

Photoinduced Charge Separation in Organic–Organic Heterojunctions Based on Porphyrin Electropolymers. Spectral and Time Dependent Surface Photovoltage Study.

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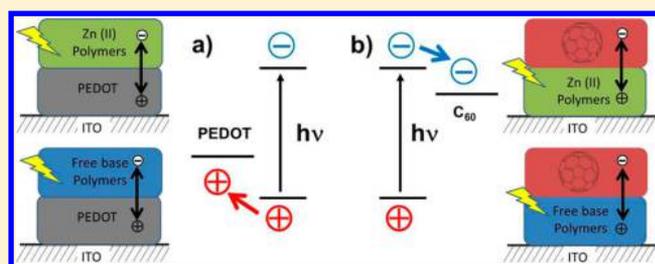
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Supporting Information

ABSTRACT: Photoactive heterojunctions formed by porphyrin polymers were electrochemically generated and analyzed by both transient and spectral dependent surface photovoltage. Indium tin oxide/organic polymer heterojunction photovoltages showed to be dependent on the presence of Zn (II) as central metal on the porphyrin polymer structure. The porphyrin electropolymers were also successfully formed on the top of a poly 3,4-ethylenedioxythiophene layer, generated by electropolymerization. The presence of the hole transport polymer dramatically altered the formation and diffusion process of the photocarriers created by excitation of the porphyrin films. A marked increase in the generated photovoltages was observed when the porphyrin electropolymer external surfaces were modified with a layer of a strong electron acceptor (C₆₀ buckminsterfullerene), showing that these heterojunctions could be used in the development of new solar energy technologies.



1. INTRODUCTION

In the development of organic-based optoelectronic devices the understanding of the processes that take place in the heterogeneous junction regions are a crucial issue. For example, in organic solar cells (OSC) the dissociation of excitons and charge recombination processes have a direct influence in cell efficiencies.^{1,2} Heterojunction regions are formed by boundaries created between electron donor and electron acceptor materials in close contact, but also the interface between the conductor substrate and the organic material plays a determinant role in the device operation.^{3,4} Indium tin oxide (ITO) is often the chosen contact for the translucent electrode, due to its optical and electronic properties.⁵ In a recent report⁶ we showed, by surface photovoltage spectroscopy (SPV), the generation of photoinduced charge separation states and charge migration in ITO/porphyrin polymer photoelectrodes. Several studies on the development of organic optoelectronic devices incorporate porphyrins and related metallized and unmetallized tetrapyrrolic compounds, because of their spectral, magnetic, and electronic properties.^{7–15} Electropolymerization is a relevant alternative technique to produce organic–organic heterojunctions because it is a practical method that allows the synthesis of subsequent conducting films.^{16–23} In our case the films over ITO substrate were produced by electrochemical polymerization of functionalized porphyrin monomers, with and

without central metal.^{6,16} Both modulated SPV and laser-induced transient photovoltage experiments demonstrated that the photogenerated electrons preferentially traveled in opposite directions, depending on the porphyrin formulation.⁶ For the polymer built with free base porphyrin, the electrons were separated toward the internal ITO/polymer interface, and for the Zn(II)-porphyrin polymer, the electrons were separated toward the external surface. In the present work, we conducted, by spectral and time dependent surface photovoltage analysis, a systematic study on the effect of the photoelectrode structures in the generation of photoinduced charge transfer states by porphyrin based electropolymer materials. Twelve different systems were generated: three configurations (ITO/photoactive polymer, ITO/hole transport material/photoactive polymer, and ITO/photoactive polymer/C₆₀ electron acceptor) with four different electropolymers in order to evaluate their potential application in the development of solar energy conversion devices. Thus, another two porphyrin polymers derivate from 5,10,15,20-tetrakis-[4(-N,N-diphenylamino)-phenyl]-porphyrin, (PTPA), and zinc(II) 5,10,15,20-tetrakis-[4(-N,N-diphenylamino)phenyl]]porphyrin, (PTPAZn),

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were electrodeposited as thin films on ITO substrate and their surface photovoltage properties were investigated. It was observed that independently of the porphyrin polymer structure, the photogenerated holes and electrons were preferentially separated in opposite directions, depending on the presence of Zn(II) as central metal in the porphyrin macrocycle. Furthermore, the four photoactive organic films were successfully formed on top of ITO electrodes modified with poly(3,4-ethylenedioxythiophene) (PEDOT) layer generated by electropolymerization. The presence of this hole transport polymer dramatically alters the formation and diffusion process of the photocarriers generated by excitation of the porphyrin films, demonstrating the crucial role of the organic–organic heterojunctions built by electropolymerization in the generation of photovoltaic effects.⁶ On the other hand, when the external surface of the porphyrin electropolymers was modified with a layer of a strong electron acceptor (C₆₀ buckminsterfullerene) the photovoltage signal obtained under similar experimental conditions rose up to near two hundred times, showing that devices formed by combining the here reported porphyrin conducting electropolymers (as light harvesting, electron donor and hole-transport layers) and fullerenes (as electron acceptor and electron transport) could present high efficiency in the conversion of solar radiation into electrical energy,²⁴ and are promising to be used in the development of new solar energy technologies.

