

# Influenced of the Donor-Acceptor Interface Morphology on Electrical Properties of Organic Solar Cells Based on Soluble TsNiPc

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**Abstract**—We present a simple method to modify the surface morphology of spin coated nickel phthalocyaninetertrasulfonic acid tetrasodium salt (TsNiPc) thin films by means of their immersion in different organic solvents followed by letting them dry under ambient conditions. Photovoltaic devices, based on treated TsNiPc films as donor and perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) layers as acceptor, were fabricated and tested. The electrical response of the treated devices under illumination showed significant enhancement and increased short-circuit current density ( $I_{sc}$ ) compared to the untreated devices. We attributed this electrical improvement to the increased charge carrier transport within the devices' active area, produced by the modified surface morphology of the donor layer that was caused by the solvent treatment. This morphological variation was found to increase the interfacial area between the donor-acceptor components, thereby promoting a higher yield of photo-generated charge carriers.

**Index Terms**—soluble phthalocyanine, TsNiPc, PTCDA, surface morphology, solvent treatment.

## I. INTRODUCTION

Organic photovoltaic devices have recently received considerable attention for their cost effectiveness, light weight, and low energy requirements during their fabrication process [1]-[3]. Nevertheless, compared to inorganic solar cells, the power conversion efficiency of these devices is still low for some unsolved nanoscale morphological-related reasons. One of the basic problems arising during the fabrication of organic solar cells (OSCs) is the poor capability of excitons (bounded electron-hole pairs) to dissociate into free charge carriers and then transport towards their respective electrodes [4], [5]. Consequently, improvements at the interface of donor-acceptor to overcome the short exciton diffusion length and to increase the photogenerated charge carriers [6], [7]. It is known that improving the donor-acceptor interface

via the formation of nanostructures will lead to a larger interface area for efficient exciton dissociation, thus ensuring a better charge carrier transport as discussed in some literatures [8]-[11]. Moreover, it also provides percolation path for the dissociated charge carrier to migrate to its respective electrode [12].

Previous works on bulk heterojunction photovoltaic device prove that the efficiency of the device is improving since this device is designed to create a three-dimensional (3-D) inter-penetrating network between the donor and acceptor in order to increase the interface area and prevent recombination of the free charge carrier [13]. In the case of bilayer photovoltaic device, some researchers produce the nanostructure using surface modification process which include the slow solvent vapor treatment and solvent ratio and the donor layer to achieve the same objectives as the bulk heterojunction device [14], [15].

In this work, phthalocyanine is used as the donor layer of the device since phthalocyanine exhibits outstanding optoelectronic, chemical, and thermal properties [16]. The use of phthalocyanine derivatives, possessing different central metal atoms (e.g. nickel, palladium, and platinum) in the process of fabricating organic solar cells, has shown pronounced effects on the open-circuit voltage, short-circuit current density, and power conversion efficiency of the devices [17]. Phthalocyanine with nickel as the central atom, substituted by tetrasulfonatedtetrasodium salt to produce nickel phthalocyaninetertrasulfonic acid tetrasodium salt (TsNiPc) was selected as donor and perylene-3, 4, 9, 10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) as acceptor. The role of PTCDA as an n-type organic semiconductor was to assist TsNiPc films in generating free charge carriers This was done because of the high hole mobility and weak charge carrier generation possessed by the single layered TsNipc films [17]. Moreover, the solubility of TsNiPc has allowed us to deposit its films using a simple spin coating technique rather than the conventional thermal evaporation process.

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Hence, the current paper is devoted to report a simple solvent treating method to modify the surface morphology of the TsNiPc films, thereby enhancing the electrical performance of the fabricated organic solar cell devices based on TsNiPc/PTCDA heterostructure.

## II. EXPERIMENTAL DETAILS

The organic semiconductors, TsNiPc and PTCDA, were purchased from Sigma-Aldrich and used as received. Fig. 1 shows the chemical structure of these materials. Commercially available indium tin oxide (ITO) coated glass substrates with a sheet resistance of  $7 \Omega/\text{square}$  were cut and cleaned with subsequent detergent solutions of acetone, isopropyl alcohol and deionized water.

