

Electrogenerated Chemiluminescence in Poly(dibutoxyphenylenevinylene) Coatings<sup>†</sup>

U. Janakiraman and K. Doblhofer\*

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*

C. Fischmeister and A. B. Holmes

*Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Cambridge, CB2 3RA, U.K.**Received: January 7, 2004; In Final Form: April 13, 2004*

Electrochemiluminescence (ECL) experiments were carried out in acetonitrile electrolytes with platinum electrodes coated with poly(2,3-dibutoxy-1,4-phenylenevinylene), DB-PPV. By application of alternating anodic and cathodic potential steps, positive and negative polarons were produced in the polymer. The annihilation reaction resulted in ECL transients. Model calculations were conducted for analyzing the electron and ion transport processes in the deposit as well as the kinetics of the annihilation reaction. Very good agreement with the experiments was found when the charging of the interfacial double layer was taken into account. The annihilation reaction was concluded to proceed under diffusion control. The emission spectrum was found to have its maximum at 480 nm. This is a shift by  $-10$  nm with respect to the fluorescence spectrum of DB-PPV in chloroform, and by  $-40$  nm with respect to the electroluminescence spectrum observed from the solid-state. The ECL emission spectrum did not depend on the sequence in which the positive and negative polarons were formed, in agreement with the expectation for an ECL mechanism.

## Introduction

When anodic and cathodic products of electrochemical processes react with each other under formation of an electronically excited state, the resulting light emission is termed electrogenerated chemiluminescence or electrochemiluminescence (ECL). This is a well-understood process.<sup>1</sup> The anodic and the cathodic reactions may proceed simultaneously at two electrodes located in such close a distance that the products are transported by diffusion, migration, and/or convection toward each other, and produce ECL when and where they meet.<sup>2,3</sup> Alternatively, the reactants for the chemiluminescence reaction may be produced sequentially by applying to one electrode anodic and cathodic potential steps in succession.<sup>4</sup>

In presence of a concentration gradient and/or electric field, the electron self-exchange reaction between the reactant and the product of each individual electrode process leads to an electron hopping process of charge transport in the homogeneous phase, which acts in a way as if the redox species were moving faster than it actually does.<sup>5,6</sup> The contribution of electron hopping becomes the more significant the larger the electron exchange rate constant and the smaller the physical mobility of the species are. Thus, in “light emitting electrochemical cells, LECs”,<sup>7–12</sup> in particular when they operate in the frozen junction mode, the “motion” of the oxidized and reduced redox ions is actually electron hopping across the redox sites. In some cases, electroactive polymers have been applied as insoluble coatings to electrode surfaces and subjected to ECL experiments in inert electrolytes.<sup>13–17</sup> Aside from the remarkable light emission, such experiments are of interest because the redox and charge-transport properties of the polymers can be conveniently

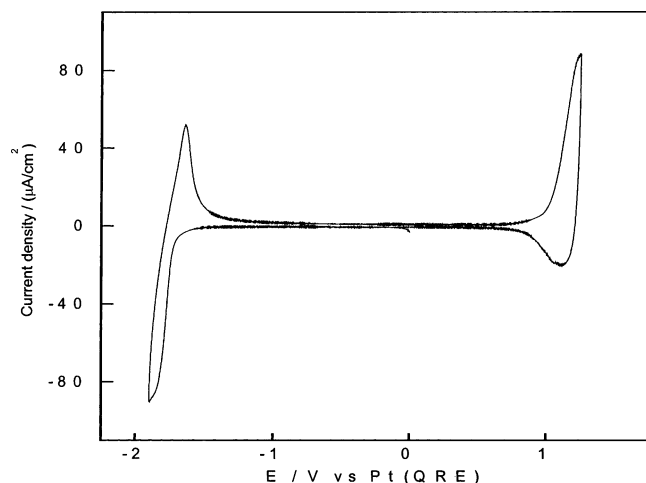
characterized under well-defined conditions. In the present work, the results of an investigation of this kind are presented. Platinum electrodes are coated with poly(2,3-dibutoxy-1,4-phenylenevinylene), DB-PPV.<sup>18</sup> This material is found to be more stable, in particular toward electrochemical oxidation in acetonitrile electrolyte, than the poly(2-ethylhexyloxy-5-methoxy-1,4-phenylenevinylene), MEH-PPV, used previously.<sup>15–17</sup> The classical method of applying alternating anodic and cathodic potential steps to the coated electrodes is employed. Thus, the ECL transients can be simulated conveniently by model calculations, and new insights into the mechanisms of electron and ion transport in the solvated polymer phase are obtained.