2. EXPERIMENTAL SECTION

2.1. Porphyrin Monomers Synthesis. The synthesis of PCBZTPAZn, PCBZTPA, and PTPA have been previously reported.^{6,25} PTPAZn was prepared from PTPA. Thus, a solution of PTPA (50 mg, 0.039 mmol) in 8 mL of DCM was treated with 2 mL of a saturated solution of zinc(II) acetate in methanol. The mixture was stirred for 1 h in argon atmosphere at room temperature. After that, the reaction mixture was treated with water (30 mL) and the organic phase was extracted with three portions of DCM (20 mL each). The solvents were evaporated under reduced pressure yielding 51 mg (98%) of pure PTPA. Spectroscopic data of PTPAZn coincide with those previously reported.²⁶ ESI–MS [*m/z*] 1345.9680 [M + H]⁺ (1344.4545 calculated for C₉₂H₆₄N₈Zn). The chemical structure of the monomers is show in Supporting Information.

2.2. Instrumentation and Measurements. Absorption spectra were recorded at 25.0 ± 0.5 °C using a 1 cm path length quartz cells on a Shimadzu UV-2401PC spectrometer. The voltammetric characterization of the redox processes and electropolymerization deposition of the porphyrins was performed with a potentiostat-galvanostat Autolab (Electrochemical Instruments) in a conventional three-electrode cell. Two kinds of working electrodes were used: Pt and indium tin oxide (ITO, Delta Technologies, nominal resistance 8–12 Ω/square). ITO was employed to form the single and double layers photoelectrodes used in SPV and UV–vis spectroscopy experiments. When large area ITO electrodes were used the counter electrode was isolated from the monomer solution by a glass frit in order to avoid interference with the redox reactions occurring at the working electrode. Electrochemical studies of porphyrins were carried out in 1,2-dichloroethane (DCE) deoxygenated solution (nitrogen bubbling), with 0.10 M tetra-*n*-butylammonium hexafluorophosphate ((TBA)PF₆) as supporting electrolyte. All the electrochemical responses of the electropolymerized films were carried out in (DCE) deoxygenated solution (nitrogen bubbling), with 0.10 M ((TBA)PF₆)

as supporting electrolyte. In all the electrochemical measurements a large area Pt counter electrode, and a silver wire quasi-reference electrode were used. After each voltammetric experiment, ferrocene was added as an internal standard, and the potential axis was calibrated against the formal potential for the saturated calomel electrode (SCE). The Pt working electrode was cleaned between experiments by polishing with 0.3 μm alumina paste followed by solvent rinses. The porphyrin layers were grown cycling the porphyrin solution in the corresponding potential range until an absorbance of around 0.1 at the Soret band was reached. PEDOT layers were electropolymerized using a 1 mM EDOT solution in DCE containing (TBA)PF₆. The films were prepared in Pt and ITO electrodes, cycling them in the –0.8/1.5 V range at 100 mV/s for 10 cycles. Evaporation of the C₆₀ layer was carried out in a Balzers ultrahigh-vacuum (UHV) evaporation chamber under pressure of about 10^{–8} mbar.

Spectroelectrochemical experiments were carried out in a homemade cell built from a commercial UV–visible cuvette. The ITO-coated glass was used as working electrode, the Pt counter electrode was isolated from the monomer solution by a glass frit, and an Ag wire as the reference electrode. The cell was placed in the optical path of the sample light beam. The background correction was obtained by taking an UV–vis spectrum of a blank cell (an electrochemical cell with an ITO working electrode without the film) with conditions and parameters identical to those of the polymer film experiment.

The measurements of modulated surface photovoltage (SPV) were performed in the fixed capacitor arrangement with chopped light (modulation frequency 6 Hz) from a quartz prism monochromator (SPM2) and a halogen lamp (100 W). The SPV signals were detected with a high impedance buffer (measurement resistance 10 GΩ). The measurements were carried out in vacuum using an already described setup.²⁷ The SPV spectra were not normalized to the photon flux, and the ITO electrodes were illuminated from the front side (active layer facing the light). The in-phase (equivalent to the sine) and phase-shifted by 90° (equivalent to the cosine) signals were measured with the two-phase lock-in amplifier (EG&G, model 5210). The phase shift has been calibrated with a Si photodiode.²⁷ The amplitude of the modulated SPV signal is defined as the square root of the sum of the squared in-phase and 90° phase-shifted SPV signals.

In SPV transient experiments the samples were excited with laser pulses (wavelength 600 nm, time of laser pulses 5 ns, intensity about 3 mJ/cm²), and the signals were recorded with a sampling oscilloscope (GAGE compuscope CS 14200) at a resolution of 10 ns.

