Electrogenerated Chemiluminescence in SiO_2 Sol−Gel Polymer Composites

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Electrogenerated chemiluminescence (ecl) is a well-established means for forming emitting excited states.[1] Polypyridyl complexes of Ru(II),[2] Os(II),[3] and Re(I)[4] have been of particular interest as luminophores because of their metal-to-ligand charge transfer (MLCT) excited states, which are well understood from the results of numerous photophysical and photochemical investigations.[5] The most thoroughly investigated complex for ecl studies has been $[Ru(bpy)_3]^{2+}$, which has been studied both in fluid solution[2a,c,d,6] and immobilized on electrode surfaces.[2e,7] Electrogenerated chemiluminescence from reactions between $[Ru(bpy)_3]^{3+}$ and amines[8] or oxalate anion[2c,9] has led to development of ecl-based detection devices and chemical sensors for a variety of biologically important molecules.[1e,7c,8a,9,10] The MLCT excited state, $[Ru(bpy)_3]^{2+}*$, can be also generated by electron transfer between electrogenerated $[Ru(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{+}$

$$[\mathrm{Ru(bpy)_3}]^{3+} + [\mathrm{Ru(bpy)_3}]^{+} \rightarrow [\mathrm{Ru(bpy)_3}]^{2+}* + [\mathrm{Ru(bpy)_3}]^{2+} \qquad \Delta G° = -0.5\ \mathrm{eV} \quad (1)$$

This reaction has been proposed as a basis for inorganic light-emitting diodes (LED's) and ecl displays.[2d,11] Electrogenerated chemiluminescence from thin-film-modified electrodes based on Ru-bpy derivatives has also been reported.[12] Given the low applied potentials required and high chemical stabilities, these inorganic LED's could potentially complement the already successful organic (OLED) technology based on conjugated polymers such as poly(*p*-phenylenevinylene).[13]

SiO_2-based gels are an attractive matrix for a variety of applications. In addition to having chemical inertness and excellent optical transparency, they are physically rigid and highly abrasion resistant and have proven to be useful matrixes for the incorporation of heat sensitive, optically and electrochemically active chromophoric materials.[14] There have been many reports of photophysical studies of SiO_2 sol−gel/composite materials with a variety of organic and inorganic chromophores. Dvorak and De Armond[15] were the first to report that $[Ru(bpy)_3]^{2+}$ incorporated into SiO_2 sol−gels on the surfaces of Pt and ITO (In_2O_3:Sn) has well-defined electron transfer and excited-state properties. Their studies were complicated by diffusional loss of the complex into external solutions. We have discovered that stable SiO_2 sol−gel composites can be formed by utilizing preformed Ru-bpy derivatized polystyrene polymers which retain the basic electron and excited-state properties[16] of the complex and report here, in a preliminary account, the photophysical properties of this novel composite material and its application in electrogenerated chemiluminescence.

The composites were prepared by doping the derivatized polymer $[PS-CH_2CH_2NHCO-(Ru^{II})_{18}]Cl_{36}$ into the

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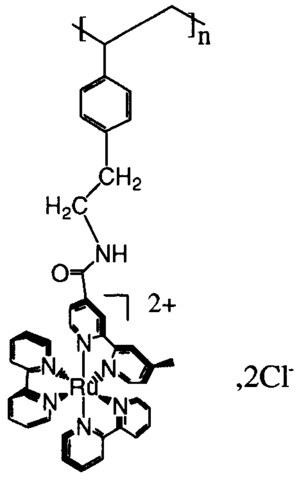
Table 1. Photophysical properties of $[PS-CH_2CH_2NHCO-(Ru^{II})_{18}]^{36+}$ in H_2O, EtOH, CH_3CN, and Thin Composite Sol–Gel Films on ITO