## Experimental Section

Platinum cylinders of diameter 3 mm and length 4 mm were used as the electrodes. With a thin platinum wire attached to one circular face, they were molten into glass tubes so that only the other circular face of the platinum cylinders was exposed. This free surface was polished with 0.7  $\mu\text{m}$  diamond paste and cleaned ultrasonically. The polymer was synthesized in the authors' laboratories in Cambridge, U.K..<sup>18</sup> It was deposited on the cleaned platinum surface by applying (with a syringe) a defined volume of a solution of the polymer in chloroform ( $10^{-4}$  g of DB-PPV in 1  $\text{cm}^3$  of chloroform). The film thicknesses given in the following were obtained by assuming that the evaporation of the solvent yields a homogeneous polymer film. The coated, glass-mantled electrodes were inserted into the electrochemical glass cell that contained the salt used as background electrolyte. To remove thoroughly water and atmospheric oxygen, which both react vigorously with the polarons, the electrode and the salt were heated in the cell to 50 °C under vacuum for 2 h. Eventually, the acetonitrile was transported by argon pressure from the original bottle (Aldrich, <0.01% water) into the glass cell, where the dissolution of the

\* Corresponding author. Telephone: +49-30-8413 5123. Fax: +49-30-8413 5106. E-mail: doblhofer@fhi-berlin.mpg.de.

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**Figure 1.** Cyclic voltammogram obtained with a platinum electrode coated with 0.3  $\mu\text{m}$  DB-PPV, in an electrolyte with 0.1 M (TBA)BF<sub>4</sub> in acetonitrile. Sweep rate: 100 mV/s.

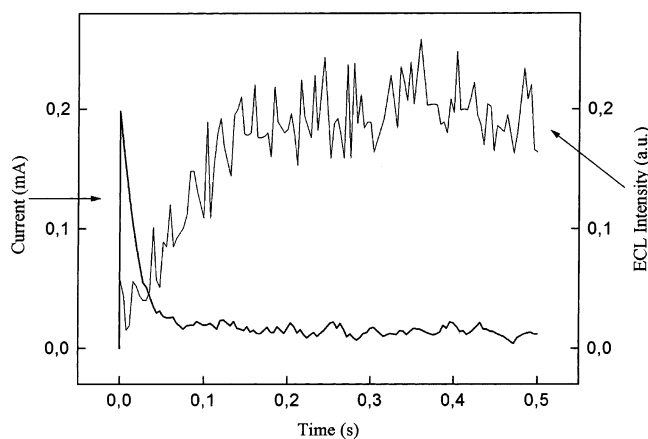
salt was accelerated by a magnetic stirrer. The electrochemical experiments were carried out with conventional potentiostatic equipment in the one-compartment cell. Both the quasi-reference and the counter electrodes were platinum wires. The total light emission intensity was measured with an RCA photomultiplier tube type 7326 supplied with 1000 V. The ECL emission spectra were measured with a Hamamatsu High Sensitivity spectrometer model C7473-36, provided by Hamamatsu Deutschland GmbH, Herrsching, Germany.

For comparison, the ECL emission from the very efficient<sup>1</sup> classical 9,10-diphenylanthracene (DPA) system<sup>4</sup> was studied along with the ECL emission from the polymer-coated electrodes. The DPA-ECL intensities were determined in the same electrochemical cell, with an uncoated platinum electrode operating in an acetonitrile electrolyte that contained 1 mM 9,10-diphenylanthracene, at a comparable faradaic current, and with the same photomultiplier geometry. Under these conditions, the emission intensities observed with the polymer-coated electrodes were at least 2 orders of magnitude smaller than the corresponding DPA-ECL intensities. Thus, under the described experimental conditions the quantum efficiency of the ECL process in the PPV-type polymer film was concluded to be at the most of the order of 0.1%.