3. RESULTS AND DISCUSSION

3.1. PCBZTPAZn, PCBZTPA, PTPAZn, and PTPA Single Layer Polymers. **3.1.1. Electrochemistry.** The electropolymerization, film formation and characterization of PCBZTPAZn, PCBZTPA, and PTPA, have been previously reported.^{6,16} Here we describe the PTPAZn polymer synthesis by the application of successive reduction/oxidation cycles in DCE, in a fashion similar to the method reported by Subbaiyan and co-workers.²⁸ Cyclic voltammetry of PTPAZn presents two one electron reversible couples at 0.53 and 0.60 V, and two irreversible peaks at more anodic potentials during the first anodic scan (Figure 1a). The first two oxidations are attributed to reversible oxidation of the tetrapyrrolic macrocycle, while the oxidation of the triphenylamine groups is responsible for the two most

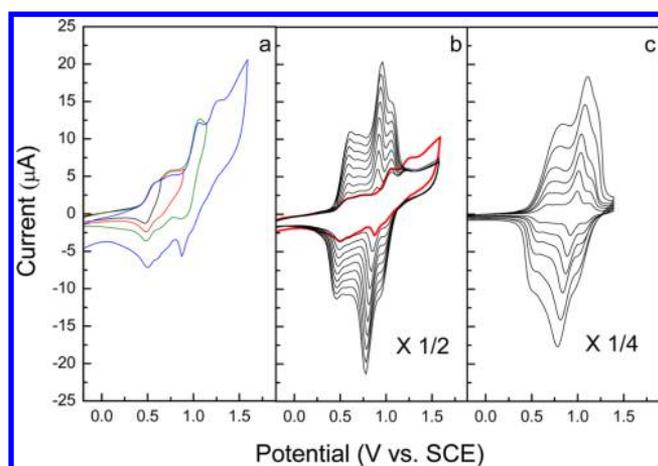


Figure 1. (a) Cyclic voltammograms (at different inversion potentials), and (b) Repetitive anodic sweeps of PTPAZn, a total of 10 scans are shown. (c) Cyclic voltammograms of electropolymerized films of PTPAZn in DCE containing only supporting electrolyte. Scan rates: 200, 150, 100, 75, 50, and 25 mV/s. All measurements were done in DCE containing (TBA)PF₆ using a Pt working electrode.

anodic peaks.^{16,26} If the electrode is cycled between -0.2 V and the most anodic peak, an increase in the oxidation/reduction currents occurs, indicating the formation of a film on the electrode surface (Figure 1b). When the electrode was removed from the porphyrin solution and placed in a solution containing only support electrolyte it showed two redox couples at 0.67 and 0.95 V. The anodic and cathodic peak currents were proportional to the scan rate, confirming that an electroactive film is irreversibly absorbed on the electrode (Figure 1c). It must be remarked that the film is not formed when the first two oxidation waves are scanned (couples at 0.53 and 0.60 V), thus the macrocycle oxidation does not conduct to polymer formation. Therefore, the polymerization mechanism involves the coupling of two TPA radical cations which form tetraphenylbenzidine (TPB) residues.^{29,30} PTPAZn holds four TPA groups which can be oxidized and involved in TPB formation. As a result, a polymer where the porphyrin units are connected by TPB units is formed.¹⁶

3.1.2. Absorption Properties of PCBZTPAZn, PCBZTPA, PTPAZn, and PTPA Electropolymerized Films. Figure S1 shows the absorption spectra of PCBZTPAZn, PCBZTPA, PTPAZn, and PTPA films electropolymerized on ITO. The polymers present the typical porphyrin Soret band and also the two and four Q characteristic bands of Zn(II) derivative and free base porphyrins, respectively, confirming that the tetrapyrrolic macrocycle has not been altered during the polymerization process. Also, for all polymers a band at around 320–330 nm is detected and attributed to absorption of the TPB/dicarbazole (for PCBZTPAZn and PCBZTPA) and TPB (for PTPAZn and PTPA) units.^{6,16} The apparition of these bands supports the polymerization mechanism already proposed.

3.1.3. Surface Photovoltage Spectroscopy. Figure 2 shows the SPV (surface photovoltage) spectra of PCBZTPAZn, PCBZTPA, PTPAZn, and PTPA single layer polymers electropolymerized on ITO. The sign of the in-phase SPV signal is positive (negative) if the photogenerated electrons are preferentially separated toward the internal (external) surface. All polymers present a SPV spectrum similar to the absorption spectra of the polymers electrodeposited on ITO, indicating

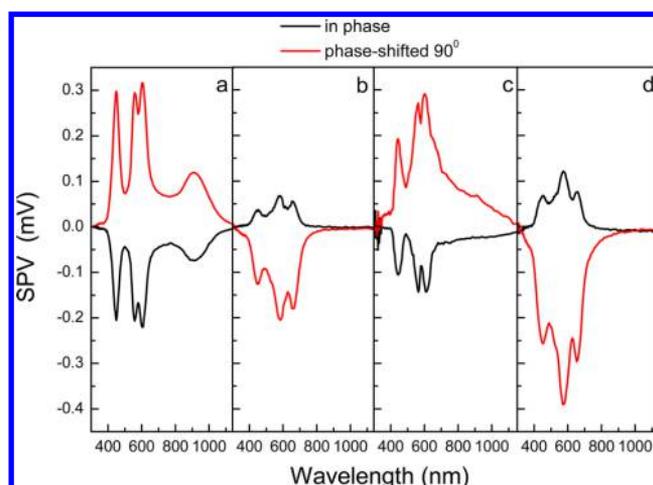


Figure 2. SPV (surface photovoltage spectra) of (a) PCBZTPAZn, (b) PCBZTPA, (c) PTPAZn, and (d) PTPA on ITO electrodes.