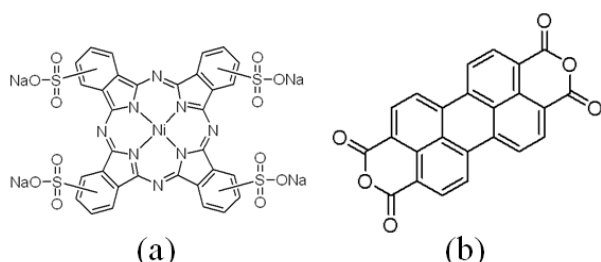


Figure 1. The chemical structure of (a) TsNiPc and (b) PTCDA

The TsNiPc solution was prepared by dissolving the powder in de-ionized water to produce a concentration of 35 mg/ml. Using this solution and the spin coating technique, films of TsNiPc with a thickness of about 100 nm were coated onto the patterned ITO substrates. For the sake of modifying the surface morphology, the TsNiPc films were immersed in toluene or chloroform for 20 minutes, and subsequently dried under ambient conditions. A 60 nm thin film of PTCDA was thermally deposited onto the treated TsNiPc films to form heterojunction active layer structures. Finally, aluminum electrode was vacuum-deposited onto these active layers to form a set of organic photovoltaic devices composed of ITO/treated TsNiPc/PTCDA/Al.

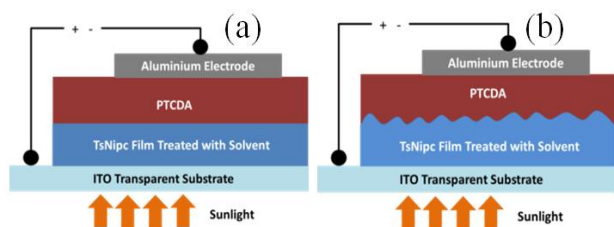


Figure 2. The schematic diagram of the organic solar cells composed of (a) untreated TsNiPc/PTCDA, and (b) treated TsNiPc/PTCDA bilayer heterojunction structures

The schematic diagram of the devices is shown in Fig. 2. In order to elucidate the modified morphology of the TsNiPc films that resulted from the treatment with different solvents, a Leica S440 Digital Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) was used. A Jasco V-570 UV-Vis-NIR spectrophotometer in the wavelength range from 200 to 800 nm was utilized to record the absorption spectra of the active layers deposited on the glass substrates.

Furthermore, a KLA Tensor P-6 surface profilometer instrument was used to measure the thickness of the films. The thickness of the TsNiPc thin films was determined at about 100 nm, while that of the treated TsNiPc/PTCDA active layers was about 130 to 140 nm. Finally, for the purpose of analyzing the electrical response, the current-voltage characteristics of the devices were measured under ambient conditions using a Keithley 2400 sourcemeter under AM 1.5G standard conditions with a white light irradiation at  $100 \text{ mW}/\text{cm}^2$  from an Oriel solar stimulator.

## III. RESULTS AND DISCUSSION

Fig. 3 shows the SEM images captured for both the untreated TsNiPc films and those treated with toluene and chloroform, respectively. A modified surface morphology of the treated films is a clear result of the treatments. Both the toluene and chloroform treated films showed the formation of a fiber-like structure with random orientation. However, the fiber shapes did not form during immersion in the poor solvents, but started to aggregate in the course of the solvent evaporation [18]. Since the boiling point of toluene is higher than that of chloroform, films treated with toluene took longer time to aggregate and to form such shapes. Thus, and because the TsNiPc was more soluble in chloroform than in toluene, clearer aggregations were produced when the films were treated with chloroform.

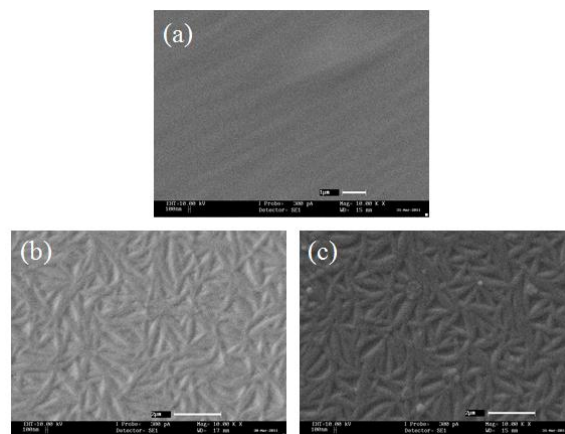


Figure 3. SEM images of TsNiPc films; (a) as-cast, treated with (b) toluene, and (c) treated with chloroform.

