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# Spectroelectrochemical Study of Electron and Energy Transfer in Poly(fluorene-*alt*-phenylene) with Perylenediimide Pendant Groups

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Electrochemical and spectroelectrochemical studies have been performed on a (fluorene-*alt*-phenylene) polymer with perylenediimide pendant groups. This polymer can be *p*-doped by oxidation of the conjugated chain, whereas the reduction occurs on the electron-acceptor perylenediimide units. The photoluminescence of this polymer in solid state is greatly inhibited by a photoinduced electron transfer from the conjugated chain to neutral perylenediimide aggregates. Several changes have been observed in the emission from polymers upon electrochemical treatments. On the other hand, the oxidation of the main chain induces the quenching of the remaining emission from the conjugated fluorophoric main chain, whereas the emission from the side groups is not affected. Remarkably, the evolution of the emission of the perylenediimide pendant groups upon electrochemical reduction allows discrimination between aggregated and nonaggregated perylenediimide groups in the polymer. As a result of the formation of the perylenediimide radical anion, the electron transfer from the main chain is inhibited and the fluorescence from the alternated fluorene–phenylene chain increases. Besides, the emission from the conjugated chain suffers a quenching process by resonance energy transfer to the electrochemically formed perylenediimide radical dianion.

## 1. Introduction

The design and synthesis of conjugated polymers functionalized with groups providing specific physical and chemical properties constitute an inspiring area in the field of materials chemistry. This approach has been explored for the preparation of materials with exciting properties and applications, such as sensors<sup>1</sup> or energy conversion materials.<sup>2–4</sup> In the latter regard, electron-donor polymers substituted with electron-acceptor groups and exhibiting photoinduced electron transfer have been synthesized as promising candidates for the preparation of enhanced devices, anticipating a favorable organization of the pendant groups in these systems.<sup>4</sup> Thus, polymer backbones carrying fullerenes,<sup>5</sup> tetracyanoanthraquinodimethane,<sup>6,7</sup> or anthraquinone<sup>8–10</sup> as the pendant electron acceptors have been reported so far. Perylenediimide (PDI) derivatives have evolved into one of the most fascinating materials in both industry and academics due to their good chemical, thermal, and photostability.<sup>11,12</sup> PDI also shows remarkable good electron accepting ability and high absorption of light in the visible range, which has prompted the preparation of a good number of electron donor–acceptor oligomers and other molecular and supramolecular architectures.<sup>13–17</sup> Interestingly, PDIs have been also covalently linked to conjugated polymers, and it has been shown that an appropriate threshold in the PDI content and the tailored matching between the band gaps of both electroactive fragments are prerequisites that greatly determine their usefulness in optoelectronic applications.<sup>18–22</sup> As it has been previously mentioned, an essential consideration in this type of materials

is the degree of interaction between the pendant PDI units in the polymeric chain. Although the strong  $\pi$ – $\pi$  stacking tendency of PDIs to form the so-called H-aggregates and to construct 1D aggregates has been well established both in the solid state<sup>23,24</sup> and in solution,<sup>25–29</sup> the observation of this phenomenon in functionalized PDI polymers is very rare. Indeed, we have recently demonstrated the inherent formation of H-aggregates between the pendant PDI units in polymer PFP–PDI, and we have also carried out an investigation of the photophysical behavior of this material, mainly in solution.<sup>30</sup> Thus, UV–vis absorption, steady-state fluorescence, and excitation spectroscopy carried out on polymer PPF–PDI evidenced the existence of PDI aggregates in different solvents. The presence of these aggregates was further confirmed by temperature-dependent studies, in which a clear correlation between the emissive properties of aggregated/nonaggregated perylenediimide moieties was found with respect to the temperature and also with the solvent investigated. The high content of PDI and the careful design of the HOMO–LUMO band gap between the polymer main chain and the pendant PDIs enabled photoinduced electron transfer not only from the polymer backbone to the PDI units but also, and more remarkably, to the formed  $\pi$ -stacked PDI aggregates. Photoinduced electron transfer does not only occur in solution but also in the solid state, as it was further confirmed by photoinduced absorption spectroscopy. This electron transfer process is responsible for the intense fluorescence quenching of the polymeric backbone. Finally, PIA measurements corroborated these results and indicated that electron transfer also occurs in the solid state.

In-depth information about the influence of injected charges on the photophysical processes of this type of materials can be obtained by means of spectroelectrochemical techniques. Fluorescence spectroscopy coupled to an electrochemical system is

