Photoredox pathways for the polymerization of a pyrrole-substituted ruthenium tris(bipyridyl) complex

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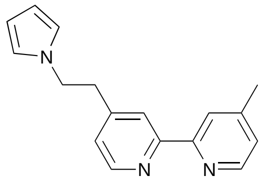
The oxidative quenching by a diazonium salt of the excited state of a pyrrole-substituted Ru(bpy)$_3$$^{2+}$ complex in acetonitrile leads to its polymerization, forming a soluble metallopolymer. The same phenomena is observed with dioxygen as the quencher. The data are consistent with the initial oxidation of the pyrrole moieties by Ru^{III} species formed upon electron-transfer quenching of [Ru(bpy)$_3$]$^{2+*}$ by O$_2$. This process appears competitive with pyrrole oxygenation by singlet oxygen formed by energy transfer, due to the subsequent fast polymerization reaction.

Photopolymérisation par transfert d'électron d'un complexe tris(pyridine) de ruthenium(II) substitué par un groupe pyrrole. L'inhibition par un sel de diazonium de l'état excité d'un complexe du type Ru(bpy)$_3$$^{2+}$ substitué par un groupe pyrrole conduit dans l'acétonitrile à sa photopolymérisation, pour former un polymère soluble. Le même phénomène est observé en présence d'oxygène moléculaire, l'ensemble des résultats étant en accord avec un mécanisme dans lequel les groupes pyrrole sont oxydées par les espèces Ru^{III}, formées à la suite de l'inhibition par transfert d'électron de [Ru(bpy)$_3$]$^{2+*}$ par O$_2$. Ce processus est compétitif avec les réactions d'oxygénation du pyrrole par l'oxygène singulet formé par transfert d'énergie, en raison de la grande vitesse de la réaction de polymérisation consécutive au transfert d'électron.

The fabrication of redox-active metallopolymers is an important subject in the construction of electrochemical and photochemical devices.[1] The applications include electrocatalysis, electroanalysis, molecular display, and energy conversion. Polymers for these purposes are readily deposited as films on electrode surfaces by oxidative electropolymerization of functionalized pyrroles.[2] In contrast, the photosensitized polymerization of pyrroles has only rarely been applied to the synthesis of polypyrroles.[3–6] The photochemical approach is of great interest for depositing polypyrroles onto any type of surface: conducting,[5,6] semiconducting,[3] or even insulating[4–6] materials, and might provide an entry into soluble transition-metal-complex-based polymers. Photopolymerization of pyrrole is readily effected in multicomponent solutions containing a photoactive species and an irreversible electron acceptor, *e.g.* [Ru(bpy)$_3$]$^{2+}$ (bpy is 2,2′-bipyridine) with [Co(NH$_3$)$_5$Cl]$^{2+}$ [4] or [Cu(dpp)$_2$]$^{+}$ (dpp is 2,9-diphenyl-1,10-phenanthroline) with *p*-nitrobenzyl bromide.[5] Photopolymerization of a pyrrole-functionalized [Ru(bpy)$_3$]$^{2+}$ complex with the reversible oxidative quencher 1,1′-dimethyl-4,4′-bipyridinium was also proved possible,[6] but the mechanism remains to be fully elucidated.

This paper reports the oxidative photopolymerization of the pyrrole-substituted ruthenium complex [Ru(bpy)$_2$(bpy-pyr)]$^{2+}$ with a diazonium salt as an irreversible oxidative quencher to form a soluble metallopolymer. Since we have recently shown that adsorbed layers of amphiphilic pyrrole-substituted polypyridyl ruthenium(II) complexes can be readily photopolymerized with dioxygen, as the only quencher in both organic and aqueous electrolytes,[7] we report here a test of this unconventional polymerization process in fluid solution with [Ru(bpy)$_2$(bpy-pyr)]$^{2+}$. This study is of great interest in the much debated question of the electron transfer quenching of the excited state of [Ru(bpy)$_3$]$^{2+}$ by molecular oxygen.[8]



