Charge Transport in Luminescent Polymers Studied by in Situ Fluorescence Spectroscopy

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Modulation of the photoluminescence of poly-[2,7-(fluorene)-1,4-(phenylene)] can be attained by reversible electrochemical modification of the conjugated chain (p- or n-doping). Controlled injection of charge quenches the fluorescent emission of the conjugated polymer. The injection of holes completely eliminates the emission, while the electrons only quench up to one-third of the initial fluorescence of the polymer. Analogous quenching effects have been previously reported for solid-state organoelectronic devices. Electrochemical Stern–Volmer plots permit the estimation of the relative mobility of charge carriers in the polymer layer. The mobility of holes is 1 order of magnitude higher that the mobility of electrons, as determined by this method.

1. Introduction

Fluorescence spectroscopy coupled to electrochemical systems, electrochemical in situ fluorescence spectroscopy, has been employed for the characterization of the redox behavior of several systems, that is, hydrogels,[1] indole trimers,[2] perylenes,[3] and lipidic layers.[4] Scarce literature can be found concerning the characterization of conductive polymers by in situ fluorescence spectroscopy;[5,6] however, this technique is a powerful tool for the characterization of conductive polymers with emissive properties.

Fluorene-based conjugated polymers are highly efficient emitters and have applications as fluorescent sensors[7] or blue emitters in organic displays (OLEDs).[8,9] An advantage of this polymer is the facile functionalization of the side-chain at the C9 site that provides the possibility of improving the solubility and processability.[10,11]

The quantum efficiency of the fluorescent emission of luminescent polymers is lowered during its function as diodes due to the quenching of the fluorescence by the injection of charges. This is a well-known phenomenon extensively studied by P. F. Barbara and co-workers using novel fluorescence–voltage single-molecule spectroscopy.[12] The authors have shown that the fluorescent emission of a polymer in a hole-transporting device depends on the applied bias potential.[12–15]

The oxidation of conjugated polymers and formation of a polaron (radical-cation) increases its conductivity, due to the introduction of charge carriers (p-doping) with a high mobility along the conjugated chain. Many conjugated polymers are good hole conductors with a mobility ranging from 10^{-1} to 10^{-7} cm^2 V^{-1} s^{-1}; however, it is less habitual to find electron-conductive polymers.[16,17] Concretely, fluorene-based polymers can be doped both by oxidation (p-doping) and by reduction (n-doping), but the mobility of electrons is usually 2–3 orders of magnitude lower than the hole mobility.[18]

The spectroelectrochemical behavior of a neutral poly-[2,7-(fluorene)-1,4-(phenylene)] was performed in this work to clarify the doping mechanism and to determine the relative charge carrier mobility in this conjugated polymer.

2. Experimental Section

Poly[9,9-bis(6′-bromohexylfluoren-2,7-diyl)-*alt*-co-(benzen-1,4-diyl)], shown in Chart 1, has been synthesized via the Suzuki coupling reaction using 1,4-phenyldiboronic acid and 2,7-dibromo-9,9-bis(6′-bromohexyl)-fluorene as starting materials. The average molecular weight of the produced polymer was $M_W = 25.7 \times 10^3$ g/mol, yielding a 35 monomer units (fluorene-phenylene) per polymer chain. Details on the preparation and characterization of the polymer were presented in a previous paper.[10]

CHART 1
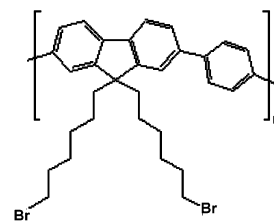
Solutions of the polymer (5 mg/mL in THF) were spin-casted over ITO conductive glass. The solvent for electrochemical measurements was acetonitrile (Merck, HPLC grade), and tetrabutylammonium tetrafluoroborate (Aldrich 99%) was used as supporting electrolyte. A platinum wire was used as auxiliary electrode. The potentials are referred to an Ag/AgCl electrode (3 M KCl, Crison) immersed in the same solution. The oxygen was purged from the electrochemical cell by an argon flow.

Spectroelectrochemical measurements (in situ fluorescence) were performed in a modified fluorescence cell (1 cm-length quartz cell), the design of which is shown in Figure 1.