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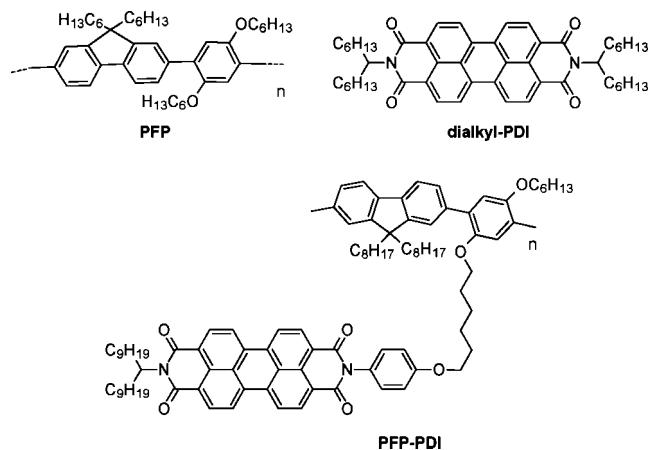
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a powerful tool for the characterization of conjugated polymers.<sup>31–33</sup> Several properties can be determined by simply following the emission intensity as a function of the applied potential. Furthermore, the technique provides a prediction tool for the working performance of conjugated polymers in organic electronic devices, like diodes or transistors. The mobility of the charge carriers,<sup>34</sup> the diffusion coefficient of the exciton,<sup>35</sup> or the electrodegradation mechanisms can be determined in detail by means of this novel technique.<sup>36</sup>

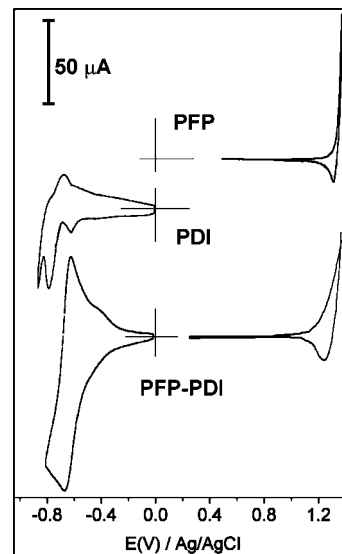
The present work represents a further step in the investigation of the aggregation phenomena between the PDI units within polymer PFP–PDI, to draw information that can be used as a feedback for the design of materials with enhanced properties regarding its application in optoelectronic devices. Thus, in this article we present the spectroelectrochemical investigation of polymer PFP–PDI and reference materials PDI and PFP (Chart 1). In contrast to our previous article, mostly dealing with the synthesis and photophysical investigation of these materials in solution,<sup>30</sup> the present work has been performed in solid state, in which the formation of aggregates is more likely to take place than in solution. Besides, the results obtained with these investigations can be more easily extrapolated to the actual behavior of these polymers in solid-state devices.



## 2. Experimental Section

This work has been focused in the characterization of the compounds depicted in Chart 1 in solid state. The synthesis and preliminary photophysical investigations of perylenediimide functionalized polymer PFP–PDI and reference polymer PFP and perylenediimide (PDI) materials have been previously reported.<sup>30</sup> The molecular weights of PFP–PDI and PFP were determined by SEC analysis in *o*-dichlorobenzene (*o*-DCB) at 80° using polystyrene standards and show  $M_w$  and  $M_n$  values of 101 000 and 16 400 g/mol ( $pd = 6.2$ ) for PFP–PDI and 38 000 and 13 100 g/mol ( $pd = 2.9$ ) for reference compound PFP. These values, combined with the molecular weights of the corresponding monomers, give 9 and 19 as the number of repeating units in each polymer.

The solvent for the 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 reference electrode was a Ag/AgCl electrode for organic solvents (3 M KCl, Crison) for the conventional electrochemical cell and a silver wire as the pseudoreference electrode for the spectroelectrochemical cell, immersed in the same electrolytic solution. Spectroelectrochemical measurements were performed



**Figure 1.** Stabilized cyclic voltammograms for PFP, PDI, and PFP–PDI deposited onto ITO electrodes; scan rate, 100 mV s<sup>−1</sup>.

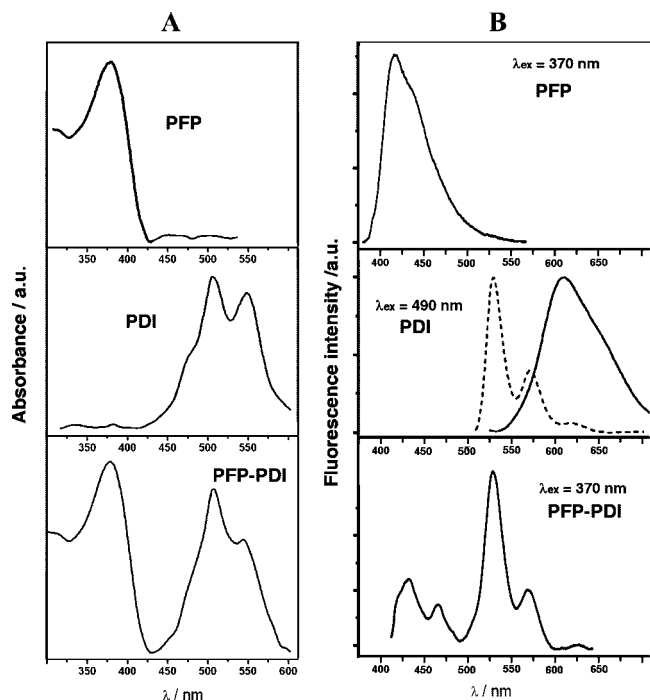
in a modified fluorescence cell (1 cm length quartz cell). Details on the cell design have been shown in a previous article.<sup>32</sup> The working electrode was a transparent ITO-glass electrode covered with the material to be investigated. A 10 μL aliquot of a solution of the compound (1 mg/mL in chloroform) was spin-casted over 1 cm<sup>2</sup> of ITO conductive glass (60 S cm<sup>−1</sup>). Oxygen was purged from the electrochemical cells by bubbling argon for 20 min, and the argon atmosphere was maintained during all the experiments. Fluorescence-spectra measurements were performed at room temperature using a PTI QuantaMaster Model QM-62003SE spectrofluorometer. UV–vis experiments were performed with an Avantes fiber optics spectrophotometer, using an AvaSpec-256–2 double channel detector and Avantes DH-2000 Deuterium-Halogen light source. All the spectroelectrochemical experiments were reproduced at least three times.

