23

J. Electroanal. Chem., 190 (1985) 287—291
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary note

PHOTOCURRENTS ARISING FROM PHOTOLYSIS OF SYNTHETICALLY CONTROLLED CHROMOPHORE—QUENCHER STRUCTURES IN POLYMERIC FILMS

JOSEPH T. HUPP, JOSEPH P. O'TRUBA, STEPHEN J. PARUS and THOMAS J. MEYER
Department of Chemistry, The University of North Carolina, Chapel Hill, NC 27514 (U.S.A.)

(Received 14th May 1985)

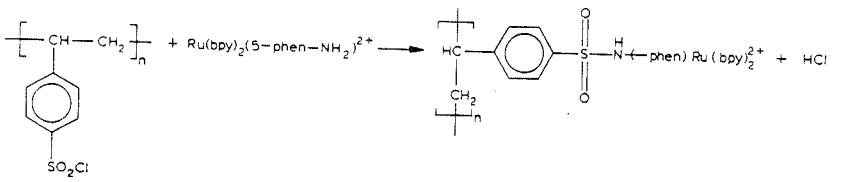
In several recent accounts it has been reported that photolysis of polymeric films on electrodes which contain polypyridyl ruthenium(II) chromophores in the presence of quenchers can lead to photocurrents [1—7]. The photocurrents appear to originate from electron-transfer reactions involving metal-complex excited states confined within the films, e.g.,

$$Ru(bpy)_3^{*2+} + PQ^{2+} \rightarrow Ru(bpy)_3^{3+} + PQ^{+} \quad (1)$$

$$Ru(bpy)_3^{*2+} + NR_3 \rightarrow Ru(bpy)_3^{+} + NR_3^{+} \quad (2)$$

(bpy is 2,2′-bipyridine; PQ^{2+} is 4,4′-dimethyl-bipyridinium ion) via processes which are well established in fluid solution [8]. We report here what appears to be a general strategy for the assembly of chromophore—quencher combinations in polymeric films, and further, that the strategy can lead to the fabrication of controlled structures within the films. Photolysis of the resulting films can lead to significant per-photon photocurrent quantum yields.

The fabrication procedure has its basis in the initial covalent attachment of the chromophore within a preformed film of chlorosulfonated polystyrene on an electrode surface [9], e.g.,



(5-phen-NH_2 is 5-amino-1,10-phenanthroline)

followed by: (1) exposure to an external solution containing a film-permeable quencher, e.g. $N(C_6H_4Br)_3$ or, more effectively, by (2) hydrolyzing the remaining $-SO_2Cl$ sites (by soaking in aqueous carbonate buffer. pH = 9.5) to

0022-0728/85/$03.30

give $-SO_3^-$ sites and thereby creating a cation exchange environment for the incorporation of quencher cations, e.g. PQ^{2+}.

In a typical experiment 2×10^{-5} g of polymer (prepared by chlorosulfonation of polystyrene; molar mass = 4000± 300 g) were deposited onto a 0.125 cm^2 platinum disk by evaporation from 10^{-5} l of acetone, followed by soaking in CH_3CN solutions of the chromophore $Ru(5\text{-phen-}NH_2)_3^{2+}$, as described previously [9]. (Control experiments based on $Ru(phen)_3^{2+}$ show that while this complex can be transiently introduced into the polymer matrix, persistent attachment is achieved only with amino ligands.) A detectable emission occurs from the films with λ_{max} = 610 nm [10]. Emission—time profiles (dry films in air) are complex but typically can be resolved into components having lifetimes of 600—800, 260 and 80 ns.

Incorporation of PQ^{2+} via ion exchange following hydrolysis was verified by the appearance of a substantial membrane-diffusion wave at $E_{1/2}$ = −0.39 V vs. SCE in acetonitrile containing PQ^{2+}, and by the appearance of oxidation and reduction waves for the $PQ^{2+/+}$ couple in films which were removed from the quencher solution, rinsed thoroughly, and placed in a fresh solution free of external PQ^{2+}. In the absence of PQ^{2+} in the external solution, the incorporated quencher does leave the film slowly. If the hydrolysis step is eliminated, the photocurrent responses described later are essentially absent and th film-based luminescence remains unquenched.

Direct evidence for the existence of a controlled spatial array of the chromo phore within the polymeric films has been obtained from depth-profiling exp iments based on ion microprobe techniques. (Full details will be given elsewhere.) In these experiments a modified film constructed from $Ru(5\text{-phen-}NH_2)_3^{2+}$ was prepared as described above, and subjected to sputtering by O_2^+. Ru^+ ions removed by sputtering were detected by Secondary Ion Mass Spectrometry (SIMS). Although only preliminary results are available, they clearly illustrate that the Ru-based chromophore is spatially isolated in the outermos 10—20% of the film.