that these are responsible for the observed photoeffect. The SPV spectra present the typical Soret absorption band, the Zn derivative polymers (PCBZTPAZn and PTPAZn) show two well-resolved Q bands, while free base polymers (PCBZTPA and PTPA) present four Q bands which appear as two bands with two shoulders (Figure 2). For both polymers formed by Zn containing porphyrin (PCBZTPAZn and PTPAZn) the sign of the in-phase SPV signal is negative indicating that the photogenerated electrons are separated in direction to the external surface. Contrarily free base porphyrin polymers (PCBZTPA and PTPA) show a positive in-phase SPV signal, which denotes that the photogenerated electrons are separated toward the internal surface.

The spectral dependence of the phase angle²⁷ is almost constant in the range where the polymers present SPV signals (Figure 3). A constant phase angle means that the mechanisms

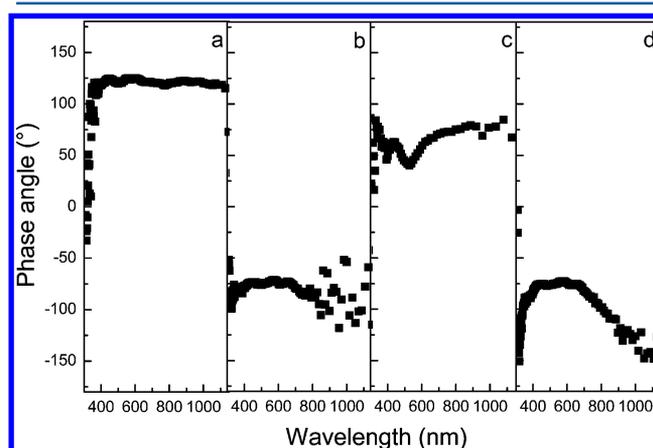


Figure 3. Phase angle spectra of (a) PCBZTPAZn, (b) PCBZTPA, (c) PTPAZn, and (d) PTPA on ITO electrodes.

of charge separation, transport and recombination are independent of the photon energy, i.e., excitation of the Q and Soret bands is equivalent with respect to charge separation and relaxation processes. However, the phase angles strongly depend on the presence of the Zn central metal in the porphyrin core, in agreement with the sign of the generated photovoltage.

The fact that the photogenerated electrons are preferentially separated toward opposite directions depending on the presence or absence of Zn(II) for both porphyrin cores is a very interesting result. It means that the photoinduced charge transfer phenomenon in the polymer/ITO interface can be modulated by the introduction of metals in the porphyrin structure. Under the present experimental conditions (ultrahigh vacuum) there are not donor or acceptor species in the vicinity of the external surface. However, when gases (air, N₂, O₂, Ar) were added to the chamber, results similar to the already described results were observed for both, free base and Zn(II) derivative polymers. Therefore, it is possible that direction of the photoinduced charge separation is an effect originated in the ITO/polymer interface. To analyze this point we modify the photoelectrode structure by introduction of a hole conducting polymer (PEDOT) between the ITO and the porphyrin polymer film.

3.2. PEDOT/PCBZTPAZn, PEDOT/PCBZTPA, PEDOT/PTPAZn, and PEDOT/PTPA Double Layer Polymers.

3.2.1. Electrochemistry. The PEDOT/porphyrin bilayers were formed by electropolymerization of a first layer of PEDOT, and a second one of porphyrin polymer. Figure 4

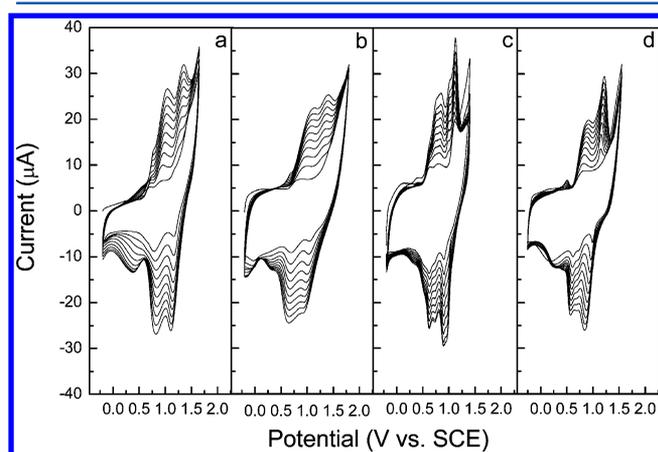


Figure 4. Repetitive anodic sweeps of (a) PCBZTPAZn, (b) PCBZTPA, (c) PTPAZn, and (d) PTPA, on top of a PEDOT layer, a total of 10 scans are shown. All measurements were done in DCE containing (TBA)PF₆ using a Pt working electrode.

shows repetitive voltammetric cycles of the porphyrin monomers on top of a previously electropolymerized PEDOT layer. Increments in the oxidation/reduction currents are visible after each cycle, indicating the successful deposition of an electroactive film on the PEDOT modified ITO electrode. In order to analyze the stability under oxidation/reduction processes of porphyrin films deposition on top of the PEDOT layer, the electrodes were placed in a solution containing only support electrolyte, and CV scans were recorded. The voltammetric responses (Figure S2) are similar to those obtained when the films were formed on ITO,^{6,16} with the exemption that they are superimposed on the PEDOT oxidation/reduction currents.