Based on Fig. 4a, 4b and 4c the roughness of the film varies from 41.426 nm, 15.902 nm and 8.593 nm respectively. As can be clearly seen from Fig. 4, the granular structure size and interval region between them for the untreated film is slightly larger than that of the treated films indicating that etching effect occurs on the films. This explains why the treated film has smaller rms roughness value compared to the untreated film. The film treated with chloroform has rougher surface which provides larger interface between donor-acceptor of the photovoltaic device since the size of the granules is larger as compared to film treated with toluene. Although in this research the surface roughness did not affect the absorption coefficient as shown in

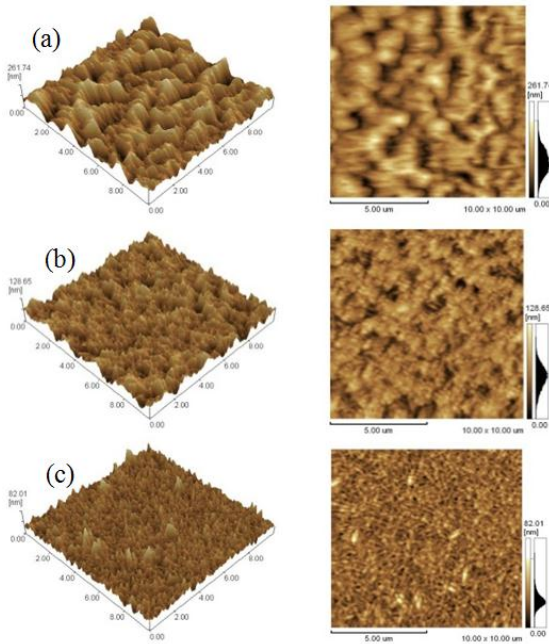


Figure 4. AFM images of NiTsPc films in 3-D (on the left) and in 2-D (on the right) for the (a) untreated, treated with (b) chloroform, and treated with (c) toluene.

Fig. 5, when fabricated into heterojunction photovoltaic device the surface roughness gives significant changes to the electrical properties of the device as shown in Fig. 6. Fig. 5-(a) shows the absorption coefficient spectra of the TsNiPc and PTCDA thin films. It can be noticed that the PTCDA film absorbs light in the visible region (400 – 600 nm), while the TsNiPc film is absorbent in two regions of 300 - 400 nm and 550 - 750 nm, respectively. The peak that occurred at a wavelength of 630 nm was due to the dimer absorption of the TsNiPc molecule [19], while the absorption peaks in the high wavelength regions were usually a result of the electronic transitions between the molecular bonding and anti-bonding orbitals,  $\pi-\pi^*$  [20].

Fig. 5-(b) shows the absorption coefficient of untreated and treated TsNiPc/PTCDA heterostructures. No pronounced difference in the peak absorption coefficients was observed. However, a relative red shift in the chloroform treated TsNiPc/PTCDA film can be seen, which suggests a higher photogenerated charge transfer between the donor-acceptor components compared to those of the acetone treated and untreated ones.

We attribute this phenomenon to the effects of solvent treatment on the morphology of the TsNiPc. As expected, in the case of the chloroform treatment, the surface modification was preferentially matched with the PTCDA acceptor to facilitate a higher donor-acceptor interface area, thereby enhancing the photo-induced charge transfer. The shape consistency between the absorption spectra of TsNiPc/PTCDA structures with those of PTCDA indicates the predominance of PTCDA photoabsorption upon blending or bringing TsNiPc into contact with PTCDA.

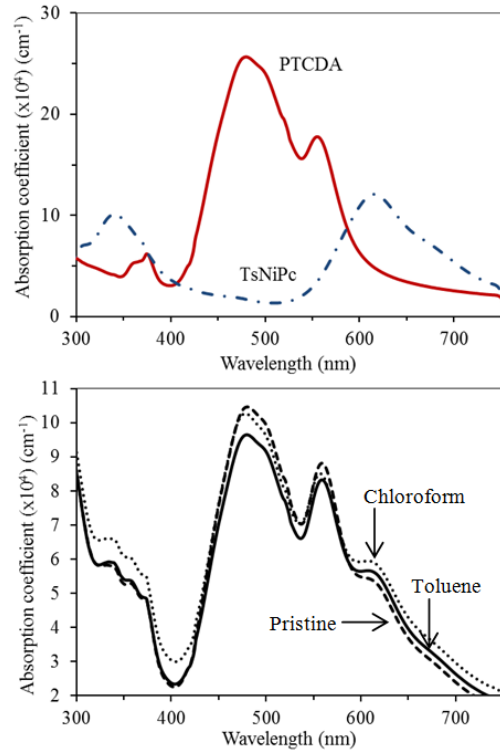


Figure 5. The absorption coefficient spectra of TsNiPc, and PTCDA films (a). As well as, untreated and treated TsNiPc/PTCDA heterostructures (b).