Visible photolysis of chromophore ($Ru[5\text{-phen-}NH_2)_3^{2+}$) and quencher ($PQ^{2+}$) containing films at constant applied potential produces significant *oxidative* photocurrents as shown in Fig. 1. In the absence of a scavenger for Ru^{III} in the external solution (CH_3CN, 0.1 *M* $[NEt_4](ClO_4)$), the photocurrent decays rapidly. In fact, the magnitude of the photocharge obtained by integration of the current—time curve (Fig. 1a) is roughly equivalent to th expected for complete oxidative quenching of the Ru^{II} chromophore (see below). Sustained photocurrents were obtained for up to 3 h in the presence of known scavengers for Ru^{III}, and in particular, with added triethanolamine (TEOA; $N(C_2H_4OH)_3$); note Fig. 1b for a shorter timescale experiment.

Several observations are consistent with Scheme 1 as the origin of the photocurrents in the presence of TEOA*: (1) The photoelectrochemical acti spectrum coincides with the absorption spectrum of the chromophore. (2) T

*Small photocurrents are observed even in the absence of the polymeric film or chromophore. The photoelectrochemical action spectrum indicates that they arise from irreversible charge-transfer photolysis of the PQ^{2+}—TEOA donor—acceptor complex. Note, for example, ref. 11.

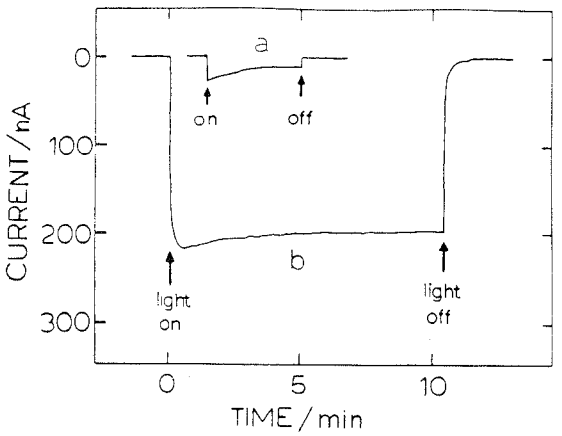


Fig. 1. Photocurrent responses at λ=460 nm from an optically-dilute polymeric film (see text) on a Pt electrode in acetonitrile solution containing: (a) 0.002 *M* [PQ]$(PF_6)_2$ and 0.1 *M* TEAP([NEt_4](ClO_4)): (b) 0.002 *M* [PQ]$(PF_6)_2$, 0.1 *M* TEAP, and 0.05 *M* TEOA. The applied potential is −100 mV vs. SCE. Light intensity = 2.5×10^{-10} mol photons s^{-1}.

sense of the photocurrent (oxidative) is consistent with PQ^+ as the electron carrier to the electrode. Also consistent is the fall off in photocurrent as the applied potential approaches the formal potential of the $PQ^{2+/+}$ couple. (3) Under the conditions of the experiment the film-based luminescence is quenched by PQ^{2+} but not by triethanolamine. (4) Blank experiments in which either PQ^{2+} or triethanolamine is omitted yield negligible sustained photocurrents (<10 nA). (5) Photocurrents increase with concentration of both added quencher and scavenger, with a plateau reached at $[PQ^{2+}]>1$ m*M*.

SCHEME 1

$$Ru(5\text{-phen-NH})_3^{2+} \xrightarrow{+h\nu} Ru(5\text{-phen-NH})_3^{2+*} \quad (4)$$

$$PQ^{2+} + Ru(5\text{-phen-NH})_3^{2+*} \rightarrow PQ^+ + Ru(5\text{-phen-NH})_3^{3+} \quad (5)$$

$$PQ^+ \xrightarrow{-e^-} PQ^{2+} \quad \text{(electrode)} \quad (6)$$

$$Ru(5\text{-phen-NH})_3^{3+} \xrightarrow{\text{TEOA}} Ru(5\text{-phen-NH})_3^{2+} \quad \text{(outer film)} \quad (7)$$

The role of the TEOA scavenger is crucial in obtaining sustained photocurrents since re-reduction of the oxidized form of the chromophore by TEOA, eqn. (7), is in competition with "recombination" or back electron transfer in which Ru(III) is rereduced by PQ^+,

$$Ru(5\text{-phen-NH})_3^{3+} + PQ^+ \rightarrow Ru(5\text{-phen-NH})_3^{2+} + PQ^{2+} \quad (8)$$

Once oxidized by one electron to give $TEOA^+$, triethanolamine is known to undergo rapid, irreversible decomposition.

We note further that saturation of the external solution with Q_2 decreases the photocurrents by 60%, presumably because of oxidative scavenging of

PQ^+ by dioxygen. The initial photocurrent level is reestablished following deoxygenation.

An estimate has been obtained for the quantum efficiency (per photon absorbed) by evaluating absorbances for films prepared on glass slides and on SnO_2 electrodes. The extent of chromophore absorbance depends on soaking time; after 1 min, $A = 0.015 \pm 0.005$ and after 20 h, $A = 0.15 \pm 0.03$. Using the *optically dilute* film, under the conditions of Fig. 1, we obtain $\phi(460\ nm) = 0{,}03 \pm 0.01$.

