. the lifetime exhibited by Ru–C, Table 1:

$$k_{en} = 1/\tau_1 - 1/\tau_0 \tag{2}$$

In conclusion, while for the Ru–A/Os–T couple the association constant is low, $K_A \sim 10^2\ \text{M}^{-1}$ [28], for the Ru–C/Os–G couple formation of the Ru–C·G–Os associate occurs with $K_A \geq 5 \times 10^3\ \text{M}^{-1}$ and leads to detectable changes of the luminescence properties. This is thought to be ascribable to the known three-point hydrogen bonding ability of the C/G couple with respect to the less favorable two-point interaction for the A/T couple [20–22].

Thus, by using luminescence spectroscopy it is possible to obtain estimates of both the association constant for the Ru–C·G–Os associate, K_A, and the rate constant, k_{en}, for the Ru→Os energy transfer process within it [36].

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