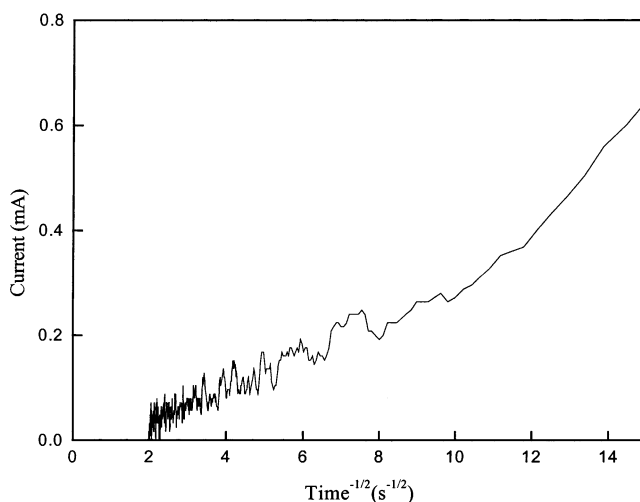
## Results

Figure 1 is the cyclic voltammogram obtained with a DB-PPV coating of thickness 0.3  $\mu\text{m}$  in an acetonitrile electrolyte containing 0.1 M tetra(*n*-butyl)ammonium tetrafluoroborate ((TBA)BF<sub>4</sub>). Note the absence of charge-transfer reactions over a potential range of approximately 2.5 V extending between the potentials of anodic oxidation and cathodic reduction of the polymer. After cycling times on the order of 10 min, the voltammetric peaks decrease markedly because of dissolution and decomposition of the polymer, which take place in particular at positive potentials.<sup>19</sup>

For generating ECL, a triple-potential step sequence is repetitively applied to the polymer-coated electrodes immersed in the nonaqueous inert electrolyte. Consider first the generation of "anodic ECL". After a waiting time,  $t_w$ , at the potential  $E = 0$  V (all polarons are discharged), a negative potential step to  $E_{\text{start}}$  is applied.  $E_{\text{start}}$  is close to the potential of the cathodic current maximum, Figure 1. After negative polarons have been produced for time  $t_f$ , the potential is stepped to the positive potential  $E_{\text{end}}$ , which is close to that of the anodic current peak,



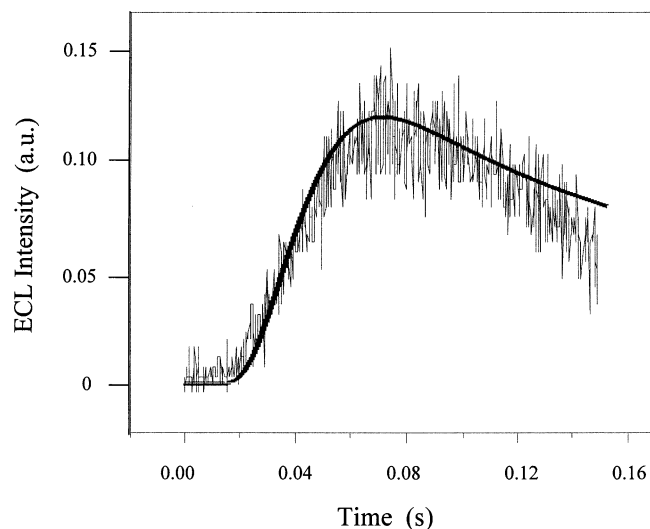
**Figure 2.** Typical current and luminescence transients measured in an "anodic ECL" experiment, with the time  $t = 0$  corresponding to the application of the large potential step. MEH-PPV coated electrode in 0.1 M TEABF<sub>4</sub>/acetonitrile electrolyte, electrode area 0.07 cm<sup>2</sup>.



