An Electro-photoswitch: Redox Switching of the Luminescence of a Bipyridine Metal Complex

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The redox couple **1/2** represents an electro-photoswitching device displaying electrochemically reversible interconversion between a non-luminescent state **1** and a luminescent state **2**.

Molecular and supramolecular devices are based on the combination of specific components arranged in as suitable manner and connected respectively by covalent bonds or by intermolecular interactions.[1] The function displayed by a given device results from the interplay of the elementary acts performed by the components. Our work has been concerned for instance with light-conversion devices[1,2] or with electron transfer by molecular wires.[1,3] We now report a molecular switching device **1/2** that effects the redox on/of switching of luminescence and combines an electroactive component with a light-emitting centre. Such a function also amounts to redox-activated optical signal generation and the corresponding device is thus of a semiochemical nature.[1b]

The $Ru(bpy)_3^{2+}$ core was chosen as the photoactive centre in view of its well-known and extensively studied luminescent properties.[4,5] The quinone/hydroquinone redox couple was selected both by virtue of its reversible electrochemical interconversion in protic media by exchange of two protons and two electrons,[6] and for the fact that the quinone unit is known to quench the luminescence of numerous photosensitive transition metal complexes.[7]

The phosphine oxide **4** was obtained by reaction with $ClP(O)Ph_2$ of the monocarbanion of 4,4′-dimethyl-2,2′-bipyridine **3** [LDA (lithiumdiisopropylamide) in THF (tetrahydrofuran) at −10 °C] (m.p. 190–191 °C, 38%).[8] The treatment of **4** with 2,5-dimethoxybenzaldehyde (NaH in THF at 50 °C) afforded ligand **5** in the *trans* configuration (m.p. 106–107 °C, 93%). The complexation of **5** with *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ followed by the addition of NH_4PF_6 provided the complex **6** as a *cis*/*trans* mixture (m.p. >300 °C, 80%), which was then catalytically reduced[9] (H_2, 10% Pd/C, EtOH/AcOH/MeCN) to the saturated analogue **7** (m.p. 146–149 °C, 98%). The complex **7** was further oxidised[10] with $Ce(NH_4)_2(NO_3)_6$-(CAN) [CAN = cerium(IV) ammonium nitrate] in aqueous MeCN to provide the complex **1** incorporating a quinone unit (m.p. 180 °C decomp., 88%). The corresponding complex **2** (m.p. 210 °C decomp.) containing a hydroquinone group was obtained in two ways: either by reduction[11] of complex **1** ($Na_2S_2O_4$ in aqueous MeCN, 71%) or by demethylation of complex **7** using boron tribromide[12] (BBr_3 in CH_2Cl_2 further quenched by water, 87%). Complex **2** was chemically reconverted into **1** by treatment with CAN. All new compounds were characterised by 200 MHz ^1H NMR and mass spectrometry, elemental analysis, and by cyclic voltammetry, electronic absorption and emission when relevant.

The position of the MLCT (metal-to-ligand-charge-transfer) band for the three complexes **1**, **2** and **7** was determined by measurements of their absorption spectra; the same value of 453 nm, characteristic of $Ru(bpy)_3^{2+}$ type complexes,[4,5] was found for these three compounds. Upon excitation in this MLCT band, the emission spectra were recorded (Fig. 1) and revealed that complexes **2** and **7** are strongly luminescent around 610 nm, whereas the emission of complex **1** is very efficiently quenched.[13] It appears that, in contrast to the 1,4-dimethoxybenzene and hydroquinone groups, the quinone moiety is an excellent quencher of the triplet state $Ru(bpy)_3^{2+*}$, especially when it is covalently connected to the photosensitive centre.‡ As a comparison, a Stern–Volmer study showed that a benzoquinone concentration of *ca.* 0.02 mol dm^{-3} was required to achieve complete luminescence quenching of $Ru(bpy)_3^{2+}$ itself.[14]

The lifetimes of the two luminescent complexes **2** and **7** were found to be 0.98 and 1.08 μs, respectively. The excited state of compound **2** has a slightly shorter lifetime, probably owing to very inefficient intramolecular electron transfer from the hydroquinone unit toward the triplet state of the chromophore (rate constant $9.4 \times 10^5 s^{-1}$).§

The study of the quinone complex **1** revealed a very short lifetime of the triplet state $Ru(bpy)_3^{2+*}$ of 100 ps.§ A very weak luminescence centred around 608 nm with a lifetime of 0.95 μs was also detected; this emission could be due to the presence of a small amount (*ca.* 8%) of the hydroquinone form.¶ In addition to the short-lived triplet state, a second component with a lifetime of 750 ps was detected; it may be assigned to a charge-separated species resulting from photoinduced electron transfer from the reductive triplet state $Ru(bpy)_3^{2+*}$ to the electron-poor quinone to form ruthenium(III) and the radical anion of the quinone. The corresponding rate constants for charge separation and charge recombination are $1.0 \times 10^{10} s^{-1}$ and $1.3 \times 10^9 s^{-1}$, respectively. The rate of charge recombination is slower than that of charge separation by a factor of 8; such a decrease in the rate of back-electron transfer is consistent with the 'inverted Marcus region'.[15] This luminescence quenching process in complex **1** is illustrated in Scheme 1.