For the study of the optical properties of PFP, PFP–PDI and PDI thin-films a 1 mg/mL solution of this compound was spin-casted onto quartz plates. Additional PDI layers were prepared for the study of aggregates. Thus, 1 mg of PDI was dissolved in 1 mL of a Nafion suspension in chloroform (100 mg/mL). This mixture was then deposited onto a quartz plate to form a solid blend PDI-Nafion (1% in weight).

## 3. Electrochemical and Optical Characterization

Figure 1 shows the stabilized cyclic voltammograms for all the compounds of Chart 1 deposited onto ITO plates. PFP polymer presents the typical electrochemical behavior of this type of fluorene-based conjugated polymers. The oxidation onset appears at 1.23 V and corresponds to the reversible *p*-doping processes of the conjugated polymer chain.

The electrochemical behavior of PDI is shown in Figure 1. In the scan of less-positive potentials, a reduction peak appears centered at −0.62 V, related to the formation of the perylenediimide radical anion (PDI<sup>•−</sup>). A second reduction peak is observed at −0.78 V which can be assigned to the formation of the perylenediimide dianion (PDI<sup>2−</sup>). The corresponding counterprocess can be observed in the reverted scan to more positive potentials, with the oxidation of the perylenediimide dianion PDI<sup>2−</sup> to PDI<sup>•−</sup> at −0.67 V and the oxidation to neutral PDI around −0.57 V.



**Figure 2.** Absorption (A) and emission (B) spectra of thin films of PFP, PDI, and PFP-PDI deposited onto quartz plates. The emission spectrum of PDI corresponds to thin films prepared by spin-casting from a 1 mg/mL solution (solid line) and a PDI-Nafion (1% in weight) blend (dashed line).

The electrochemical behavior of PFP-PDI is also shown in Figure 1. The right side of the voltammogram corresponds to the *p*-doping of the conjugated fluorene-phenylene backbone, with an oxidation onset at 1.10 V. The voltammogram on the left side corresponds to the redox processes of the pendant perylenediimide groups.

Compared with the cyclic voltammograms of nonaggregated PDI, the reduction of the pendant group in the polymer starts at more positive potentials, and a single reduction peak appears centered at  $-0.67$  V. The two one-electron reduction processes that were observed for the reference PDI compound are thus overlapped here. The corresponding oxidation peak appears in the reverted scan at  $-0.62$  V, related to the transition  $\text{PDI}^{2-}/\text{PDI}^{\cdot-}$ , and the shoulder around  $-0.4$  V can be assigned to the transition  $\text{PDI}^{\cdot-}$  to the neutral state.

Part A of Figure 2 shows the UV-vis spectrum of PFP-PDI, PFP, and PDI films deposited onto quartz plates. The spectrum of PFP shows an absorption maximum at 380 nm corresponding to the HOMO-LUMO electronic transitions of the conjugated chain. The spectrum of the PDI film is characterized by the presence of bands due to the  $\pi\pi^*$  transition of the perylenediimide units at 550 nm, due to a (0,0) vibronic transition. An additional (0,1) vibronic transition is visible at 508 nm, and a shoulder appears at 477 nm. The values of the maxima for the electronic transitions are red-shifted with respect to the spectrum measured in solution due to the  $\pi$ -stacking of perylenediimide molecules.<sup>26</sup> It has been shown that a strong vibronic coupling takes place between the cofacially arranged perylenediimide units in hydrogen aggregates, which results in an enhanced (0,1) transition. This is often used as an evidence of aggregation. Thus, the ratio between the intensity of the main vibronics is (0,0)/(0,1) = 0.93, which is lower than the ratio obtained for this compound in diluted solutions, (0,0)/(0,1) = 1.62 shown in our previous article.<sup>30</sup> This result confirms the formation of

aggregates in the PDI layer, as one would expect in a larger extension that we observed in the solution studies.

Finally the spectrum of PFP-PDI presents the absorption features of both chromophores: the maximum at 380 nm corresponds to the electronic transition of the conjugated chain, and the low-energy absorption bands are related to the transitions of the perylenediimide side groups. The ratio between the main vibronic bands of perylenediimide is (0,0)/(0,1) = 0.71. This ratio is lower than in the corresponding investigation in solution and even lower than the ratio of the solid layer of PDI, indicating that the proximity of the side groups in the polymer strongly favors the cofacial interaction between perylene groups with respect to pristine PDI in the solid state.

