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## A POLYMER-FILM BASED PHOTOELECTRODE CONTAINING IMMOBILIZED QUENCHER AND CHROMOPHORE POLYMER BLENDS

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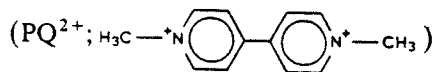
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### ABSTRACT

A strategy for the immobilization of both quencher and chromophore jointly within a polymeric film is described based on the use of a polymer blend. Photolysis of the resulting films on electrodes gives rise to significant photocurrents in the presence of an added reductive scavenger.

### INTRODUCTION

We recently reported the appearance of oxidative photocurrents following irradiation of chemically modified, polymeric films on metal electrodes [1]. The effect was obtained on the basis of excitation of a polypyridine-Ru(II), metal to ligand charge transfer (MLCT) chromophore which had been bound chemically within the films. Following excitation and oxidative quenching by added paraquat

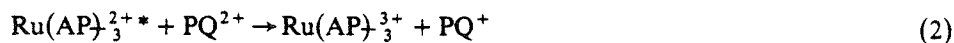


present in the film by ion exchange, and reductive scavenging of Ru(III) by added triethanolamine, significant photocurrents were observed via the series of reactions in Scheme 1.

A photoelectrode was also described based on reductive quenching of the rhenium-based MLCT chromophore  $[(\text{AP})\text{Re}(\text{CO})_3(\text{pyridine})]^+$  with dioxygen as the redox scavenger [1].

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## SCHEME 1



(AP- is 5-amino-1,10-phenanthroline chemically bound to chlorosulfonated polystyrene; TEOA is triethanolamine,  $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ )

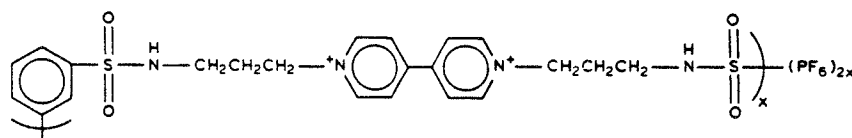
The sequence of reactions in Scheme 1 provides a basis for a photocurrent with a relatively high quantum yield per photon absorbed. However, limitations exist associated with the use of mobile, solution-based quenchers. Film-based systems where both the chromophore and quencher are immobilized could be advantageous in: (1) solid-state photoelectrochemical devices, (2) devices based on geometrically isolated, structured arrays of quenchers and chromophores, or (3) flow systems, where a solution-phase quencher would be depleted rapidly.

We describe here a strategy for fabricating polymeric films containing both immobilized quenchers and chromophores based on polymer blends, and illustrate the utility of the approach in a photoelectrode application.

## EXPERIMENTAL

## Materials

Chlorosulfonated polystyrene ( $\text{PSSO}_2\text{Cl}$ ) [2], *ortho*-polyxylylviologen dibromide  $[(\text{PXV}(\text{Br})_2)_x]$  [3],  $[\text{Ru}(\text{AP})_3](\text{PF}_6)_2$  [4],  $[\text{Ru}b_2(\text{AP})](\text{PF}_6)_2$  [4] (b is 2,2'-bipyridine), and  $[\text{Re}(\text{CO})_3(\text{py})(\text{AP})](\text{PF}_6)$  [5] (py is pyridine) were prepared according to literature methods. The sulfonamide-based polyviologen,  $[\text{PPQ}(\text{PF}_6)_2]_x$ ,



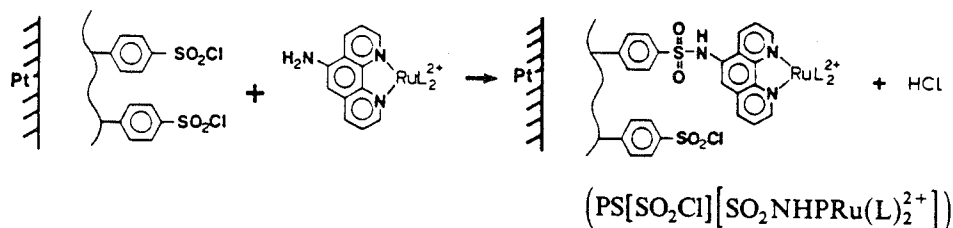
was supplied by Dr. Larry Margerum. Its preparation was based on that for a closely related polyviologen described by Simon and Moore [6]. Briefly, 2.38 g *N,N'*-bis( $\alpha$ -aminopropyl)dipyridiniumbromide [6] was dissolved in 70 ml water containing 0.85 g  $\text{Na}_2\text{CO}_3$ . 1.21 g 1,3-benzenedisulfonylchloride (recrystallized from hexane) was dissolved in 20 ml dichloroethane and the two solutions were combined. After stirring for 2 h, the dichloroethane was removed by rotary evaporation, and the aqueous solution was added to a large excess of acetone. A yellow oil was isolated, which resisted recrystallization from acetone, isopropanol and ethanol. The

oil was dissolved in water, precipitated by adding aq.  $\text{NH}_4\text{PF}_6$ , collected on a glass frit and dried with ether. This material was redissolved in acetone, filtered into excess ether, and collected as a white solid.