3.2.2. Absorption Properties. The electropolymerization of porphyrins on top of PEDOT was carried out on ITO, and it was also confirmed by UV-vis spectroscopy and spectroelectrochemistry. Absorption spectra of ITO/PEDOT/PCBZTPA double layer at different applied potentials were taken and the one at -0.8 V (neutral state) was subtracted from each individual spectrum, and then the resulting spectra were plotted

as Δ Abs. The same procedure was carried out for ITO/PEDOT single layer, and the results are shown in Figure 5,

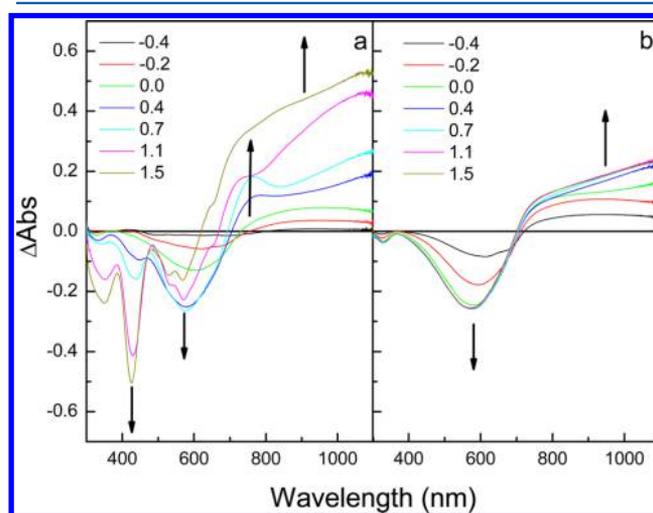


Figure 5. Difference spectra of (a) PCBZTPA and (b) PEDOT, deposited on ITO, at different applied potentials.

parts a and b. As can be seen, between -0.4 and 0.0 V the bilayer presents a negative Δ Abs between 400 and 720 nm, with maxima at about 580 nm, and a positive broad band that extends from 700 nm to the near-IR. In the same potential and wavelength range, ITO/PEDOT shows the same negative and positive bands than those observed for the PEDOT/porphyrin bilayer, indicating that PEDOT is oxidized, while the porphyrin remains unaltered.^{31,32} At more anodic potentials (0.4 and 0.7 V) both, a negative (580 nm) and a positive band (broad band that extends to the near-IR) keep growing. Also, the bleaching of the Soret band and a new positive band at around 760 nm (which is not present in ITO/PEDOT) are observed, indicating that PEDOT and porphyrin layers get oxidized (Figure 5a). Between 1.1 and 1.5 V the bleaching of the Soret band increases, and also the bleaching of the Q bands can be detected. The positive broad band that extends to the near-IR is also increased, but the intensity of this band is higher compared to ITO/PEDOT single layer. The positive band observed at 760 nm is characteristic of the TPB and Dicarbazole (DCBZ) radical cations, and the other one developed at 1.5 V is attributed to both, TPB/DCBZ dication, and PEDOT oxidized (see Figure 5b for comparison). This same behavior is observed for the other PEDOT/porphyrin layers. Absorption spectra at two different applied potentials are shown in Figure S3. All the described processes are fully reversible for several oxidation/reduction cycles.

The results above shown demonstrate that the PEDOT layer is electrochemically active (it can be reduced/oxidized) when the porphyrin layer is present at the top of the PEDOT film. Also, the presence of the bands developed at 0.7 and 1.5 V applied potentials (characteristic of the TPB and DCB radical cation, and dication) confirm that porphyrin polymerization mechanism on top of PEDOT is the same than that proposed when the PEDOT layer is not present.^{6,16} These facts demonstrated the successful generation of polymer/polymer heterojunction by a simple electropolymerization procedure.

3.2.3. Surface Photovoltage Spectroscopy. The SPV spectra of all the PEDOT/porphyrin layers, with and without Zn (II), present a negative in-phase and a positive phase shifted

by 90°, indicating that the electrons move to the external surface (Figure 6). These results are different to those obtained

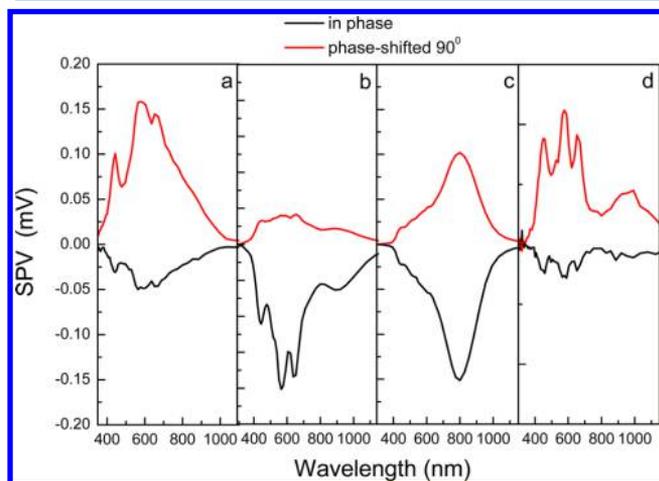


Figure 6. SPV (surface photovoltage) spectra of electropolymerized films of (a) PEDOT/PCBZTPAZn, (b) PEDOT/PCBZTPA, (c) PEDOT/PTPAZn, and (d) PEDOT/PTPA on ITO electrodes.