Part B of Figure 2 shows the fluorescence spectra of the compounds of Chart 1 deposited onto quartz plates. The PFP polymer shows an emission maximum at 416 nm, similar to the results obtained in solution,<sup>30</sup> with a poorly defined vibronic feature around 440 nm, indicative of low exciton-phonon coupling.

The spectrum of the PDI thin film spin-casted from a 1 mg/mL solution shows an emission maximum at 620 nm corresponding to the emission from aggregated perylenediimides.<sup>37</sup> Figure 2 also shows the spectrum of a PDI layer dispersed in a Nafion matrix (1% PDI in weight, dashed line). In this matrix, the emitting features of nonaggregated perylenediimide can be observed with much higher emission intensity than in the layer containing aggregated (pristine) perylenediimide. An emission maximum at 529 nm corresponding to the  $S_0 \rightarrow S_1$ , and additional vibronic features appear at 571 and 618 nm.

The spectrum of the PFP-PDI polymer film shows the emission maximum at 430 nm with a vibronic feature at 467 nm corresponding to the emission from the conjugated backbone. The emission of the perylenediimide pendant groups appear with emission maxima at 529 and 560. The low-intensity emission band at 624 nm may be related to the emission from aggregated perylenes. The emission comes mainly from non-aggregated species, which have an emission quantum yield much higher than the aggregated species. The quantum yield for the emission of this polymer in the solid state is very low due to the existence of a photoinduced charge-separation process from the PFP chain to the pendant PDI units, as we have previously mentioned.<sup>30</sup>

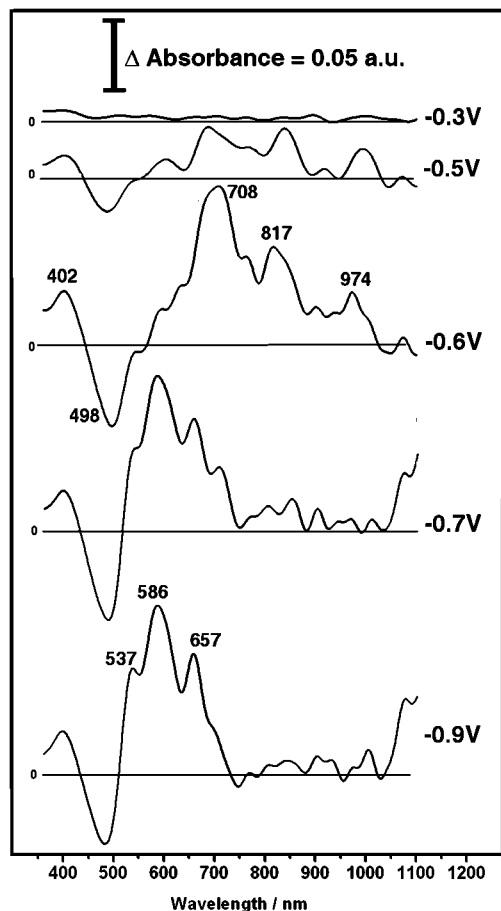
#### 4. Spectroelectrochemical Study

**4.1. In Situ Electrochemical UV-vis.** To obtain a maximal sensitivity, the in situ UV-vis experiments were performed in the following manner: the ITO/PFP-PDI was immersed in the electrochemical cell at a controlled potential (0.0 V), and a reference spectrum was taken at that potential. Then, the potential was stepped to a different value acquiring the sample spectrum. The Electrochemically-Induced Absorption (ECIA) spectrum presented is the difference between the sample and the reference spectra. The presence of positive bands in the ECIA spectrum corresponds to the formation of new electronic transitions at the applied potential, induced by the electrochemical treatment, whereas negative bands indicate the inhibition of electronic transitions at that potential.

Figure 3 shows the ECIA spectra of an ITO/PFP-PDI electrode at different potentials. As the potential is stepped from 0.0 V (reference potential) to negative values a series of electrochemically induced absorption bands appear from  $-0.3$  V onward as a result of the reduction of the perylenediimide units.

Three positive bands appear at 708, 817, and 974 nm, reaching a maximum in intensity at  $-0.6$  V. These bands are





**Figure 3.** Electrochemically induced absorbance spectra of an ITO/PFP-PDI electrode; reference potential, 0.0 V. Sample potentials are depicted close to the corresponding spectrum.

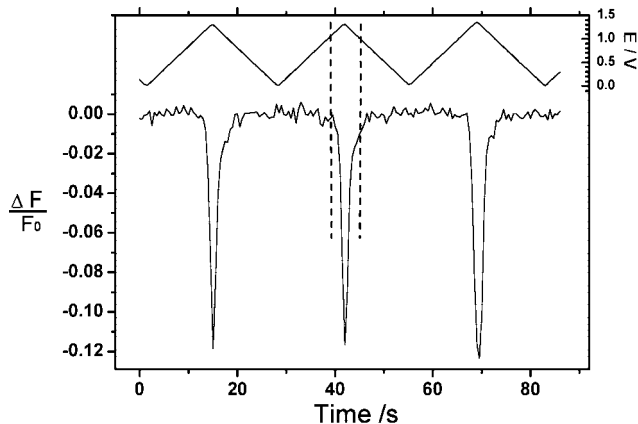
related to  $D_0 \rightarrow D_n$  transitions of the half-filled orbital of the perylenediimide radical anion formed upon electrochemical reduction.<sup>19,38,39</sup> Related to this process, a negative band at 498 nm indicates the disappearance of the  $S_0 \rightarrow S_n$  transition modes of the neutral perylene.