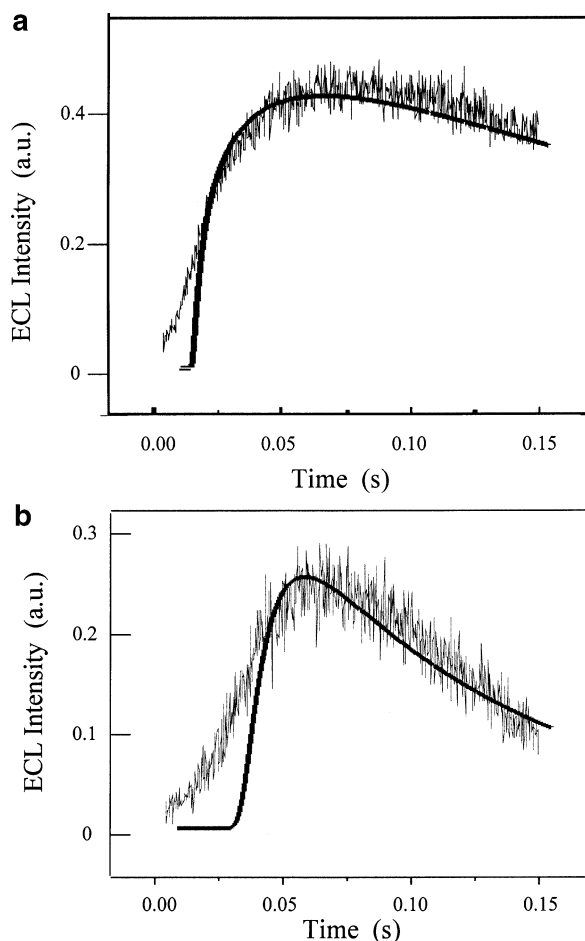
**Figure 3.** Current transient following a potential step from 0.0 to 1.3 V, on the  $t^{-1/2}$  scale ("Cottrell plot"). The system is the same as in Figure 1.

Figure 1. The positive polarons formed at  $E_{\text{end}}$  react in the annihilation reaction with the negative polarons present in the polymer, generating "anodic ECL" for time  $t_r$ . Thereafter, the potential is stepped back to  $E = 0$  V. For "cathodic ECL" the pulse sequence is inverted. Good signals of both negative and positive ECL could be observed with  $t_f = t_r = 150$  ms and a waiting time  $t_w = 200$  ms.

Figure 2 shows the rise and decay of current and luminescence intensity following a typical positive potential step that induces "anodic ECL". Note that the luminescence intensity rises relatively slowly after the decay of the current. This is strong support for the view that the light emission is the result of the chemiluminescence reaction between the positive and negative polarons. The slower the transport of the polarons the longer will be the duration of the ECL. Thus, ECL from the polymer-coated electrodes is normally of larger duration (up to seconds) than that in the solution phase (of the order of milliseconds<sup>4</sup>). If the luminescence mechanism were of the solid-state electroluminescence type,<sup>1</sup> the variation of the emission intensity would be strictly coupled with the time-dependent rate of charge injection across the electrode/polymer interface, which is clearly not the case here. Figure 3 shows a current transient following a potential step from 0.0 to 1.3 V, on the  $t^{-1/2}$  scale (positive polarons are formed from the neutral polymer).