for single layer polymers, where the free base polymers presented a positive in-phase value and the Zn(II) derivatives showed negative in-phase values. The SPV spectra are similar to the absorption spectra of the bilayers with the difference that the Soret and Q bands are not very well resolved. However, all polymers present a constant phase in the range 300–1150 nm (Figure 7), which indicates that the photovoltage generation and recombination mechanisms are not dependent on the electronic transitions involved in the light absorption processes.

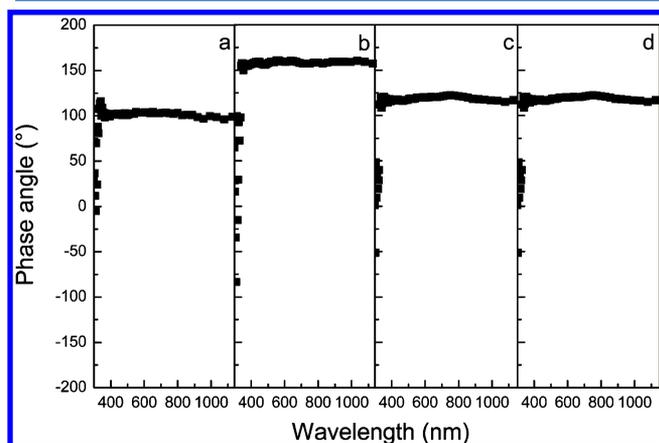


Figure 7. Spectra of the phase angle of electropolymerized films of (a) PEDOT/PCBZTPAZn, (b) PEDOT/PCBZTPA, (c) PEDOT/PTPAZn, and (d) PEDOT/PTPA on ITO electrodes.

The sign of the SPV was also confirmed by using time-resolved SPV measurements (Figure 8). All PEDOT-porphyrin bilayers show a negative surface photovoltage, the same sign than that observed in light chopped experiments, confirming that after light excitation the movement of the electrons is in the direction of the external layer, and the holes are directed toward the internal layer (PEDOT). It must be remarked that for free base polymers deposited on naked ITO (single layers), the transient SPV signal is positive.⁶

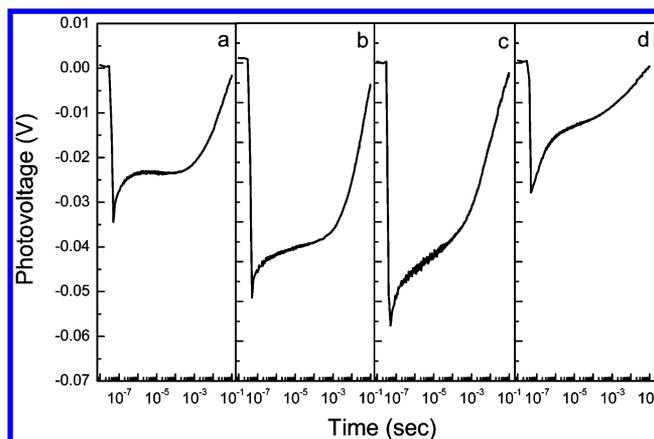


Figure 8. Time resolved SPV signals of electropolymerized films of (a) PEDOT/PCBZTPAZn, (b) PEDOT/PCBZTPA, (c) PEDOT/PTPAZn, and (d) PEDOT/PTPA on ITO electrodes.

All of these results clearly indicate that there is a change in the charge separation mechanism as a result of the presence of PEDOT between the ITO and porphyrin layer. These behaviors could be explained taking into account that PEDOT is a good hole transporter. When the porphyrin is excited, and the hole–electron pair is formed, a hole can be injected in the PEDOT layer, leaving the positive charge in the ITO/PEDOT interface and the negative charge in the external porphyrin layer (see Figure 12a).

Because of the fact that the introduction of a hole transporter produces a remarked effect on the photovoltage generated by light absorption of the porphyrin polymers, the presence of a strong electron acceptor should be analyzed. Thus, ITO/porphyrin films were modified by the deposition of an external C₆₀ layer.

3.3. PCBZTPAZn/C₆₀, PCBZTPA/C₆₀, PTPAZn/C₆₀, and PTPA/C₆₀ double layer films. **3.3.1. Absorption Properties.** Porphyrin polymer/C₆₀ bilayers were fabricated by evaporation of a layer of C₆₀ on top of the electropolymerized porphyrin films. The absorption spectra of the bilayer films looked similar to the absorption spectra before the evaporation, with the exception that there is an increment and a shift in the band located at around 340 nm compared to single layer polymers (Figure S1 and S4). C₆₀ presents an absorption band in the UV region,^{33,34} therefore it is possible that the increase observed at 340 nm corresponds to absorption of the C₆₀ layer.

