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Electrochemistry and electrogenerated chemiluminescence  
of films of the conjugated polymer  
4-methoxy-(2-ethylhexoxyl)-2,5-polyphenylenevinylene ☆

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# Electrochemistry and electrogenerated chemiluminescence of films of the conjugated polymer 4-methoxy-(2-ethylhexoxyl)-2,5-polyphenylenevinylene ☆

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## Abstract

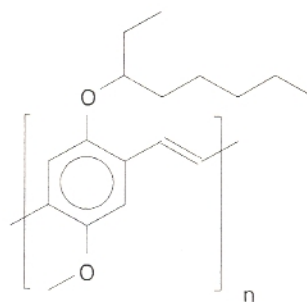
The thin film electrochemistry and electrogenerated chemiluminescence (ECL) of the title compound were obtained on Pt electrodes (CH<sub>3</sub>CN/0.1 M tetrabutylammonium fluoroborate). Orange luminescence ( $\lambda_{\text{max}} = 622$  nm) was obtained by pulsing the potentials between +0.40 and -2.35 V versus Fc/Fc<sup>+</sup> as well as by oxidizing the system in the presence of TPAH (TPAH = tri-*n*-propylamine), which generates the strongly reducing intermediate TPA<sup>•</sup>, and by reducing the system in the presence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, which produces the strongly oxidizing intermediate SO<sub>4</sub><sup>•-</sup>.

## 1. Introduction

We report here the surface electrochemistry and electrogenerated chemiluminescence (ECL) resulting from the reaction between reduced and oxidized centers in the polymer 4-methoxy-(2-ethylhexoxyl)-2,5-polyphenylenevinylene [MEH-PPV] (f.w. = 10<sup>5</sup> to 10<sup>6</sup>, degree of polymerization  $\approx 2000$ ), which was cast onto the surface of a Pt disk electrode. Moreover, when the polymer was oxidized in the presence of tri-*n*-propylamine (TPAH) ECL was also observed. To our knowledge this is the first report of ECL in polymer films of this kind.

The title compound (see below) is a member of a broad class of light-emitting conjugated polymers based on the poly(*p*-phenylenevinylene) backbone which have received a great deal of attention in re-

cent years [1–6]. This is due for the most part to the discovery that conjugated polymers of this type can be made into light emitting diodes (LEDs) in solid state polymer devices [1–6], where combination of injected electrons and holes in layers produce light emission.



MEH-PPV

☆ This Letter numbers 56 in our publications of our studies in the area of electrogenerated chemiluminescence.

ECL involves the production of light by the electron-transfer reactions between electrogenerated species [7]. Typically, the excited states are produced by an electron-transfer reaction between an oxidized species (often a radical cation) and a reduced species (radical anion) both of which are generated at an electrode by alternate pulsing of the electrode potential. Alternatively, the excited state can be produced in a single potential step in a reaction between the oxidized and reduced form of the parent species and an intermediate generated by bond cleavage to form a strong oxidant or reductant (e.g.  $S_2O_8^{2-}$ ,  $C_2O_4^{2-}$ , TPAH). For example, with tri-*n*-propylamine (TPAH), oxidation is believed to lead to the strong reductant TPA $\cdot$  which can then undergo an electron-transfer reaction with the oxidized parent species (R) to generate light via the following reaction sequence [8,9]<sup>1</sup>:



Previous studies of the ECL of polymer films [10–13] have utilized electroactive and emitting moieties attached to a nonconjugated polymer backbone (e.g. poly(vinyl-9,10-diphenyl anthracene), poly(4-vinyl-4'-methyl-2,2'-bipyridyl)ruthenium(II)) or ion-exchanged into a polyelectrolyte film ( $Ru(bpy)_3^{3+}$  in nafion). Electrochemical and ECL studies on polymers of the type discussed here can provide information about the properties of these conjugated polymers. Potential applications, for example, display devices, are also possible.

