



Measurement of exciton diffusion lengths of phthalocyanine derivatives based on interlayer excitation transfer

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ABSTRACT

The exciton diffusion length (L_D) of several phthalocyanines (Pcs) was investigated by use of organic photovoltaic cells, where two different p-type organic semiconductor materials, including a Pc layer, were laminated, and interlayer excitation energy transfer occurred between them. The distribution of excitons in the Pc layer that accept energy from the other p-type semiconductor material by excitation transfer should be much narrower than that of excitons created by light absorption directly. This delta-function-like generation of excitons allowed the simple analysis of exciton diffusion. The results of the analysis indicated that the planar Pcs (copper Pc and metal-free Pc) showed shorter L_D s of around 5 nm, as compared to the 18.5 ± 4.8 nm shown by the pyramidal-shaped Pc (tin Pc).

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1. Introduction

Organic photovoltaics (OPVs) have received a lot of attention because of their potential in large-scale and low-cost solar energy conversion [1,2]. The generally accepted formation mechanism of an OPV is as follows: (1) absorption of photons by p-type and/or n-type organic semiconducting materials and creation of their excitons, (2) diffusion of excitons to the interface of both materials (p/n junction), (3) dissociation of excitons into electrons and holes at the junction, and (4) collection of the charged carriers at the electrodes. State-of-the-art OPV cells with high power conversion efficiency are based on bulk heterojunction (BHJ) [3] or p-i-n [4] architecture in order to overcome a fundamental issue of organic semiconducting materials, i.e., the short exciton diffusion length (L_D). In photoactive layers, the heterojunctions required for dissociating an exciton into charged carriers should be located within the L_D of the light-absorbing layers from any part of the photoactive layer. Thus, the BHJ architecture is important; however, in the case of planar heterojunction architecture, the thickness of the light-absorbing layer should be shorter than its L_D . Hence the L_D of the semiconductors is a pivotal material property for OPVs.

To date, the reported values of L_D obtained mainly by the photoluminescence quenching technique have ranged widely for various materials [5–10]. Although this technique is arguably most useful for luminescent materials, it cannot be applied to nonluminescent materials.

Phthalocyanine (Pc) and its derivatives are widely used as a p-type semiconductor material in OPV, but most of them are not luminescent. The thickness dependence of the photocurrent response in solar cells is another technique to determine L_D , but a simple exponential distribution of excitons based on optical penetration depth could be misleading because of the optical interference arising from the reflective metal counter electrode [11]. Some literature taking this influence into account has been published, but we believe it is controversial to determine L_D from the thickness dependence of photocurrent response on the basis of reported L_D values that can vary from a few to tens of nanometers; like for example, in the case of copper Pc (CuPc) [12–17].

Recently, we demonstrated OPV cells exhibiting a photoenergy collection and transfer system based on interlayer excitation transfer (ET) [18]. The cells have two different p-type organic semiconductor layers, with one layer absorbing photons and transferring its exciton energy to the other layer (from p1 to p2), as shown in the inset of Fig. 1. Excitons in the ET-accepting p-type layer should be produced very near the p/p interface, unlike in the case of optical excitations. These situations are schematically illustrated in Fig. 1. This is believed to occur because the interaction length of the exciton energy transfer should be much shorter than the optical penetration length of organic semiconductors, even if the transfer is based on Förster resonance energy transfer (FRET) [19,20], which is known to be efficient and long ranged [21]. Note that the critical distance of FRET is usually within a few nanometers, even for two-dimensional-layer energy-acceptor systems [22]. We believe that an initial distribution of excitons this narrower could be advantageous for determining the L_D of nonluminescent materials by using the photocurrent response of PV cells. Here we will demonstrate the measurement of the L_D of several Pc derivatives with different

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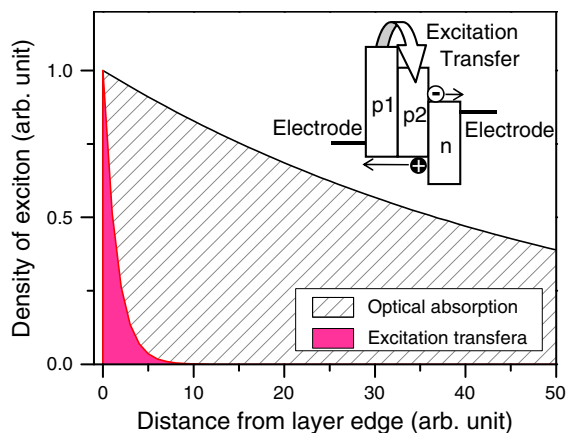


Fig. 1. Schematic illustration of exciton distributions formed by ET and optical absorption in the conditional layer. Light incidences from an edge at distance = 0. Inset: Schematic of OPV cell based on interlayer ET.

metal ions at their center (MPc; $M=H_2$, Cu, and Sn) by using OPV cells that exhibit interlayer excitation energy transfer. We measure MPc-thickness-dependent photocurrent responses of OPV cells with two p-type organic semiconductor layers: α , ω -diphenyl-sexithiophene (P6T) and MPc.