The cell is capped with a silicone plate, which also serves as electrode support. The working electrode was a transparent ITO-glass electrode covered with the polymer. The electrode was placed with an angle near 45°. The counter electrode was a platinum wire, and a silver wire was used as the pseudo-

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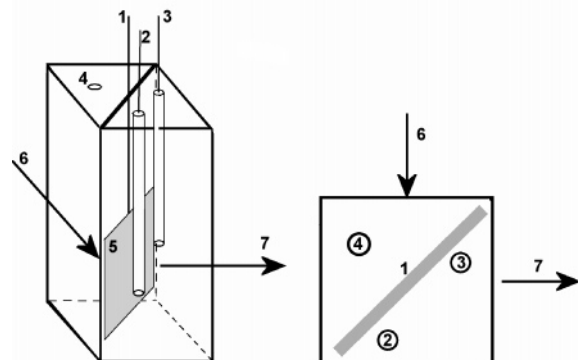*J. Phys. Chem. B, Vol. 110, No. 12, 2006* **5915**

Figure 1. Spectroelectrochemical cell for in situ fluorescence: (1) connection for working electrode, (2) counter electrode, (3) reference electrode, (4) gas inlet, (5) working electrode: ITO glass, (6) source excitation beam, and (7) emission beam to detector.

reference electrode, both immersed in the same solution and protected by a glass capillary tube. Fluorescence spectra were acquired at room temperature using a PTI QuantaMaster model QM-62003SE spectrofluorimeter. Samples were excited a 370 nm (0.5-nm band-pass). The emission spectra were collected between 380 and 650 nm, and the total time of acquisition was 27 s per scan.

3. Results and Discussion

A series of spectra were recorded in the oxidation (p-doping) of the polymer in a voltammetric scan at low scan rate (1 mV s^{-1}) performed in the spectroelectrochemical cell. The electrode was immersed in the electrochemical cell at a controlled potential of 0.9 V, and the scan started toward more positive potentials. Figure 2a shows the fluorescence spectra obtained during a positive scan up to 1.6 V.

The initial fluorescence spectrum of the polymer obtained at open circuit and at the initial potential (0.9 V) shows an emission peak in the blue zone with a maximum at 422 nm and a well-defined vibronic feature at 443 nm. As the potential grows, the shape of the spectrum does not change substantially and there is no shift in the position of the emission bands. Figure 2b shows the value of integrated intensity of the fluorescence spectra as a function of the applied potential. The intensity values remain unvaried at potentials lower than 1.10 V with the polymer in the semiconducting state. The intensity of the spectrum starts to decrease at potentials more positive than 1.10 V, reaching a minimum of emission at 1.45 V. At this potential, the fluorescence of the polymer is completely quenched and further oxidation does not modify this situation. The fluorescent emission of the polymer in its initial states comes from the flourophore units. As positive charges are introduced, the polymer suffers the quenching of its fluorescence. This result is analogous to the quenching of the photoluminescence related to the injection of holes in hole-transporting diodes.[12] Attending to the shape of the intensity versus potential curve, which is very similar to the evolution of resistivity versus potential for conductive polymers,[19] the doping level of the polymer reaches a maximum from 1.45 V, and the electronic band that promotes the conductivity is charge-saturated from that potential.