## 2. Experimental

ECL and photoluminescence spectra were taken with an Aminco-Bowman spectrofluorometer (SPF) in conjunction with a Princeton Applied Research

<sup>1</sup> It has been postulated that upon oxidation of TPAH a short-lived radical cation is formed, e.g.  $N(CH_2CH_2CH_3)_3 - e^- \rightarrow \cdot^+N(CH_2CH_2CH_3)_3$ , which then loses a proton from an alpha carbon to form the strongly reducing intermediate  $(CH_2CH_2CH_3)_2N(\cdot CH-CH_2CH_3)$ .

(PAR) model 1215 OMA2 optical multichannel analyzer including a silicon intensified target vidicon detector with a vacuum UV scintillator. The experiments employed a conventional 3-electrode cell. The total cell volume was 1–2 ml with the cell designed to fit into the sample holder of the spectrofluorometer. A platinum disk electrode (0.7 cm diameter) was employed as the working electrode with a Pt wire as the auxiliary electrode and a silver wire as the quasi-reference electrode (QRE), whose potential was calibrated with respect to the ferrocene/ferrocenium ( $Fc/Fc^+$ ) couple. The MEH-PPV/working electrode was produced by briefly submerging a clean Pt electrode in a 0.1%–0.2% (w/v) xylene solution containing the electroactive polymer and then letting the solvent evaporate to leave a thin film  $\approx 0.1 \mu m$  thick, as determined by profilometry. The electrode was placed in a MeCN solution with 0.1 M tetrabutylammonium fluoroborate ( $Bu_4NBF_4$ ) as the supporting electrolyte and the entire system deoxygenated with argon for several minutes. The polymer is insoluble in MeCN, so that the polymer film remained intact over a broad range of potentials during the electrochemical experiments. The ECL emission intensity was determined using a single-photon-counting system (Hamamatsu Corp., Bridgewater, NJ) utilizing a Hamamatsu R928P photomultiplier tube cooled to  $-20^\circ C$ .

## 3. Results and discussion

### 3.1. Electrochemistry

Cyclic voltammograms for an electrode coated with MEH-PPV in  $CH_3CN/0.1 M Bu_4NBF_4$  showed fairly well-defined, chemically reversible, waves at  $\approx +0.4$  and  $\approx -1.9$  V versus  $Fc/Fc^+$  on scanning up in voltage and  $\approx +0.25$  and  $\approx -2.2$  V versus  $Fc/Fc^+$  on scanning down in voltage (Fig. 1). The separation between the two waves (oxidation versus reduction of MEH-PPV) is approximately 2.4 V. This value is in agreement with the peak in the  $\pi-\pi^*$  absorption ( $\hbar\omega \approx 2.4$  eV) of MEH-PPV films cast from solution. A linear dependence of peak current on scan rate ( $\nu$ ) with a zero intercept was observed for  $\nu < 50$  mV/s (Fig. 2), providing evidence that the electrochemical reactions occur within the thin film on the elec-

