



Article Deposition and Characterization of Heterostructures Based on Doped Ferrocene for Film-Device Applications

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Abstract: Novel heterostructures based on ferrocenium hexafluorophosphate (FcPF₆), 2,6-dihydroxyanthraquinone (DHAQ) or 2,6-diaminoanthraquinone (DAAQ), zinc phthalocyanine (ZnPc) and nylon 11 were deposited by the high-vacuum thermal evaporation (HVTE) technique. Morphological and mechanical characterizations of these organic heterostructures FcPF₆:DHAQ/nylon(ZnPc) and FcPF₆:DAAQ/nylon(ZnPc) were carried out. Subsequently, corresponding optical parameters were calculated. The heterostructure with FcPF₆:DHAQ presented the lowest optical band gap and fundamental band gap at 1.55 eV and 2.45 eV, respectively. The nylon(ZnPc) layer favors the optical behavior and places these heterostructures within organic low-bandgap semiconductor range. Additionally, devices were fabricated, and their electrical behavior was evaluated. The ITO/FcPF₆:DHAQ/nylon(ZnPc)/Ag device exhibits ohmic behavior, and the ITO/FcPF₆:DAAQ/ nylon(ZnPc)/Ag device exhibits ohmic behavior at low voltages, but at V \geq 5V, its behavior changes to Space Charge Limited Current (SCLC). This device carries a maximum current of 0.02 A, three orders of magnitude higher than the current carried by the device with the DHAQ. The SCLC conduction mechanism showed a hole mobility of 9.27×10^{-8} (cm²)/Vs, the concentration of thermally excited holes of 3.01×10^{23} m⁻³, and trap concentration of 3.93×10^{21} m⁻³. FcPF₆:DHAQ/nylon(ZnPc) and FcPF₆:DAAQ/nylon(ZnPc) are potential candidates for organic devices as an emitter layer and active layer, respectively.

Keywords: organic heterostructure; film; optical properties; band gap; electrical properties

1. Introduction

Metallocenes are organometallic compounds consisting of a transition metal atom (iron, manganese, ruthenium, titanium, and zirconium) bonded to the faces of two parallel plane cyclopentadienyl (Cp) ligands [1,2]. Metallocenes' planar chirality relates to their three-dimensional sandwich-like spatial arrangement, where two Cp ligands hold a metal atom between them [1]. Ferrocene (M=Fe) is among the most important member of the metallocene family (Fc) [3] with the first sandwich complex being discovered during the 1950s [4,5]. The Fc compound has stable covalent bonds, is diamagnetic, does not have unpaired electrons, and has an effective dipole moment of zero. Moreover, the strong interaction between Fe(II) and the Cp rings endows Fc with thermal stability and tolerance to light, oxygen and moisture; furthermore, it has good solubility in all common organic solvents and is easily functionalized [1,6]. The possible chiral structure gives Fc its stability, and reactivity to benzene [1,7,8]. Fc possesses exceptional structural and electronic characteristics [1,3]. Similarly, it has metallic and nonmetallic features; the unique bonding between the metallic species (d-orbital) and nonmetallic species (π bond) provides an electronic transfer pathway, suggesting potential molecular sensitizer applications [7,9]. Additionally, Fc is employed as a reference compound for calibration in electrochemistry, such as in cyclic voltammetry [1,6,10-12]. Considering its low oxidation potential [6,10] and a partial negative charge in the Cp rings, Fc has electron donor properties and may undergo



Citation: Sánchez Vergara, M.E.; Toledo Dircio, E.; Zubillaga Serrano, R.I. Deposition and Characterization of Heterostructures Based on Doped Ferrocene for Film-Device Applications. *Coatings* **2022**, *12*, 1859. https://doi.org/10.3390/ coatings12121859