bpy–pyr

Results and Discussion

The electrochemical behavior and oxidative electropolymerization of pyrrole-substituted ruthenium tris(bipyridyl) complexes in acetonitrile electrolyte have already been investigated.[9] The cyclic voltammetry curve for [Ru(bpy)$_2$(bpy-pyr)]$^{2+}$ [Fig. 1(*a*), curve a] shows three well-behaved pairs of peaks in the negative potential area, due to the successive one-electron reductions of the ligands.[10] Upon oxidation, the Ru$^{II/III}$ couple appears to be weakly reversible and is characterized by an abnormally high anodic peak. Since N-alkylpyrroles are known to be oxidized around 1.3 V,[12] this behavior has been attributed to the catalytic two-electron irreversible oxidation of the pyrrole group by Ru^{III} species, leading to a functionalized polypyrrole. In fact, thin poly[pyrrole ruthenium(II) complex] films could be grown on a platinum electrode by repeated scans over the -0.1 to 1.6 V range.[9] However, the film-forming ability of [Ru(bpy)$_2$(bpy-pyr)]$^{2+}$, which contains only one pyrrole group, is poor in acetonitrile electrolyte. Exhaustive oxidation at 1.3 V consumed 3.6 electrons per molecule of complex and led mainly

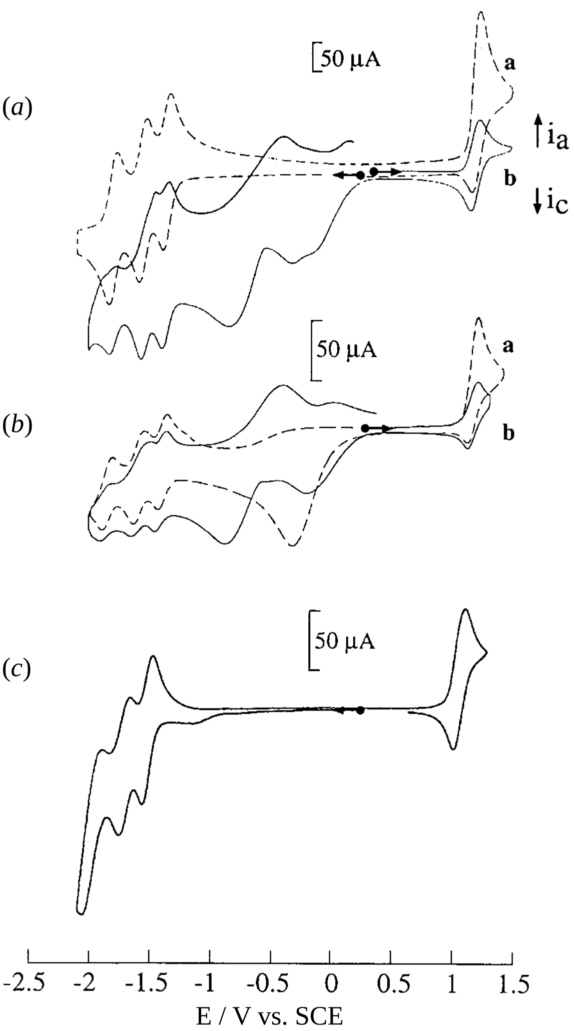


Fig. 1 Cyclic voltammograms at v = 0.1 V s^{-1} in CH_3CN + 0.1 M TBAP. (*a*) 2 mM $[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$ before (curve a) and after (curve b) exhaustive oxidation at 1.3 V on a large platinum gauze. (*b*) 1 mM $[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$ + 2.3 mM *p*-$CH_3C_6H_4N_2{}^+$ before (curve a) and after (curve b) visible irradiation under argon. (*c*) 1 mM $[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$ after visible irradiation under air

to a solution of oligomers and/or polymer in a Ru^{III} form.[9] The cyclic voltammetry curve of these oxidized species [Fig. 1(*a*), curve b] presents a fully reversible $Ru^{II/III}$ wave and ill-behaved waves for the ligand-centered reductions, along with several broad peaks due to protons released upon polymerization (two protons per pyrrole ring[2]). It must be emphasized that no wave corresponding to the regular polypyrrole electroactivity can be seen on the voltammogram. Obviously the conductivity of the polypyrrole matrix, and hence its electroactivity, have been destroyed by over-oxidation, due to the high anodic potential used for its synthesis.[13]