sample	E_{abs} (nm)	$E_{em}{}^{a}$ (nm)	$\varphi_{em} \times 10^2$	$\tau_1(I_1)^b$ (ns)	$\tau_2(I_2)^b$ (ns)	$\tau_3(I_3)^b$ (ns)	$\langle\tau\rangle^c$ (ns)
$[PS-Ru_{18}]Cl_{36}(H_2O)^d$	458	665	4.2	30(0.39)	182(0.27)	685(0.34)	294
$[PS-Ru_{18}]Cl_{36}(EtOH)^d$	458	650	7.1	32(0.37)	200(0.26)	1140(0.37)	486
$[PS-Ru_{18}](PF_6)_{36}(CH_3CN)^d$	458	645	7.4	43(0.35)	279(0.23)	1354(0.42)	648
$ITO/SG-[PS-Ru_{18}]Cl_{36}$(air)	458	648		38(0.42)	270(0.30)	1101(0.28)	405
$ITO/SG-[PS-Ru_{18}]Cl_{36}$(Ar)	458	648		34(0.42)	260(0.32)	1137(0.26)	393
$ITO/SG-[PS-Ru_{18}]Cl_{36}/H_2O^e$	458	660		31(0.38)	242(0.33)	890(0.29)	350
$ITO/SG-[PS-Ru_{18}]Cl_{36}/EtOH^e$	458	650		27(0.43)	240(0.32)	1062(0.25)	354
$ITO/SG-[PS-Ru_{18}]Cl_{36}/CH_3CN^e$	458	648		28(0.42)	242(0.31)	1155(0.27)	399

[a] Emission energies obtained from corrected spectra, excitation wavelength $\lambda_{exc} = 458$ nm. [b] $\lambda_{exc} = 456$ nm, excitation power 50 $\mu J/mm^2$ per pulse; I_1, I_2, and I_3 are the preexponential factors derived from fits to eq 1. [c] Average lifetime calculated as $\langle\tau\rangle = (I_1\tau_1 + I_2\tau_2 + I_3\tau_3)/(I_1 + I_2 + I_3)$. [d] Dearated solution, $[Ru^{II}] < 1 \times 10^{-5}$ M. [e] $[Ru^{II}]$ in the sol–gel = 0.2 M (Si/Ru = 50); no difference in photophysical properties was observed upon exposure of the films to aerated or deaerated solvents.

forming SiO_2 gel as described previously.[15,17] The molecular structure of the polymer repeat unit is illustrated below. The polymer, which was available from a previous study as the PF_6^- salt,[16] was prepared by amide derivatization of a silyl-protected precursor amine prepared by living anionic polymerization. The PF_6^- salt was converted into the Cl^- salt by metathesis in acetone by using $[N(n-C_4H_9)_4]Cl$.



$[PS-CH_2CH_2NHCO-(Ru^{II})_{18}]Cl_{36}$ (n = 18)

In preparing the composites, 20.1 mg of $[PS-CH_2CH_2-NHCO-(Ru^{II})_{18}]Cl_{36}$ was dissolved in 1.7 mL of absolute EtOH with stirring. To the continuously stirred solution was added 5 drops (~0.08 g) of the surface active agent Triton X-100 (Aldrich), 0.1 mL of 0.01 M HCl, and 0.2 mL of TMOS (tetramethylorthosilicate, $Si(OCH_3)_4$). This composition corresponds to the molar ratio Si/Ru = 50. The solution was stirred for an additional 30 min. The resulting sols were aged, typically for 24 h, and deposited as a film on an ITO electrode by spreading with a glass slide or spin-coating at 5000–8000 rpm. It was allowed to dry for 2 h at room temperature and for an additional 24 h at 100 °C in the air. The thickness of the films was determined by step profilometry and varied between 700–1500 nm for films prepared by spreading and 100–400 nm for films prepared by spin-coating. The concentration of Ru^{II} in the films was estimated by UV–visible measurements ($\epsilon_{456} = 15\,300$ M^{-1} cm^{-1} for $[PS-CH_2CH_2NHCO-(Ru^{II})_{18}](PF_6)_{36}$ in CH_3CN)[18] to be $[Ru^{II}] = 0.20$ mol dm^{-3}. The resulting sol–gel/polymer composite films are stable toward leaching into an external solution and display novel redox properties.[17]