#### Blended films

In an inert atmosphere, freshly prepared solutions of  $\text{PSSO}_2\text{Cl}$  and  $[\text{PPQ}(\text{PF}_6)_2]_x$  in acetone (2 mg/ml) were combined in proportions of 3:2. Upon mixing, turbidity was immediately evident and if allowed to sit, one or both polymers salted out within a few minutes. Consequently, we cast the films as quickly as possible by solvent evaporation from 10  $\mu\text{l}$  aliquots placed on platinum disks ( $0.125\text{ cm}^2$ ) or 100  $\mu\text{l}$  aliquots on platinum squares ( $1\text{ cm}^2$ ). The coated electrodes were then placed in a vacuum port for several hours to remove residual acetone. In a similar fashion, blended films based on  $[\text{PXV}(\text{Br})_2]_x$  and  $\text{PSSO}_2\text{Cl}$  were cast from dimethylformamide + methanol mixtures with the solvent removed by vacuum evaporation. Residual solvent was removed by heating ( $50^\circ\text{C}$ ) for 1.5 h in a vacuum oven. A useful criterion for adequate solvent removal was film insolubility in acetonitrile solutions containing 0.2 M tetraethylammonium bromide ( $[\text{TEA}]\text{Br}$ ). Blends were also cast onto glass cover slips, but invariably the resulting films were crystalline and poorly adhesive.

As detailed earlier [2] the chromophores were incorporated into films by chemical attachment to  $-\text{SO}_2\text{Cl}$  sites through sulfonamide formation ( $\text{L} = 2,2'$ -bipyridine or 5-amino-1,10-phenanthroline),



Given the multiple binding site capability of the tris-chelate, there is probably crosslinking in films in which it is incorporated. The attachment process involved soaking the film-coated electrodes for 1 h in a 5 mM stock solution ( $\text{CH}_3\text{CN}$ ) which also contained 0.2 M  $[\text{TEA}]\text{Br}$ , followed by rinsing and soaking in two additional  $\text{CH}_3\text{CN}$  solutions containing 0.2 M  $[\text{TEA}]\text{Br}$  for 30 min each to remove any unreacted, entrapped complex. We estimate the degree of loading on a per  $-\text{SO}_2\text{Cl}$  site basis to be less than a few percent.

#### Measurements

Time-resolved luminescence decays were obtained by laser flash photophysics using instrumentation described previously [7]. Photocurrents were obtained under potentiostatic control using a standard three electrode cell arrangement. The photolysis source was a 1000 W high-pressure mercury lamp (Hanovia), with the output

first passing through a condensing lens and a Bausch and Lomb Model 33-86-79 high-intensity monochromator.

## RESULTS AND DISCUSSION

Cyclic voltammetry (Fig. 1 of the  $[\text{PPQ}(\text{PF}_6)_2]_x/\text{PSSO}_2\text{Cl}$  blended film in  $\text{CH}_3\text{CN}$  with 0.1 *M* tetraethylammonium perchlorate shows chemically reversible waves at  $E(1) \sim -0.52$  V and  $E(2) \sim -1.02$  V (vs. SSCE) corresponding to successive one-electron viologen-based reductive couples [8,9]. The electrochemical response of the  $[\text{PXV}(\text{Br})_2]_x/\text{PSSO}_2\text{Cl}$  film is similar, but with reductive waves appearing at  $E = -0.35$  V and  $-0.85$  V. For the latter film, but with  $[\text{Ru}(\text{AP})_3](\text{PF}_6)_2$  incorporated, photolysis over a 4 h period in  $\text{CH}_3\text{CN}$  with 0.2 *M*  $[\text{TEA}]\text{Br}$  resulted in substantial loss ( $> 80\%$ ) in  $\text{PXV}^{2+/+}$  electroactivity but the photocurrent response (see below) remained relatively unaffected.