The voltammogram of $[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$ remains the same upon visible irradiation ($\lambda > 405$ nm) of the solution for hours under an argon atmosphere. We checked that the luminescence of the excited state $[Ru(bpy)_3]^{2+*}$ in deaerated acetonitrile was not quenched by pyrrole, even when present in large excess. This result was further corroborated by the determination of the luminescence lifetime ($\sim$950 ns) and the emission quantum yield (0.064) of $[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$, which are very close to those of $[Ru(bpy)_3]^{2+}$.[14] It should be noted that the absorption and emission spectra of the pyrrole-substituted complex in acetonitrile solution at room temperature are also identical to those exhibited by $[Ru(bpy)_3]^{2+}$.

In contrast, we found that $[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$ was readily photopolymerized in deareated acetonitrile and in the presence of a slight excess (2.3 equivalents) of *p*-methylbenzenediazonium salt. This compound is known[15] to efficiently quench $[Ru(bpy)_3]^{2+*}$ to form $[Ru(bpy)_3]^{3+}$ ($k_q = 1.8 \times 10^9$ M^{-1} s^{-1}) with a good quantum yield ($\Phi = 0.13$). The cyclic voltammetry curve recorded after visible irradiation [Fig. 1(*b*), curve b] shows that the $Ru^{II/III}$ wave has become well-reversible, and that the diazonium salt has been almost fully consumed, as demonstrated by the disappearance of its irreversible reduction wave [$E_p = -0.23$ V;[15] Fig. 1(*b*), curve a]. In addition, the appearance of several new reduction waves can be explained by the presence of protons released during the photoprocess. Comparison between curves b of Fig. 1(*a*) and (*b*) shows that the visible irradiation of the pyrrole-substituted complex in the presence of this oxidative quencher gives the same result as its electrooxidation. This means that the complex is photopolymerized in the presence of a diazonium salt to give a soluble polymer, as a consequence of pyrrole oxidation by the photogenerated Ru^{III} species. We have verified that the photopolymerization is incomplete in the presence of less than two equivalents of diazonium salt. The overall process is close to that reported for the photosensitized polymerization of regular pyrrole with $[Ru(bpy)_3]^{2+}$ as the sensitizer and $Co(NH_3)_5Cl$ as the oxidative quencher.[4] However, here the process is probably intramolecular, since the pyrrole group is covalently linked to the photosensitizer. Highly irreversible oxidative quenching of $[Ru^{II}(bpy)_2(bpy\text{-}pyr)]^{2+*}$ by the diazonium salt (denoted $ArN_2{}^+$) (eqn 1) leads to $[Ru^{III}(bpy)_2(bpy\text{-}pyr)]^{3+}$. Fast intramolecular electron transfer can then occur between Ru^{III} and the pyrrole moities (eqn 2), giving rise to the polymerization of the complex (eqn 3). Owing to the moderate quenching rate of the excited complex by the diazonium salt and the rather low overall photopolymerization quantum yield (see below), some back reactions and other deactivation pathways are expected to take place. For clarity they are not discussed here.

$$[Ru^{II}(bpy)_2(bpy\text{-}pyr)]^{2+*} + ArN_2{}^+ \rightarrow$$
$$[Ru^{III}(bpy)_2(bpy\text{-}pyr)]^{3+} + ArN_2{}^{\bullet} \quad (1)$$
$$ArN_2{}^{\bullet} \rightarrow Ar^{\bullet} + N_2{}^{\bullet}$$
$$Ar^{\bullet} + SH \rightarrow ArH \qquad (S = \text{solvent})$$
$$[Ru^{III}(bpy)_2(bpy\text{-}pyr)]^{3+} \rightarrow [Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet+})]^{3+} \quad (2)$$
$$n\,[Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet+})]^{3+} \rightarrow \text{poly}[Ru^{II}(bpy)_2(bpy\text{-}pyr)]^{2+} \quad (3)$$