Academic Editor: Manish Kumar

Received: 10 November 2022 Accepted: 25 November 2022 Published: 30 November 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). electrophilic substitution [13,14]. Owing to these properties, Fc derivatives have found application in several fields such as catalysis [15], material sciences [16–19], push-pull dyes [10], medicinal chemistry [20], and chiroptical spectroscopy [21–23]. Interestingly, Fc's inter-ring distance measures about 3.3 Å: suitable for hydrogen bonding [24] and, in principle, for other noncovalent interactions, between attached groups on the two Cp rings [25]. Therefore, Fc has been studied as a doped semiconductor member of the active donor:acceptor layer, for organic optoelectronic devices and applications [26,27]. Furthermore, Nar et al. [28] developed an organic field-effect transistor with ferrocenyl-carborane linked to the phthalocyanine (Pc) ring through a phenylethynyl spacer, and Akutsu et al. [29] prepared the semiconductor BEDT-TTF-based salt in which ferrocenyl-based is the counter-anion. These examples show potential applications of Fc-doped semiconductors, in the manufacture of optoelectronic devices (e.g., organic light-emitting diodes (OLEDs) [26,27], flash memories [30], organic transistors [28], and solar cells [31]).

The present and growing energy demand remains a great challenge, and alternative technologies, such as solar cells, present a solution for the excessive consumption of fossil fuels [31]. A simple solar cell consists of two semiconductor layers: the first layer type-p, has a lower electrons charge, while the second one, has a greater electron charge. These sheets joined together, are placed on two metal contacts or electrodes. The most common cells are silicon based; however, their technological complexity comes with high production costs. Organic solar cells present an opportunity to reduce costs. Their structure resembles conventional cells, replacing the type-n layer with a donor compound film, and exchanging the type-p layer with an acceptor compound film [31,32]. Within this context, we present a comparative study on organic heterostructures based on ferrocenium hexafluorophosphate (FcPF₆) doped with 2,6-dihydroxyanthraquinone (DHAQ) or 2,6-diaminoanthraquinone (DAAQ) to achieve a donor:acceptor structure in active layers [27]. The heterostructures transformed into an acceptor form to surpass the limit imposed by the exciton length in organic materials [30,33,34]. Hence, the photogenerated excitons can be dissociated instantly into charge-free carriers [33,34].

Pursuing new active layers with good performance characteristics, as well as improving device manufacturing, is a major issue. Moreover, it is important to consider that the application of solar cells requires a specific organic compound structure with excellent absorption in the visible region of spectra [35]. To meet this need, devices manufactured in this work, include a hybrid layer of zinc phthalocyanine (ZnPc) embedded in nylon 11. The Pcs exhibit strong absorption of ultraviolet spectra from 300–350 nm (B-band) and of visible spectra from 600–700 nm (Q-band) [35]. Additionally, the nylon 11 can protect heterostructures from environmental conditions such as humidity, saline environments, or thermal changes. Nylon 11's flexible and thermodynamically metastable structure allows for molding in treatments such as thermal relaxation [36,37]. During thermal relaxation, homogeneous dispersion of ZnPc particles enables for their stable attachment to the polymer [36,37]. These unusual thermal, physical, and mechanical properties make the Nylon 11 and ZnPc composite film the prime candidate for this work, which provides a novel perspective on high-value optical and electrical heterostructures with applications in optoelectronics and photovoltaics.

2. Materials and Methods

2.1. General Remarks

Ferrocenium hexafluorophosphate (FcPF₆: $C_{10}H_{10}F_6FeP$), 2,6-dihydroxyanthraquinone (DHAQ: $C_{14}H_8O_4$), 2,6-diaminoanthraquinone (DAAQ: $C_{14}H_{10}N_2O_2$), zinc phthalocyanine (ZnPc: $C_{32}H_{16}N_8Zn$), and nylon 11 (Polyundecanolactam: [-NH(CH₂)₁₀CO-]_n) were obtained from commercial suppliers (Sigma-Aldrich, St. Louis, MO, USA), and used without further purification. Organic semiconductors were produced with donor/acceptor structure: FcPF₆:DHAQ and FcPF₆:DAAQ, using reported procedures [27].