The demonstration that the excitation–quenching sequence in Scheme 1 can be transferred from solution to the polymeric film with a relatively high quantum efficiency (per photon absorbed) is notable. It is perhaps more notable that the chromophore is constrained to the outer edge of the film since within the film: (1) excitation, quenching, and redox product separation occur, but in contrast to the solution experiment, (2) there is a net charge separation and directed charge transfer character. Oxidation ($PQ^+ \rightarrow PQ^{2+}$) and reduction ($Ru(5\text{-phen-NH}\rightarrow_3^{3+} \xrightarrow{TEOA} Ru(5\text{-phen-NH}\rightarrow_3^{2+}$) of the photoproduced redox carriers occur in separate parts of the film, oxidation at the electrode–film interface and reduction near the film–solution interface.

We have obtained a photoelectrochemical response of the same magnitude using chemically attached $Re(CO)_3(pyridine)(5\text{-phen-NH}_2)^+$ as the chromophore within the film but based on reductive quenching by $N(C_6H_4Br)_3$. $N(C_6H_4Br)_3$ was added to the solution (CH_3CN, 0.1 *M* $[NEt_4](ClO_4)$) external to the unhydrolyzed film. In the half cell: (1) Reductive photocurrents are observed as far positive as ca. +1.05 V, consistent with the reduction of $N(C_6H_4Br)_3^+$ at the electrode. ($E_{1/2}$ = +1.1 V vs. SCE for $N(C_6H_4Br)_3^{+/0}$.) (2) Sustained photocurrents are observed in aerated solutions in the presence of added acid. Apparently, following reductive quenching within the film (eqn. 9),

$$Re^{I}(CO)_3(py)(5\text{-phen-NH}\rightarrow^+ + NR_3 \xrightarrow{+h\nu} Re^{II}(CO)_3(py)(5\text{-phen-NH}\rightarrow + NR_3^+$$

the role of O_2 is to reoxidize the highly reduced form of the chromophore ($E_{1/2}$ for $[Re(CO)_3(py)(5\text{-phen-NH}_2)]^{+/0}$ = −1.2 V vs. SCE in acetonitrile). This process (eqn. 10),

$$Re(CO)_3(py)(5\text{-phen-NH}\rightarrow^0 + H^+ + O_2 \rightarrow Re(CO)_3(py)(5\text{-phen-NH}\rightarrow^+ + HO_2 \quad (10)$$

is in competition with back electron transfer with NR_3^+,

$$Re(CO)_3(py)(5\text{-phen-NH}\rightarrow + NR_3^+ \rightarrow Re(CO)_3(py)(5\text{-phen-NH}\rightarrow^+ + NR_3 \quad (11)$$

From the potential dependence of the cell, the electrode reaction is the reduction of NR_3^+,

$$NR_3^+ \xrightarrow{+e^-} NR_3 \qquad \text{(electrode)} \quad (12)$$

Results obtained earlier [12] in a related solution-based cell were consistent with H_2O_2 as the ultimate reduction product via

$$H^+ + HO_2 + NR_3 \rightarrow H_2O_2 + NR_3^+ \quad (13)$$

ACKNOWLEDGEMENTS

We would like to acknowledge support of this research from the Department of Energy under grant no. DE-ASO5-78ERO6034. Acknowledgements are made also to S.R. Bryan, D.P. Griffiths and R.W. Linton for SIMS experiments with the Cameca IMS-3f ion microscope facility at North Carolina State University.

REFERENCES

1 N. Oyama, S. Yamaguchi, M. Kaneko and A. Yamada, J. Electroanal. Chem., 139 (1982) 215.
2 N. Oyama, S. Yamaguchi, M. Kaneko and A. Yamada, Makromol. Chem. Rapid Commun., 3 (1982) 769.
3 T. Yamamura and Y. Umezawa, J. Chem. Soc. Dalton Trans., (1982) 1977.
4 M. Kaneko, S. Moriya, A. Yamada, H. Yamamoto and N. Oyama, Electrochim. Acta, 29 (1984) 115.
5 T.D. Westmoreland, J.M. Calvert, R.W. Murray and T.J. Meyer, J. Chem. Soc. Chem. Commun., (1983) 65.
6 L.D. Margerum, T.J. Meyer and R.W. Murray, J. Electroanal. Chem., 149 (1983) 279.
7 M. Krishnan, X. Zhang and A.J. Bard, J. Am. Chem. Soc., 106 (1984) 7371.
8 C.R. Bock, J.A. Connor, A.R. Guitterez, T.J. Meyer, D.G. Whitten, B.P. Sullivan and J.K. Nagle, J. Am. Chem. Soc., 101 (1984) 4815.
9 C.D. Ellis and T.J. Meyer, Inorg. Chem., 23 (1984) 1748.
10 C.D. Ellis, Ph.D. dissertation, University of North Carolina, 1983.
11 B.P. Sullivan, W.J. Dressick and T.J. Meyer, J. Phys. Chem., 86 (1982) 1473.
12 J.P. Otruba, G.A. Neyhart, W.J. Dressick, J.L. Marshall, B.P. Sullivan, P.A. Watkins and T.J. Meyer, J. Am. Chem. Soc., submitted.