

Electrochemical Modulation of Luminescence from an Interfacial Probe during Redox Switching of Polypyrrole

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Steady-state measurements were used to demonstrate how luminescence from an interfacial probe such as pyrene or $[\text{Ru}(\text{bpy})_3\text{Cl}_2](\text{bpy} = 2,2'\text{-bipyridine})$ may be modulated by redox switching of a polypyrrole electrode between the insulating and electronically conductive states.

Polypyrrole is an important member of an emerging family of electronically conductive polymers which can be electrochemically redox-switched between the oxidized, conductive form and the neutral, insulating state.¹ There has been considerable interest in this switching phenomenon; the order-of-magnitude conductivity changes, optical transitions, and ionic fluxes that accompany the redox switching offer much scope for exploitation.² The possibility of utilizing luminescence from a probe molecule close to the polymer surface to monitor environmental changes during the switching was intriguing to us. Specifically, we expected that the luminescence from such a molecule could be *reversibly* modulated in a manner which tracked the corresponding variations in polymer conductivity. The strategy is shown schematically in Figure 1. The efficacy of this approach rests on the extent to which the probe molecules can be constrained within the critical distance for energy-transfer quenching³ from the polymer surface.

A custom-designed thin-layer luminescence cell, similar to

that employed for spectroelectrochemistry,⁴ was positioned at a 45° angle in a 1 cm quartz cuvette. The substrate for the polymer was a Au minigrad electrode (Buckbee-Mears/Interconics; 100 wires per inch) which was sandwiched between the two slides. Polypyrrole was anodically electrodeposited⁵ on this minigrad in a separate electrochemical cell. The nominal deposition potential was +0.65 V (all potentials herein are quoted with respect to the non-aqueous $\text{Ag}^{+/0}$ reference electrode); the deposition bath was MeCN–2% (v/v) H_2O –0.1 M LiClO_4 containing 0.2 M pyrrole. The polypyrrole films were nominally a few μm thick. All luminescence measurements were performed on MeCN containing 0.1 M tetrabutylammonium perchlorate (TBAP). This solution, containing the requisite concentration of the probe molecule, was placed as a reservoir pool in the quartz cuvette. Capillary rise within the thin-layer cell was completed prior to measurement. The reference and counter electrodes were placed in the solvent pool to complete the cell assembly.

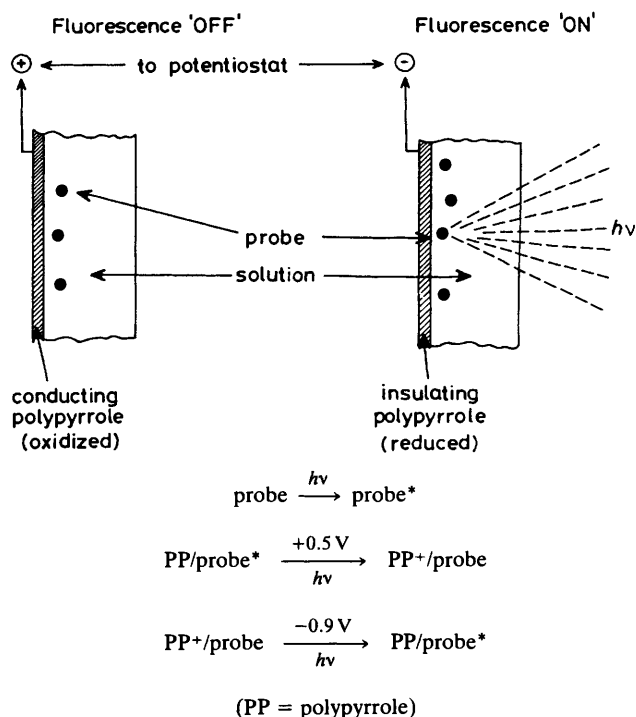


Figure 1. Strategy for monitoring electrochemical modulation of luminescence from an interfacial probe molecule during redox switching of a polypyrrole electrode

Pyrene and tris(2,2'-bipyridine)ruthenium(II) chloride, $[\text{Ru}(\text{bpy})_3\text{Cl}_2]$, were used as candidate probe molecules to demonstrate the luminescence modulation strategy. Key results are contained in Figure 2. Figure 2(a) shows steady-state fluorescence spectra of pyrene. When the potential of the polypyrrole is poised at 0 V, the fluorescence intensity is drastically attenuated (*ca.* 90%) relative to the situation at -0.9 V, when the polypyrrole is switched to its neutral, insulating form [cf. spectra (A) and (B) in Figure 2(a)].[†] Subsequent oxidation of the polymer at $+0.5$ V returns the emission intensity to the level corresponding to the original (quenched) state [spectrum (C)]. This sequence may be repeated over many cycles of the polypyrrole electrode. The spectrum at -0.9 V mirrors that obtained in a 'blank' experiment without either gold or polypyrrole in the thin-layer cell cavity.

Cyclic voltammetry has established potential regimes for the oxidized and reduced forms of polypyrrole.¹ Thus, at potentials lower than *ca.* -0.5 V, the polymer is in the reduced (insulating) state; at potentials higher than this value, the material can be redox-switched to the oxidized (electronically conductive) form. The conductivity changes accompanying this redox process span several orders of magnitude. The important conclusion from the data in Figure 2 is that the polymer in its oxidized form is an effective excited-state quencher. On the other hand, the polymer in the reduced state shows little proclivity for quenching luminescence from a probe molecule. The generality of these trends is illustrated by the corresponding data in Figure 2(b) for the $[\text{Ru}(\text{bpy})_3\text{Cl}_2]$ probe. This latter molecule perhaps could prove more useful

[†] The spectra in Figure 2 pertain to the situation when a steady-state has been attained in terms of intensity changes. The latter occur over several seconds after the potential is switched. The temporal aspects of the luminescent modulation will be addressed elsewhere.