2.2. Heterostructures Assembly and Characterization

The $(FcPF_6:DHAQ)/nylon(ZnPc)$ or $(FcPF_6:DAAQ)/nylon(ZnPc)$ heterostructures were produced through stacked or planar heterojunction, of two disperse heterojunction films. The first layer contains doped ferrocene, while the second one holds ZnPc embedded in the nylon 11 matrix. The FcPF₆:DHAQ and FcPF₆:DAAQ semiconductors films were deposited on glass, PET and monocrystalline silicon (100) using a high vacuum thermal evaporation system (HVTE) (Intercovamex, S.A. de C.V., Cuernavaca, Morelos, México). In this technique each semiconductor was placed within a tantalum crucible that was introduced inside the evaporation system; subsequently, pressure inside the vacuum chamber was reduced, reaching a minimum of 10^{-5} torr; lastly, the temperature in the system was increased up to the point where the semiconductor evaporated. The gaseous semiconductor was deposited at a deposition rate of 1 A/s as a thin film, when got in contact with the substrates, after experimenting the nucleation and growth processes. Nylon 11 and ZnPc were sequentially integrated and, after each integration, nylon 11 was subject to thermal relaxation at 120 °C for 10 min. Layer thicknesses were measured using a quartz crystal microbalance monitor SISMONI-1C-3 mHz (Intercovamex, S.A. de C.V., Cuernavaca, Morelos, México) connected to a thickness sensor. The film thicknesses are: FcPF₆:DHAQ (212 nm)/nylon(ZnPc) (755 nm) and FcPF₆:DAAQ (34 nm)/ nylon(ZnPc) (755 nm).

The equipment used for the chemical and morphological characterizations of the heterostructures was a Bruker microanalysis system coupled to a ZEISS EVO LS 10 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) operated at 20 kV and a focal distance of 25 mm. AFM measurements of the films were performed in contact mode with a static tip with a Nanosurf Naio microscope (Nanosurf, Liestal, Switzerland). For the optical characterization, the ultraviolet-visible spectroscopy was obtained on a UV– Vis 300 Unicam Spectrophotometer (Thermo Fisher Scientific Inc., Waltham, MA, USA), measurements went from 200 to 1100 nm corresponding to the UV-Vvis spectrum. In order to evaluate the electrical behavior, the heterostructures were deposited on indium tin oxide (ITO: $\ln_2O_3 \cdot (SnO_2)_x$)-coated glass slide (glass-ITO). ITO works as transparent anode, while the silver was deposited at the end of the process as cathode (Figure 1). The electrical characterization was carried out using the four-tip collinear method by an auto-ranging Keithley 4200-SCS-PK1 (Tektronix Inc., Beaverton, OR, USA). The devices were illuminated using a lighting and temperature controller circuit from Next Robotix (Comercializadora KMox, S.A. de C.V., Mexico City, Mexico), using commercial LEDs with the light colors: UV (2.70 eV), blue (2.64 eV), green (2.34 eV), yellow (2.14 eV), orange (2.0 eV), and red (1.77 eV).



Figure 1. Scheme of the organic heterostructures with ITO and Ag electrodes.

