



# Boron subphthalocyanine chloride crystalline thin film with a long range exciton diffusion length grown assisted by negative surface charges



Jingchuan Wang, Pan Yang, Xiaochong Zhao, Lijun Yang \*

Institute of Materials, Chinese Academy of Engineering Physics, Jianguo 621907, China

## ARTICLE INFO

### Article history:

Received 17 February 2017  
Received in revised form 21 June 2017  
Accepted 1 July 2017  
Available online 01 July 2017

### Keywords:

Crystalline SubPc film  
Exciton diffusion length  
Organic photovoltaics

## ABSTRACT

Boron subphthalocyanine chloride (SubPc) crystalline thin film has been fabricated under the help of negative surface charges and its growth mechanism is discussed as well. This thin film is composed of triangular grains and shows turbostratic-graphite-like microscopic structure, which is verified by atomic force microscope and elliptical diffraction pattern in transmission electron microscopy. The exciton diffusion length of this crystalline thin film can reach to  $95 \pm 2$  nm, which is 5.5 times larger than that of amorphous one fabricated by thermal evaporation. This long exciton diffusion length is comparable with the optical absorption depth in the visible light spectrum, which can be expected to enhance the performance of SubPc-based organic solar cells.

© 2016 Published by Elsevier B.V.

## 1. Introduction

The exciton diffusion length defines the effective domain size or thickness of active layer in organic solar cells. Outside of this range, exciton cannot dissociate at donor/acceptor interface and there is no contribution to performance of solar cells. Generally, the exciton diffusion length of organic semiconductor thin films is reported around 8–20 nm [1,2], which is smaller than the light absorption depth in the visible spectrum,  $\alpha^{-1} \sim$  hundreds of nm ( $\alpha$  is the absorption coefficient). It is considered to be one of major limitations of organic photovoltaic [3]. A long range exciton diffusion length was reported in highly ordered rubrene crystals [4], moreover, an improved charge carrier mobility was also reported in ordered small molecule and well organized conjugated polymers thin films [5,6]. Therefore, an expectation is that the ordered molecular arrangement would benefit for the organic solar cells.

Boron subphthalocyanine chloride (SubPc) is a 14  $\pi$ -electron umbrella-shaped molecule with a strong dipole moment ( $\mu \sim 4.5$  D) oriented along the Cl–B bond direction [7]. Recently, SubPc shows very impressive photophysical properties and has been applied in nonlinear optics, OLEDs and photovoltaic devices [8,9]. The SubPc thin film is conventionally deposited by thermal evaporation under vacuum, which tends to be disordered amorphous [9]. The exciton transport in this thin film will be disturbed, since the excited energy transfer between molecules is sensitive to the related dipole orientation and spatial distance according to the Förster theory [10]. Therefore, the exciton

diffusion length is expected to be enhanced by ordering the molecule arrangement through increasing Förster radius. Methods of in situ or post-annealing [11,12], templating [13], and molecule structure design [14,15] have been adopted to prepare an ordered molecular arrangement and furthermore to improve the performance of organic photovoltaics. Electric-field assistance method has been applied to grow perpendicularly oriented CdS nanorod (30 nm  $\times$  5 nm,  $\sim 220$  D dipole moment) superlattices [16], protein crystals [17], and even alter the water freezing point [18]. All of above utilized the interaction between molecule dipole and charges (or electric-field) to produce an ordered molecular arrangement [19–22]. In this research, a crystalline SubPc thin film with long exciton diffusion length has been grown on negatively charged Si substrate.

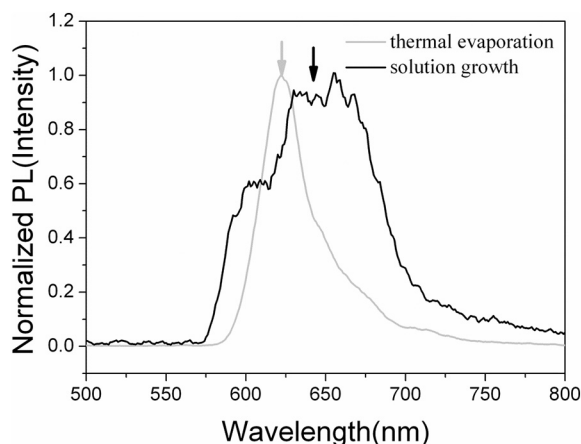
## 2. Experimental

### 2.1. Materials and films fabrication

All organic materials, SubPc (Aldrich), C<sub>60</sub> (Aldrich), BCP (Aldrich) were used as received. SubPc was dissolved in toluene and forms a saturated solution at room temperature ( $20 \pm 2$  °C). The thermal evaporation rate of organic layers (SubPc, C<sub>60</sub> and BCP) is around 1 Å/s under a base pressure of  $< 8 \times 10^{-7}$  Torr. Quartz, ITO glass, heavily doped n-type silicon and silicon with 150 nm oxide layer substrate were ultrasonically cleaned in detergents, acetone and isopropyl alcohol. After cleaning, the substrates were dried by 99.995% pure nitrogen before using.

A  $1 \times 10^4$  V/cm DC electric field was applied between two electrodes, which were separated by Teflon at a distance of 2 mm, and a high voltage 2 kV was applied. A 30 sccm nitrogen flow was supplied to maintain

\* Corresponding author.  
E-mail address: [sherry\\_yang@live.cn](mailto:sherry_yang@live.cn) (L. Yang).



**Fig. 1.** The PL emission of the amorphous SubPc thin film and crystalline thin film. The arrows inserted show the emission peak used for exciton diffusion measurement.

a steady inert gas condition in the solution. A crystallized thin film was grown at room temperature during 24 h with humidity around 60–70%.