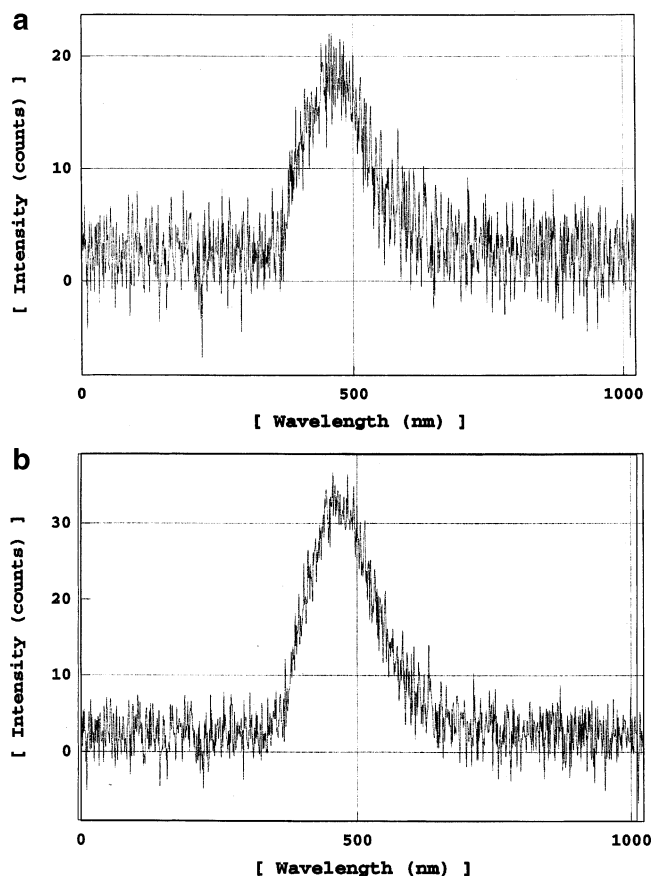


**Figure 4.** ECL transient following a “cathodic ECL” potential step from +1.3 V to −1.85 V. The experiment was conducted shortly ( $\approx 1$  min) after the platinum electrode coated with DB-PPV had been immersed into 0.1 M (TBA)BF<sub>4</sub>/acetonitrile. The solid line represents the simulated transient, with  $k_{\text{ex}} = 4 \times 10^4 \text{ mol}^{-1} \text{ L s}^{-1}$ ,  $D^{\text{app}} = 4.5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ ,  $R_u = 19\,150 \, \Omega$ , and  $C_{\text{dl}} = 1.3 \, \mu\text{F}$ .



**Figure 5.** (a) “Anodic” and (b) “cathodic ECL” with a DB-PPV film and (TBA)BF<sub>4</sub>/acetonitrile electrolyte as in Figure 4. However, the experiments were conducted after about 10 min experimenting in the electrolyte. The solid line represents the simulated transients obtained with the following fit parameters: (a)  $k_{\text{ex}} = 3 \times 10^4 \text{ mol}^{-1} \text{ L s}^{-1}$ ,  $D^{\text{app}} = 6 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ ,  $R_u = 1200 \, \Omega$ , and  $C_{\text{dl}} = 1 \, \mu\text{F}$ ; (b)  $k_{\text{ex}} = 1 \times 10^4 \text{ mol}^{-1} \text{ L s}^{-1}$ ,  $D^{\text{app}} = 1 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ ,  $R_u = 1200 \, \Omega$ , and  $C_{\text{dl}} = 3 \, \mu\text{F}$ .

The reported experiments are conducted with (TBA)BF<sub>4</sub> as the background electrolyte. When (TBA)ClO<sub>4</sub> is used instead,



**Figure 6.** ECL emission spectra obtained from “cathodic” (upper picture) and “anodic ECL” with a DB-PPV-film. Electrolyte: 0.1 M (TBA)BF<sub>4</sub> in acetonitrile.

the voltammetric oxidation current at a given positive potential is smaller, indicating that the mobility of ClO<sub>4</sub><sup>−</sup> in the polymer phase is significantly smaller than that of BF<sub>4</sub><sup>−</sup>. On the other hand, there is little difference between electrolytes containing tetra(ethyl)ammonium (TEA) and tetra(*n*-butyl)ammonium tetrafluoroborate, except in the case of cross-linked films where the cathodic current can be suppressed in the case of (TBA)-BF<sub>4</sub>.<sup>19</sup>

Figure 4 shows an ECL transient with a particularly well pronounced delay between the potential step and the onset of luminescence. This can be associated with the large value of  $R_u$  of the coating freshly immersed into the electrolyte. The delay becomes shorter as the value of  $E_{\text{end}}$  is increased. It also tends to decrease with continued pulsing, because  $R_u$  decreases as a consequence of better solvation and swelling of the film. The two ECL transients of Figure 5 were obtained after about 10 min of experimenting, i.e., after the film had swollen. The two transients appear similar, suggesting that there is little difference between “anodic” and “cathodic” ECL. Also, the emission spectra of “anodic” and “cathodic” ECL are identical, which strongly supports this view (see Figure 6).