3. Results and Discussion

3.1. Morphological and Mechanical Characterization of Ferrocene Heterostructures

Heterostructures were produced through HVTE technique, with identical temperature, pressure, deposition speed, and equipment parameters. After HVTE deposition, the morphological characterization of the organic heterostructures was carried out. The microphotographs at $100 \times$ for FcPF₆:DHAQ/nylon(ZnPc) and FcPF₆:DAAQ/nylon(ZnPc) are shown in Figure 2a,b, respectively. Both present a heterogeneous morphology with particles of irregular shape and size, yet the structure of the doped semiconductor affects this morphology. Fabrication begins with the deposition of the active layer, integrated by the semiconductor FcPF₆:DHAQ or FcPF₆:DAAQ, during which, the formation of nuclei is generated on the substrates. Apparently, the difference in the type of dopant, DHAQ or DAAQ, is the main cause of the shape in the nucleus, their subsequent growth, and the morphology of the film. Furthermore, Catania et al. [38] showed the effect of substrate choice during nucleation, for example, glass generates a greater number of heterogeneous nuclei. This is due to the initial processes that occur during the formation of thin films. Physisorption occurs first, with the first atoms approaching the substrate being adsorbed on its surface. Once the atom is attached to the surface, strain energy is generated at the substrate's surface due to the atoms' bonds on the surface in response to the atom's adsorption. This strain is determined by the substrate's crystalline structure. Moreover, adhering an atom to the surface produces extra energy, so there must be a force that overcomes this barrier, the nature of which depends on the deposition technique used. Nucleation at the substrate surface in HVTE is determined by the relative surface energy of the different interfaces: (i) substrate-vapor, (ii) film-substrate, and (iii) film-vapor, but HVTE ultimately reduces surface energy. The nucleation and subsequent growth of the nuclei will result in the film's final microstructure and the substrate influences the morphology of the films. It should also be noted that the heterostructure in this work is made up of two films. After the formation of FcPF₆:DHAQ and FcPF₆:DAAQ films, the layer integrated by nylon 11 and ZnPc is deposited and subjected to thermal relaxation for integration of ZnPc particles into the polymer matrix. The final morphology of the heterostructure, observed in Figure 2a,b, will depend on the dopant and its film FcPF₆:DHAQ or FcPF₆:DAAQ. The EDS performed on FcPF₆:DHAQ/nylon(ZnPc) or FcPF₆:DAAQ/nylon(ZnPc) heterostructures is shown on Figure 2c,d. Iron can be seen due to the presence of ferrocene in the active layer; the presence of zinc is shown because of phthalocyanine embedded in the polymer; oxygen is present in both the dopant and nylon 11; and nitrogen is present in ZnPc, in nylon, and in the DAAQ, regarding heterostructure FcPF₆:DAAQ/nylon(ZnPc). Heterostructures' EDS elemental analyses were performed on the entire SEM area and, they can be considered semi-quantitative measurements due to films' heterogeneity (see Table 1). However, when comparing the results of the heterostructure with the DHAQ dopant, with respect to the heterostructure with the DAAQ dopant, the heterostructure with DAAQ presents a higher percentage of nitrogen, while the one with DHAQ presents a higher percentage of oxygen, due to the amine groups and hydroxy substituents, respectively, on each dopant (see Figure 1).

To complement the information corresponding to the morphology of the heterostructures FcPF₆:DHAQ/nylon(ZnPc) and FcPF₆:DAAQ/nylon(ZnPc), it is important to analyze their topography through AFM. The smooth surface of the heterostructures plays an important role to improve the transport and mobility of charges in devices such as organic solar cells [39]. Figure 3 shows the image for a 10 μ m \times 10 μ m area, and the RMS (Root Mean Square) roughness and the Ra (Average Roughness) are provided in Table 2. The RMS represents the average of the squared deviations, with respect to the average height of the heterostructures, and is greater than Ra, which represents the arithmetic average of the absolute values of the heights of the heterostructures. However, the RMS and Ra of the heterostructure $FcPF_6$:DHAQ/nylon(ZnPc) is practically triple than roughness present in the heterostructure with the diamino anthraquinone. This is mainly due to the effect of the dopant DHAQ or DAAQ during the deposition of the ferrocene film. According to what has been reported in the experimental section, the DAAQ generates a thinner film that allows the upper nylon(ZnPc) film to be deposited more uniformly and with less roughness. The smooth surface in FcPF₆:DAAQ/nylon(ZnPc) is connected to the reduction of the interface charge traps, and so, to the production of an excellent interface between the FcPF₆:DAAQ layer and the nylon(ZnPc) layer [39].



Figure 2. The SEM microphotographs for (**a**) FcPF₆:DHAQ/ nylon(ZnPc) and (**b**) FcPF₆:DAAQ/ nylon(ZnPc). EDS for (**c**) FcPF₆:DHAQ/nylon(ZnPc) and (**d**) FcPF₆:DAAQ/nylon(ZnPc).

 Table 1. EDS analysis of the heterostructures.

Sample	C (%)	N (%)	O (%)	Fe (%)	Zn (%)
FcPF ₆ :DHAQ/nylon(ZnPc)	67.48	10.84	13.7	0.16	7.82
FcPF ₆ :DAAQ/nylon(ZnPc)	71.45	18.03	6.75	0.03	3.73



Figure 3. The AFM images for (a) FcPF₆:DHAQ/nylon(ZnPc) and (b) FcPF₆:DAAQ/nylon(ZnPc).

