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## Exciton Dissociation at Indium Tin Oxide/Indium doped Zinc Phthalocyanine Interface

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**Abstract.** A new intercalation of Indium and zinc phthalocyanine (ZnPc) thin film is developed by using thermal co-evaporation technique. The exciton dissociation at the interface of Indium Tin Oxide (ITO) electrode and Indium doped ZnPc upon laser irradiation is observed through the transient photovoltage measurement technique in comparison with the interfacial exciton dissociation occurred at ITO/pristine ZnPc interface. The occurring transient photovoltage spike is regarded as the effect of exciton dissociation at ITO/In-doped ZnPc interface and depends on the amount of free carrier separation by built-in field or charge carrier concentration according to doping ratio. The experiments demonstrate the existence of exciton dissociation at ITO/In-doped ZnPc interface, the direction of charges transfer is that holes are injected to ITO, whereas electrons are left in bulk film. A thin insulating layer of 6 nm thick lithium fluoride (LiF) is inserted between ITO and In-doped ZnPc to prevent the exciton dissociation at ITO/In-doped ZnPc interface and insist on the phenomenon of interfacial exciton dissociation. Further photoelectron spectroscopy experiments prove that In-doped ZnPc is hole transport material.

### Introduction

The performance of organic photovoltaic cells has been in progress since Tang's excellent article was published [1], which is directly attributed to the theory of donor/acceptor (D/A) interface that functions as a site for efficient dissociation of excitons [1,2,3]. In organic photovoltaic cells, the dissociation of photoinduced excitons is a very vital process to produce photocurrent [4]. However, the process of exciton dissociation in organic photovoltaic cells is still not fully understandable. In order to enhance the efficiency of organic photovoltaic cells, a proper understanding of the exciton dissociation mechanism is an essential requirement [5].

Song *et al* first introduced a transient photovoltage study of exciton dissociation process at the interface of ITO and N,N'-Bis(naphthalene-1-yl)-N,N'-bis(phenyl) benzidine (NPB) [6]. They have discovered a polarity transition of transient photovoltage from negative to positive of ITO/NPB/Al (Al grounded). This phenomenon was explained that it is attributed to a combination of interfacial dissociation of excitons at ITO/NPB interface and the free carrier separation by built-in field in NPB bulk, experimentally demonstrates that the exciton dissociation certainly exists at the ITO/NPB interface and after the dissociation, electrons are injected into ITO whereas holes are left in NPB film.

In addition, a negative to positive polarity change in transient photovoltage upon pulse laser irradiation was also observed at the interface of ITO and copper phthalocyanine (CuPc) [7]. They also explained that the polarity change is regarded as a combination of the exciton dissociation at ITO/CuPc interface (fast process) and the field-induced free carrier separation (slow process). The experiments verified the existence of exciton dissociation at ITO/CuPc interface, and the direction of which is electrons are injected into ITO with holes left in CuPc film.

Both findings mentioned above employed transient photovoltage measurements in nano-second time domain in order to capture the rapid polarity change from negative pulse to positive pulse upon pulsed laser irradiation. Their findings indicate that, at first electrons are injected into ITO whereas holes are left in organic thin film (fast process) and secondly, the directions of them are reversed, holes are injected into ITO while electrons are left in organic thin film (slow process). The whole process was described in detail, the fast process (negative pulse) is due to the interfacial exciton dissociation in nanosecond time domain and the slow process (positive pulse) spontaneously arise from free carrier separation in the built-in field which can be measured in micro-second time domain.

We are interested in studying the transient photovoltage at the interface of ITO and phthalocyanine materials in slow process or in a few millisecond interval time domain, to properly investigate whether such a positive transient photovoltage is the effect of the exciton dissociation at the interface or not.

In the present research, indium doped ZnPc is selected as the organic semiconductor material to study the phenomenon of transient photovoltage at the interface of ITO electrode, especially in the interval of millisecond time domain, or focus only on the positive transient photovoltage. In-doped ZnPc with different Indium doping ratio can vary in its charge-carrier concentration and induce similar but not the same shape of transient photovoltage in comparison with that of undoped ZnPc.

