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An Unusual Photosensitizer: Dyad of Eosin–Tris(2,2′-bipyridine)Ru(II)

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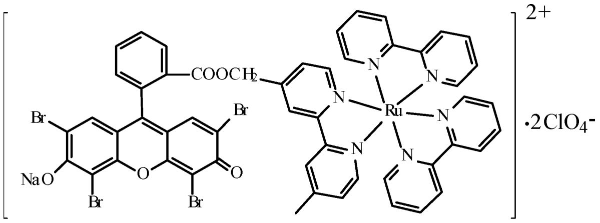
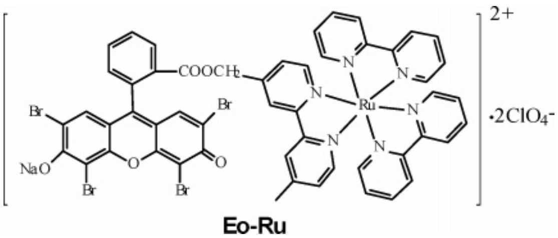
ABSTRACT



Eo-Ru

A dyad of eosin and tris(2,2′-bipyridine)Ru(II) was prepared, and its photophysical properties were investigated. The photosensitization of eosin is greatly enhanced by introduction of tris(2,2′-bipyridine)Ru(II), which is verified via photooxygenation of anthracene derivatives. The electron-transfer mechanism of photosensitization is also discussed.

Polypyridine ruthenium complexes[1] and xanthenes[2] have been widely used in many areas such as photochemistry, electrochemistry, photoelectrochemistry, photocatalysis, artificial photosynthesis and related solar energy conversion, laser dyes, fluorescence depolarization diagnostic devices, photomedicine, molecular probes, and quantum counters. The interest in such compounds is very active. Polypyridine ruthenium, especially tris(2,2′-bipyridine)Ru(II), has an absorption maximum in the range of 400−500 nm, and eosin, a xanthene, strongly absorbs the light in the range of 500 nm to 600 nm with a very small extinction coefficient below 500 nm. Combination of these two chromophores would be expected to produce some new properties compared to the individual compounds since the dyad of eosin and Ru possesses several advantages. First, the complementary absorption spectra of eosin and Ru provide an extended absorption range for the dyad, which would favor the collection of light. Second, an intramolecular electron transfer from eosin to Ru would take place upon the excitation of eosin moiety or Ru moiety according to the Rehm−Weller equation[3] (free energy changes, $\Delta G = -0.33$ and -0.12 eV, respectively, calculated from the data listed in Table 1). Furthermore, since Ru(I) is relatively more stable than many organic species,[1a] a relatively long-lived photoinduced charge separation state ($Eo^{+\bullet}-Ru^{-}$) would be expected. This is useful for the dyad to take part in the secondary reaction after an initial photoinduced electron transfer. This communication reports the unusual photosensitization of a novel dyad: eosin−tris(2,2′-bipyridine)Ru(II) (Eo−Ru).



Eo-Ru

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Table 1. Photophysical and Electrochemical Data of Model Compounds and Dyad[a]

item	EoEt	$Ru(bpy)_3^{2+}$	Eo in Eo-Ru
λ_{abs} (nm)	538	454, 462[b]	542
λ_{em} (nm)	562	620	561
Φ_F	0.41	0.04[d]	0.003
Φ_{IST}	0.39	~1.0[d]	0.54
Φ_{IC}	0.20	0.00[d]	0.20
Φ_{ET}			0.257
t (ns)	3.68	760	0.362 (47%), 3.14 (53%)
E_S/E_T (eV)	2.31/1.90[c]	2.75/2.12[d]	
E_{ox}/E_{red}(V)	0.80/−1.04[c]	1.26/−1.26[d]	

[a] λ_{abs} = absorption wavelength, λ_{em} = fluorescence wavelength; Φ_F, Φ_{IST}, Φ_{IC} = fluorescence quantum yield, intersystem crossing quantum yield, and internal conversion quantum yield, respectively; Φ_{ET} = electron transfer quantum yield statically and dynamically; t = lifetime of fluorescence; E_S/E_T = singlet/triplet energy; E_{ox}/E_{red} = oxide/reduction potential. [b] In Eo-Ru. [c] Cited from ref 2e. [d] Cited from ref 1a.

The preparation of Eo−Ru was accomplished by esterifying the carboxyl group of eosin with 4-bromomethyl-4′-methyl-2,2′-bipyridine, followed by a coordination substitution reaction with $Ru(bpy)_2Cl_2{\cdot}H_2O$.