## Discussion

The cyclic voltammogram of Figure 1 shows absence of faradaic current flow in the potential range between anodic oxidation and cathodic reduction of the polymer. It resembles that of polycyclic aromatic compounds, such as 9,10-diphenyl-anthracene.<sup>4</sup> This is in agreement with the view that the anodic oxidation of the polymer corresponds to extraction of an electron from the highest occupied  $\pi$  orbital of the extended conjugated system, forming the positive polaron, P<sup>+</sup>. Cathodic reduction

corresponds to injection of an electron into the lowest unoccupied  $\pi^*$  orbital, producing the negative polaron,  $P^-$ . The polarons  $P^+$  and  $P^-$  react with each other, forming the excited state,  $P^*$  that may decay under emission of light,  $h\nu$ :



The system is analyzed by using the electrochemical concepts developed for permeable polymer coatings.<sup>20</sup> The transport of the polarons and the kinetics of the annihilation reaction in the polymer are treated on the basis of the following three reaction/diffusion equations:

$$\frac{\partial C_P}{\partial t} = -\frac{\partial J_P}{\partial x} + 2k_{\text{ex}}C_{P^+}C_{P^-} \quad (2a)$$

$$\frac{\partial C_{P^+}}{\partial t} = -\frac{\partial J_{P^+}}{\partial x} - k_{\text{ex}}C_{P^+}C_{P^-} \quad (2b)$$

$$\frac{\partial C_{P^-}}{\partial t} = -\frac{\partial J_{P^-}}{\partial x} - k_{\text{ex}}C_{P^+}C_{P^-} \quad (2c)$$

where  $C$  and  $J$  are the concentrations and the fluxes, respectively, of the species defined by the subscript, and  $k_{\text{ex}}$  is the rate constant of the homogeneous annihilation reaction.

The fluxes of charged species in the polymer phase are defined by both activity gradients (diffusion) and the electric field (migration).<sup>20–22</sup> For simplification, in the present analysis this diffusion–migration transport is treated in terms of the mathematics of pure diffusion. This is considered acceptable because electroneutrality coupling between the polarons and counterions will effectively lead to transport of neutral ion pairs. It is known that the response of electrochemical diffusion/migration systems normally follows the same functional relationship as that of systems controlled by pure diffusion.<sup>21,22</sup> Indeed, the current transient represented in Figure 3 on the  $t^{-1/2}$  scale shows straight-line behavior at longer times, as expected for diffusional transport. Of course, the effective diffusion coefficients involved in this treatment are affected by migration, and may thus deviate significantly from the physical diffusion coefficients of the individual ionic species.

Assuming that four DB–PPV units constitute one polaronic site, and that the density is  $0.6 \text{ g cm}^{-3}$ , the concentration of polaronic sites is  $C_P = 6.1 \times 10^{-4} \text{ mol cm}^{-3}$ . With this value, the analysis of the transient of Figure 3 on the basis of Cottrell's equation yields an apparent diffusion coefficient of positive polarons,  $D^{+\text{app}} = 2.6 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ . Such a small value is in agreement with the above considerations that the rate of charge transport is largely defined by the mobility of the counterions, in the considered case by  $\text{BF}_4^-$ . By applying potential steps from 0 to  $-1.7 \text{ V}$ , Cottrell plots corresponding to the formation of negative polarons are obtained. The analysis yields values of the apparent diffusion coefficient  $D^{-\text{app}}$  that are smaller by typically 30% than  $D^{+\text{app}}$ . Clearly, the cause for this is the greater mass and bulkiness of the counterions  $(\text{C}_4\text{H}_9)_4\text{N}^+$ . However, the reproducibility of such determinations of diffusion coefficients was not better than about 30%. Furthermore, both polaronic diffusion coefficients increased with time, starting with the order of  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ , Figure 4, and arriving normally at about  $1 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  after 10 min pulsing, Figure 5. Thus, in the simulations, the further simplifying assumption was introduced that the apparent diffusion coefficients for positive and negative polarons would be equal, i.e.,  $D^{-\text{app}} \approx D^{+\text{app}} \approx D^{\text{app}}$ .