Voltafluorograms were obtained by recording the intensity of the emission at 420 nm while a cyclic voltammogram was performed. Figure 3 shows the cyclic voltammogram and the simultaneous voltafluorogram obtained at a scan rate of 100 mV s^{-1}. The quenching of the fluorescence is observed in the forward scan from 1.10 V. The initial fluorescent intensity of
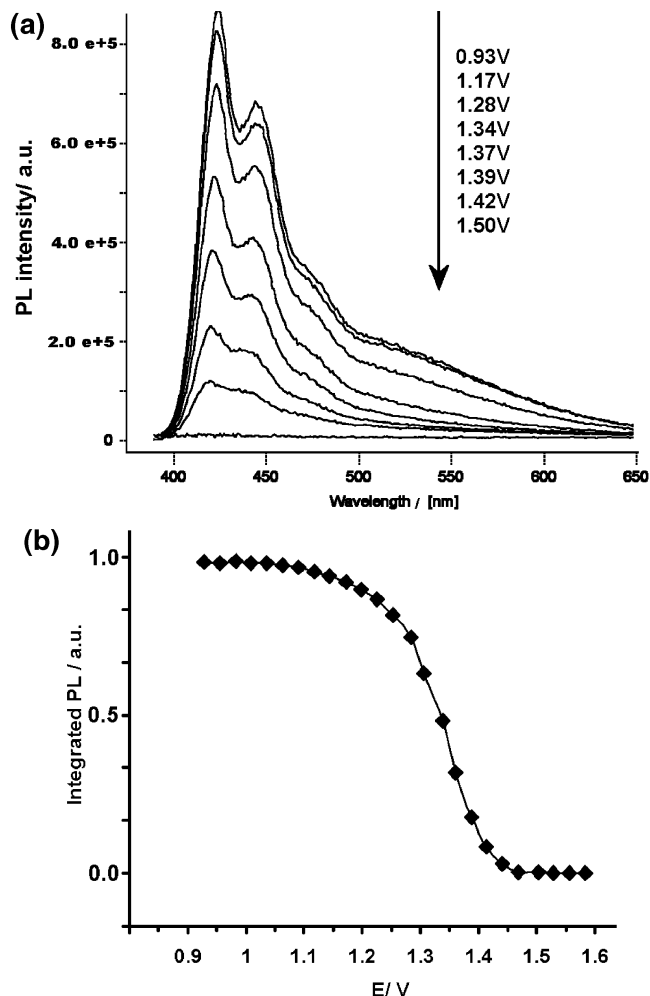

Figure 2. (a) Selected fluorescence spectra of ITO-polymer electrode obtained during an oxidation scan (potentials indicated in the figure). Scan rate 1 mV s^{-1}, excitation wavelength 370 nm. (b) Integrated intensity of the emission spectra between 380 and 650 nm as a function of the applied potential.
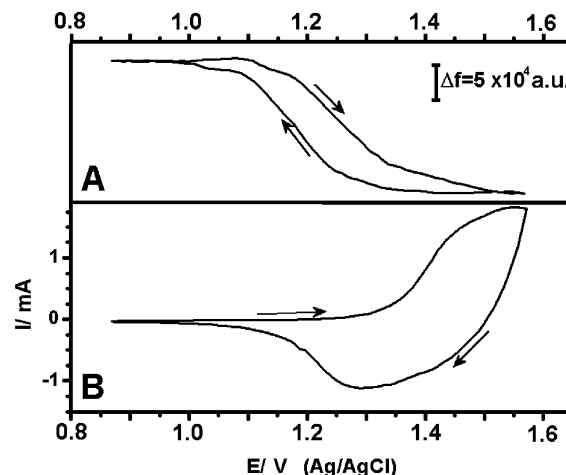

Figure 3. Cyclic voltafluorogram (A) and cyclic voltammogram (B) of an ITO-polymer electrode in a solution of 0.1 M tetrafluoroborate tetrabutylammonium in acetonitrile. Scan rate 100 mV s^{-1}. Excitation 370 nm, emission 420 nm.

the polymer is recovered after the dedoping process in the backward scan, indicating the reversibility of p-doping.

To correlate the emission intensity with the redox state of the polymer, the plots of fluorescence intensity were recorded as a function of voltammetric charge. Figure 4 shows the
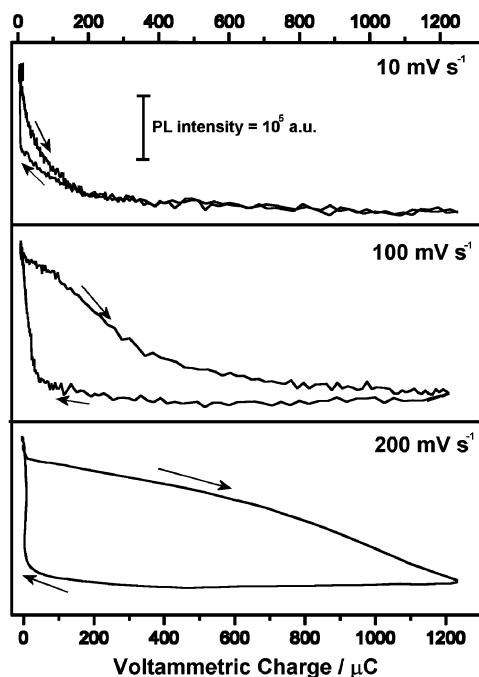
Figure 4. Fluorescence−voltammetric charge plots obtained during the cyclic voltammogram of an ITO-polymer electrode at different scan rates. Polarization program: 0.85 V → 1.6 V → 0.85 V.