The photopolymerization can be followed by ^1H NMR experiments conducted in deuterated acetonitrile solutions of complex and diazonium salt. At the end of the photolysis, the aromatic resonances at 5.64 ppm for the H atoms of the pyrrole ring have vanished, as have those at 8.32 and 7.72 ppm of the diazonium (Fig. 2). The quantum yield of the photopolymerization at 436 ± 4 nm was evaluated from the decrease of the pyrrolic ^1H NMR signals. An overall quantum yield of 0.08 was obtained when 73% of the initial complex (1 mM in CD_3CN) was polymerized in the presence of an excess of *p*-methylbenzenediazonium salt (4 mM). Thus the polymerization by Ru^{III} species is 64% efficient, taking into account that these species are formed with a quantum yield of 0.13 [15] in these experimental conditions.

In addition, the FTIR spectrum of the isolated photopolymer (see Experimental) shows a carbonyl band at 1685 cm^{-1}, typical of the formation of some pyrrolidone moeties in the polymer.[16] A similar band was found at 1703 cm^{-1} in the polymer synthesized by oxidative electropolymerization. These observations indicate that the polypyrrole matrix has been over-oxidized during the photopolymerization process, since Ru^{III} is a strong oxidizing agent.

In a similar fashion, the $Ru^{II/III}$ couple of $[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$ becomes well-reversible after visible irradiation for a few minutes under air or dioxygen [Fig. 1(*c*)]. This observ-

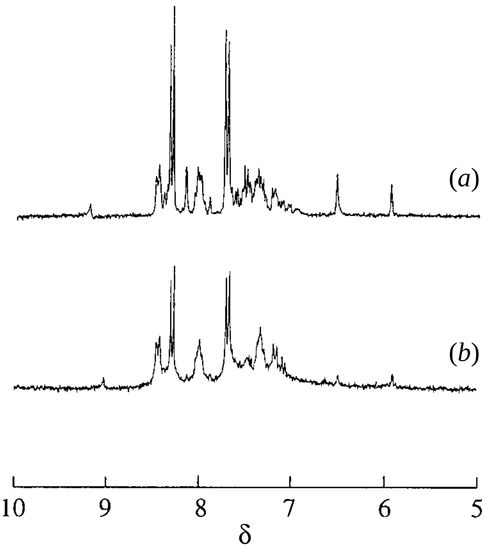


Fig. 2 250 MHz ^{1}H NMR spectra of $[Ru(bpy)_2(bpy\text{-}pyr)][PF_6]_2$ + 4 mM p-$CH_3C_6H_4N_2{}^+$ in CD_3CN before (*a*) and after (*b*) visible irradiation under argon

ation suggests that the complex is also photopolymerized in these experimental conditions. It is noteworthy that no peak due to the reduction of protons released upon pyrrole polymerization can be seen in the voltammogram. We will see in the proposed photopolymerization scheme that released protons are quantitatively trapped by $O_2{}^{\bullet-}$. This photopolymerization could also be followed by recording the ^{1}H NMR spectra of $[Ru(bpy)_2(bpy\text{-}pyr)][PF_6]_2$ in aerated CD_3CN solution before and after visible irradiation (Fig. 3). After photopolymerization, the aromatic resonances for the H atoms of the pyrrole ring have vanished while new small peaks in the 5.4–6.9 ppm range appear. The spectra now exhibit broad resonances in the aliphatic region. After the photopolymerization process the signal corresponding to the methylene group adjacent to the pyrrole ring is strongly disturbed and is shifted about 0.6 ppm downfield with respect to the monomer. The resonance for the methylene group adjacent to the bpy moieties broadens but is not shifted, and that for the methyl group in the 4′ position of the ligand is unchanged after polymerization. It should also be noted that the spectrum remains essentially the same in the aromatic region. Owing to the extreme insolubility of most polypyrroles, very little information on their ^{1}H NMR spectra can be found in the literature. However, similar features have been reported for the ^{1}H NMR spectra of poly(3-butylsulfonate pyrrole), which is slightly soluble in D_2O.[17] It should be noted that the FTIR spectrum of the isolated photopolymer is very similar to that of the electropolymer and of the photopolymer synthesized in the presence of diazonium salt. In particular, it shows a strong carbonyl band at 1709 cm^{-1}, typical of the over-oxidation of the polypyrrole matrix (see above).