Table 2. Roughness and	d mechanical	parameters of the	heterostructures
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Sample	RMS (nm)	Ra (nm)	Area (m ²)	σ _{max} (Pa)	ε	НК
FcPF ₆ :DHAQ/nylon(ZnPc) FcPF ₆ :DAAQ/nylon(ZnPc)	11.34 3.83	8.72 2.83	$6.01 imes 10^{-6} \ 6.12 imes 10^{-6}$	$\begin{array}{c} 1.65\times10^8\\ 1.62\times10^8\end{array}$	0.776 0.776	0.59 0.58

Considering a maximum applied force of 900 N, a series of mechanical properties of organic heterostructures were analyzed. The outcomes of determining the maximum stress (σ_{max}), the unitary deformation (ε), as well as the Knoop microhardness (HK) under these conditions, are presented in Table 2. The mechanical properties of both heterostructures are remarkably similar from each other. Reason apparent, the doped Fc does not exert a significant influence and the nylon(ZnPc) film absorbed stress in the heterostructures. While the stress and hardness values are congruent with this type of heterostructures and deposition methods, the high strain reported results from a highly plastic region within the structure. Therefore, mechanical stress or loads under service conditions should be avoided.

3.2. Evaluation of Optical Properties

Since radiation absorption and emission are essentials for optoelectronic and photovoltaic equipment, the following analysis of the UV–Vis spectrum was conducted on the semiconductor films. The results shown in Figure 4a are, as expected, given the heterostructure's opacity, with the lowest transmittance produced by FcPF₆:DHAQ/nylon(ZnPc). According to Aslan et al. [40], the transmittance of the investigated heterostructures was detected to be relatively weak and in line with the observation. Interestingly, in the region between 600 and 700 nm the transmittance of both heterostructures, decreases significantly, a behavior related to the charge transfer transition between the Fe(II) and cyclopentene in de Fc [41–44]. The presence of opaque nylon 11 should also be considered as an important cause of low transmittance in heterostructures. Finally, in the transmission spectra, one can observe a relation between lower transmission Q (in the visible region) and B (in the near ultraviolet region) bands of the ZnPc [34], which are tied to the orbitals of the aromatic system and to the overlapping orbital on the zinc atom [34,45,46].



Figure 4. (a) Transmittance spectra, (b) spectral behavior of absorption coefficient, and (c) variation of $(\alpha h v)^{1/2}$ with hv of the organic heterostructures.

By means of absorption spectra, the different electronic transits taking place between the fundamental state and the excited state of the semiconductor films, registered because of radiation absorption from different wavelengths. The UV–Vis spectra for FcPF₆:DHAQ/nylon(ZnPc) and FcPF₆:DAAQ/nylon(ZnPc) have been studied to evaluate the absorption coefficient (α), optical band gap and nature of the transition involved. Figure 4b shows the photon energy ($h\nu$) dependence of the α for the two organic heterostructures. In these spectra, one can observe a well-defined vibrational structure whose bands can be assigned to the different transitions π – π * of Fc and ZnPc; they show a red shift in the absorption edge for FcPF6:DHAQ/nylon(ZnPc), and the intensity of the absorption peaks increases for this heterostructure [27,45,46]. This behavior is because of the DHAQ dopant on the heterostructure; however, an intense absorption of the B-band is shown from the two heterostructures at 1.85 eV. The absorption peaks, labeled the Q-band, are observed at 1.7 eV. Additionally, two bands appear in the UV region at 1.92 and 2.04 eV, labeled with N and M, respectively [45].