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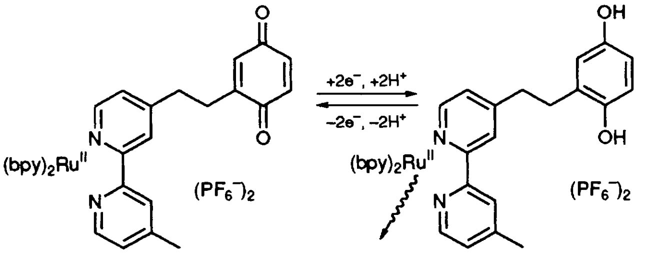
† URA 422 of the CNRS.

‡ An even stronger luminescence quenching than shown in Fig. 1 would be expected with stronger acceptor groups[14] such as substituted quinones as found in porphyrin–quinone systems, see ref. 7(*e*).

§ All the photophysical studies were made in argon-saturated acetonitrile. The lifetimes were measured by transient absorption spectroscopy following excitation at 532 nm with a 30 ps laser pulse. The shorter-lived (*i.e.* 100 and 750 ps) transient species were monitored by ps pump-probe techniques and the longer-lived (*i.e.* 1 μs) transient species were monitored with a pulsed xenon lamp. The transient species having a lifetime of 100 ps was detected by transient absorption; it would not be detected by time-resolved luminescence because the signal is far too weak. Its differential absorption spectrum agreed well with that observed for compounds **2** and **7** and, consequently, it can safely be assigned to the triplet excited state of the chromophore. The transient species displaying a lifetime of 750 ps was also detected only by transient absorption spectroscopy; it was not observed in the time-resolved luminescence decay records, for which the time resolution was *ca.* 100 ps. Lifetimes of both species were measured at 450 nm, by monitoring the return to ground state. The relative amplitude of the signal at 450 nm carries no significance because different species are being monitored. The differential absorption spectra recorded for the 100 and 750 ps species differ in the region around 390 nm. The 750 ps species is not the triplet excited state; it is most likely a mixture of the redox species as illustrated in the Scheme. The very long lived species (lifetime *ca.* 1 μs) was detected by both time-resolved emission and transient absorption spectroscopy.

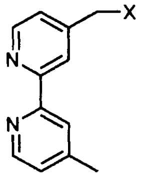
¶ The assignment of 8% for the emission from the 'impurity' in complex **1** was derived by comparing the integrated emission signals from optically matched solutions of **1** and **7** following excitation with a 30 ps laser pulse at 532 nm. The actual percentage may vary slightly with excitation wavelength and, presumably, depends on the state of oxidation of the appended group.

The oxidation [+0.96 V *vs.* SCE (saturated calomel electrode)] and reduction (−0.44 V *vs.* SCE) potentials of the electroactive quinone and hydroquinone groups of complexes **1** and **2** have been determined by cyclic voltammetry in aqueous MeCN. Exhaustive coulometric electrolysis of solutions of compounds **1** and **2** (10^{-5} mol dm^{-3}) was conducted in aqueous MeCN (1.5% H_2O, 0.1 mol dm^{-3} $TBAPF_6$) by application of potentials −0.60 and +1.10 V (*vs.* SCE), respectively, slightly superior to the anodic and cathodic peaks corresponding to the reduction and oxidation of the quinone and hydroquinone moieties. These electrolyses were followed

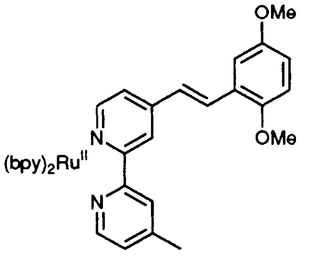


1
Non-luminescent

2
Luminescent



3; X = H
4; X = POPh$_2$



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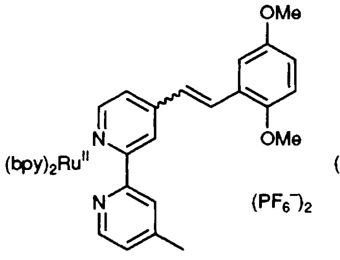
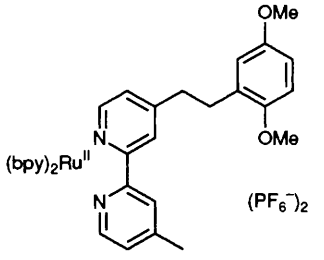