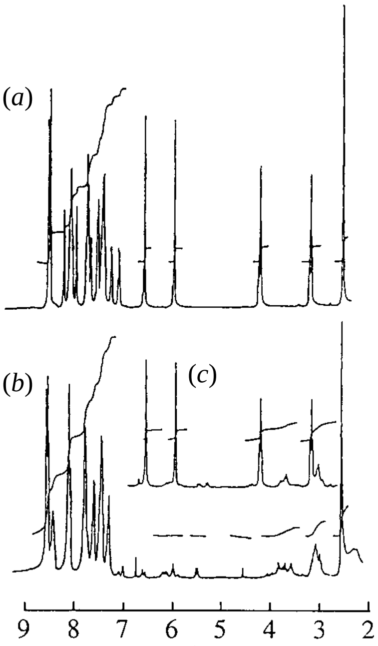


Fig. 3 250 MHz ^{1}H NMR spectra of $[Ru(bpy)_2(bpy\text{-}pyr)][PF_6]_2$ in CD_3CN before (*a*) and after (*b*) visible irradiation under air; spectrum (*c*) was recorded after about 30% of the initial complex was photopolymerized

Additional experiments have been carried out to obtain more information on this photoprocess. First, the quantum yield of the photopolymerization at 436 nm was evaluated from the evolution of the ^{1}H NMR spectra of the complex. A quantum yield of 0.36 for the overall process was obtained when 80% of the initial complex (1 mM in aerated CD_3CN) was transformed.

It is well-known that the quenching of the excited states of $[Ru(bpy)_3]^{2+}$ and related complexes by molecular oxygen can occur *via* both electron transfer and energy transfer processes.[18] Since the polymerization reaction must involve first the oxidation of the pyrrole moieties of the complex,[2,9] we outlined a possible photopolymerization mechanism in the presence of oxygen on the basis of the excited state and redox properties of $[Ru^{II}(bpy)_2(bpy\text{-}pyr)]^{2+}$ and O_2. The known energy levels for this system are shown in Fig. 4. On the basis of the energy level diagram, oxidative quenching of $[Ru^{II}(bpy)_2(bpy\text{-}pyr)]^{2+}$ by O_2 (eqn 4) can take place with formation of the $O_2{}^{\bullet-}$ superoxide radical anion and $[Ru^{III}(bpy)_2(bpy\text{-}pyr)]^{3+}$. Before the back-electron-transfer reaction (eqn 5) takes place, $[Ru^{III}(bpy)_2(bpy\text{-}pyr)]^{3+}$ can rearrange by intramolecular electron transfer to $[Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet+})]^{3+}$ (eqn 2), as seen above.[19] At this stage, other back-electron-transfer reactions can occur, leading to $[Ru^{II}(bpy)_2(bpy\text{-}pyr)]^{2+}$ and either ground state oxygen (eqn 6) or singlet oxygen (eqn 7). Some $[Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet+})]^{3+}$ molecules, however, can escape the back reactions and polymerize (eqn 3). Scavenging of $O_2{}^{\bullet-}$ by H^+ to form a hydroperoxyl radical and free Ru^{III} complex (eqn 8) can of course

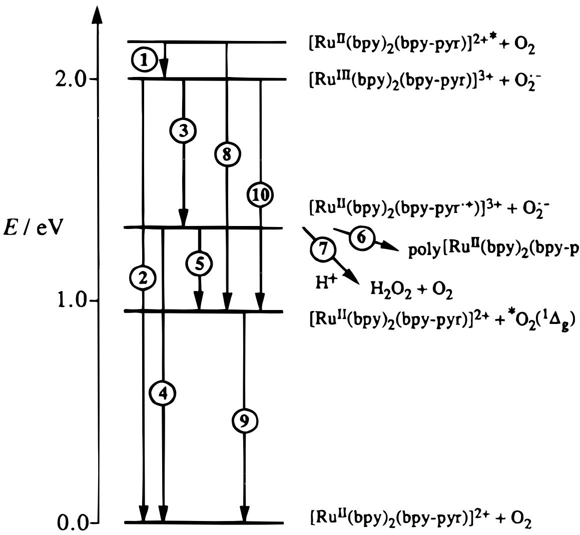


Fig. 4 Energy level diagram for $[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$ and O_2 (CH_3CN solution)