As mentioned before, valuable optical heterostructures depend keenly on the optical band gap (E_g) and transport energy band gap (E_t) [40,47–51]. At the absorption edge $\alpha > 10^4$ cm⁻¹ (see Figure 4b), the energy dependence of the band gap absorption coefficient is given by Equation (1) [47,48] using the Tauc plot method [39]:

$$\alpha = \frac{A}{h\nu} (h\nu - E)^n \tag{1}$$

where *A* is constant, *E* represents the band gap, and *n* assumes values of $\frac{1}{2}$, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. For allowed indirect types of transitions:

$$\alpha h\nu = A(h\nu - E)^2 \tag{2}$$

Thus, a plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ depicts a straight line whose intercept on the energy axis gives the *E* as shown in Figure 4c. The straight-line nature of the plots over a wide range of *hv* indicates the indirect type of transitions for amorphous films. From the graphs of Figure 4c, the dopants DHAQ and DAAQ evidently exert an important effect on the optical band gap of the heterostructures. Table 3 shows optical band gap E_g values, which corresponds to the onset of optical absorption and formation of a bound electron–hole pair [49,50], and the E_t corresponds to the transitions between the orbitals of DHAQ or DAAQ and the Fc structure [27,49,51]. The heterostructure with DHAQ displays lower E_g and E_t values, which could indicate a greater charge transport with respect to FcPF₆:DAAQ/nylon(ZnPc). It is important to consider lower E_g and E_t values for both heterostructures with respect to those previously reported for Fc-base, doped semiconductors [27,40,52]. The main causes of the phenomenon could be: (i) the intermolecular interactions between Fc and its dopant, (ii) the alternate between the electron-donor Fc and the electron-acceptor DHAQ/DAAQ, which generates rich zones and electron-deficient zones favoring the charge transport, and (iii) the presence of the ZnPc and its π - π * transitions, both HOMO-LUMO between their symmetry orbitals a_u and b_g (Q band), and from their occupied symmetry orbitals b_u and a_u of lower energy, to the LUMO (B band). This last one could be the most important, because the ZnPc contained in nylon(ZnPc) favors the optical behavior and places these heterostructures within an organic low-bandgap semiconductor range [53]. On the other hand, the E_t values are higher than the E_g , and their difference corresponds to the binding energy of the exciton [40,54]. According to previous studies [40,55,56], the binding energy (EB) values for FcPF₆:DHAQ/nylon(ZnPc) and FcPF₆:DAAQ/nylon(ZnPc) are in the range between 0.5 and 1.5 eV (see Table 3). The optical characteristics of the studied heterostructures favor their application in optoelectronic and photovoltaic devices.

 Table 3. Optical parameters for the organic heterostructures.

Sample	E_g (eV)	E_t (eV)	EB (eV)
FcPF ₆ :DHAQ/nylon(ZnPc)	1.55	2.45	0.9
FcPF ₆ :DAAQ/nylon(ZnPc)	1.76	2.57	0.81

3.3. Fabrication of Thin Film Device and Electrical Characterization

Thin film devices were fabricated with the heterostructures, according to the scheme shown in Figure 1 and the orbital diagram shown in Figure 5. The ITO with a work function $\phi = 4.7$ eV was used as the anode, while Ag with $\phi = 4.2$ eV was used as the cathode. According to the diagrams in Figure 5, which are based on the calculations of the HOMO and LUMO orbitals in doped Fc [27], the electrical conduction process for each device is expected to consist of the injection of holes and electrons in opposite directions. The ferrocene base film that acts as active layer in the device, is in contact with the anode, while the nylon(ZnPc) film whose function is to support the layer of doped Fc, in the absorption of radiation and generation of charge carriers, which give place to the photocurrent, is in contact with the cathode.



Figure 5. Energy levels of (a) FcPF₆:DHAQ/nylon(ZnPc) and (b) FcPF₆:DAAQ/nylon(ZnPc) devices.