## Experiment

All devices prepared in this work were fabricated with different stacking structures as depicted in Fig. 1. Glass substrates coated with ITO ( $12 \Omega/\square$  sheet resistance) were cleaned and heated to  $120^\circ \text{C}$  before loaded into high vacuum chamber. ZnPc powder purchased from Aldrich was chosen as the matrix material for the present study. Undoped ZnPc and Indium doped ZnPc thin films were deposited by thermal evaporation method at a base pressure of  $2 \times 10^{-5}$  mbar. With Indium dope, the molar doping ratio of Indium and ZnPc was specifically designed to be 1:4, 1:8 and over dope 1:1 ratio. The film thickness were continuously monitored during evaporation using two independent quartz crystal oscillators at a deposition rate of  $0.4 \text{ nm/s}$  for ZnPc and  $0.1 \text{ nm/s}$  for Indium (1:4). ZnPc and Indium were grown simultaneously on the substrates. The thickness of pristine ZnPc and In-doped ZnPc is varied from  $50 \text{ nm}$ ,  $100 \text{ nm}$  to  $350 \text{ nm}$ . The film on ITO glass substrate was fabricated as Schottky diode in order to measure its electrical characteristics because ITO electrode has proved to be an effective ohmic contact to many organic semiconductor materials. Another electrode, the  $100 \text{ nm}$  thick aluminum electrode was deposited as Schottky contact by using thermal evaporation method as well. The complete devices have an effective area of approximately  $2 \times 2 \text{ mm}^2$  for both pristine ZnPc and In-doped ZnPc. The transient photovoltage measurement was carried out by illuminating the device from the ITO side with laser light source ( $\lambda = 532 \text{ nm}$ ) while the Al cathode was grounded and the transient signal was recorded by a Lecroy oscilloscope.

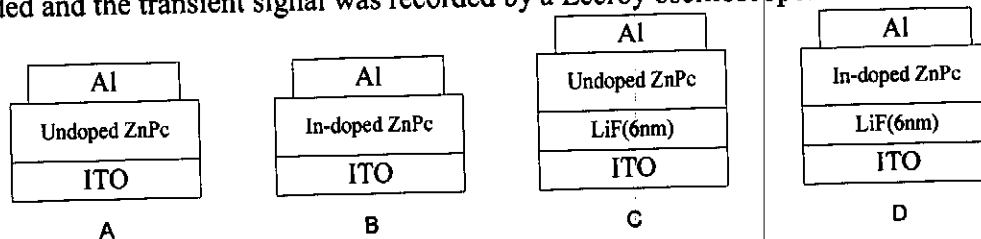


Fig. 1. The stacking structure of devices.

## Results and Discussions

### Transient Photovoltage Measurement

Fig. 2 shows the screen of oscilloscope which measure the transient photovoltage evolution of the devices versus time upon pulsed laser irradiation. The laser pulse control signal is generated from the arbitrary signal generator with  $400 \text{ millisecond (mSec)}$  pulsewidth rectangular wave. The transient

photovoltage of ITO/pristine ZnPc(50nm)/Al device is recorded in Fig. 2 a). It is immediately noticeable that the photoinduced voltage response is composed of two parts. The first one is the sharp positive spike (yellow) arise immediately after the rising edge of the laser pulse (violet) and reach its maximum amplitude at 400 mV in a few nSec before decaying down exponentially to about 200 mV within 70 mSec. The second part is the photoinduced voltage responded to the rectangular wave laser pulse in which it start to appear at about 70 mSec after the first part. Its amplitude voltage increase exponentially until reach the steady state amplitude at more or less 400 mV. When the laser pulse is off at 400 mSec, the photovoltage is decayed suddenly to 0 volt within a few mSec.

To prove that such a sharp positive rising edge directly result from the exciton dissociation at the interface between ITO and ZnPC, the layer of LiF(6nm) is inserted between ITO and ZnPC because LiF will be able to block the exciton transferred at the interface and the photoinduced sharp positive spike will be vanished.

