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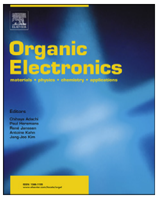

# Improved photovoltaic response of a near-infrared sensitive solar cell by a morphology-controlling seed layer

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## ABSTRACT

We demonstrate that a thin seed layer of indium phthalocyanine chloride (ClInPc) annealed under mild conditions effectively controls the morphology of both post-annealing deposited ClInPc films and ClInPc:$C_{60}$ mixed films, introducing the triclinic phase into the commonly monoclinic phase dominating film. ClInPc/$C_{60}$ planar solar cells and ClInPc:$C_{60}$ (1:1) planar-mixed solar cells with and without the triclinic phase were studied. Increased short circuit current ($J_{sc}$), fill factor (FF), external quantum efficiency (EQE) and internal quantum efficiency (IQE) of the devices containing triclinic phase is attributed to the enhanced absorption in the near infrared (NIR) region and decreased series resistance. The correlation between open circuit voltage ($V_{oc}$) and dark saturation pre-exponential factor ($J_{so}$) was analyzed to investigate $V_{oc}$ loss upon annealing. The overall performance of device is considerably improved by introducing the triclinic phase of ClInPc.

## 1. Introduction

The compatibility with low-cost materials and processing renders organic photovoltaics (OPVs) great potential to contribute to future energy needs [1,2]. However, although the power conversion efficiency of organic solar cells has steadily increased due to tremendous efforts in tuning molecular structure, morphology and device architecture [3–8], the performance of OPVs requires further improvement for commercial application. One of the limiting factors is solar spectrum loss arising from narrow absorption range of each particular conjugated organic small molecule or polymer. One approach to this issue is to establish tandem devices by stacking subcells with photoactivity in different wavelength regions, thus ensuring wide spectrum coverage [9–12]. Most organic solar cells underperform in the near infrared (NIR) wavelength region, which is a region of high solar photon flux, with 40% of the solar power being lost due to inefficient absorption in the NIR. Therefore, optimizing NIR absorption offers the opportunity to further increase the short circuit current of OPVs [13–16].

Donor materials that have NIR response include donor-acceptor conjugated oligomers and polymers [9,17], carbon nanotubes [18,19], and phthalocyanine (Pc) materials [15,20–24]. Various Pc materials are most frequently used due to their chemical tunability. Incorporating metal centers into Pc ring changes the shape of the molecule, which, in turn, tunes the morphology, crystallinity, and optical and electronic properties of the resulting films [24]. Divalent metals, such as Cu, Zn, Co and Ni, give planar metal-Pc complexes, which form herringbone stacks in films. Two similar polymorphs, assigned as the α- and β-phase, are induced from two different intermolecular tilt angles within the herringbone stack [25,26]. The high similarity of the two phases gives rise to similar absorption features, with the most intense Q-band located between 500 and 750 nm [21,27]. On the contrary, non-planar Pc materials, including PbPc, ClAlPc, TiOPc, VOPc and ClInPc, exhibit vastly different polymorphs, which are assigned as monoclinic phase and triclinic phase [28–30]. Monoclinic form consists of molecules stacking in a face-to-face fashion, giving rise to metal ions in a linear chain [28,31]. Triclinic form consists of molecules stacking in a head-to-tail fashion, alternately orienting convex and concave sides [28,32]. The monoclinic form displays a blue-shifted absorption band compared to the monomer absorption, while the triclinic phase displays a red-shifted absorption band compared to the monomer [22,33–36]. In PbPc, for example, the absorption maximum of the triclinic form is at 900 nm while that of the monomer is at 690 nm[23, 33]. Thus, the triclinic phase of non-planar Pc materials, in particular, renders them very interesting NIR absorbers for organic

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solar cells. Phase transformations between monoclinic and triclinic and/or mixtures of the two phases in thin films can be accessed by varying the deposition rate, tuning the substrate temperature during deposition, solvent annealing, or templating via a crystalline interlayer.

Tuning the organic film crystallinity, molecular orientation and aggregation by a templating layer toward better performance of organic solar cells has been drawing interest. The templating layers are focused on semiconducting organic molecules [37–39] and copper halide [33,35,40,41]. However, organic templating materials would cause competent light absorption, as well as additional interfacial energetics to be considered. Copper halide is light sensitive and is detrimental to stability of organic materials [42]. The aforementioned limitations evoke endeavors to investigate alternative strategies to achieve the same outcome.

In this work, we demonstrate that annealing a thin (5 nm) seed layer of ClInPc under mild conditions is a useful strategy to introduce the triclinic phase in subsequently deposited ClInPc film or ClInPc:$C_{60}$ mixed films. Triclinic phase evolution was proved by morphology and absorption studies. Introducing the triclinic phase into ClInPc solar cells enhances device absorption and EQE beyond the 800 nm region and significantly increases IQE throughout the entire ClInPc photoactive region, which leads to increased $J_{sc}$, FF and power conversion efficiency (PCE) in both planar and planar-mixed solar cells. The loss of $V_{oc}$ with increasing triclinic phase was investigated and was explained by an increased dark saturation pre-exponential factor, $J_{so}$. The device performance is consistent with the previous study that adjacent molecules in triclinic phase have stronger $\pi$-$\pi$ interaction than those in monoclinic phase [34]. On one hand, the stronger intermolecular interaction is responsible for the more delocalized electronic states [34] favoring charge generation and collection. On the other hand, the stronger intermolecular interaction enhances recombination at donor/acceptor (D/A) interfaces leading to higher $J_{so}$. Hence, the molecular aggregate structure in non-planar phthalocyanine films needs to be carefully studied and engineered to fully utilize this NIR sensitive solar cell material.