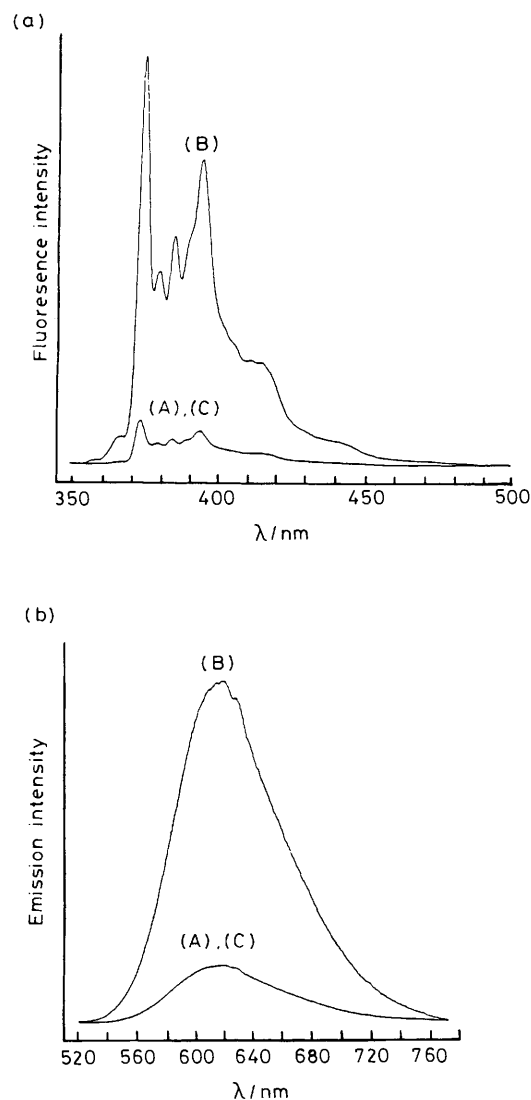


Figure 2. (a) Fluorescence modulation from the pyrene probe at a polypyrrole/acetonitrile interface; solution MeCN-0.1 M TBAP, containing 1.48×10^{-5} M pyrene; excitation wavelength 330 nm; slit widths for emission and excitation 1.5 and 8 nm, respectively. (b) Luminescence modulation from the $[\text{Ru}(\text{bpy})_3\text{Cl}_2]$ probe at a polypyrrole/acetonitrile interface; solution as in (a) containing 1.55×10^{-4} M probe; excitation wavelength 440 nm; slit widths for emission and excitation 2 and 8 nm, respectively. Refer to text for spectral notation and switching sequence: (A) oxidized PP at E 0 V; (B) neutral PP at E -0.9 V; (C) oxidized PP at E $+0.5$ V (PP = polypyrrole).

in a practical sense (*i.e.* in device development) in that its luminescent emission lies in the visible range.

It should be noted that the probe molecules themselves undergo no electrochemical changes within the potential limits (-0.9 V to 0.5 V) employed for redox-switching polypyrrole. For example, the oxidation of $[\text{Ru}(\text{bpy})_3]^{2+}$ occurs at $+0.90$ V. Pyrene is electro-oxidized (or electro-reduced) at even more extreme potentials.

Control experiments were also performed with bare Au minigrad electrodes in the thin-layer cell. These experiments with the two probes yielded emission spectra in each case similar to those labelled (A) and (C) in Figure 2. Thus, oxidized polypyrrole exhibits a propensity for energy-transfer luminescence quenching, similar in magnitude to that for the

Au substrate. Importantly, however, switching of the Au potential between the limits identified in Figure 2 does not cause modulation of the luminescence intensity. The majority of the experiments in this study were not conducted on deaerated solutions. Interestingly enough, any potential-induced modulation observed with Au, would have signalled the influence of dissolved O₂ as a contributory factor to the data in Figure 2. This is because O₂ would be expected to be electroreduced and reoxidized on switching the potential from -0.9 V to +0.5 V. Such is not the case here.

The literature precedent on optical changes in polypyrrole during redox switching⁶ prompted us to check whether the observed attenuations in luminescence intensity could be due to inner-filter effects.⁷ The latter arise from absorption of the excitation (primary) and/or emission (secondary) light by the quencher. Excitation spectra of both pyrene and [Ru(bpy)₃Cl₂] in the blank cell were identical, with the gold electrode in place, and with polypyrrole in either the conductive or insulating states. The fact that neutral polypyrrole has higher absorbance than the oxidized form, over a wavelength range germane to this study,⁶ also renders unlikely an explanation for the observed modulation in terms of inner-filter effects.

A Förster-type energy transfer model⁸ appears adequate to explain the luminescence intensity trends in Figure 2. The fact that 'background' intensities amount to ca. 10% with either Au or oxidized polypyrrole in the thin-layer cell, suggests contributions from the luminescence of molecules situated beyond the critical, quenching distance in the thin-layer cell. ‡

‡ Comparisons of the thickness of the solution layer in the present luminescence cells (~0.025 mm) and nominal values of the critical quenching distance for Förster energy transfer (1–10 nm), as well as other experiments, indicate strong adsorption of pyrene and [Ru(bpy)₃Cl₂] on the polypyrrole surface. We thank a referee for pertinent comments on this aspect of the work which will be elaborated upon in a full paper.

We are attempting to evaluate this effect by covalent anchoring of the probe molecules to the polymer surface *via* well defined molecular spacers.

To our knowledge, the data in Figure 2 constitute the first examples of electrochemical luminescence modulation caused by redox switching of an electronically conductive polymer. Specific reagent-induced fluorescence modulations have been reported, however, in studies aimed towards sensor development.⁹

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