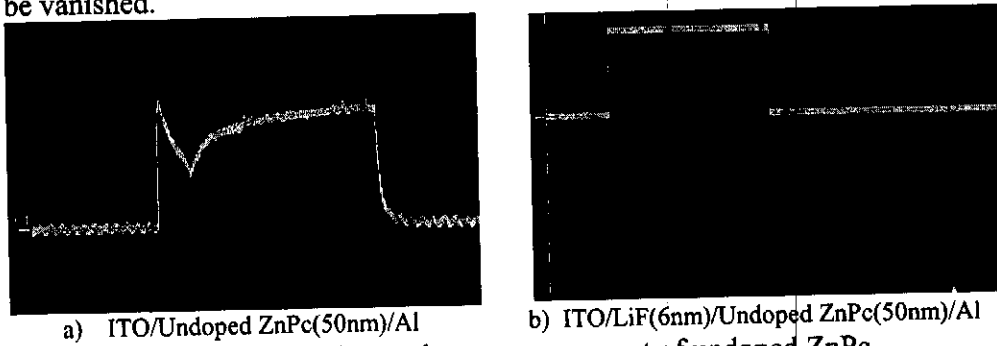


Fig.2. Transient photovoltage measurement of undoped ZnPc.

Fig. 2 b) shows the photovoltage of ITO/LiF(6nm)/pristine ZnPc(50nm)/Al. It is surprisingly that the sharp positive spike disappear as expected. The photoinduced voltage response (violet) rise exponentially until reach about 400 mV within a few hundred mSec and decay exponentially to 0 volt after the laser pulse is off (yellow). This experiment reveal that there is a phenomenon of exciton dissociation at the interface of ITO and ZnPc. The observed sharp positive pulse photovoltage indicates that the exciton dissociation at the ITO/ZnPC interface occurs in such a way that holes are injected into ITO and leaving electrons in the ZnPc film. This phenomenon should be confirmed further by investigation the existence of interfacial exciton dissociation of ITO and Indium doped ZnPc because the free-carrier charge concentration of ZnPc should be risen upon Indium doping. Then it will lead to the conclusion that such a photoinduced sharp positive pulse is directly relevant to the amount of carrier concentration.

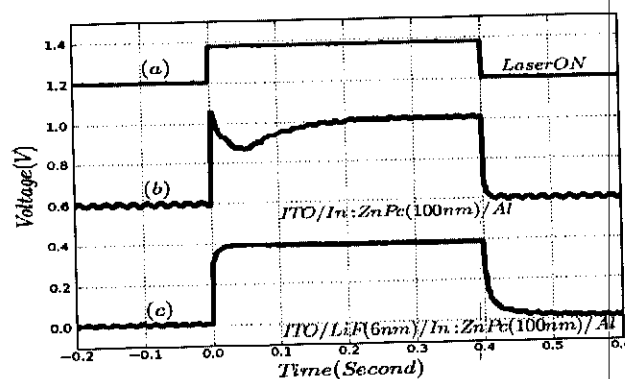


Fig.3. Transient photovoltage measurement of Indium doped ZnPc(1:8 ratio) with 100 nm thick.

The photovoltage measurement of Indium doped ZnPc devices is illustrated in Fig. 3. The doping ratio of Indium and ZnPc is intentionally selected to be 1: 8 for first experiment. As can be seen in graph b) and c), the phenomenon of interfacial exciton dissociation occurs at ITO/In-doped ZnPc(100nm) interface as well. The sharp positive spike increase immediately upon laser irradiation(400 mS pulsewidth) until reach its maximum voltage at about 450 mV before decaying

down to 250 mV within 50 mS. In case of inserting LiF(6nm) exciton blocking layer, there is no such a sharp positive spike as well which indicates that LiF is capable of blocking interfacial exciton dissociation at ITO/In-doped ZnPc. And the photoinduced voltage response is risen exponentially faster than that of pristine ZnPc to the steady voltage of 400 mV.

In order to observe the relationship of interfacial exciton dissociation of ITO/In-doped ZnPc and the amount of free-charge carrier concentration, the Indium doping ratio will be varied and the thickness of In-doped ZnPc is selected to be 350 nm. Because with thicker film, the photoinduced amplitude voltage due to the rectangular wave laser pulse or unit step response will decline. Therefore, the change of the transient photovoltage according to the interfacial exciton dissociation(spike) with different doping ratio can be particularly noticeable.

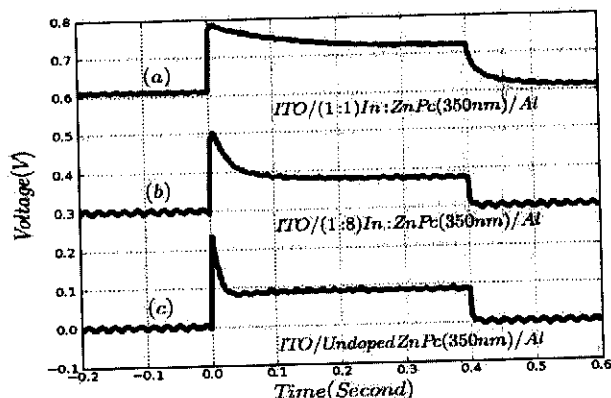


Fig.4. Transient photovoltage measurement of Indium doped ZnPc (350 nm thick).