## 2. Materials and methods

ClInPc was purchased from Lumtec Corp., $MoO_3$, $C_{60}$ and BCP were purchased from Sigma-Aldrich Company. Organic thin films were grown on 10 nm $MoO_3$ pre-deposited on indium-tin-oxide coated glass substrate (ITO/glass) in high vacuum ($<10^{-6}$ Torr) at rate of 0.5 Å/s, with the substrate maintained at room temperature during deposition. ClInPc:$C_{60}$ (1:1) blend films were prepared by co-deposition with both rates at 0.5 Å/s. Annealing of 5 nm seed layer of ClInPc was conducted on a hot plate in $N_2$ environment at 60 °C, 80 °C or 100 °C for 15 min $MoO_3$ and the subsequent organic layers were deposited without a mask, while the top Ag electrode was deposited with a metal mask to yield a final device area of 1.21 $mm^2$.

The optical absorption was obtained by measuring the transmittance and reflectance of the ClInPc films on ITO/glass deposited with 10 nm $MoO_3$ using an Evolution 220 UV–Visible Spectrophotometer with ISA 220 integrating sphere. The morphology of the films was characterized in air using an Agilent 5500 atomic force microscope (AFM). All devices related operation and measurement were performed in a nitrogen filled glovebox. Current-voltage characteristics of organic solar cells was measured under dark and simulated AM 1.5G solar illumination from a solar simulator with a Xe-arc lamp. A crystalline Si reference cell was used to measure the intensity of the solar simulator, which was adjusted to 1 sun.

## 3. Results and discussion

### 3.1. Film morphology

First, we characterized the morphologies of a 5 nm seed layer of ClInPc as-deposited or annealed at different temperatures (shown in Fig. 1). Fig. 1a of bare ITO surface morphology shows clusters of tens of nanometers in diameter with root mean square (RMS) roughness of 1.23 nm. A 5 nm ClInPc seed layer (Fig. 1b–e) as-deposited or annealed covers the ITO cluster morphology, suggesting the presence of a continuous wetting layer. The as-deposited film is mostly uniform with sparsely distributed islands. RMS roughness of ClInPc films increases along with the annealing temperature, which is 2.2 nm for as-deposited film, 3.2 nm, 5.6 nm and 6.1 nm for films annealed at 60 °C, 80 °C or 100 °C, respectively. The roughness partially arises from the lateral growth of islands. To understand the vertical growth behavior of islands at different temperatures, the height density distribution was plotted in Fig. 1f. The as-deposited ClInPc film exhibits a density maximum at 4.7 nm, a shoulder at 5.8 nm, and a tail extending to 10 nm. Upon annealing, all density distributions are broadened, with the maxima shifting to 5.5 nm. The distribution tail extends to 12 nm for the film annealed at 60 °C, and to 30 nm for the film annealed at 80 °C or 100 °C. Therefore, we can conclude that larger size clusters evolve with higher annealing temperature.

Next, we investigated the morphologies of films with an additional 15 nm ClInPc grown on the aforementioned 5 nm seed layers (Fig. 2a–d). Significant differences in film morphology were observed for films grown on seed layers annealed at 80 °C and higher. The domain size of ClInPc films also increased with increasing seed layer annealing temperature: RMS roughness of 15 nm ClInPc films grown on seed layers as-deposited or annealed at 60 °C, 80 °C or 100 °C were 3.5 nm, 4.2 nm, 6.7 nm and 7.1 nm respectively.

Fig. 2e–f shows surface morphology of ClInPc:$C_{60}$ (1:1) blend films used for planar-mixed solar cells. The films were prepared as follows: seed layer either as-deposited or annealed at 80 °C was prepared on $MoO_3$ covered ITO/glass. An additional 5 nm ClInPc and 10 nm ClInPc:$C_{60}$ (1:1) blend was subsequently deposited. The surface of a ClInPc:$C_{60}$ (1:1) blend film is smoother than that of neat ClInPc films. The RMS roughness of the blend film on the seed layer as-deposited is 1.2 nm and on the annealed seed layer is 5.6 nm. The observed larger cluster size and higher RMS roughness of the ClInPc films and ClInPc:$C_{60}$ (1:1) blend films grown on the annealed seed layer suggest better crystallinity.

### 3.2. Film absorption

Fig. 3a shows the absorption of 15 nm ClInPc film grown on 5 nm ClInPc seed layer. As was observed for non-planar phthalocyanine materials, PbPc, VOPc and TiOPc, the triclinic phase induces stronger $\pi$-$\pi$ interaction between adjacent Pc rings and causes broadening of the Q-band spectrum toward NIR [43–48]. The reason for this broadening is the prevalent exciton coupling in the coordinated complex [22,49]. For the as-deposited film, the dominant peak at 730 nm can be assigned to the monoclinic phase of ClInPc. Upon annealing at 60 °C, a very weak shoulder evolves at 830 nm, which can be assigned to the triclinic phase of ClInPc. Increasing absorption at 830 nm, corresponding to an increasing concentration of the triclinic phase, is observed with increasing annealing temperature. Examining the integral of the total absorption spectra of these films, it is apparent that the integral of all 20 nm ClInPc film are identical at wavelengths below 800 nm but diverge above 800 nm. The triclinic phase in films annealed at 80 °C or 100 °C significantly contribute to the total absorption.