2. Experimental details

Fig. 2a shows the chemical structures used in this study. The band gap of P6T is larger than those of the MPcs, as indicated in the figure; interlayer ETs from P6T to all MPcs are promising and have been confirmed in previous literature except for the combination of P6T and H_2 Pc [18]. The chemicals P6T (Sumitomo Seika Chemicals), H_2 Pc (Aldrich), SnPc (Aldrich), and bathocuproine (BCP, TCI) were

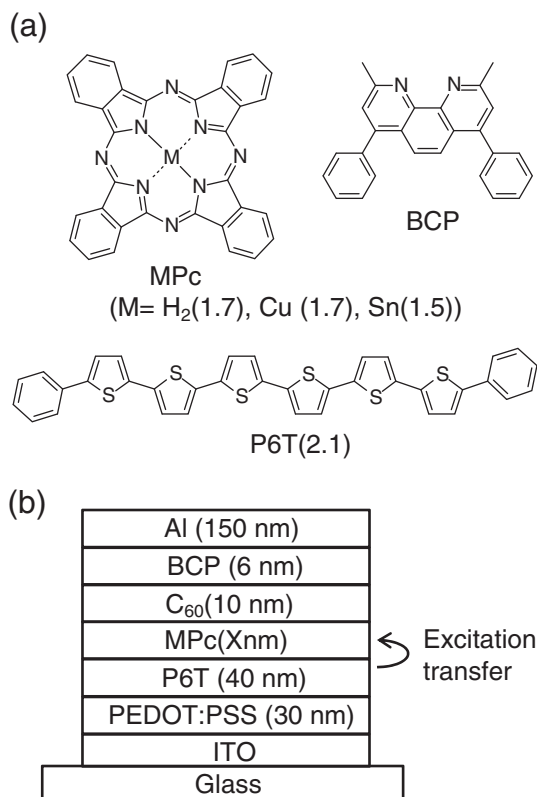


Fig. 2. Structures of chemicals (a) and device (b) used in this study. Parenthetical values in panel (a) show the band gap of each material in electron volts.

purified before use by temperature-gradient train sublimation with Ar gas flow. We also used C_{60} purchased from Frontier Carbon (nanom purple SUH grade) and CuPc (organic light-emitting device grade) donated by Nippon Steel Chemicals, both without further purification. Fig. 2b shows the schematic of the device employed in the present study. Fig. 3 shows the absorption spectra of 40-nm-thick P6T, 10-nm-thick C_{60} , and 40-nm-thick CuPc layers. We prepared the devices by sequentially depositing several materials onto commercially available indium-tin-oxide (ITO) coated glass substrates, with a sheet resistance of $15 \Omega/\text{square}$. The substrates were washed with detergent water, pure water, and 2-propanol under ultrasonication and treated with O_2 plasma at 50 W for 5 min. We prepared a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer on the substrates by spin coating a commercially available formula (Heraeus, Clevis P Al 4083). We deposited several organic layers by thermal evaporation under vacuum (2.0×10^{-4} Pa) at a rate of $0.6 \text{ \AA}/\text{s}$. Finally, the aluminum electrode was prepared on top of the organic layer stack by thermal evaporation under vacuum at a rate of $10 \text{ \AA}/\text{s}$. The active area of each cell was $\sim 6 \text{ mm}^2$. We mounted the produced devices in a small chamber with a quartz window and evacuated the chamber using a rotary pump. We recorded the incident photon-current conversion efficiency (IPCE) spectra of the devices with a source meter (Keithley 2400) under monochromatic light irradiation from a light source (Bunko Keiki SM-25A); monochromatic light intensity for each wavelength was measured with a calibrated silicon photodiode (Hamamatsu Photonics S1337-1010BQ).

3. Results and discussion

Fig. 4a shows the IPCE spectra of OPV cells exhibiting the P6T and CuPc interlayer excitation energy transfer system with CuPc thicknesses varying from 7 to 25 nm. The two peaks at 600–700 nm are attributed to direct optical absorption by the CuPc layer, as shown in Fig. 3. Roughly speaking, the IPCE values for CuPc do not vary as the CuPc thickness increases. However, the IPCE values decreased drastically at 400–550 nm, as shown in Fig. 4b. According to our previous report [18], the IPCE values at 400–550 nm are due to P6T. The incident light is absorbed by P6T, then interlayer excitation energy transfer converts P6T excitons into CuPc ones, and finally these CuPc excitons transform into charged carriers at the CuPc/ C_{60} interface. For charge separation of CuPc excitons, the excitons have to diffuse (migrate) from the vicinity of the P6T/CuPc interface to the CuPc/ C_{60} interface. Thus, the thickness of the CuPc layer strongly influences the sensitization.

Here we would like to derive the fraction (F) of excitons generated by excitation transfer for the charge separation at the CuPc/ C_{60} interface. For simplicity, we consider only the direction of thickness

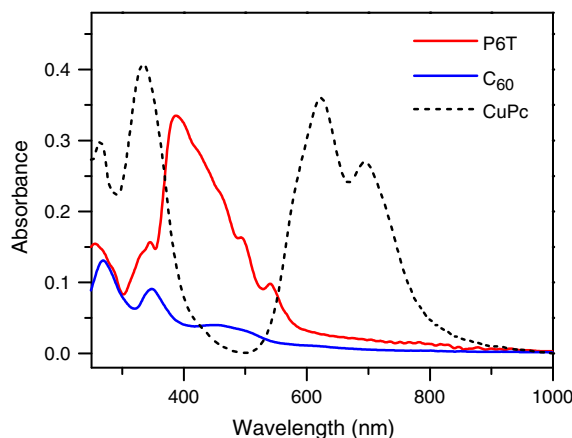


Fig. 3. Optical absorption spectra of P6T (40 nm), C_{60} (10 nm), and CuPc (40 nm) thin films. The P6T layer was prepared on a 30-nm-thick PEDOT:PSS covered quartz substrate, but the CuPc and C_{60} layers were on a bare one.

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