With different doping ratio in comparison with pristine ZnPc, the transient photovoltage of the devices are displayed in Fig. 4. Now focusing on the duration of the decay time of the sharp positive spikes of each one. The decay time of the spike of undoped ZnPc device decline to a voltage of steady state at about 50 mSec(graph c) while that of In-doped ZnPc(1:8 ratio) reduce to a steady state voltage at about 200 mS(graph b). The third graph, the decay time of the transient photovoltage of In-doped ZnPc(1:1 ratio) which is over doped(graph a), it takes longer than 350 mS to decay to steady state. When the laser pulse is off at 400 mS, the photoinduced voltage of over doped ZnPc devices also decay slower than that of the others. The resulting more decay time of In-doped ZnPc devices indicates that In-doped ZnPc thin film has more carrier concentration than that of undoped ZnPc device.

In other words, the exciton dissociation at the interface of ITO/Phthalocyanine materials occurs with light irradiation and attributed to free-charge carrier separation by built-in field. The more carrier concentration the longer decay time of the transient photovoltage comes into existence.

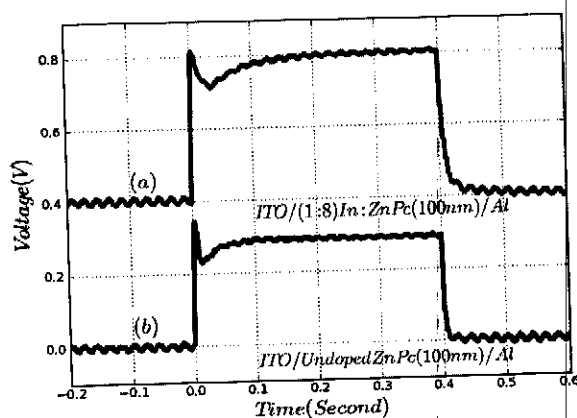


Fig.5. Comparison of transient photovoltage measurement of (a) In-doped ZnPc(1:8 ratio) and (b) undoped ZnPc.

Fig. 5 shows the comparison of transient photovoltage of the undoped ZnPc device and In-doped ZnPc device which fabricated with 100 nm thick. The resulting response is the same as in the case of 350 nm thick, that is, the decay time of the spike in case of undoped ZnPc has a duration about 12 mSec(graph b) whereas the decay time of In-doped ZnPc(1:8 ratio) device takes longer time, it has a duration about 35 mS(graph a). This experiment also confirms that In-doped ZnPc thin film has more carrier concentration than that of undoped ZnPc device.

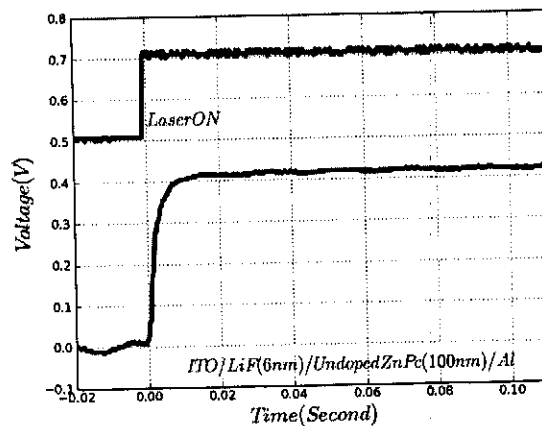


Fig. 6. Photovoltage measurement of ITO/LiF(6nm)/undoped ZnPc(100nm)/Al

Exciton blocking layer, 6 nm thick LiF layer is an insulator used to prevent charge transfer from ZnPc or In-doped ZnPc to ITO as shown in Figure 2. b), Fig. 3(graph c) and as well as Fig. 6. In Fig. 6, the photoinduced voltage response of pristine ZnPc device(100nm) is plotted in comparison with the laser pulse signal. It is noticed that, with LiF exciton blocking layer, the output photovoltage takes only 15 mSec to rise up from 0 volt to the steady state amplitude of 0.4 volt. But, without LiF, it takes almost 100 mSec as shown in graph b of Fig. 5. This special characteristic can also be observed in In-doped ZnPc device(Fig. 3).