It is clear that the effective interfacial electrode potential,  $E_F$  (causing faradaic current), differs from the applied potential  $E$  by  $IR_u$ , where  $R_u$  is the uncompensated resistance of electrolyte and film. Consider the large potential step from  $E_{\text{start}}$  to  $E_{\text{end}}$  (regularly near 3 V), which produces the second polaronic species, and thus luminescence. This potential step generates a large current transient  $I_C(t)$  associated with the charging of the interfacial double layer of capacitance  $C_{\text{DL}}$ . Furthermore, the faradaic reaction of polarons (which have been produced in the forward step) leads to a significant current  $I_F(t)$  that flows before  $E_F$  reaches values near  $E_{\text{end}}$ , at which the electrochemical production of the second polaronic species starts to proceed at a significant rate. These two processes lead to a delay between the moment of the potential step (from  $E_{\text{start}}$  to  $E_{\text{end}}$ ), and the beginning of the second charge-transfer reaction, as  $E_F$  approaches  $E_{\text{end}}$ .

$$E_F(t) = E_{\text{start}} + \int_0^t \frac{I_C(t)}{C_{\text{DL}}} dt \quad (3)$$

$$I(t) = I_F(t) + I_C(t) \quad (4)$$

The additional uncompensated resistance introduced by the coating enhances the time constant for charging the double-layer. Thus, it tends to increase the delay between the application of the potential step and the rise of ECL, as observed in particular in the experiment of Figure 4.

The simulation of the concentration profile and the current associated with the formation of the first polaronic species (at  $E_{\text{start}}$  in the “forward” step, see Figure 3) is conducted analytically on the basis of the Cottrell concept; i.e., it is assumed that at the interface the polymer is instantaneously oxidized or reduced to the polaronic state, and the rate of interfacial charge-transfer is determined by the diffusional flux of polarons from the interface into the bulk polymer.<sup>23–25</sup> This straightforward treatment appears appropriate, considering first that in the sequence of potential steps each “forward” step is preceded by a relaxation time of the system at  $E = 0 \text{ V}$ , at which the polymer phase is transformed into the neutral state. Second, the concentration profile of interest for the ECL analysis is the one established by the end of the period  $t_f$  (typically 150 ms), at which time the delayed start of the charge-transfer reaction caused by double-layer charging is negligible.

The simulation of the concentration profiles, the current, and the ECL transient following the second, large potential step (to  $E_{\text{end}}$ ) is computed by the finite difference method.<sup>24,25</sup> The reaction/diffusion problem is solved as discussed by Bard and Faulkner<sup>25</sup> and, in particular, as described previously<sup>4</sup> for solution-ECL with DPA. As indicated above, for obtaining model transients that reproduce this delayed onset of luminescence, it is necessary to evaluate  $E_F$  on the basis of eqs 3 and 4 for each time step. Values of  $C_{\text{DL}}$  and  $R_u$  in the presence of the coating are obtained by analyzing the current decay following small potential steps in the potential range between the voltammetric peaks (the values of  $C_{\text{DL}}$  are assumed to be independent of the electrode potential). With such values of  $E_F$ , the concentrations of polarons and neutral polymer sites at the interface metal/polymer are obtained via the Nernst equation at each time step (with the activities assumed to be equal to the concentrations). The rate of the interfacial charge-transfer is then determined as the diffusional flux of polarons from/to the interface. For the numerical analysis, first the duration of the experiment and a time increment are chosen. Starting values of apparent diffusion coefficients of polarons for the simulation



are obtained via the Cottrell equation from experiments as shown in Figure 3. With this information the vertical distance between the parallel planes dividing the polymer space in front of the metal electrode is defined. Finally, a value of the annihilation rate constant is estimated, and the development of the concentration profiles of positive and negative polarons and of neutral polymer sites is calculated for successive time intervals in the same way as described in our previous work with DPA.<sup>4</sup> The decay of the excited state formed in the annihilation reaction is always considered instantaneous. Consequently, the obtained rate of the annihilation reaction is directly taken as the simulated luminescence emission intensity, and correlated with the experimental luminescence transient. The values of the apparent diffusion coefficient and of the annihilation rate constant are then varied until a reasonable match between simulation and experiment is obtained; see the model transients included as solid lines in Figures 4 and 5.