charge−fluorescence plots obtained at three different scan rates (10, 100 and 200 mV s^{-1}). For the experiment performed at 10 mV s^{-1}, the slow introduction of charge produces the complete quenching of the fluorescence at values around +300 μC (100% doping). Further oxidation of the polymer produces an over-population of the conducting band. During the dedoping process (reverse scan of Figure 4), the excess of charge is removed without modification of the fluorescence intensity, reaching a charge around +300 μC where the fluorescence is recovered.

As the sweep rate is increased, the curve presents a significant hysteresis, which is more evident at the highest scan rate 200 mV s^{-1}. Now, the injection of charge in the ITO|polymer interface and its migration across the polymer chains to the outer surface of the electrode is a fast process. During the doping process at high scan rate, the fluorescent species in the polymer film suffer a slow kinetic conversion to nonfluorescent species. This is indicative that the charge added to the polymer is initially placed in the conjugated chains near the polymer|solution interface and the charge injected overpopulates the conductance band of the polymer in those regions. The complete doping of the complete polymeric layer happens when the charge diffuses in a slow process controlled by the electrolyte diffusion along the whole polymer.[20] Conversely, the curve fluorescence versus charge during the dedoping process is similar for all of the scan rates studied, indicating a nonkinetically hindered process for the recovery of fluorescent species. The film of the polymer in the reduced form has a compact structure that may impede the transients of the ions that balance the electronic charge introduced in the polymer upon oxidation. The reorganization of the polymer chains and the swelling of the polymer produce an open more accessible film upon oxidation. The diffusion process occurring during the dedoping happens in the open-oxidized polymer in a fast manner.[2]

The shape of the voltafluorograms obtained are very similar to the single-molecule field-induced fluorescence modulation obtained with photooxidized poly[2-methoxy, 5-(2′-ethylhexyl-oxy)-*p*-phenylenevinylene] (MEH-PPV) in hole transporting electronic devices.[12] These authors also show slow kinetics for
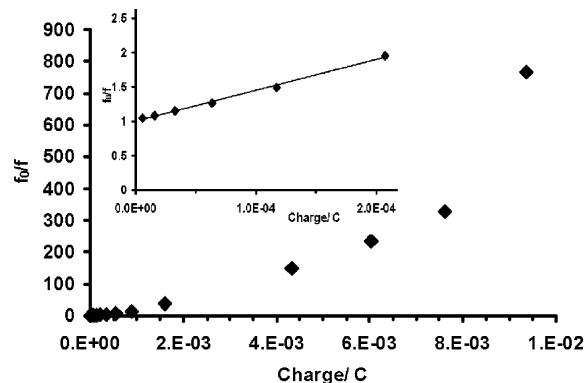

Figure 5. Electrochemical Stern−Volmer plot obtained in the oxidation of ITO-polymer electrode (positive charge vs normalized fluorescence). Scan rate 1 mV s^{-1}. Excitation 370 nm, emission 380−650 nm. Inset: Magnification of the plot between 0 and +0.2 mC.

the charge-transfer rate in this type of polymer, as studied at different sweep rates for the bias potential. The results obtained in this work by electrochemical methods present several analogies with the work performed by Gesquiere et al. in solid-state electronic devices,[14] indicating an equivalence of the phenomenology described for electronic devices and electrochemical systems.