The results of absorption, emission, and excited-state lifetime measurements for $[PS-CH_2CH_2NHCO-(Ru^{II})_{18}]^{36+}$ in water, EtOH, CH_3CN, and thin composite films are summarized in Table 1. MLCT absorption spectra in the films are very similar to those in solvents with $\lambda_{max(abs)} = 458$ nm, but emission in dry films is blue-shifted compared to those in H_2O and EtOH. The blue shift is expected given the rigid nature of the medium.[19] When the films are exposed to water or EtOH, the emission energies shift gradually (for approximately 1 h) from the values obtained in dry films to values close to those for the pure solvent (the emission energies observed 1 h after exposure to solvent are summarized in Table 1). The dynamics of this change presumably parallel the rate of solvent exchange into film pores partially filled with the Triton X-100 surfactant.

Emission lifetimes both in solution and in the composite films (dry or exposed to solvent) follow complex decay kinetics but could be fit to eq 1. The results are summarized in Table 1.

$$I = \sum_{i=1}^{3} I_i \exp(-t/\tau_i) \qquad (1)$$

In this equation I is the total emission intensity at time t and I_i and τ_i are the intensity and lifetime of component i. The complexity of the decay kinetics is a consequence of having a distribution of emitters in the heterogeneous polymer composite environment and of excited state–ground state and excited state-excited state interactions between the closely packed Ru sites in the polymer.[20] On the basis of the lifetime measurements, there is no sign of oxygen quenching in the dry films, indicating that gas diffusion into the dry films may be restricted. Exposure to water and EtOH influences excited-state lifetimes, as expected on the basis of the shifts in E_{em}, although the effect is partially masked by the complexity of the decay kinetics.

As shown in Figure 1 the Ru^{II} sites in the films can be reversibly oxidized (at polymer concentrations $[PS-CH_2CH_2NHCO-(Ru^{II})_{18}]^{36+} \gtrsim 0.01$ M) by stepping the

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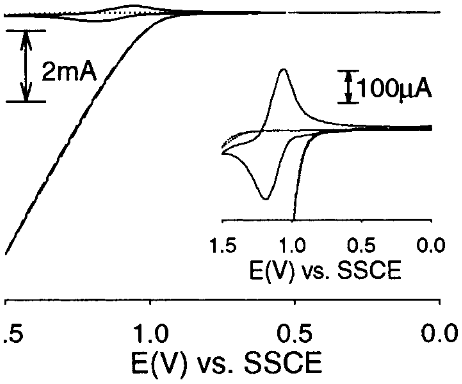

Figure 1. Cyclic voltammogram of ITO/SG−[PS−CH_2CH_2-NHCO−$(Ru^{II})_{18}$]Cl_{36} in 0.2 M Na_2SO_4 (H_2O), pH ~ 5 (solid line); ITO/SG in 0.2 M Na_2SO_4 (H_2O) with added 50 mM of $Na_2C_2O_4$ (dotted line); and ITO/SG−[PS−CH_2CH_2NHCO−$(Ru^{II})_{18}$]Cl_{36} in 0.2 M Na_2SO_4 (H_2O) with added 50 mM of $Na_2C_2O_4$ (dashed line). Inset shows the same data on an expanded scale. All voltammograms were measured at 100 mV/s.