A positive band appears at 402 nm and it is related to electronic transitions in the PFP backbone.<sup>40</sup> The positive character of this band indicates the growth of HOMO-LUMO transitions on the polyfluorene conjugated chain induced by the reduction of the perylenediimide side groups.

When the potential of the electrode is stepped to  $-0.7$  V, a sudden change in the shape of the spectrum can be observed. New positive bands appear at higher energies (537, 586, and 657 nm) related to singlet transitions of the perylenediimide dianion formed upon further reduction.<sup>19,41</sup> The intensities of these bands reach a maximum at the most negative potential explored ( $-0.9$  V). All of these processes are completely reversible, and the initial spectrum is recovered when the potential is reverted to the initial value.

**4.2. In Situ Electrochemical Fluorescence.** The evolution of the emissive properties of the different compounds was studied as a function of the applied potential. The variation of the fluorescence is presented as normalized relative difference of the emission  $\Delta F/F_0$ , with  $F_0$  being the emission intensity from the spectroelectrochemical cell at the initial potential.

Figure 4 shows the evolution of the emission maximum of the PFP polymer ( $\lambda_{\text{ex}} = 370$  nm,  $\lambda_{\text{em}} = 415$  nm) as a function of time during three consecutive voltammetric cycles between an initial potential of 0 and an anodic limit of  $+1.3$  V.



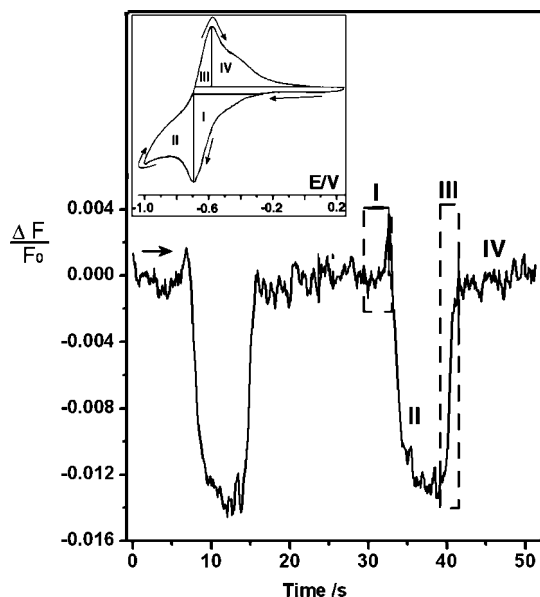
**Figure 4.** Evolution of the emission of PFP during successive potential scans between 0 and 1.3 V (upper graph). The zone between dashed lines corresponds to the potentials where the polymer is doped;  $\lambda_{\text{ex}} = 370$  nm,  $\lambda_{\text{em}} = 415$  nm; scan rate  $100 \text{ mV s}^{-1}$ .

The variation of the fluorescent emission is similar to that obtained during the doping of other light emitting polymers.<sup>32,34</sup> In the range of potentials between 0 and  $+1.1$  V, the emission intensity remains unmodified, as this potential range correlates to the semiconducting state of the polymer. At potentials more positive than  $+1.1$  V, the transition from the semiconducting to the doped state of the polymer is observed and the fluorescence is quenched. Thus, the intensity of the quenching is proportional to the doping level of the polymer.<sup>32</sup> When the potential scan is reverted at 1.3 V, the corresponding dedoping process is reflected in the recovery of the initial value of the fluorescence intensity.

A similar experiment was performed with a PDI film deposited onto an ITO plate ( $\lambda_{\text{ex}} = 490$  nm,  $\lambda_{\text{em}} = 530$  nm). The evolution of the emission intensity was measured as a function of time during a series of voltammetric cycles between  $+0.25$  V and a cathodic limit of  $-0.75$  V. The emission starts to be quenched at potentials less positive than  $-0.45$  V, corresponding to the first reduction process (neutral PDI to  $\text{PDI}^{\cdot-}$ ). The fluorescence is completely quenched when the  $\text{PDI}^{\cdot-}$  is formed. The second reduction process to  $\text{PDI}^{2-}$  does not modify the emissive state of the molecule that remains quenched. The initial fluorescence of the PDI film is recovered after the reoxidation of the  $\text{PDI}^{\cdot-}$  to the neutral state, at potentials more positive than  $-0.31$  V. Similar results were obtained by Dias et al. in a detailed study of the fluorescence emission of perylenediimide species as a function of the electrochemical potential.<sup>42</sup>

The variation of the emission from the PFP-PDI polymer as a function of the applied potential will be discussed in the following section. During the *p*-doping of the conjugated chain the emission from the backbone ( $\lambda_{\text{em}} = 415$  nm) shows a reversible quenching due to the injection of positive charges, similarly to that of the PFP polymer. The emission of the perylenediimide pendant groups ( $\lambda_{\text{em}} = 530$  nm) remains unaffected upon such electrochemical treatment. More interesting is the change of the emitting properties upon electrochemical reduction of the perylenediimide groups.