3.3.2. Surface Photovoltage Spectroscopy. Figure 9 shows the SPV spectra of the different ITO/polymer/C₆₀ double layer photoelectrodes. As can be seen, all bilayers present a negative in-phase SPV signal, indicating that electrons are separated toward the external surface. Although the SPV spectra are broadened and the maxima are not very well resolved, the SPV signals are similar to the absorption spectra of the bilayer electrodeposited on ITO. They present the Q bands, and the Soret bands are observed as a shoulder. It must be noted that for all systems the SPV amplitudes are increased in comparison with single layer polymers. For example, PCBZTPAZn/C₆₀ photoelectrode generates a SPV amplitude of around two hundred times larger than that observed for PCBZTPAZn single layer under similar experimental conditions.⁶ Also, the introduction of the external C₆₀ layer produces a change in the charge separation mechanism detected for free base polymers single layers. The photogenerated electrons are preferentially separated toward the external surface when the C₆₀ is present.

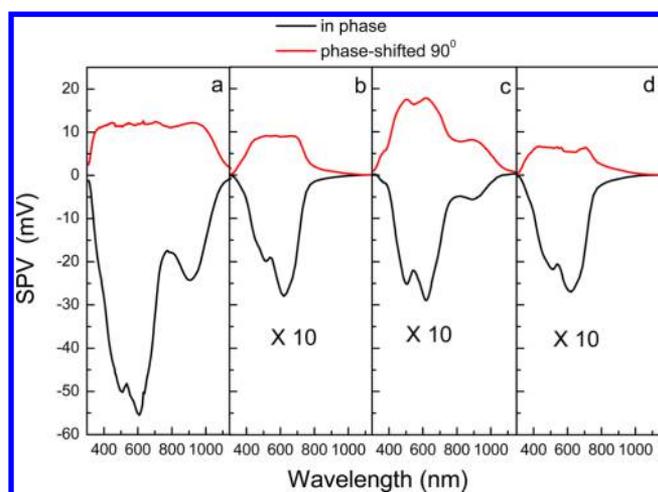


Figure 9. SPV (surface photovoltage) spectra of electropolymerized films of (a) PCBZTPAZn, (b) PCBZTPA, (c) PTPAZn, and (d) PTPA on ITO electrodes with a layer of evaporated C_{60} on top of the films.

Moreover, the phase angles are nearly constant for all the double layer systems in the 350–750 nm range, indicating that the mechanisms of charge separation, transport and recombination are independent of the photon energy (Figure 10).

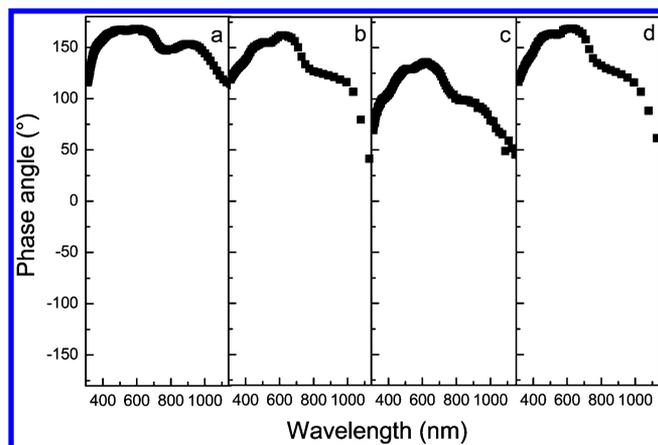


Figure 10. Spectra of the phase angle of electropolymerized films of (a) PCBZTPAZn, (b) PCBZTPA, (c) PTPAZn, and (d) PTPA on ITO electrodes with a layer of evaporated C_{60} on top of the films.

However, for free base polymers the phase angle changes respect to those obtained for free base single layer films (see Figures 3, and 10, parts b and d) in agreement with the change photogenerated charge distribution.

In concordance with the light cooped results the sign of the time-resolved SPV measurements is negative for all the bilayers (Figure 11). Zn derivative polymers present a very similar behavior, which is characterized by a very fast increase in the SPV signal of around 60 mV after pulse excitation, decreases to 50 mV, remains almost nearly constant until 0.01 μ s after laser pulse, and then decreases. Free base polymers show comparable time-resolved SPV traces. In both cases SPV signal increases within the laser pulse, then they continue increasing until 10^{-4} s, and finally decreases. These increases in the SPV signals in time are an indication of ongoing charge separation by diffusion, i.e. preferential migration of one kind of photo-generated charge carriers.