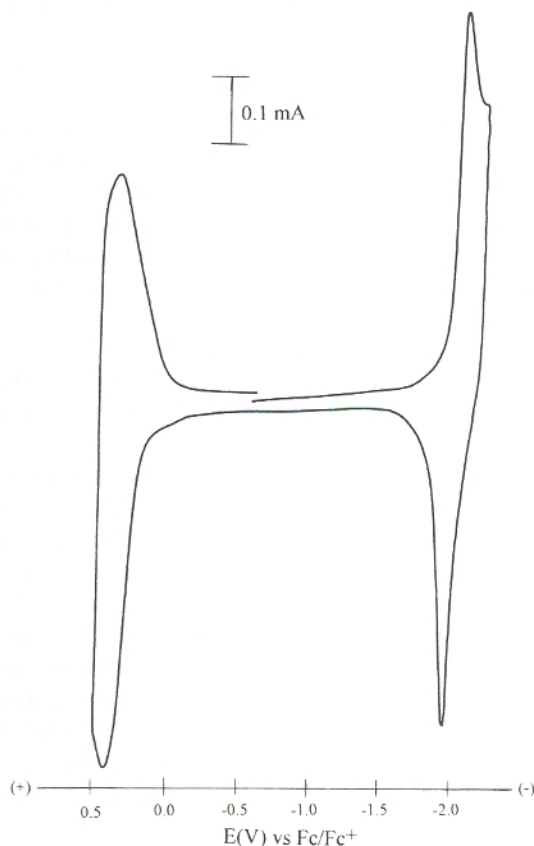


Fig. 1. Cyclic voltammogram of a cast film of MEH-PPV on a Pt disk (0.5 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ ) at a scan rate of 100 mV/s.

trode surface and not in solution. At faster scan rates, the  $i_p/v$  value decreases, suggesting the onset of kinetic or diffusive limitations. Repeated cycling over this potential range or extension of the scans to more positive potentials produced a decrease in peak heights, probably because of some dissolution of the oxidized form of the polymer. Integration of the cyclic voltammogram yields  $1.2 \times 10^3$  C of charge injected into the surface-confined polymer during the anodic sweep. This corresponds to approximately 200 monolayers of polymer on the electrode surface or, assuming each monolayer is  $\approx 5 \text{ \AA}$  thick, a film thickness of 0.1  $\mu\text{m}$ , in general agreement with the value obtained by profilometry. Thus, essentially all of the polymer film is electrolyzed during an electrochemical scan.

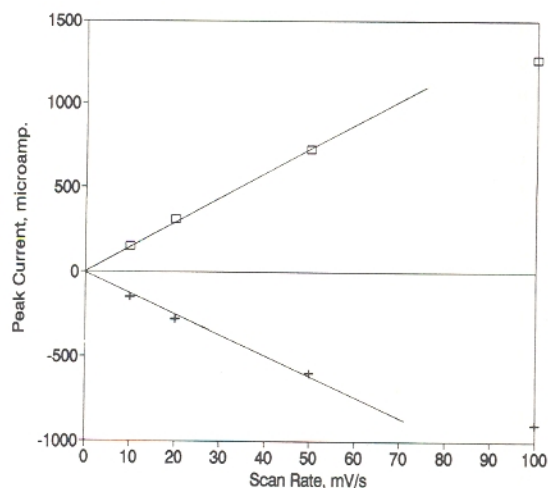


Fig. 2. Scan rate dependence of the peak current of a cast film of MEH-PPV on a Pt disk electrode (0.5 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ ). ( $\square$ ): anodic peak at +0.36 V versus  $\text{Fc}/\text{Fc}^+$ . ( $+$ ) cathodic peak at  $-2.12$  V versus  $\text{Fc}/\text{Fc}^+$ .

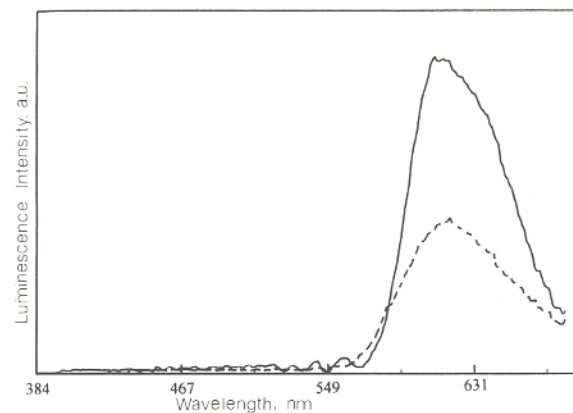


Fig. 3. Luminescence spectra of a cast film of MEH-PPV (0.5 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ ). (—) Photoluminescence spectrum excited at 350 nm. (---) ECL spectrum obtained by pulsing the electrode potential between 0.4 V versus  $\text{Fc}/\text{Fc}^+$  for 1 s and  $-2.35$  V versus  $\text{Fc}/\text{Fc}^+$  for 0.5 s. All spectra are recorded at room temperature.