Irradiation of a blended film of  $[(\text{PPQ}(\text{PF}_6)_2)_x/\text{PS}[\text{SO}_2\text{Cl}][\text{SO}_2\text{NHPRu}(\text{AP})_2^{2+}]]$  at 430 nm in the presence of 1.3 *M* TEOA gave the steady-state photocurrent-versus-potential response shown in Fig. 2. Similar results were obtained with  $[(\text{AP})\text{Re}(\text{CO})_3(\text{py})]^+$  as the chromophore and  $[\text{PXV}(\text{Br})_2]_x$  in place of  $[\text{PPQ}(\text{PF}_6)_2]_x$  as oxidative quencher. In Fig. 2, the sense of the photocurrent (oxidative) together with its disappearance when the electrode is polarized at  $-0.50$  V are both consistent with oxidative quenching by the  $\text{PPQ}^{2+}$  sites followed by electron migration to the electrode based on the  $2 + / +$  polyviologen couple in the film. The photocurrent action spectrum shows that  $[\text{SO}_2\text{NHPRu}(\text{AP})_2]^{2+}$  is the chromophore. In the absence of complex, a background photocurrent of tens of nA is still observed, but only when TEOA is present in the external solution. Its origin is probably in direct excitation of the donor-acceptor complex between  $\text{PPQ}^{2+}$  sites and TEOA in the film.

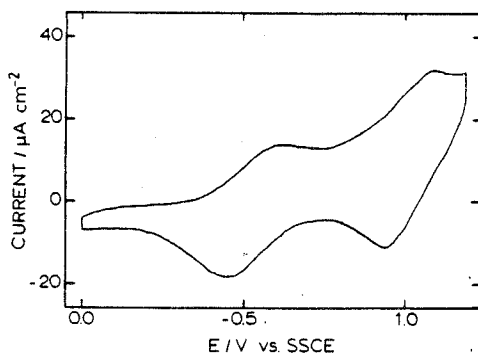


Fig. 1. Cyclic voltammetry in  $\text{CH}_3\text{CN} + 0.1$  *M* TEAP of a blended film of  $[\text{PPQ}(\text{PF}_6)_2]_x + \text{PSSO}_2\text{Cl}$  on a platinum disk. Scan rate = 50 mV/s.

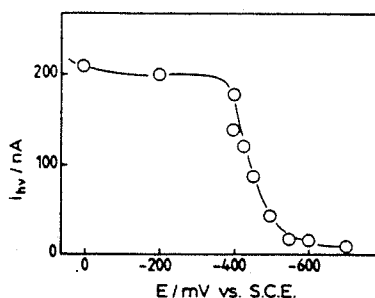


Fig. 2. Potential dependence of steady-state photocurrents in  $\text{CH}_3\text{CN} + 0.1 \text{ M TEAP}$  and  $1.3 \text{ M TEOA}$ , from a blended film of  $[\text{PPQ}(\text{PF}_6)_2]_x$  and  $\text{PS}[\text{SO}_2\text{Cl}][\text{SO}_2\text{NHPRu}(\text{AP})_2]^{2+}$ . Excitation wavelength is  $430 \text{ nm}$ .  $0.125 \text{ m}^2$  electrode.

The film-based dynamics of excited-state quenching by blended  $[\text{PXV}^{2+}]_x$  were investigated using time-resolved luminescence. Figure 3 shows the emission decay curves from  $[\text{SO}_2\text{NHPRu}(\text{AP})_2]^{2+}$ , monitored at  $625 \text{ nm}$ , following excitation at  $450 \text{ nm}$  with a  $\text{N}_2$ -pumped, pulsed-dye laser (pulse width =  $10 \text{ ns}$ ). Curve *a* shows emission decay from a film (on a platinum electrode) consisting of  $\text{PS}[\text{SO}_2\text{Cl}][\text{SO}_2\text{NHPRub}_2^{2+}]$ ; curve *b* is the decay from a blended film containing both  $\text{PS}[\text{SO}_2\text{Cl}][\text{SO}_2\text{NHPRub}_2^{2+}]$  and  $[\text{PXV}^{2+}]_x$ . The relative intensities for *a* and *b* show that quenching in the blend is virtually ( $\geq 99\%$ ) complete.

As commonly found for film-based emitting chromophores of this type, excited state decay in both types of films is non-exponential [10]. Nonetheless, except for the difference in emitted intensity, the decay traces are approximately superimposable (after the first  $15 \text{ ns}$ ) and, for example, at long times ( $> 500 \text{ ns}$ ) each can be fit reasonably well with a single decay constant of  $\tau = 600\text{--}800 \text{ ns}$ . This is a significant observation on two counts, the first being that it indicates that the environment of

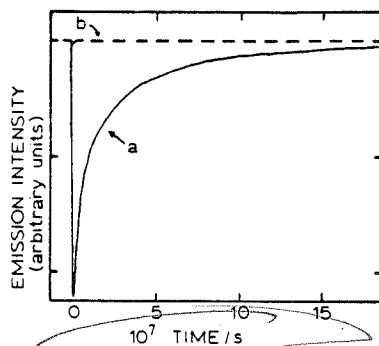


Fig. 3. Emission decay curves from  $[\text{SO}_2\text{NHPRub}_2]^{2+}$  following laser flash photolysis of: (a) a  $\text{PS}[\text{SO}_2\text{Cl}][\text{SO}_2\text{NHPRub}_2^{2+}]_n$  film on platinum foil in  $\text{CH}_3\text{CN}$ , and (b) a  $\text{PS}[\text{SO}_2\text{Cl}][\text{SO}_2\text{NHPRub}_2^{2+}] + [\text{PXV}(\text{Br})_2]_x$  blended film on platinum foil in  $\text{CH}_3\text{CN} + 0.2 \text{ M TEA}[\text{Br}]$ . Pulse width =  $10 \text{ ns}$ . Both solutions were deoxygenated. Obtained on a  $1 \text{ cm}^2$  electrode.