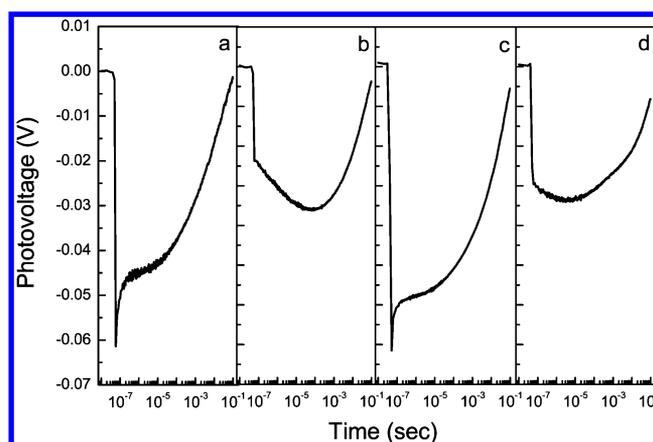


Figure 11. Time resolved SPV signals of electropolymerized films of (a) PCBZTPAZn, (b) PCBZTPA, (c) PTPAZn, and (d) PTPA on ITO electrodes with a layer of evaporated C_{60} on top of the films.

All bilayers show an increase in the SPV magnitude respect to the single layer polymers. As it was mentioned above, the observed high value could be explained analyzing the energetic states in the different layers. Both, free base and Zn polymers have a LUMO state with an energy higher than the corresponding to the C_{60} layer, and electron transfer from the polymers to C_{60} is energetically allowed (see Figure 12b). It

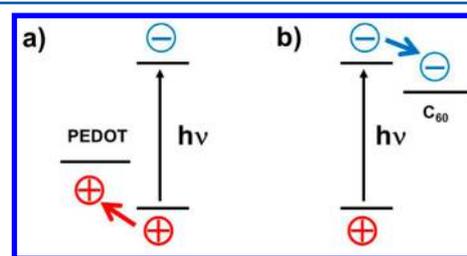


Figure 12. Energy level diagram showing the preferential movement of the photogenerated charges.

is interesting to highlight the fact that, although all photoelectrodes showed an increment in the generated photovoltage due to the presence of C_{60} electron acceptor layer, there is a marked difference in the case of ITO/PCBZTPAZn/ C_{60} photoelectrodes (Figure 10a). The huge increase observed in the SPV signal compared to ITO/PCBZTPAZn single layer could be originated from a series of characteristics of the porphyrin containing photovoltaic electropolymer. It is known that Zn (II) porphyrins are better electron donors than the corresponding free bases.^{23,35} We have demonstrated³³ that the Zn porphyrin- C_{60} dyad generated more efficiently photoinduced charge separated states than the homologue free base dyad. Although, PCBZTPAZn and PTPAZn polymers are formed by Zn(II) porphyrins, their structures are quite different. PCBZTPAZn has two carbazole (CBZ) and two triphenylamine (TPA) electro-dimerizable residues, while PTPAZn holds four electro-dimerizable TPA groups. These features conduce to differences in the polymer structures; due to the fact that CBZ and TPA have different radical cation coupling rate constants (4–5 magnitude orders higher for CBZ respect to TPA.) As a result, it is possible that PCBZTPAZn form a linear polymer with some degree of intercrossing, while PTPAZn could form a starburst like structure. This structural difference could affect the processes of charge separation and charge diffusion that

produce the photovoltage effect. Photoinduced charge separation states have been observed before in porphyrin/ C_{60} systems, where the porphyrins act as the donor unit and the C_{60} as the acceptor.^{28,33,34,36}

4. CONCLUSIONS

The effect of Zn(II) as central metal in the photoinduced charge separation process involved in ITO/porphyrin polymer heterojunctions was established through time-resolved and spectral dependence surface photovoltage. For free base polymers the electrons were preferentially separated toward the internal surface, while for Zn(II) derivatives the electrons traveled in the opposite direction. Although it is clear that the presence of Zn(II) as central metal changes the sign of the generated photovoltage in ITO/electropolymer interfaces, the origin of this phenomenon is still unknown. A more deeply study involving related tetrapyrrolic macrocycles (porphyrins and phthalocyanines) in the polymer structure is actually under development in order to clarify the causes of the observed effects.

The porphyrin films were also successfully electropolymerized on top of a PEDOT layer. Electrochemical and spectroelectrochemical experiments showed that both, PEDOT and porphyrin layers can be reversibly oxidized and reduced, demonstrating that the generation of these organic/organic heterojunctions produces electroactive and photoelectroactive films, where photogenerated charge carriers are preferentially separated, as it was demonstrated by SPV. For all PEDOT/porphyrin heterojunctions the electrons were separated toward the external surface, while the holes were transferred to the PEDOT layer. On the other hand, after deposition of a C_{60} buckminsterfullerene layer on top of the porphyrin based electropolymers, the SPV data showed that the electrons were separated in the direction of the external surface, while the holes were located in the porphyrin internal surface. The photoelectrodes exhibited a marked increase in the generated photovoltages, due to the presence of the strong electron acceptor layer. All these results show that the heterojunctions are efficient in the generation of charge separated states, and that the electrochemical generated bilayers could be used in the development of new solar energy conversion technologies.

■ ASSOCIATED CONTENT

■ Supporting Information

Chemical structures of the monomers, absorption spectra of electropolymerized single layer films, PEDOT/porphyrin polymers films, and porphyrin polymer/ C_{60} bilayers, and cyclic voltammograms of electropolymerized porphyrin films on top of PEDOT layers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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