### 3.2. Electrogenerated chemiluminescence

When the potential is pulsed between +0.40 and  $-2.35$  V, a pumpkin-orange emission is observed from the electrode surface upon the cathodic pulse (Fig. 3). The emission is essentially the same as the photoluminescence spectrum (Fig. 3) and can be assigned to an excited state formed in an annihilation

reaction between electrogenerated oxidized and reduced centers in the immobilized film, as seen in previous ECL polymer film studies [10–13].

The ECL was rather short-lived, lasting  $\approx 1$ –2 min when the potential was continually pulsed between +0.40 and  $-2.35$  V versus Fc/Fc<sup>+</sup> with a 1 s anodic pulse duration and a 0.5 s cathodic pulse duration. Upon oxidation, the film changes color from bright red to blue/black. When the potential is held at +0.40 V, the colored oxidized species can be seen to dissolve in the MeCN solution and diffuse away from the electrode surface, resulting in irreversible cyclic voltammograms.

An orange luminescence was also observed at the polymer-covered electrode surface when the potential was swept to +0.475 V versus Fc/Fc<sup>+</sup> in a deoxygenated MeCN solution containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> and 0.1 M TPAH. ECL was not observed under these conditions in MeCN solutions containing only TPAH or with the MEH-PPV in the absence of TPAH. The ECL was moderately intense to the dark-adapted eye, but could not be observed by the nondark-adapted eye. The polymer film was lost from the electrode surface after 2–3 sweeps through the 0/+1 couple resulting in a loss of observable ECL. Quickly switching the potential after passage through the 0/+1 couple did not result in a substantial increase in film lifetime as was observed during the electrochemistry experiments in the absence of TPAH.

Emission was also observed when the potential was swept to  $-2.0$  V versus Fc/Fc<sup>+</sup> in a deoxygenated MeCN solution containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> and 10 mM (TBA)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (TBA = tetra-*n*-butyl ammonium)<sup>2</sup> [14,15]. As in the experiment involving TPAH, the ECL could be seen with a dark-adapted eye. The ECL could be observed for several minutes when the potential was held at  $-2.0$  V with a gradual loss of both emission intensity and polymer integrity. However, even after 10 min, a faint ECL emission could be observed. An estimate of the ECL efficiency (photons generated per e<sup>-</sup> injected) was obtained by

comparing the integrated intensity of the MEH-PPV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system to that of Ru(bpy)<sub>3</sub><sup>3+</sup>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (bpy = 2,2'-bipyridine), assuming an ECL efficiency of 5% for the latter system [14,16,17]. The integrated ECL intensity of the MEH-PPV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system was measured in MeCN utilizing 10 mM S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>. Similarly, the Ru(bpy)<sub>3</sub><sup>3+</sup>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> reference system utilized 1 mM Ru(bpy)<sub>3</sub><sup>3+</sup>, 10 mM S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, and 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>. By comparing the ratios of the integrated emission intensity to the number of Coulombs consumed in the forward electrolysis, an initial ECL efficiency of  $\approx 0.4\%$  was obtained for the MEH-PPV system. This decreased with time, due primarily to loss of polymer from the electrode surface.

Fig. 4 depicts the proposed mechanism for the reactions at the polymer/electrode interface. In the solid-state polymer devices, the light emitting polymer is sandwiched between metal electrodes. The emission process is usually described in terms of a semiconductor model, where one electrode injects electrons into the conduction band and the other injects holes into the valence band. Electroluminescence results from the electron-hole annihilation process. To achieve high electroluminescence efficiency, metals with low work functions (i.e. Ca) must be used for electron injection.