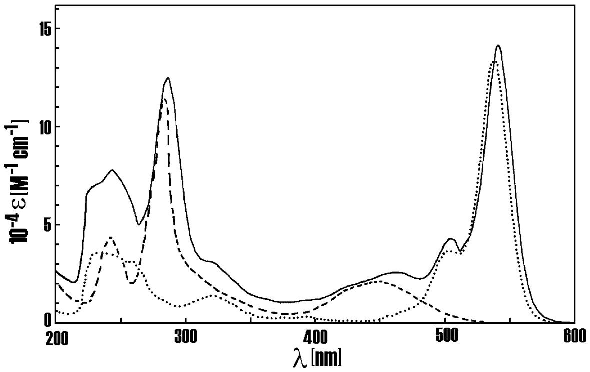

Figure 1. Absorption spectra of dyad of Eo−Ru and model EoEt in acetonitrile: (—) Eo−Ru; (···) EoEt; (- - -) $Ru(bpy)_3^{2+}$.

The absorption spectrum of Eo−Ru (Figure 1) is characterized by a simple combination of $Ru(bpy)_3^{2+}$ (Ru) and eosin ethyl-ester (EoEt). The metal to ligand charge transfer (MLCT) band of Ru and absorption band of Eo in the visible region in Eo−Ru have a red shift of 8 and 4 nm, respectively, in acetonitrile compared to their individual components. This suggests the existence of a ground state static electric interaction between positively charged Ru and negatively charged eosin ethyl ester, which is similar to the fluorescence quenching of other xanthenes by viologen.[2f] The quantum yield of generating singlet oxygen (Φ^1O_2) of eosin in Eo-Ru is 0.54, directly measured through the time-resolved emission of $^1\Delta_gO_2$ in the near infra region (1270 nm).[4]

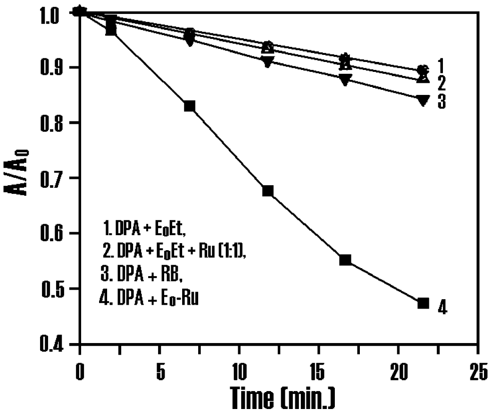

Figure 2. Absorbance of DPA at 392 nm versus irradiation time under light >510 nm in the presence of different sensitizers. [DPA] ≈ 1×10^{-4} M; [sensitizer] ≈ 2×10^{-6} M. A_0 and A: absorbance before and after irradiation, respectively.

Generally, the quantum yield of singlet oxygen is approximately equal to the quantum yield of intersystem crossing (Φ_{ISC}). Compared to the intersystem crossing quantum yield of EoEt ($\Phi_{ISC} = 0.39$), the heavy atom Ru in Eo−Ru enhances the intersystem crossing of eosin from 0.39 to 0.54. Although both EoEt ($\Phi_F = 0.41$) and $Ru(bpy)_3^{2+}$ ($\Phi_F = 0.04$) have strong photoluminescence, very weak emission ($\Phi_F = 0.003$) was observed in Eo−Ru when the Eo moiety was selectively excited at 540 nm and no emission was measured for the Ru moiety, excited at 450 nm. In the dyad, the fluorescence lifetime of the eosin moiety exhibits a double exponential decay, 3.14 ns (54%) and 0.362 ns (46%), respectively. The long-lived component comes from the ground-state static electric interaction, whereas the shorter one can be attributed to the intramolecular photoinduced electron transfer from the excited eosin moiety to the Ru moiety as well as the intramolecular "heavy atom effect". The total quantum yield of dynamic and static electron transfer (Φ_{ET}) from the excited Eo moiety to Ru moiety is $\Phi_{ET} = 1 - \Phi_F - \Phi_{ISC} - \Phi_{IC} = 1 - 0.003 - 0.54 - 0.20 = 0.257$; here $\Phi_{IC} = 0.20$ was cited from the literature[5] and assumed no change in Eo-Ru. The lack of emission of Ru moiety can be caused by triplet−triplet energy transfer from the excited Ru moiety to eosin moiety and electron transfer from eosin moiety to excited Ru moiety. Both processes are thermodynamically allowed with a free energy change of −0.22 and −0.12 eV, respectively. The photophysical and electrochemical data of EoEt, $Ru(bpy)_3^{2+}$, and Eo−Ru are partly listed in Table 1.