Data of the normalized integrated photoluminescence (f_0/f) as a function of the introduced charge are shown in Figure 5, where the extent of the fluorescence quenching due to the injection of positive charges can be measured. To avoid kinetic problems by electrolyte diffusion and to consider only the effects produced by charge mobility across the polymer, the experiment was performed in quasi-stationary conditions (scan rate 1 mV s^{-1}), acquiring simultaneously the complete emission spectrum. We assume that upon doping at low scan rate the polymer can be considered as a nonstoichiometric material, homogeneously oxidized.[20] The oxidation of the polymer does not yield a number of oxidized or reduced single chains while the rest of polymer remains in semiconducting form, but the whole polymeric layer is partially oxidized due the delocalization of the charge along the conjugated backbone.[21]

Figure 5 is equivalent to a Stern−Volmer plot, considering the amount of positive charge injected as quencher. This electrochemical Stern−Volmer plot (ESV plot) shows a linear range up to +0.2 mC (inset of Figure 5). For the analysis of these results, an equivalent electrochemical Stern−Volmer equation can be derived as:

$$\frac{f_0}{f} = 1 + K_E^+[C] = 1 + K_V^+ Q \qquad (1)$$

where f_0 and f are the fluorescent emissions in the absence and presence of quencher, respectively, K_E^+ is the electrochemical quenching constant, $[C]$ is the positive charge introduced per unit volume of polymer (V), Q is the charge injected, and K_V^+ is the ESV constant per volume of polymer. The charge introduced in the polymer is delocalized along the conjugated chain due to the mobility of the hole in this polymer. In conventional Stern−Volmer plots, the Stern−Volmer constant K_D is proportional to the diffusion coefficient of the quencher, as expressed by the Smoluchowski equation:

$$K_D = 4\pi R N \tau_0 D \qquad (2)$$

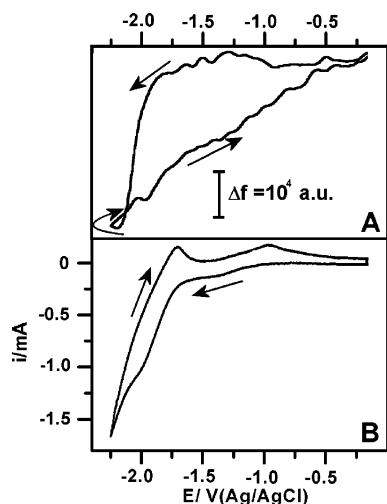where R is the collision radius, N is Avogadro's number, τ_0 is

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Figure 6. Cyclic voltafluorogram (A) and cyclic voltammogram (B) of an ITO-polymer electrode in a solution of 0.1 M tetrafluoroborate tetrabutylammonium in acetonitrile. Scan rate 100 mV s^{-1}. Excitation 370 nm, emission 420 nm.

the lifetime of the excited state in the absence of quencher, and D is the diffusion coefficient.

An equivalent formulation for the electrochemical quenching would drive one to consider K_E^+ proportional to the diffusion coefficient of the quencher (D^+) along the polymer film:

$$K_E^+ = \phi D^+ \tag{3}$$

In the oxidative quenching of the polymer, the positive charge injected diffuses through the polymer film, and its diffusion is equivalent to its mobility as expressed by the Einstein relation:

$$D^+ = \frac{k_b T}{z} \mu_h \tag{4}$$

with z being the charge of the carrier, k_b the Boltzmann constant, and T the temperature. Finally, by the combination of eqs 3 and 4, we obtain:

$$K_E^+ = \rho \mu_h \tag{5}$$

Therefore, the electrochemical quenching constant can be used for the estimation of the mobility of the charge carriers (holes for p-doped polymers). The proportionality constant ρ has dimensions of resistivity (Ω cm) and depends on intrinsic properties of the polymer, such as the lifetime of the excited state in semiconductor state. An equivalent formulation can be assumed for the n-doping (electrochemical reduction) of the polymer, as will be shown later.