The simulated luminescence transient represented in Figure 4 (full line in the figure) is obtained with the rather large series resistance,  $R_u \approx 19 \text{ k}\Omega$ . The series resistance decreases within 10 min of operation to approximately  $1 \text{ k}\Omega$ , because the film takes up electrolyte and swells. This leads to a decrease of the time constant  $R_u C_{dl}$ , i.e., in the swollen state  $E_F$  approaches  $E_{end}$  faster. The analysis for two swollen films is shown in Figure 5. It yields apparent diffusion coefficients of the polarons that are 2 orders of magnitude larger than in the unswollen film. The relatively poor fit of the rising portion of the ECL transients is most probably caused by inhomogeneities of the coating, in particular of its thickness.

The shape of the model-ECL transients depends quite strongly<sup>4</sup> on the model-rate constant of the annihilation reaction,  $k_{ex}$ . Thus, the value  $k_{ex} \approx 10^4 \text{ mol}^{-1} \text{ L s}^{-1}$  obtained in the procedure of varying the fit parameters is considered precise to within a factor of 2. Comparing this value of  $k_{ex}$  with that of a diffusion-controlled homogeneous electron exchange reaction in liquid solutions<sup>26</sup> ( $\approx 10^{10} \text{ mol}^{-1} \text{ L s}^{-1}$ ), it appears small. However, taking into account the differences in the diffusion coefficients (the apparent diffusion coefficients of polarons,  $D^{app} \approx 10^{-11} - 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ; the diffusion coefficients in liquid solutions,  $D \approx 10^{-5} - 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ), the determined values of  $k_{ex}$  point to a diffusion-controlled rate of the annihilation reaction in the homogeneous polymer phase.

The emission spectra of "anodic ECL" and "cathodic ECL" are shown in Figure 6. The emission maxima, at 480 nm, are the same for both "anodic" and "cathodic" ECL. This is exactly what would be expected for an ECL process, in which the annihilation reaction between  $P^+$  and  $P^-$  yields the excited-state independent of the order in which  $P^+$  and  $P^-$  were formed. The emission maximum is found to differ little from the fluorescence maximum of the polymer dissolved in chloroform (490 nm), which is in line with the consideration that the  $\pi^* \rightarrow \pi$  transition involves a small change in molecular dipole moment and thus a small dependence on the dielectric constant of the medium. The emission of the solid-state EL device based on DB-PPV as well as the photoluminescence from solid DB-PPV is known<sup>18</sup> to have both the maximum at 519 nm.

## Summary and Conclusions

The ECL results presented above demonstrate that coatings of DB-PPV on platinum electrodes in acetonitrile electrolyte behave as permeable electroactive films with both mobile electronic and ionic charge carriers. For the polarons, relatively small values of apparent diffusion coefficients are found ( $10^{-11} - 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ). This is proposed to be caused by electroneu-

trality coupling with counterions, which largely determine the rate of transport of the ion pairs.

For obtaining "anodic ECL", at first the negative polarons are produced at a negative potential; then a large positive potential step (up to 3 V) leads to formation of the positive polarons. The annihilation reaction between negative and positive polarons in the film proceeds with a rate constant  $k_{ex} \approx 10^4 \text{ mol}^{-1} \text{ L s}^{-1}$ . It is proposed that this rate is close to diffusion control, the relatively small absolute value being caused by the small apparent diffusion coefficients of the polarons. The overall quantum yield of the luminescence produced in the annihilation reaction is small, corresponding to less than 1% of that observed from solutions of 9,10-diphenylanthracene under similar conditions on uncoated noble-metal electrodes. The sequence of potential steps may be inverted, producing "cathodic ECL". The emission spectra obtained in anodic and cathodic ECL are identical, and the luminescence transients are similar. This indicates that indeed the reaction between the positive and negative polarons produces the excited state, independent of the sequence of their formation.

The transport of the polarons into the polymer phase is analyzed on the basis of a semi-infinite linear diffusion model. The transport processes in the film, caused by the large potential step, are simulated under consideration of charging of the electric double layer and of the current for discharging the polaronic species formed in the first potential step. These currents produce an  $IR_u$  drop that hinders the effective potential  $E_F$  from reaching the value required for significant production of the second polaronic species, thus retarding the appearance of ECL (see in particular Figure 4).

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