Figure 5 shows the evolution of the emission at 530 nm (corresponding to the emission from the perylenediimide groups) during voltammetric scans performed for the study of reduction processes (the voltammogram obtained in the spectroelectrochemical cell is shown in the inset of Figure 5). The initial potential is settled at  $+0.25$  V. When the potential is stepped to less positive values, a reduction current can be observed from



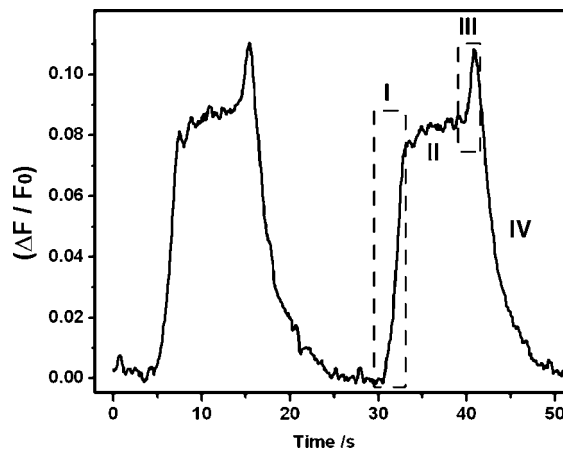
**Figure 5.** Evolution of the emission of PFP-PDI during successive potential scans between +0.25 and -1.0 V;  $\lambda_{\text{ex}}=370$  nm;  $\lambda_{\text{em}}=530$  nm. Four zones have been marked corresponding to different zones of the voltammogram (inset); scan rate  $100 \text{ mV s}^{-1}$ .

-0.2 V due to the electrochemical reduction of perylenediimide groups to  $\text{PDI}^{\cdot-}$  (zone I in the voltammogram).

The emission from the perylenediimide moieties remains stable in spite of its reduction to  $\text{PDI}^{\cdot-}$  species in that zone of potentials. This result is indicative of the reduction of nonemissive perylenediimide species, that is, perylenediimide aggregates, as this aggregates only emit above 600 nm. The  $\pi$ -stacked species are reduced at more positive potentials than the corresponding nonaggregated (and light-emitting) perylenediimides. Similar results were obtained by Meijer et al. in the study of a perylenediimide derivative. The authors show that hydrogen-bonded perylenediimide dimers can be formed in  $\text{CH}_2\text{Cl}_2$  solutions. These dimers present more positive reduction potentials than the nonaggregated materials.<sup>43</sup>

Only after the reduction maximum current is reached (from -0.67 V onward) the emission intensity of nonaggregated perylenediimides decreases due to its reduction to  $\text{PDI}^{\cdot-}$  (zone II). Simultaneously, the concurrent reduction of aggregated  $\text{PDI}^{\cdot-}$  to  $\text{PDI}^{2-}$  was observed at this potential by *in situ* UV-vis (Figure 3, -0.7 V). The emission intensity reaches a stable minimum from -0.84 V, and this situation remains, even in the reverted scan from -1.0 to -0.67 V. The counterprocesses start in the positive-going scan from -0.67 V (zone III), where an increase of the emission from PDI units can be observed due to the oxidation of nonaggregated  $\text{PDI}^{\cdot-}$  to PDI. The initial value of fluorescence intensity is recovered in the positive-going potential from -0.57 V (zone IV), where all of the PDI species are transformed to the neutral state.

Quantification of the amount of perylenediimide aggregates can be obtained from these experiments. The voltammetric charge passed through the electrode in the negative-going scan from -0.2 to -0.67 V (zone I) corresponds to the reduction of aggregated perylenes while nonaggregated groups remain in neutral state because there is no modification of the emission intensity at 530 nm. The charge employed for this reduction is  $Q_I$  and corresponds to  $1e^-$  per PDI molecule in the aggregates. From -0.67 V (zone II), the voltammetric charge passed ( $Q_{II}$ ) is employed in two processes: part of the charge is used for quenching the emission from emissive nonaggregated perylene-



**Figure 6.** Evolution of the emission of PFP-PDI during successive potential scans between +0.25 and -1.0V;  $\lambda_{\text{em}} = 415$  nm,  $\lambda_{\text{ex}}=370$  nm. Four zones have been marked corresponding to the zones of the voltammogram shown in the inset of Figure 5; scan rate  $100 \text{ mV s}^{-1}$ .