The value of K_V^+ measured from the linear range (up to +0.2 mC) of the ESV plot in Figure 5 is 4500 ± 100 C^{-1} for positive charge (holes). The positive deviation for higher values of charge is related to a high extent of quenching and is interpreted in terms of "sphere of action" of the quencher.[22] At high concentrations of quencher, a static contribution of the quenching constant appears due to the presence of a quencher adjacent to the flourophore at the moment of the excitation. Another possible explanation for this phenomenon may be related to the superquenching effect that has been observed for polyfluorenes by Fan et al.[23] The conductive character of this polymer produces a delocalization of the introduced charge along the conjugated chain by an efficient internal charge transfer.
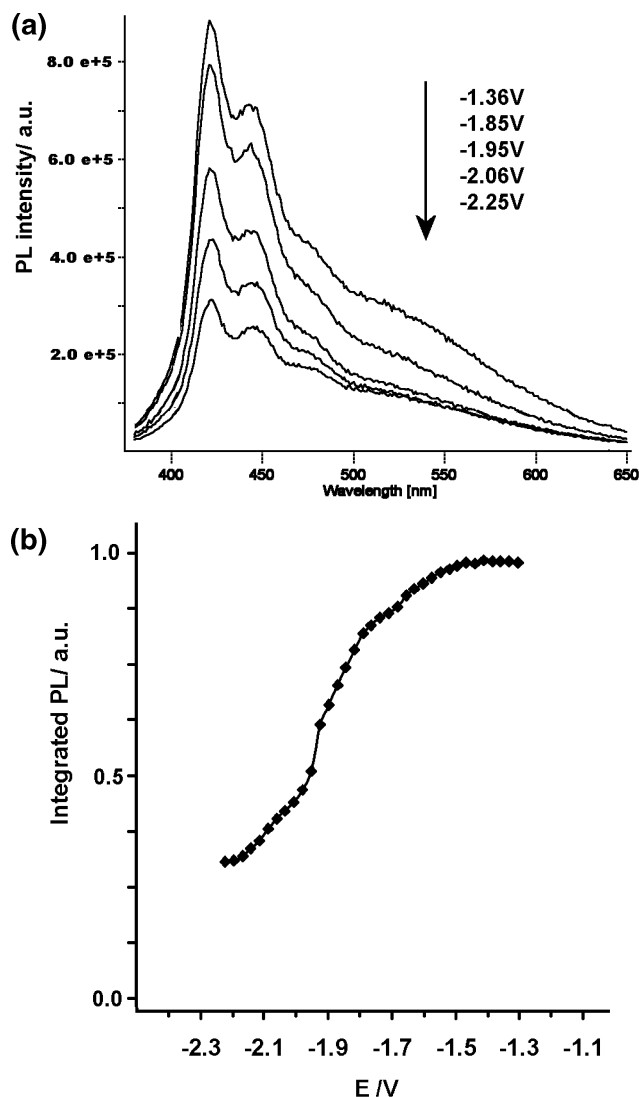

Figure 7. (a) Fluorescence spectra of an ITO-polymer electrode obtained during the reduction scan at different potentials (indicated in the figure). Scan rate 1 mV s^{-1}. Excitation wavelength 370 nm. (b) Integrated intensity of the emission spectra between 380 and 650 nm as a function of the applied potential.

A similar study was performed for the characterization of the n-doping processes. Figure 6 shows the voltafluorogram and the voltammogram recorded during the reduction of the polymer in the spectroelectrochemical cell. The electrode was initially immersed in the cell at −0.2 V, and the scan started toward less positive potentials. The negative current appearing at −1.70 V is due to the reduction of the polymer (n-doping). The quenching of the fluorescence is observed from that potential. The minimum of fluorescence is reached at −2.10 V, corresponding to a 100% doping level. The shape of the curve is similar to the curve for p-doping. Two oxidation peaks appear in the reverse voltammetric scan at −1.70 and −1.00 V, related to the dedoping process. It can be observed in the voltafluorogram that the initial fluorescence intensity is recovered slowly, indicating that the dedoping process is hindered. This slow kinetics in the dedoping scan may be related to the formation of localized anions in the conjugated chain. Only after the oxidation at −1.0 V is the fluorescence completely recovered.