help avoid the back electron transfer.[8]

$$[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+}* + \mathrm{O_2} \rightarrow [\mathrm{Ru^{III}(bpy)_2(bpy\text{-}pyr)}]^{3+} + \mathrm{O_2}^{\bullet -} \tag{4}$$

$$[\mathrm{Ru^{III}(bpy)_2(bpy\text{-}pyr)}]^{3+} + \mathrm{O_2}^{\bullet -} \rightarrow [\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+} + \mathrm{O_2} \tag{5}$$

$$[\mathrm{Ru^{III}(bpy)_2(bpy\text{-}pyr)}]^{3+} \rightarrow [\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet +})}]^{3+} \tag{2}$$

$$[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet +})}]^{3+} + \mathrm{O_2}^{\bullet -} \rightarrow [\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+} + \mathrm{O_2} \tag{6}$$

$$[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet +})}]^{3+} + \mathrm{O_2}^{\bullet -} \rightarrow [\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+} + {}^*\mathrm{O_2}(^1\Delta g) \tag{7}$$

$$n\ [\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet +})}]^{3+} \rightarrow \mathrm{poly}[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+} \tag{3}$$

$$\mathrm{O_2}^{\bullet -} + \mathrm{H^+} \rightarrow \mathrm{HO_2}^{\bullet} \rightarrow \tfrac{1}{2}\mathrm{H_2O_2} + \tfrac{1}{2}\mathrm{O_2} \tag{8}$$

$$[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+}* + \mathrm{O_2} \rightarrow [\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+} + {}^*\mathrm{O_2}(^1\Delta_g) \tag{9}$$

$${}^*\mathrm{O_2}(^1\Delta_g) \rightarrow \mathrm{O_2}(^3\Sigma_g) + h\nu(1260\ \mathrm{nm}) \tag{10}$$

$$[\mathrm{Ru^{III}(bpy)_2(bpy\text{-}pyr)}]^{3+} + \mathrm{O_2}^{\bullet -} \rightarrow [\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+} + {}^*\mathrm{O_2}(^1\Delta_g) \tag{11}$$

$$[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+} + {}^*\mathrm{O_2}(^1\Delta_g) \rightarrow \text{photooxygenation products} \tag{12}$$

$[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+}*$ can also be quenched by $\mathrm{O_2}$ *via* energy transfer (eqn 9). It is well-known[20] that the quantum yield of $^*\mathrm{O_2}$ $(^1\Delta_g)$ formation upon excitation of the regular $[\mathrm{Ru(bpy)_3}]^{2+}$ complex in aqueous solution is only 0.5, indicating that there is some other deactivation path that competes with the energy-transfer mechanism. It has also been established[20,21] that for $[\mathrm{Ru(bpy)_3}]^{2+}$ the yield of the electron-transfer products $[\mathrm{Ru(bpy)_3}]^{3+}$ and $\mathrm{O_2}^{\bullet -}$ is negligible. In $\mathrm{CH_3CN}$, for example, it is lower than 10^{-3}.[21] It was concluded[20] that $[\mathrm{Ru(bpy)_3}]^{2+}$can be quenched by oxygen *via* both energy- and electron-transfer processes, and that the electron-transfer products cannot be easily evidenced because of the fast back electron transfer of the ion pair within the solvent cage. However, it has been very recently demonstrated[8] that $[\mathrm{Ru(bpy)_3}]^{3+}$ can be released from the solvent cage by protonation of $\mathrm{O_2}^{\bullet -}$ upon excitation in acidic solutions. Formation of $[\mathrm{Ru(bpy)_3}]^{2+}$ was obtained with a limiting quantum yield of 0.49 at infinite acid concentration, showing the efficiency of the photoredox process in these conditions. In a similar fashion, in the case of $[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+}$ the fast intramolecular electron transfer from the pyrrole moiety to the oxidized $\mathrm{Ru^{III}}$ center (eqn 2) can compete with the back electron transfer (eqn 6 and 7), allowing for the photopolymerization process.