#### Photoelectron Spectroscopy Study

The basic principle of doping in organic semiconductor is equivalent to that in inorganic materials. Free charge carriers are generated by adding impurities which either transfer an electron to the electron conducting(LUMO) states(n-type doping) or remove electron from the hole conducting(HOMO) states(p-type doping). Generally, the type of semiconductor materials can be investigated by measuring the significant Fermi level shift towards the corresponding transport conducting states using photoelectron spectroscopy. For organic materials such as phthalocyanine, ultraviolet photoemission spectroscopy(UPS) is generally used to determine the HOMO peak position at binding energy of valence band emission. And inverse photoemission spectroscopy(IPES) is always used to investigate the LUMO peak position at binding energy of conduction band emission. Therefore, it requires both UPS and IPES to identify the type of doped organic semiconductor whether it is electron doped or hole doped material. However, x-ray photoemission spectroscopy(XPS) is going to be used to carry out investigation instead due to some reason.

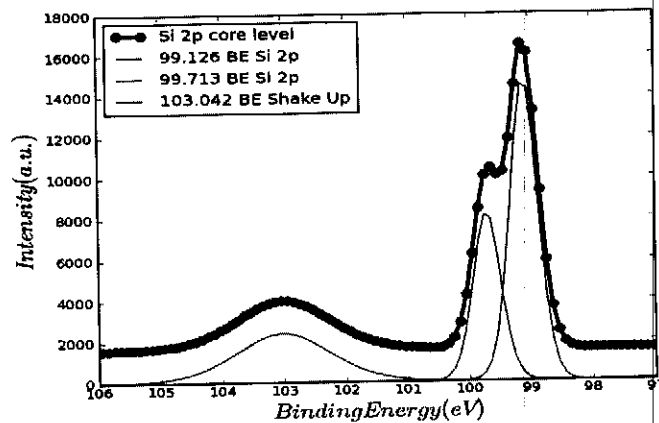


Fig.7. Si 2p core level XPS measurement of intrinsic Silicon substrate, Si(111)

Fig. 7 shows the binding energies of Si 2p bulk component of the intrinsic Silicon substrate used throughout the experiment. This XPS spectrum (blue dot line) of Si 2p emission is composed of 99.126 eV, 99.713 eV components and the shake up component at 103.042 eV. The cleaned intrinsic silicon substrate will be used as the substrate for deposition of 2 nm thick ZnPc and another one, 2 nm thick In-doped ZnPc(1:4). Because the Si 2p binding energy can vary for extremely p-doped to extremely n-doped samples between 98.8 eV and 99.9 eV. Then, the physical interaction of phthalocyanine and intrinsic silicon at their interface should be observed directly from XPS spectrum of Si 2p.

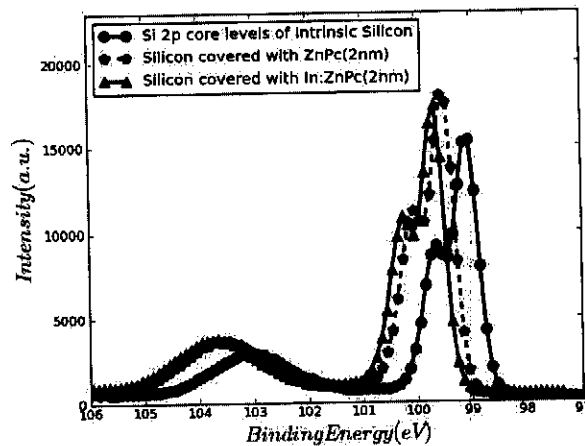


Fig.8. Si 2p core level XPS measurement of intrinsic Silicon substrate, ZnPc on Silicon, In-doped ZnPc on Silicon.

The line shape of the substrate Si 2p emission of silicon substrate covered with 2 nm ZnPc and silicon substrate covered with 2 nm In-doped ZnPc(1:4) are demonstrated in Fig. 8. Silicon covered with ZnPc which is p-type semiconductor, its Si 2p emission spectrum shift to higher binding energy of 99.488 eV (red dash line). With Indium dope, Si 2p emission spectrum of silicon substrate covered with In-doped ZnPc(1:8) move further to higher binding energy of 99.603 eV (soft blue dot line in Fig. 9). For higher doping ratio, In-doped ZnPc(1:4), its Si 2p emission spectrum also move further to higher binding energy of 99.680 eV (up triangle line).