Fig. 6 shows the electrical photovoltaic performance of the solar cells incorporated with untreated and treated TsNiPc active layers. In comparison to the untreated devices, it was observed that the values of the short circuit current density ( $J_{sc}$ ) for the toluene and chloroform treated devices were increased by factors of four and ten, respectively. This is where a non-considerable change in the open circuit voltage ( $V_{oc}$ ) was detected (see Fig. 6). It is accepted that the  $J_{sc}$  depends on the absorption properties of the films and their charge carrier transport. On the other hand, the open-circuit voltage,  $V_{oc}$  can be approximated by the difference in the electrodes' work function or by the difference in the Highest Occupied Molecular Orbital (HOMO) of the donor and the Lowest Unoccupied Molecular Orbital (LUMO) of the acceptor [21].

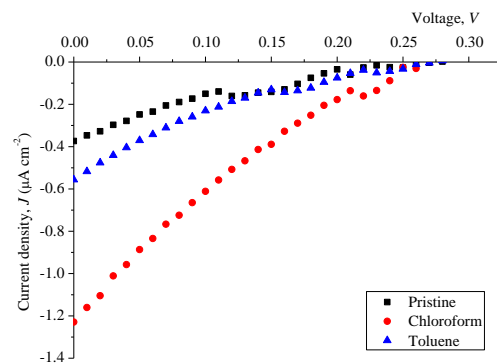


Figure 6. The current density – voltage ( $J$ - $V$ ) characteristics of ITO/TsNiPc/PTCDA/Al and ITO/treated TsNiPc/PTCDA/Al devices under light illumination

Consequently, from the  $J$ - $V$  results shown in Fig. 6, it is clear that the solvent treatment does not affect the HOMO and LUMO molecular energy levels of the materials. Since the same electrodes were used in the fabrication of both devices, similar  $V_{oc}$  resulted for the untreated and treated solar cells. Referring to Fig. 5-(b), as was previously discussed, a successive red shift in the absorption spectra of the treated TsNiPc/PTCDA was prominent compared to those of the untreated structures.

The dependency of  $J_{sc}$  on the photoinduced charge carriers' transport between the donors and acceptors suggests that in the current work, the exciton dissociation at the interfaces between TsNiPc/PTCDA would have been enhanced. Therefore, we may conclude that for the chloroform treated solar cells, a larger interface area between the TsNiPc donor and the PTCDA acceptor was produced, leading to a larger  $J_{sc}$  (11  $\mu$ A) compared to that of the toluene treated ones (6  $\mu$ A).

This can be explained with the higher solvent effect of chloroform to aggregate the soluble TsNiPc moieties to form larger fiber-like shaped structures and to produce a greater amount of humps and valleys along the surface area of the treated films (see Fig. 2 and Fig. 3). Ultimately, as a result of this morphological modification, a more suitable matching towards achieving a higher interfacial area is generated.

#### IV. CONCLUSIONS

In this work, a simple method was demonstrated for the modification of the the surface morphology of spin coated TsNiPc thin films, with the aim of enhancing the electrical properties of TsNiPc/PTCDA based organic solar cells. This was realized by means of immersing the TsNiPc films in poor solvents such as toluene and chloroform, and then allowing them to dry under ambient conditions. The electrical response of the treated devices under illumination showed significant enhancement and increased short-circuit current density ( $J_{sc}$ ). The toluene and chloroform treatments increased the  $J_{sc}$  values of the devices by about four and ten times, respectively, compared with the untreated devices. We attribute this electrical improvement to the increased charge carrier transport within the devices' active area due to the modified surface morphology of the donor layer that was caused by the solvent treatment. This morphological variation was seen increase the interfacial area between the donor-acceptor components, thereby promoting a higher yield of photo-generated charge carriers.

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