However, a photoprocess involving singlet oxygen cannot be ruled out since formation of singlet oxygen in our system is proved by the observation of the sensitized infrared (1260 nm) luminescence of singlet oxygen (eqn 10) upon excitation of $[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+}$. We found that the quantum yield of singlet oxygen formation for $[\mathrm{Ru(bpy)_2(bpy\text{-}pyr)}]^{2+}$ is essentially the same as that found for $[\mathrm{Ru(bpy)_3}]^{3+}$. Besides energy transfer (eqn 9) there are in principle two other reaction paths for singlet oxygen formation: (i) back electron transfer from $\mathrm{O_2}^{\bullet -}$ to $[\mathrm{Ru^{III}(bpy)_2(bpy\text{-}pyr)}]^{3+}$ (eqn 11), which does not occur for $[\mathrm{Ru(bpy)_3}]^{2+}$ [22] and can probably also be excluded for $[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr)}]^{2+}$, and (ii) back electron transfer from $\mathrm{O_2}^{\bullet -}$ to the oxidized pyrrole moiety of $[\mathrm{Ru^{II}(bpy)_2(bpy\text{-}pyr^{\bullet +})}]^{3+}$ (eqn 7). It can then be anticipated that the pyrrole groups could be photooxygenized by singlet oxygen (eqn 12), rather than undergo oxidative polymerization, since the photosensitized oxygenation of pyrrole and its derivatives is well-established.[23] In order to investigate this other possible photoprocess, we have photolyzed $[\mathrm{Ru(bpy)_2(bpy\text{-}pyr)}]^{2+}$ in aerated $\mathrm{CD_3CN}$ in the presence of singlet oxygen quenchers. We first chose 2,5-dimethylfuran, which is known to react with $^*\mathrm{O_2}$ $(^1\Delta_g)$ with a high rate constant ('preferred value':[24] $2.3 \times 10^{-8}\ \mathrm{M^{-1}\ s^{-1}}$). In the presence of one molar equivalent of this quencher, the quantum yield for the reaction of pyrrole dropped from 0.36 to 0.10. This result might indicate that, in the absence of singlet oxygen quencher, pyrrole consumption is mainly due to its oxygenation rather than to its oxidative polymerization. However, we found that 2,5-dimethylfuran is readily oxidized by $\mathrm{Ru^{III}}$ species. This was easily demonstrated by a CV experiment conducted in a solution of $[\mathrm{Ru(bpy)_3}]^{3+}$ in acetonitrile electrolyte, which showed that the $\mathrm{Ru^{II/III}}$ couple became fully irreversible in the presence of one molar equivalent of 2,5-dimethylfuran. Thus, this compound is able to quench photogenerated $\mathrm{Ru^{III}}$ species as well as singlet oxygen. Additional quenching experiments have been carried out using the less oxidizable 2,3-dimethyl-2-butene (tetramethylethylene, TME), which is know to react with singlet oxygen with a good rate constant ('preferred value':[24] $3 \times 10^{-7}\ \mathrm{M^{-1}\ s^{-1}}$), to give 2,3-dimethyl-3-hydroperoxy-1-butene.[25] ^{1}H NMR measurements have shown that photolysis of the pyrrole-substituted complex (1 mM in $\mathrm{CD_3CN}$) in the presence of TME (3 mM) only resulted in a small decrease of the quantum yield for pyrrole consumption (0.25, against 0.36 without quencher). An important result is that this yield remained the same upon increasing the concentration of TME, up to 10 molar equivalents. The efficiency of the quenching of singlet oxygen by TME in these experimental conditions can be evaluated from ^{1}H NMR spectra, since the hydroperoxide formed presents characteristic resonances at 8.81 ppm (—OOH) and 4.89 ppm ($=\mathrm{CH_2}$). The quantum yield for TME photooxygenation was high (0.30) and remained the same regardless of the amount of added TME (3, 6, or 10 molar equivalents). In addition, we have verified in separate experiments that 2,3-dimethyl-3-hydroperoxy-1-butene was also formed upon visible irradiation of a pyrrole-free complex $\{[\mathrm{Ru(bpy)_2(dmbpy)}]^{2+}$, dmbpy = 4,4′-dimethyl-2,2′-bipyridine$\}$ 1 mM in aerated $\mathrm{CD_3CN}$ together with 3 mM TME; quantum yield: 0.5, even in the presence of 1 mM *N*-methylpyrrole.