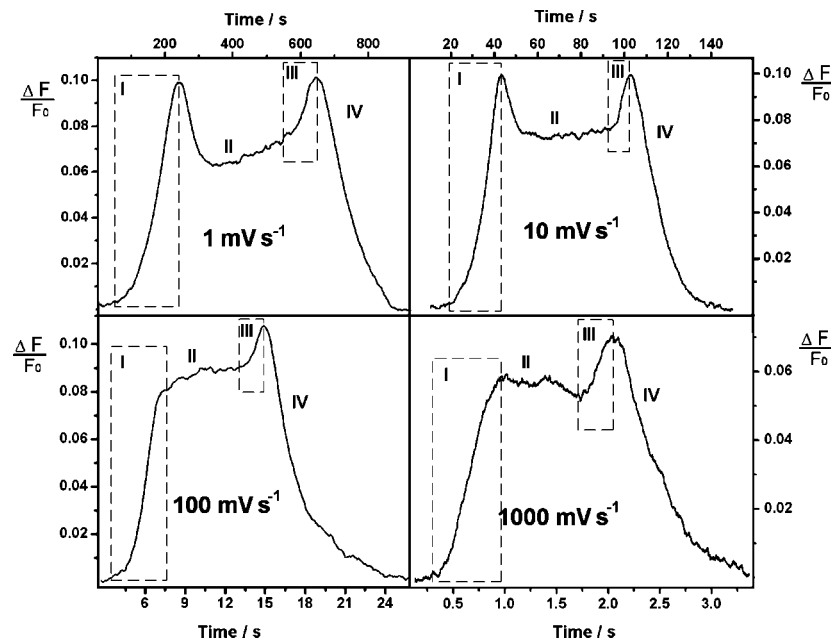
diimides by the reduction  $\text{PDI} \rightarrow \text{PDI}^{\cdot-}$  ( $Q_n$ ,  $1e^-$  per nonaggregated molecule) and the other portion of the voltammetric charge passed ( $Q_a$ ) is employed to the second reduction process of aggregated  $\text{PDI}^{\cdot-}$  to  $\text{PDI}^{2-}$  corresponding to  $1e^-$  per  $\text{PDI}^{\cdot-}$  molecule in aggregates, and therefore  $Q_a = Q_I$ . The total charge passed in those processes is  $Q_I = -0.404 \text{ mC}$  and  $Q_{II} = (Q_n + Q_a) = -0.465 \text{ mC}$ . The difference between the values of charges ( $Q_{II} - Q_I$ ) =  $Q_n = -0.061 \text{ mC}$ , being to the charge for the reduction of nonaggregated PDI species.  $Q_n/Q_{II}$  ratio relates to the ratio (nonaggregated PDI molecules)/(total perylenediimide molecules). From the results obtained in several PFP-PDI films, the  $87 \pm 7\%$  of pendant groups is in the form of aggregates. Whereas in the previous solution study, aggregation could be exclusively ascribed to the formation of intramolecular aggregates, in our present solid state investigation both intra but principally intramolecular aggregation is also expected to occur.

The evolution of the emission from the perylenediimide groups with the applied potential is the same upon direct excitation of the perylenediimide groups ( $\lambda_{\text{ex}} = 490$  nm), and therefore the emitting processes previously exposed are not affected by the presence of photoinduced charge-separated states formed upon the photoexcitation of the conjugated main chain.

The same experiment was performed following the emission from the conjugated backbone ( $\lambda_{\text{ex}} = 370$  nm,  $\lambda_{\text{em}} = 415$  nm) during the scan from +0.25 to -1.0 V. Figure 6 shows the evolution of the emission of the PFP backbone during the electrochemical reduction of the pendant perylenediimide groups.

At the initial potential, the PFP-PDI polymer is in the form of a charge separation complex, being the PFP chain, the electron donor, and the PDI the electron acceptor, and the fluorescence from the PFP backbone is inhibited by the presence of positive charges, whereas negative charges are localized in the PDI groups. The emission intensity of the backbone starts to grow simultaneously to the reduction of the perylenediimide moieties to  $\text{PDI}^{\cdot-}$  (zone I). The maximum intensity is reached at the onset of the zone II, corresponding to the second electron transfer to the PDI groups.

The emission intensity stays at this plateau until the zone III of potentials in the reverted scan to positive-going potentials. The dianionic perylenediimide groups are oxidized to  $\text{PDI}^{\cdot-}$ , and a sharp increase of the fluorescence of the PFP backbone is observed in the zone III. Finally, the fluorescence of PFP



**Figure 7.** Evolution of the emission of PFP-PDI during the reduction of perylenediimide groups at different scan rates. The scan rate is indicated close to the corresponding chronofluorescence spectrum. Four zones have been marked corresponding to the zones of the voltammogram of Figure 5 (inset);  $\lambda_{\text{ex}} = 370$  nm,  $\lambda_{\text{em}} = 415$  nm.

decays at potentials where the oxidation of  $\text{PDI}^{\cdot-}$  the neutral perylenediimide takes place (zone IV).

Further analysis of the behavior of the PFP emission upon perylenediimide reduction was performed by the study of these processes at different voltammetric scan rates. Figure 7 shows the profile of the PFP emission ( $\lambda_{\text{em}} = 415$  nm) during several voltammetric scans at different scan rates.