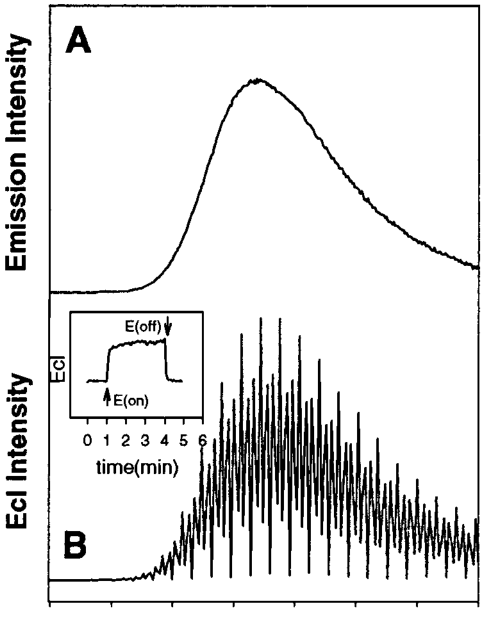

Figure 2. Photoluminescence (A) and electrochemiluminescence (B) spectra of ITO/SG−[PS−CH_2CH_2NHCO−$(Ru^{II})_{18}$]Cl_{36}. The inset in part B shows the temporal intensity profile under continuous potential cycling with 50 mM $Na_2C_2O_4$(H_2O) in the external, nondearated solution at pH = 6.0 (adjusted by 0.01 M H_2SO_4). The conditions for part A were Si/Ru = 50 (~0.2 mol of Ru per dm^3 of gel), film exposed to H_2O, excitation wavelength 460 nm. For part B the potential program was E_1 = 0 V (0.1 s), E_2 = +1.70 V (0.1 s) versus SSCE, Si/Ru = 50 (~0.2 M in Ru).

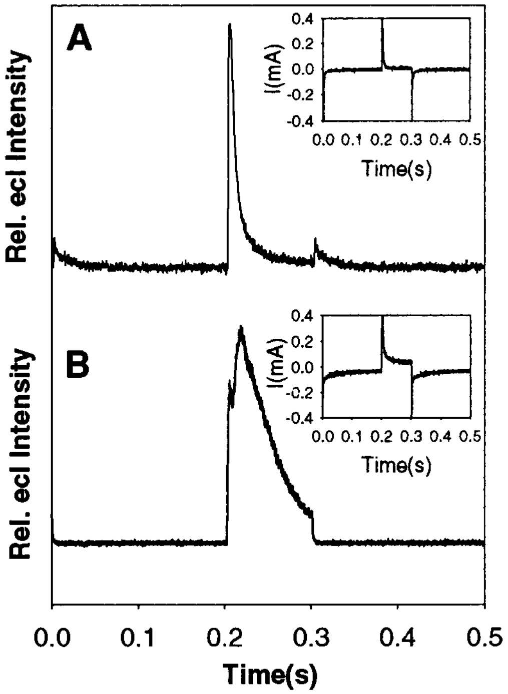

Figure 3. Electroluminescence (by annihilation) of (A) ITO/SG−[PS−CH_2CH_2NHCO−$(Ru^{II})_{18}$]Cl_{36}/MeCN and (B) ITO/[Ru(bpy)$_3$](PF_6)$_2$ in MeCN. The potential program was $E_1 = +1.40$ V (0.1 s), $E_2 = -2.00$ V (0.2 s) versus SSCE, supporting electrolyte 0.1 M [N(n-C_4H_9)$_4$]PF_6 (TBAH), solution deaerated by Ar purging for 30 min. The insets show corresponding current changes.