The current-voltage (I-V) behavior provided valuable information about the heterostructure parameters, Figure 6a,b illustrate the forward and reverse I-V characteristics at 25 °C of the glass/ITO/FcPF₆:DHAQ or FcPF₆:DAAQ/nylon(ZnPc)/Ag heterojunction device at different illumination conditions. From Figure 6a, it is evident that, in the device with the semiconductor FcPF₆:DHAQ, there is interference, probably caused by its high roughness, generated by the nylon(ZnPc) layer, even though it was deposited in a way to enhance the optical properties in the heterostructure (ZnPc) and to protect it from the environmental conditions (nylon 11) to avoid the efficient flux of electric charges. Graph I–V shows ohmic behavior in the heterostructure with FcPF₆:DHAQ under the different lighting conditions. Under natural or ambient lighting this device shows null charge transport, while against the rest of the lighting conditions, changes are generated in the electrical transport, and the greatest electrical current is generated with green lighting. On the other hand, in the device with the semiconductor FcPF₆:DAAQ (Figure 6b), the behavior is very different to the above, and it is observed a marked ambipolarity, so the heterostructure is able to transport both electrons, and holes. This device transports current with several orders of magnitude higher than the current generated by the device with dopant DHAQ. Additionally, the device containing DAAQ has no significant change in its current transport under the different lighting conditions. A notable feature is dual operating regime; al low voltages (V \leq 0.5 V), it is nearly ohmic. The current increases at a slightly lower rate after 0.5 V. The abrupt shift in slope indicates that the device has reached a Space Charge Limited Current (SCLC) regime, which is dictated by an exponential trap distribution [57–60]. By raising the voltages (V \geq 0.5 V) to increase the current, it was possible to create a condition in which the carriers do not migrate fast enough and concentrate in a region of the heterostructure. Under these conditions, the device enters the SCLC regime and parameters such as the hole mobility (μ), thermally excited holes concentration (p_0), trap concentration per energy unit (P_0), effective density of states (N_v), and total trap concentration ($N_{t(e)}$) were

calculated. Current density (current carried per unit area) in the ohmic regime is obtained from Equation (3) [59,60]:

$$V = \frac{p_0 e \mu V}{d} \tag{3}$$



1

Figure 6. I-V characteristics of (**a**) ITO/FcPF₆:DHAQ/nylon(ZnPc)/Ag and (**b**) ITO/FcPF₆:DAAQ/ nylon(ZnPc)/Ag heterojunction devices at different illumination conditions.

In addition to the previously established parameters, e denotes the electronic charge, V the applied voltage to the film, and d is the thickness of the film. Other elements are taken into consideration in Equation (4) for determining the current density in the SCLC region [59,60]:

$$I = N_v e \mu \left(\frac{\varepsilon_0 \varepsilon}{e P_0 k T_L}\right)^l \frac{V^{l+1}}{d^{2l+1}} \tag{4}$$

 ε_0 is the vacuum permittivity, ε the dielectric constant of the material, and k being Boltzmann's constant. T_L is the temperature parameter that characterizes the trap distribution, and l denotes the slope of the ohmic regime zone, which may be calculated by dividing T_L by the local temperature. Finally, Equation (5) gives the overall trap concentration [59]:

$$N_{t(e)} = P_0 k T_L \tag{5}$$

Assuming that the vacuum permittivity is $8.85 \times 10^{-14} \text{ CV}^{-1} \text{ cm}^{-1}$, a value of 3 is used for the dielectric constant of the heterostructures, a commonly accepted average value for organic semiconductors [61]. The electrical parameters evaluated in ambient lighting conditions are shown in Table 4. Only the parameters were evaluated in these lighting conditions since, according to Figure 6b, the device does not undergo significant modification when subjected to radiation of different wavelengths. It is important to consider that, currently, there are no reported values for doped ferrocene semiconductor films and even fewer electrical parameters have been reported for ferrocene-based heterostructures, which is why this work opens the possibility of studying films of ferrocene derivatives, in different types of optoelectronic devices.

Electrical conductivity (σ) was evaluated at 25 °C for ITO/FcPF₆:DAAQ/nylon(ZnPc)/ Ag device. The measurements were made for three sets at constant voltages of 0.1, 0.5 and 1.0 V, corresponding to points in the ohmic region (0.1 V) and SCLC region (0.5 and 1.0 V). The σ for the device was determined from Equations (6) and (7):

$$R = \frac{V}{I} \tag{6}$$

$$\sigma = \frac{w}{RtL} \tag{7}$$

In these expressions, R is the electrical resistance of the material, t is the thickness of the film (789 nm, see the experimental section), L is the length of the electrodes (0.477 cm) and w is the distance between the electrodes (0.159 cm). According to the results reported

in Table 4, the highest σ in the device occurs under the ohmic regime. Subsequently, and due to charge saturation, when the device enters the SCLC regime, σ begins to decrease as the voltage increases. However, the values obtained are in the conductivity range for semiconductor films of 10^{-6} – 10^{1} Scm⁻¹ [62,63], remarkable because organic semiconductors are generally defined in terms of its room temperature conductivity. The FcPF₆:DAAQ/nylon(ZnPc) heterostructure has the potential to be used as an active layer in optoelectronic devices, while the FcPF₆:DHAQ/nylon(ZnPc) heterostructure could be studied as an emitter layer.