The increase of the emission observed in the zone of potentials marked as III in Figure 6 (oxidation of  $\text{PDI}^{2-}$  to  $\text{PDI}^{\cdot-}$ ) appears at all of the scan rates studied. The most striking aspect of these experiments is the presence of an equivalent variation of the emission in the zone II of the potential (reduction of  $\text{PDI}^{\cdot-}$  to  $\text{PDI}^{2-}$ ) but only at low scan rates.

Initially the fluorescence of the polyconjugated system is inhibited by the formation of a charge-separated complex. When scanning to negative potentials, in the zone I of the voltammogram, the electrochemically injected negative charge reaches the LUMO level of perylenediimide groups. The injection of this charge inhibits the photoinduced electron transfer from PFP to PDI, recovering the neutral state of the backbone. It produces an increase of the intensity of the  $S_0 \rightarrow S_1$  excitation as observed by UV-vis (Figure 3) and the corresponding increase of the emission intensity at 415 nm ( $S_1 \rightarrow S_0$  of PFP).

The reduction of  $\text{PDI}^{\cdot-}$  to  $\text{PDI}^{2-}$  species takes place in the zone II ( $-0.67$  to  $-1.0$  V). In that moment, the fluorescence from PFP partially decays (at scan rates 1 and 10  $\text{mV s}^{-1}$ ). As observed by in situ UV-vis spectroscopy the electrochemical formation of  $\text{PDI}^{2-}$  at those potentials induces the growth of absorption bands at 510–750 nm (Figure 3), corresponding to singlet transitions of the perylenediimide dianion. The fluorescence emission spectrum of PFP shown in part B of Figure 2 partially overlaps the absorption spectrum of the electrochemically formed  $\text{PDI}^{2-}$  species. In that case, upon perylenediimide dianion formation, resonance energy transfer (RET) may occur between PFP chromophores and  $\text{PDI}^{2-}$  units. This RET process induces the partial decrease of the emission of PFP in the zone II of potentials.

Later, when the  $\text{PDI}^{2-}$  is oxidized to  $\text{PDI}^{\cdot-}$  (zone III) the RET process ceases because the absorption bands of the radical

anion appear at lower energies ending, thus, the spectral overlap. The initial situation is recovered when the neutral PDI group is recovered in the zone IV of potentials, and the charge separation complex is formed again upon photoexcitation.

The different behavior at different scan rates is indicative of different kinetic constants for the processes that quenched the emission from PFP. It is important to note that the RET process only occurs when the  $\text{PDI}^{2-}$  is formed.

At low scan rates, the complete reactivation of the fluorescence of the PFP backbone takes place at potentials more positive than the formation of the  $\text{PDI}^{2-}$  species. When the zone II of potentials is reached,  $\text{PDI}^{2-}$  species appear in the layer and RET from the polymeric backbone compete with the luminescent decay, partially quenching the emission from the backbone.

However, as the scan rate is increased the fluorescence of the polymer increases more slowly reaching a maximum plateau at less positive potentials than in the low scan rate experiments. In this case, the  $\text{PDI}^{2-}$  species are formed before all of the emission of the polymer is recovered. The electrochemical reduction of  $\text{PDI}^{\cdot-}$  to  $\text{PDI}^{2-}$  is a process faster than the charge transfer from PDI to PFP. That is, the recovery of neutral PFP, which happens by annihilation of the charge transfer complex upon reduction of PDI moieties, is slower than the electrochemical formation of  $\text{PDI}^{2-}$  species.

In the zone III and IV of potentials, the variation of the emission from PFP is almost independent of the scan rate, indicating that the reverse electrochemical transition  $\text{PDI}^{2-}$  to  $\text{PDI}^{\cdot-}$  is fast, and we observe the maximum emission from PFP before the formation of the charge separation complex. It indicates that electrochemical reactions on PDI pendant groups are faster than the photoinduced charge transfer from PFP to PDI.

## 5. Conclusions

A spectroelectrochemical study has been performed on a (fluorene-*alt*-phenylene) polymer with perylenediimide pendant groups. The photoluminescence of this polymer in the solid state

is partially inhibited by a photoinduced electron transfer from the conjugated chain to neutral perylene aggregates.

This polymer can be *p*-doped by oxidation of the conjugated chain, whereas the reduction takes place on the electron-acceptor perylenediimide units. The electrochemical oxidation induces the complete quenching of the emission from the conjugated backbone similarly to that observed in the reference polymer (PFP) without pendant perylenediimides.

More complex photophysical behavior has been observed upon electrochemical reduction of the perylenediimide units to radical anion and dianion species. The electrochemical injection of negative charges initially occurs to aggregated nonemitting perylenediimide groups. As a result of the formation of the perylenediimide radical anion, the electron transfer from the main chain is inhibited and the fluorescence from the polymer backbone increases. Once all of the perylenediimide aggregates are reduced, the electron is injected to nonaggregated and emitting perylenediimide groups, inhibiting thus the emission from these units. Finally, at larger negative potentials the emission from conjugated chain is partially inhibited by a process of resonance energy transfer to the electrochemically formed perylenediimide dianion. All of the processes related are completely reversible, and the photoinduced charge separation complex is recovered when the perylenediimide reaches again its neutral state.

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