the chromophore is not dramatically different in the blend. In addition, the loss of emitted intensity but not of lifetime shows that the quenching mechanism is by static and not by dynamic quenching since dynamic quenching would, of necessity, involve a decrease in lifetime. This is not a surprising result given the immobilized nature of the quencher. However, when combined with the observation of a high percentage of quenching, it shows that the separate quencher and chromophore-modified polymers must be extensively and somewhat homogeneously interwoven in the blended film, with nearly all of the chromophoric sites surrounded by quencher sites.

In contrast to the polyviologens, TEOA does not quench the MLCT luminescence and as suggested in Scheme 1, its role is that of a redox scavenger. On the basis of the pattern of reactions in Scheme 1 and kinetic analyses presented earlier for analogous systems in solution [11,12], the dependence of the photocurrent on [TEOA] is predicted to be of the form:

$$1/i_{hv} \propto 1/[TEOA] + \text{constant} \quad (6)$$

That the predicted inverse-inverse relationship holds is demonstrated by the plot in Fig. 4.

Because of the low levels of chromophore incorporation and our inability to cast stable blends on transparent substrates, a quantitative evaluation of the photon-absorbed photocurrent quantum efficiencies,  $\phi$ , is difficult. Nevertheless, a comparison between blended and non-blended films where the conditions for chromophore incorporation were identical, shows the photocurrent output from the blended films to be smaller by about an order of magnitude. Assuming the chromophoric loadings in the two types of films are similar, we can estimate very roughly that  $\phi = 0.002$  to  $0.02$  under optimal conditions. The low efficiency is somewhat surprising: from the time-resolved luminescence decay measurements (Fig. 3), the efficiency of excited-state quenching in the PXV/PSSO<sub>2</sub>Ru film is essentially unity and from the kinetic analysis in Fig. 4 the scavenging efficiency at high [TEOA] is greater than  $0.8$ .

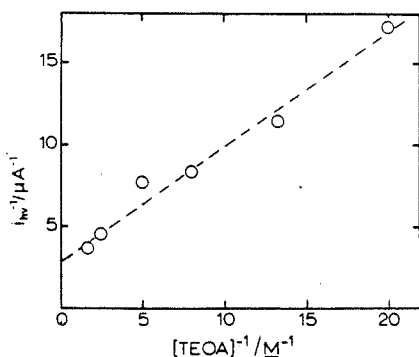
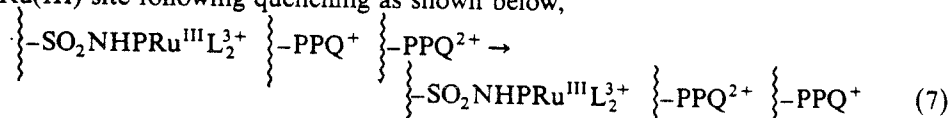
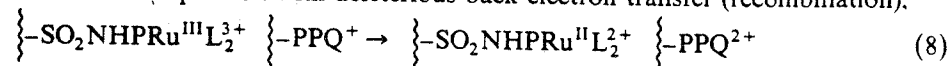


Fig. 4. Inverse photocurrent (steady state) versus inverse [TEOA] for photolysis at 430 nm of the blended film from Fig. 3b on a 0.125 cm<sup>2</sup> electrode.

However, cyclic voltammetry shows that the degree of electroactivity of the blended polyviologen is only about 5% on the basis of a comparison between integrated peak areas and the known amount of polymer cast onto the electrode. The low photocurrent quantum efficiencies may arise from slow electron transport away from the Ru(III) site following quenching as shown below,



which is in competition with deleterious back electron transfer (recombination),



Alternatively, if there are extensive regions within the film which are electroinactive,  $\text{PXV}^+$  or  $\text{PPQ}^+$  could build up locally and inhibit photocurrent production by a combination of competitive light absorption, recombination, and/or reductive quenching.

#### ACKNOWLEDGEMENTS

Dr. Larry Margerum supplied a sample of  $[\text{PPQ}(\text{PF}_6)_2]_x$ . Dr. Steve McClanahan assisted in the time-resolved luminescence experiments. We also acknowledge the Department of Energy for support of this research under grant no. DE-AS05-78ER06034.

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