The description of the ECL process, while formally the same, involves injection of charge from the Pt contact with movement of oppositely charged ions from the solution to maintain electroneutrality. This follows from previous studies of polymer modified electrodes, including those with conducting polymers such as polypyrrole and polyaniline [18–21]. As with those polymers, the injected electron represents a reduced center with an associated cation (Bu<sub>4</sub>N<sup>+</sup>), and an injected hole represents an oxidized center with an associated anion (BF<sub>4</sub><sup>-</sup>). This ECL process, where electrons and holes are injected at the Pt upon cycling the potential, is depicted in Figs. 4A, 4B and 4D.

In the experiment involving tri-*n*-propylamine, platinum serves as the hole injector (Fig. 4C) while TPA<sup>+</sup> (also formed at the platinum electrode) serves as a reductant strong enough to inject electrons into the conduction band. This also leads to electron and hole annihilation and hence ECL (Fig. 4D). Electron injection into the polymer film from a high work function metal (Pt) is possible because charge in the

<sup>2</sup> The chemical or electrochemical reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is believed to form the strongly oxidizing intermediate SO<sub>4</sub><sup>-•</sup>, which then generates light via the following reaction sequence: S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + e<sup>-</sup> → SO<sub>4</sub><sup>-•</sup> + SO<sub>4</sub><sup>2-</sup>; R + e<sup>-</sup> → R<sup>-•</sup>; R<sup>-•</sup> + SO<sub>4</sub><sup>-•</sup> → R\* + SO<sub>4</sub><sup>2-</sup>; R\* → R + hν.