Electrical Parameter	Value		
μ	$9.27 imes10^{-8}~\mathrm{cm^2/Vs}$		
p_0	$3.01 imes 10^{23}~{ m m}^{-3}$		
N_v	$1.83 imes 10^{25}~{ m m}^{-3}$		
P_0	$2.0 imes 10^{40} ext{ 1/(J m^3)}$		
$N_{t(e)}$	$3.93 imes 10^{21} ext{ m}^{-3}$		
σ at 0.1 V	$1.01 imes 10^2~{ m Scm^{-1}}$		
σ at 0.5 V	$8.45 imes10^1~{ m Scm^{-1}}$		
σ at 1.0 V	$6.78 imes10^1~\mathrm{Scm}^{-1}$		

Table 4. Electrical properties under ambient illumination for FcPF₆:DAAQ/nylon(ZnPc) device.

4. Conclusions

Heterostructures based on FcPF₆:DHAQ/nylon(ZnPc) or FcPF₆:DAAQ/nylon(ZnPc) were fabricated and morphologically characterized. Some mechanical properties of the organic heterostructures were evaluated and the maximum stress is in the order of 1.65×10^8 Pa, the unitary deformation is 0.776, and the Knoop microhardness is around 0.59 HK. The mechanical properties depend on the nylon(ZnPc) layer. On the other hand, the optical properties of the heterostructures near the fundamental absorption edge can be interpreted by considering the existence of two types of optical transitions: the optical gap (1.55–1.76 eV) and the fundamental energy gap (2.45–2.57 eV). Between these transitions there are two transitions corresponding to the trap transitions. The presence of ZnPc in nylon 11 enhances the optical behavior of the heterostructures and positions them as lowbandgap semiconductors. Finally, electrical parameters of ITO/FcPF₆:DHAQ/nylon(ZnPc)/ Ag and ITO/FcPF₆:DAAQ/nylon(ZnPc)/Ag devices were studied through their currentvoltage characteristics. The ITO/FcPF₆:DHAQ/nylon(ZnPc)/Ag device shows ohmic behavior while the device with DAAQ shows an ambipolar and ohmic behavior at voltages less than 0.5 V and at high voltages its behavior changes to SCLC. Therefore, the heterostructures FcPF₆:DHAQ/nylon(ZnPc) and FcPF₆:DAAQ/nylon(ZnPc) are potential candidates for optoelectronic applications, the DHAQ heterostructure has applications as an emitter layer, and the DAAQ heterostructure can be used as an active layer in solar cells. The influence DAHQ or DAAQ as dopants is clear: although the presence of DHAQ generates better optical properties, the DAAQ dopant enhances the electrical behavior of the heterostructure.

Author Contributions: Conceptualization, M.E.S.V.; methodology, E.T.D. and M.E.S.V.; software, M.E.S.V., E.T.D., and R.I.Z.S.; validation, M.E.S.V., E.T.D., and R.I.Z.S.; formal analysis, M.E.S.V. and E.T.D.; research, M.E.S.V.; resources, M.E.S.V.; data curation, M.E.S.V. and R.I.Z.S.; writing—original draft preparation, M.E.S.V., E.T.D., and R.I.Z.S.; writing—review and editing, M.E.S.V., E.T.D., and R.I.Z.S.; visualization, M.E.S.V.; supervision, M.E.S.V.; project administration, M.E.S.V.; and funding acquisition, M.E.S.V. All authors have read and agreed to the published version of the manuscript.

Funding: María Elena Sánchez-Vergara acknowledge the financial support from Anahuac México University, project number PI0000067.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank Lorena Valle Salas for her technical support.

Conflicts of Interest: The authors declare no conflict of interest.

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