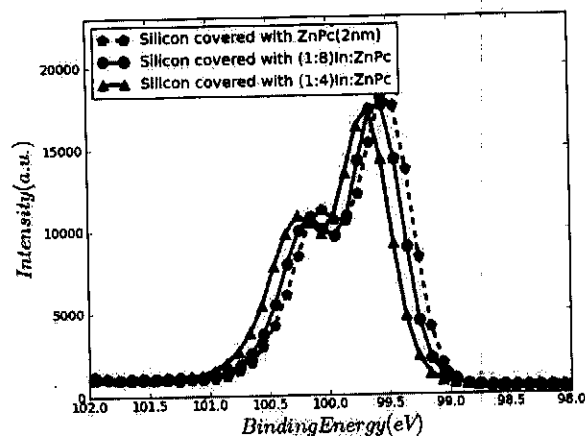


Fig.9. Si 2p core level XPS measurement of ZnPc on Silicon and In-doped ZnPc on Silicon.

With the XPS measurement results, Si 2p emission spectrum of silicon substrate covered with ZnPc shift to higher binding energy and with Indium dope, its Si 2p emission spectrum move further to higher binding energy which is directly proportional to the doping ratio. The more Indium doping ratio, the higher binding energy of Si 2p emission spectrum. ZnPc is known as p-type organic semiconductor, from the XPS result, there must be physical interaction between intrinsic silicon and ZnPc at their interface such as induce intrinsic silicon becomes p-type silicon. Thus, its Si 2p emission spectrum shift toward higher binding energy. With Indium dope, the physical interaction of Indium and ZnPc must occur in such a way that electrons from ZnPc molecules transfer to Indium atoms. Then ZnPc becomes hole doped ZnPc or In-doped ZnPc is p-type semiconductor as well. The sharp positive transient photovoltage of In-doped ZnPc device confirms that free charge carrier of In-doped ZnPc are positive charges or holes, that is In-doped ZnPc is hole transport material. With regard to this analysis, it is consistent with the shift toward higher binding energy of Si 2p emission spectrum of silicon substrate covered with In-doped ZnPc. Indium doped ZnPc is p-type, then Si 2p emission spectrum shift toward higher binding energy with higher doping ratio.

The result of transient photovoltage measurement is reasonably consistent with the p-type investigation of XPS spectroscopy results. Exciton dissociation at the interface of ITO and In-doped ZnPc generating a sharp positive spike upon laser irradiation reveals that the charge transfer from In-doped ZnPc thin film to ITO electrode are positive charges or holes. Then Indium doped ZnPc is p-type or hole doped semiconductor. The decay time of the spike due to interfacial exciton dissociation last longer proportional to the Indium doping ratio. The more Indium dope, the longer decay time, indicates that intercalation of Indium and ZnPc is successful and there must be physical interaction of Indium and ZnPc. That is, electrons are attracted from ZnPc molecules to atoms of Indium and then enable In-doped ZnPc has more charge carrier concentration(hole dope). Therefore, the higher carrier concentration achieve upon Indium doping, resulting in longer decay time. The change of decay time according to varying of Indium doping ratio also confirm that the interfacial exciton dissociation is attributed to the free-carrier separation by built-in field in In-doped ZnPc bulk. We would like to propose the method of transient photovoltage measurement and the phenomenon of exciton dissociation at the interface of ITO and phthalocyanine material to be utilized as a process to identify the type of phthalocyanine semiconductor material.

### Summary

The exciton dissociation at the interface of ITO and In-doped ZnPc is proved to occur in such a way that holes form In-doped ZnPc move toward ITO electrode and leaving electrons at In-doped-ZnPc bulk and the amount of those positive charges transfer depends on charge carrier concentration or doping ratio. This finding indicates that intercalation of Indium and ZnPc generate hole dope to ZnPc semiconductor material and thus, In-doped ZnPc is p-type. The transient photovoltage measurement

of the interfacial exciton dissociation between ITO and phthalocyanine film can be used to investigate the type of semiconductor. The shift of Si 2p emission spectrum to higher binding energy of silicon substrate covered with very thin In-doped ZnPc film confirms that In-doped ZnPc is a hole doped organic semiconductor.

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