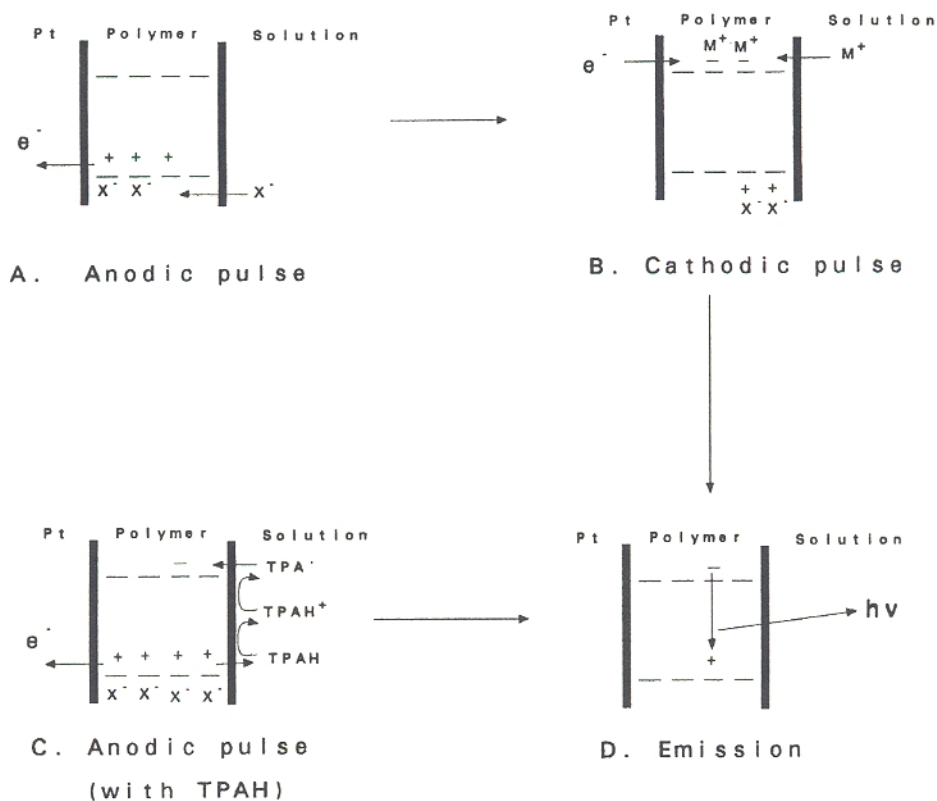


Fig. 4. Schematic of ECL from MEH-PPV coated on Pt electrode via oxidative and reductive pulsing (A and B, respectively) and oxidation in the presence of tripropylamine (C). (A) Oxidation of polymer (hole injection) at polymer/electrode surface and subsequent insertion of electrolyte anions. (B) Reduction of polymer (electron injection) at polymer/electrode surface and subsequent insertion of electrolyte cations. (C) Simultaneous oxidation of MEH-PPV on Pt surface to form holes and the oxidation of TPAH to TPA $^+$ . (D) Luminescence resulting from the annihilation of holes and electrons.

film is compensated by cations from the solution, minimizing space charge layer formation in the polymer layer. Note that the polymer layer formed in this way is quite porous, since ferrocene dissolved in the solution can be oxidized during an anodic sweep at potentials less positive than those needed for polymer oxidation. The presence of electrolyte within the polymer pores and electrode probably increases the rate of ion injection and decreases the ionic resistance of the polymer layer. Experiments are currently underway to study related polymers and both their solution and thin-film properties.

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#### References

- [1] J.H. Burroughs, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. MacKay, R.H. Friend, P.L. Burn and A.B. Holmes, *Nature* 347 (1990) 539.
- [2] P.L. Burn, A. Draft, D.R. Baigent, D.D.C. Bradley, A.R. Brown, R.H. Friend, R.W. Gymer, A.B. Holmes and R.W. Jackson, *J. Am. Chem. Soc.* 115 (1993) 10117.
- [3] N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend and A.B. Holmes, *Nature* 365 (1993) 628.
- [4] G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colareri and A.J. Heeger, *Nature* 357 (1992) 477.
- [5] D. Braun and A.J. Heeger, *Appl. Phys. Letters* 58 (1991) 1982.

- [6] Y. Cao, G.J. Treacy, P. Smith and A.J. Heeger, *Appl. Phys. Letters* 60 (1992) 2711.
- [7] L.R. Faulkner and A.J. Bard, in: *Electroanalytical chemistry*, Vol. 10, ed. A.J. Bard (Marcel Dekker, New York, 1977) pp. 1–95.
- [8] J.B. Noffsinger and N.D. Danielson, *Anal. Chem.* 59 (1987) 865.
- [9] J.K. Leland and M.J. Powell, *J. Electrochem. Soc.* 1 (1990) 257.
- [10] F.-R.F. Fan, A. Mau and A.J. Bard, *Chem. Phys. Letters* 116 (1985) 400.
- [11] H.D. Abruna and A.J. Bard, *J. Am. Chem. Soc.* 104 (1982) 2641.
- [12] I. Rubinstein and A.J. Bard, *J. Am. Chem. Soc.* 102 (1980) 6641.
- [13] I. Rubinstein and A.J. Bard, *J. Am. Chem. Soc.* 103 (1981) 5007.
- [14] H.S. White and A.J. Bard, *J. Am. Chem. Soc.* 104 (1982) 6891.
- [15] F. Bolletta, A. Rossi and V. Balzani, *Inorg. Chim. Acta.* 53 (1981) L23.
- [16] N.E. Tokel-Takvoryan, R.E. Hemmingway and A.J. Bard, *J. Am. Chem. Soc.* 95 (1973) 6582.
- [17] W.L. Wallace and A.J. Bard, *J. Phys. Chem.* 83 (1979) 1350.
- [18] P.J. Peerce and A.J. Bard, *J. Electroanal. Chem.* 114 (1980) 89.
- [19] H.S. White, J. Leddy and A.J. Bard, *J. Am. Chem. Soc.* 104 (1982) 4811.
- [20] R.A. Bull, F.-R. Fan and A.J. Bard, *J. Electrochem. Soc.* 131 (1984) 687.
- [21] J. Leddy and A.J. Bard, *J. Electroanal. Chem.* 153 (1983) 223.