Figure 7a shows the fluorescence spectra obtained during a negative scan up to −2.25 V at a low scan rate (1 mV s^{-1}). In the negative scan, the shape of the spectrum does not change substantially, and there is no shift in the position of the emission
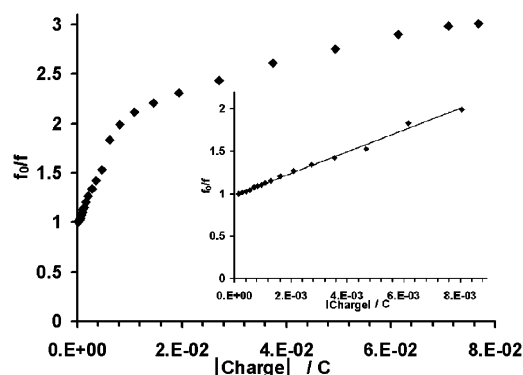
Figure 8. Electrochemical Stern−Volmer plot obtained in the reduction of ITO-polymer electrode (negative charge vs normalized fluorescence). Scan rate 1 mV s^{-1}. Excitation 370 nm, emission 380−650 nm. Inset: Magnification of the plot between 0 and −8 mC.

bands. The intensity of fluorescence remains unvaried at potentials more positive than −1.50 V. The integrated intensity of the spectrum starts to decrease from that potential, as shown in Figure 7b where its evolution with the potential can be observed.

The intensity decreases strongly from −1.50 V, reaching a minimum of emission at −2.20 V; however, some residual fluorescence is observed that is not diminished upon further reduction. This result suggests that negative charges (electrons) are less effective quenchers as compared to positive charges (holes), as was previously observed in organic light emitting diodes.[24]

The evolution of the fluorescence with respect to the negative charge introduced in the polymer is shown in the ESV plot for the reduction process in Figure 8. This plot shows a linear range between 0 and −8 mC (inset). At higher values of charge, the intensity of fluorescence tends asymptotically to 3; that is, the fluorescence is quenched up to one-third of its initial fluorescence. This result may indicate that the injected charge is not able to quench completely the fluorescence of the polymer even after complete n-doping, due to a hindered mobility of negative polarons by a partial negative charge trapping in monosubstituted C9 defective sites in the polyfluorenes.[25] From the linear range of the plot, the quenching constant for negative charges ($K_V{}^-$) is established in 124 ± 3 C^{-1}.

The electrochemical Stern−Volmer (ESV) equation for negative polarons can be derived in a manner analogous to that of the positive ESV equation:

$$\frac{f_0}{f} = 1 + K_E{}^-[C] = 1 + K_V{}^- Q \qquad (6)$$

where $K_E{}^-$ is the electrochemical quenching constant, $[C]$ is the negative charge introduced per unit volume of polymer (V), Q is the negative charge injected, and $K_V{}^-$ is the ESV constant per volume of polymer. Assuming the same character for positive and negative polarons, and following the same deduction, the electrochemical Stern−Volmer constant for electrons would be:

$$K_E{}^- = \rho \mu_e \qquad (7)$$

This equation is analogous to eq 5, with μ_e being the electron mobility in the polymer and ρ the proportionality constant depending on the polymer properties in semiconducting form.

The different values obtained for electrochemical quenching constants are indicative of the different mobilities of holes and electrons of this type of polymer. The ratio $K_V{}^+/K_V{}^-$ is equal to the ratio of the mobilities of the charge carriers μ_h/μ_e, according to eqs 5 and 7. The hole-to-electron mobility ratio calculated with this method is 36, indicating a lower mobility of electron according to the literature.[26,27] Further experiments are currently in progress to assess the relation between the ESV plots with intrinsic properties of the conjugated polymers.

4. Conclusion

In situ electrochemical fluorescence has been employed for the first time in the characterization of luminescent polymers. This is a powerful technique that can be applied to the study of conjugated polymers with application in electroorganic devices such OLEDs emissive layers. This technique permits one to characterize the properties of the emissive layer as charge carriers are injected separately, discriminating between the effects induced in the photoluminescence by the injection of holes or electrons.

Poly-[2,7-(fluorene)-1,4-(phenylene)] presents a high photoluminescence due to the presence of flourophore units with the polymer in semiconducting form. The introduction of positive or negative charges induced the quenching of the fluorescence due to the mobility of the charges along the conjugated system. The variation of the fluorescence with the charge introduced in the polymer gives information about the mobility of the charge carriers. For the polymer studied, we have determined the relative mobility of holes and electrons through the conductive polymer layer, finding a hole mobility that is 1 order of magnitude higher than the electron mobility, according to literature data.

Further work is in development to establish the chemical nature of the species formed upon oxidation or reduction of the polymer and to determine the physical meaning of the ρ parameter.

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