potential of the underlying electrode beyond the potential of the $Ru^{III/II}$ couple. Upon addition of 50 mM $Na_2C_2O_4$, the composite film shows catalytic behavior toward oxalate oxidation (Figure 1), as expected.[7a,b] Repetitive potential pulsing in 50 mM $Na_2C_2O_4$ aqueous solution between $E_1 = 0$ and $E_2 \geq 1.0$ V (versus SSCE) leads to the observation of an intense orange luminescence, easily observable under ambient lighting. The ecl spectrum of the device ITO/SG−[PS−CH_2CH_2NHCO−$(Ru^{II})_{18}$]$^{36+}$(0.2 M in Ru^{II})/$C_2O_4^{2-}$(H_2O) is compared with the photoluminescence observed from the same film in Figure 2. The match in emission maxima indicates that both photo- and electrochemiluminescence originate from the same MLCT excited state. The temporal stability of the ecl is illustrated in the inset in Figure 2. After 10−15 min, the ecl is decreased due, in part, to the decrease in oxalate concentration. Another factor possibly affecting the ecl stability is the presence of the Cl^- counterions, which can be oxidized to Cl_2 at potentials required for Ru(II) → Ru(III) oxidation. This interferes with the ecl process by oxidation of oxalate radicals. Variations in the repetition rate of the potential step between 1 and 10 Hz did not effect the observed ecl intensity markedly, but there was a ~10-fold increase when the potential step was extended past the $Ru^{III/II}$ wave at 1.26 V from +1.00 V to +1.70 V (versus SSCE). This is similar to the behavior of [Ru(bpy)$_3$]$^{2+}$ in ion-exchanged Nafion films.[7] Electron transfer in the composite films is slow under the pulse conditions used, and a longer step increases the fraction of sites undergoing electron transfer. No difference in ecl intensity is observed between stirred and unstirred solutions, showing that the film behaves as a fully permeable membrane toward oxalate anions.[21]

We have also studied electroluminescence (el) in films generated by potential steps beyond the first reduction ($E_{1/2}^{2+/+} = -1.24$ V versus SSCE) and first oxidation ($E_{1/2}^{III/II} = 1.26$ V). In Figure 3 are compared the el of 0.1 M ITO/SG−[PS−CH_2CH_2NHCO−$(Ru^{II})_{18}$]Cl_{36}/MeCN in [N(n-C_4H_9)$_4$]PF_6 (TBAH) and the el at an ITO electrode by sequential oxidation and reduction of [Ru(bpy)$_3$]$^{2+}$ in MeCN. In both cases intense orange emissions of comparable intensities are observed which match the emission spectrum of $[Ru(bpy)_3]^{2+}$. The decrease in per-site efficiency in the composite is partially due to slow electron-transfer kinetics. From chronoamperometric measurements, $D_{ct} = 1.4 \times 10^{-9}$ cm²/s,[17] where D_{ct} is the apparent charge-transfer diffusion coefficient for the Ru(II) → Ru(III) oxidation. (For the freely diffusing chromophore, the diffusion coefficient is $D_{app} \sim 5 \times 10^{-6}$ cm²/s.)[22] With this value the thickness of the diffusion layer in the film during the 0.1 s pulse is ~150 nm. Thus, for films thicker than 150 nm, only a fraction of the sol−gel-immobilized chromophores actually participate in the ecl reaction.

The stability of el by annihilation is lower than that for ecl in the presence of oxalate. Typical half-lives of 3−5 min have been observed for different electrodes after repetitive potential scans at 10 Hz. By using ITO/$[Ru(bpy)_3]^{2+}$ (MeCN, 0.1 M in TBAH) as a standard, with $\phi_{ecl} = 0.05$,[2b] ϕ_{ecl} for a series of sol−gel/composite films (determined by signal averaging within the first 500 cycles) was $\phi_{ecl} = 0.016{-}0.0012$ for different films. We are currently investigating the factors required to maximize light output and ecl stability in both types of experiments.

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(21) The penetrability of the composite films with respect to the oxalate ions seems to be in contradiction to the lifetime measurements in the dry films. They showed that there are no differences in lifetimes between dry films in air and under Ar, indicating restricted gas diffusion in the film. However, in a more recent study (Sykora, M.; Meyer, T. J. Manuscript in preparation) it was found that the compositions of dry films differ from those of films exposed to a solvent. The key difference lies in the content of the surfactant (Triton X-100 in the present work). Thus, while in the dry films the surfactant is an integral part of the composite, upon exposure to a solvent, the majority of the surfactant leaches out of the film. As a result, the pores originally filled by surfactant are filled with solvent and become accessible to dissolved ions and/or oxygen. This model is consistent with the gradual change in emission energies observed over a period of 1 h as the surfactant is replaced by solvent in the pores of the composite.

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