## 2.2. Thin film characterization

Grazing incidence X-ray diffraction (GIXRD) was performed by Rigaku 9KW Smartlab and maintain the grazing angle ( $\alpha$ )  $0.5^\circ$  using Cu  $K\alpha$  radiation. Atomic force microscope (AFM) was performed by DI Nano Scope 8 in the ambient air at room temperature. Transmission electron microscope (TEM) with selected area electron diffraction (SAED) was performed by JEOL JEM-2100F at a low operated voltage of 100 kV. The TEM samples were prepared by scratching the SubPc thin film by carbon covered cooper grid directly.

Absorption measurement was carried by an Agilent Varian Cary 4000UV/VIS/NIR spectrophotometer. The amorphous SubPc was thermal evaporated directly on the quartz substrate, and then measured the wavelength range from 200 nm to 800 nm. The solution-process SubPc crystallized thin film was fabricated on the ITO glass, then the measurement range is taken from 280 nm to 800 nm.

Photoluminescence (PL) data was measured at room temperature by Edinburgh FLS980 spectrophotometer. An incidence and detect angle of  $45^\circ$  was chosen in this research for the purpose of minimizing the discrepancy caused by the overlap between absorption and fluorescence. The PL spectra were performed by 300 nm excitation 450 W Xe lamp with 340 nm filter and the step of 1 nm was taken for data collection. The excitation spectra were collected for samples with exciton

blocking layer and quenching layer at fixed peak emission wavelength (622 nm for thermal evaporation SubPc and 648 nm for solution growth SubPc according to the PL emission peaks of thin films as the following pictures). For emission  $> 500$  nm, a filter was used to eliminate the double-wavelength light (Fig. 1).

## 2.3. Exciton diffusion length measurement

Comparing the PLE intensity of the sample with the exciton blocking layer to that with the exciton quenching layer, we obtain the normalized quenching ratio  $\eta(\alpha)$ , referring to the reported method [1].

$$\eta(\alpha) = \frac{PL_B(\alpha)}{PL_Q(\alpha)} = \frac{\alpha(\lambda)L_{ED}}{\cos\theta_\lambda} + 1 = \alpha'(\lambda)L_{EX} + 1 \quad (1)$$

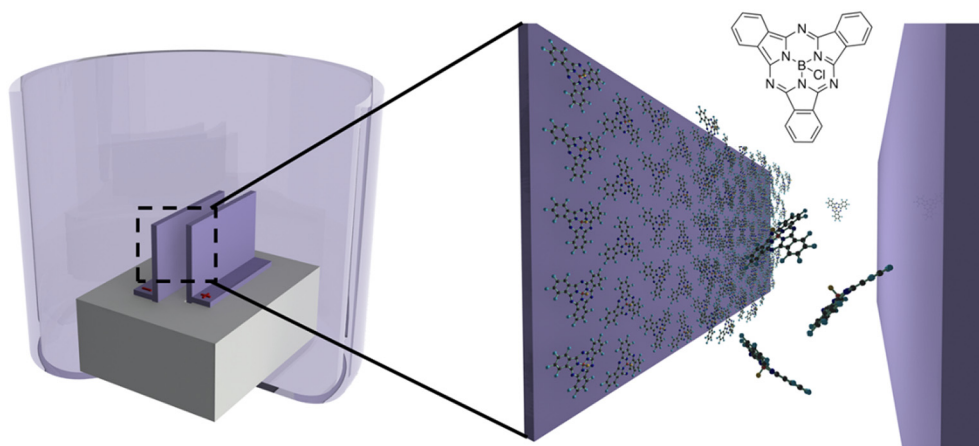
After correction of the incidence conditions, the slope of a plot of  $PL_B/PL_Q$  versus effective absorption coefficient  $\alpha'(\lambda)$  yields the exciton diffusion length. In cases where Förster energy transfer between the SubPc film and the quenching layer can be neglected due to the high quenching efficiency of exciton at interface between the C<sub>60</sub> and SubPc which has been already applied in organic solar cell system.

## 3. Results and discussion

Fig. 2 shows the schematic of experimental setup. An electric field ( $10^4$  V/cm) was applied to two electrodes which were emerged in the saturated SubPc toluene solution. The nitrogen was supplied to maintain anhydrous condition and control the evaporation of solvent to generate a steady supersaturating condition.

The morphology of SubPc film grown on the electrode is shown in Fig. 3(a). From AFM topography, it can be seen that the thin film is composed of triangle shape domains that implies a well-organized crystalline state. Similarly, nanocrystallized triangle SubPc island was reported to form on Cu(111) substrate [7]. They used the scanning tunneling microscope (STM) technique and found that these islands could be assembled by the triangle shape molecules. Therefore, it was expected that these triangle topographic domains were formed by the means of well-arranged SubPc molecules.

The crystal structure can be further verified by using of grazing incidence X-ray diffraction technology and TEM with selected area electron diffraction image. The results shown in Fig. 4(a) and (b) reveal this thin film is in crystalline state. The major diffraction peaks of GIXRD ( $17.01^\circ$ ) suggests the (001) plane is parallel to the substrate surface according to Matheus and Kietai et al.'s work [11,23]. It is worth to note the unique elliptical diffraction patterns shown in Fig. 4(b), which was observed by



**Fig. 2.** The schematic of experimental setup for crystalline SubPc thin film growth. (a) 3D drawing. (b) The schematic of thin film growth process: SubPc nucleation formed on negative electrode and then steadily deposited onto the substrate.

Download English Version:

<https://daneshyari.com/en/article/5466026>

Download Persian Version:

<https://daneshyari.com/article/5466026>

[Daneshyari.com](https://daneshyari.com)