All these results mean that the singlet oxygen formed upon photolysis of $[\mathrm{Ru(bpy)_2(bpy\text{-}pyr)}]^{2+}$ is quantitatively quenched by TME. This proves that pyrrole comsuption is mainly due to its oxidative polymerization with $\mathrm{Ru^{III}}$ species formed *via* electron-transfer quenching of the excited state of the complex with dioxygen (quantum yield 0.25). However, in the absence of a singlet oxygen quencher, some pyrrole photooxygenation is likely to take place with a lower quantum yield.

Conclusion

The present novel photosensitized polymerization procedure appears to be a useful approach for the elaboration of soluble photoredox polymers. It might also provide a way to synthesize soluble supramolecular polymers. On the other hand, experimental evidence strongly suggests that electron transfer from $[\mathrm{Ru(bpy)_3}]^{2+}*$ to molecular oxygen is able to compete with energy transfer in organic media, if $\mathrm{Ru^{III}}$ species are released from the solvent cage by a fast chemical reaction such as pyrrole oxidation and polymerization.

Experimental

Materials

The bpy-pyr ligand and $[\mathrm{Ru(bpy)_2(bpy\text{-}pyr)}][\mathrm{PF_6}]_2$ were synthesized according to literature procedures.[9] The *p*-

methylbenzene diazonium salt was prepared and purified by a standard procedure.[26] Acetonitrile (Rathburn HPLC grade S or Merck Uvasol) and deuterated acetonitrile (S.d.S.) were used as received. Tetrabutylammonium perchlorate (TBAP, Fluka puriss) was dried under vacuum at 80 °C for 3 d.

Measurements

The electrochemistry measurements in CH_3CN–TBAP electrolyte were done with a PAR 273 electrochemical system. The working electrode consisted of a 5 mm diameter platinum disc sealed in glass. Potentials are reported *vs.* the saturated calomel reference electrode (SCE).

Solutions of photopolymers were evaporated under vacuum. The resulting solids were dissolved in a minimum of CH_2Cl_2 and precipitated by the addition of Et_2O. The electropolymer was synthesized using $(CH_3)_4NBF_4$ as the supporting electrolyte. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2, which was then concentrated. The polymer was precipitated by the addition of Et_2O. IR spectra were recorded in KBr pellets.

Visible irradiations were done with the light of a 250 W Hg lamp filtered through UV and IR cutoff filters. For the determination of the quantum yield, the 436 ± 4 nm emission from a Xe lamp was isolated by using a bandpass filter (Oriel 5645). The intensity of light adsorbed by the sample was measured by a standard actinometry procedure. Quantum yields were determined from the integration of the ^1H NMR spectral signals of the sample before and after irradiation.

Luminescence lifetimes were measured with an Edinburgh single-photon-counting apparatus (N_2 lamp, 337 nm). Luminescence quantum yields were obtained following a literature procedure[27] using $[Ru(bpy)_3]^{2+}$ as a standard. All the photophysical experiments were performed on 10^{-4} M CH_3CN solutions degassed by repeated freeze–pump–thaw cycles. Near-infrared oxygen emission was measured with a home-built instrument consisting of an Ar ion laser as the excitation source ($\lambda_{ex} = 488$ nm), a monochromator (Edinburgh) with a grating of 1200 lines/nm, 1-mm blaze, and a liquid-nitrogen-cooled germanium detector and preamplifier (Northcoast, model EO-817L). The sample (air-equilibrated CH_3CN solution) was held in a 10 mm × 10 mm cuvette, and a beam chopper (Stanford Research, model SR540) was placed between the excitation source and the sample; luminescence was monitored at right angles to the excitation. A muon filter (Northcoast, model 829B) was used as an electronic signal filter, after the signal was sent to a lock-in amplifier (Stanford Research, model SR510).

References

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