6
cis / trans



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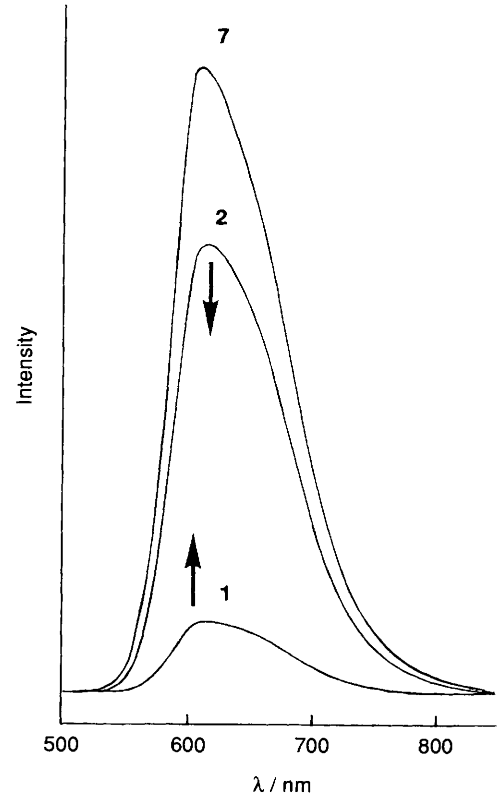
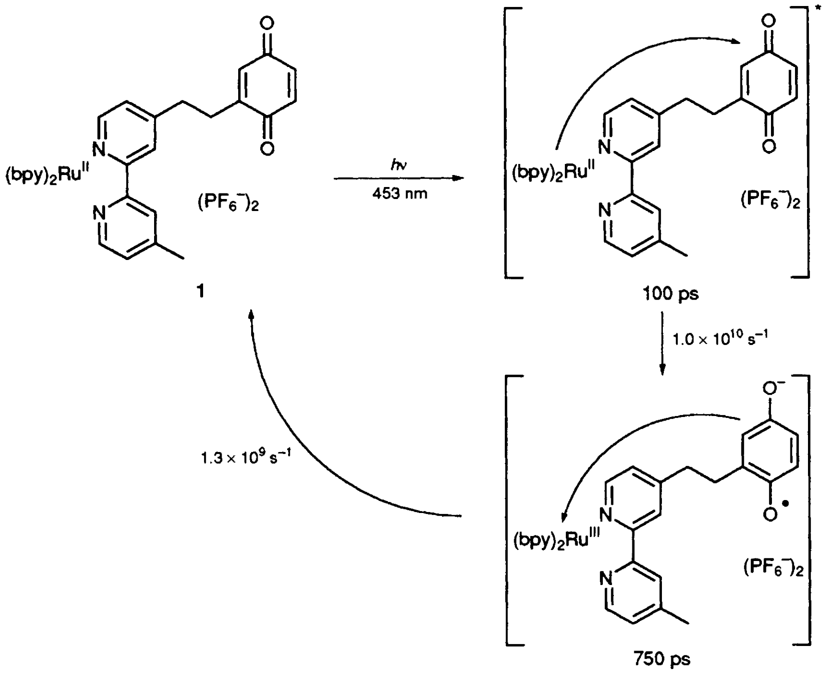


Fig. 1 Emission spectra of the complexes **1**, **2** and **7** (MeCN, λ_{ex} = 453 nm); the arrows indicate the changes observed on electrochemical interconversion of **1** and **2**



Scheme 1 Photophysical processes for the luminescence quenching of chromophore $Ru(bpy)_3^{2+}$ by the covalently connected quinone in compound **1**

by emission spectroscopy; the electrochemical cycle was initiated by the complete reduction at −0.60 V of a non-luminescent solution of the quinone **1** to form the strongly emitting hydroquinone **2**; this same electrolytic solution was then oxidised quantitatively back to the quinone at +1.10 V to afford the non-luminescent starting solution of **1**. The same cycle was effected starting with the hydroquinone solution and conducting successively oxidation and back-reduction. The electrochemical interconversion of **1** and **2**, is therefore, perfectly reversible.

The quinone/hydroquinone redox couple built into complexes **1** and **2** fulfils the requirements for the design of a bistable electro-photoswitch: both the oxidised and reduced forms **1** and **2** are isolable and stable; the reduced form **2** is luminescent, whereas the oxidised form **1** is quenched; the electrochemical interconversion of the two species is reversible.

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