The photosensitization of eosin was found greatly enhanced by introduction of the Ru complex, which was verified by the photosensitization oxygenation of 9,10-diphenylanthracene (DPA). Figure 2 shows the decrease of characteristic absorption of DPA at 392 nm in oxygen-saturated acetonitrile upon irradiation (>510 nm) in the

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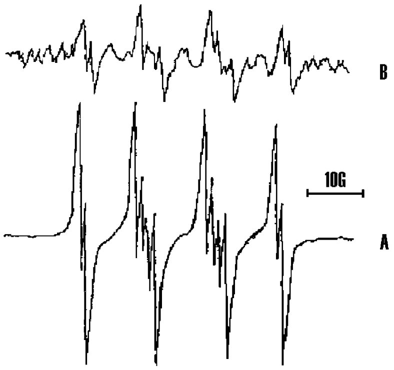
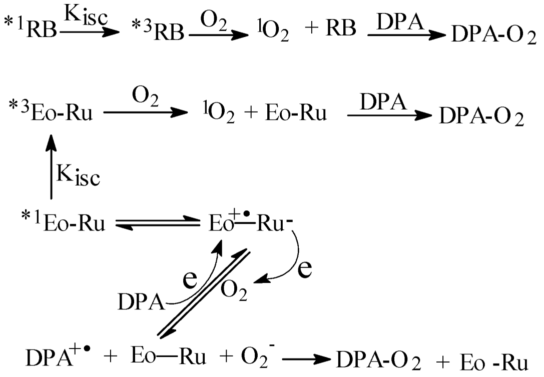


Figure 3. ESR spectra of the DMPO$-O_2^{-\bullet}$ radical adduct generated from an oxygen-saturated DMSO solution with DMPO (20 mM) upon irradiation of 532 nm laser: (A) Eo$-$Ru 0.2 mM), (B) addition of 5 mM of *p*-benzoquinone to A.

presence of different sensitizers. Rose Bengal is a typical sensitizer of singlet oxygen with a quantum yield of $\Phi^1O_2 = 0.76$.[2a] The reaction induced by RB should be more efficient than that by Eo$-$Ru ($\Phi^1O_2 = 0.54$) if both reactions are singlet oxygen mechanism. However the reaction sensitized by Eo$-$Ru is much faster than those sensitized by Rose Bengal (RB), EoEt/Ru mixture (1:1, molar ratio), or EoEt. The percentages of converted DPA are 41%, 10%, 8%, and 7% for Eo$-$Ru, RB, EoEt/Ru mixture, and EoEt, respectively, upon irradiation for 16 min. This result indicates that singlet oxygen is not the predominant mechanism for the photooxygenation induced by Eo$-$Ru. Further, the photooxygenation of different anthracene derivatives in different solvents induced by Eo$-$Ru was investigated. Apparently, polar solvent like acetonitrile strongly increases the reaction, whereas nonpolar solvent dramatically slows down the reaction. After irradiation for 15 min, the percentage of converted DPA and 9,10-dimethylanthracene (DMA) are 39%, 96% in acetonitrile and 4.6%, 42.4% in benzene, respectively. Also, an electron-donating group in the 9,10 positions accelerates the reaction, whereas an electron-accepting group in the 9,10 positions decreases the reaction rate. The reaction is very fast for DMA and 9-methlyl-anthracene (MA), with no observable reaction for 9-anthraldehyde (CHO-AN) and 9-anthracenecarboxylic acid (COOH-AN), and there is a slow reaction for anthracene (AN), 9,10-dichloroanthracene (DCA), and 9,10-dibromoanthrcne (DBA). The reaction rate decreases DMA > MA > DPA > AN > DCA ≈ DBA > CHO-AN ≈ COOH-AN. NMR and MS data prove that the isolated product from the reaction of DPA is a peroxide of 9,10-dipenylanthracene. All of these results suggest that an electron transfer mechanism is probably involved. To verify the existence of an electron-transfer mechanism, an experiment capturing superoxide anion was performed.

A typical 3 × 2 × 2 ESR signal (Figure 3) was obtained upon irradiation of an oxygen-saturated DMSO solution of Eo$-$Ru and DMPO (5,5′-dimethyl-1-pyrrodine *N*-oxide) at 532 nm, which is identical to the DMPO$-O_2$ (H) radical adduct.[6] The same signal was not observed in the absence of either oxygen or Eo$-$Ru or in the presence of EoEt or RB under the same conditions. When a quencher of O_2^- (*p*-benzoquinone)[7] was introduced to the system, the DMPO$-O_2$(H) signal disappeared. These results indicate generation of O_2^- following irradiation of the solution of Eo$-$Ru and also suggest that an electron transfer exists in the photooxygenation of anthracene derivatives induced by Eo$-$Ru. On the basis of the results above, an electron-transfer photooxygenation reaction mechanism is proposed (Scheme 1). That the initial photoinduced intramolcular electron-transfer process is responsible for the improved photosensitizaton of eosin in the dyad of Eo$-$Ru can also be concluded.

Scheme 1. Possible Electron Transfer and Singlet Oxygen Mechanism of Oxygenation of DPA Sensitized by Eo$-$Ru



The strong photosensitization ability and broad absorption range in the visible region of Eo$-$Ru suggest that this composite sensitizer has potential application in many areas such as photoinduced reaction, photocatalysis, and photosynthesis and related solar conversion. Since superoxide anion probably involves a phototherapy process,[8] this compound may find application in photodynamic therapy.

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Supporting Information Available: Experimental procedures, synthesis and spectral data for compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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