

Communications

Nanoscale Size Effects on Photoconductivity of Semiconducting Polymer Thin Films

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Thin films of semiconducting polymers and organic materials¹ are currently of wide interest for applications in electronic and optoelectronic devices such as field-effect transistors,^{2,3} light-emitting diodes,⁴ solar cells,⁵ and xerographic photoreceptors.^{6–9} Nanoscale size effects on optical, optoelectronic, electronic, magnetic, mechanical, and other properties of inorganic semiconductors, metals, oxides, and ceramics have been widely reported.^{10–12} Some of these size effects are well understood in terms of *quantum confinement in nanostructures*^{10,12} or the critical role of interfaces.^{10–12} In contrast, very little is known about nanoscale confinement size effects on the properties of electroactive and photoactive semiconducting polymers. Although quantum confinement has been invoked to explain the observed optical properties of electrochemically grown semiconducting polymer nanostructures,¹³ nanoscale size effects in electroactive and photoactive polymers need not be of quantum mechanical origin. Equally important possible physical origins of nanoscale size effects in conjugated polymers include interface- and surface-mediated processes,⁸ supramolecular structure

and morphology,^{9,13b,14} charge-transport and -trapping processes,⁸ electronic, morphological, or chemical defects, and conformational changes.¹⁵ We recently initiated studies aimed at the understanding of confinement size effects in electroactive and photoactive semiconducting polymers and related thin-film devices. We have previously reported observation of novel voltage tunable reversible color changes and dramatic enhancement of performance in semiconducting polymer heterojunction light-emitting diodes as the electroluminescent polymer layer thicknesses were varied in the nanoscale range (25–100 nm).¹⁶

In this paper, we report preliminary results of our study exploring nanoscale size effects on semiconducting (conjugated) polymers through photoconductivity experiments on bilayer photoreceptors which consist of a layer of a conjugated polymer and a layer of trap-free triarylamine-doped polycarbonate. The electric-field-dependent quantum efficiency for charge photogeneration was measured as a function of film thickness (9–195 nm) of the light-absorbing conjugated polymer. It is shown that the quantum efficiency for charge photogeneration is increased by a factor of 3 when the film thickness of the conjugated polymer layer is reduced from ~100 to ~10 nm. The observed nanoscale size effects on photoconductivity of conjugated polymers are explained in terms of exciton diffusion lengths in the materials and the interfacial nature of the photogeneration process.

Bilayer photoreceptors consisting of a thin layer (9–195 nm) of a semiconducting (i.e., conjugated) polymer, poly(2,5-pyridylenebenzobisthiazole) (PPyBT), and a thick layer (10–22 μ m) of a trap-free tri-*p*-tolylamine (TTA) doped polycarbonate (TTA:PC) were used in our studies. The molecular structures of PPyBT and TTA are shown in Figure 1. The bilayer devices were fabricated on a Ni-coated poly(ethylene terephthalate) (PET) substrate (Figure 1). Since molecularly doped polymers such as TTA:PC are known to be trap-free materials,¹⁷ the bilayer assemblies of Figure 1 provide an excellent opportunity to explore the photoinduced processes in the semiconducting polymer layer and at the semiconducting polymer (PPyBT)/molecularly doped polymer (TTA:PC) interface.^{7,8} A *trap-free* charge-transport material means that charges photogenerated or injected into the material can move through it over long distances without being trapped.¹⁷ In the case of TTA-doped polycarbonate used here, it is a trap-free *hole*-transport material.

The bilayer devices were fabricated by spin coating of isotropic solutions of PPyBT in nitromethane contain-

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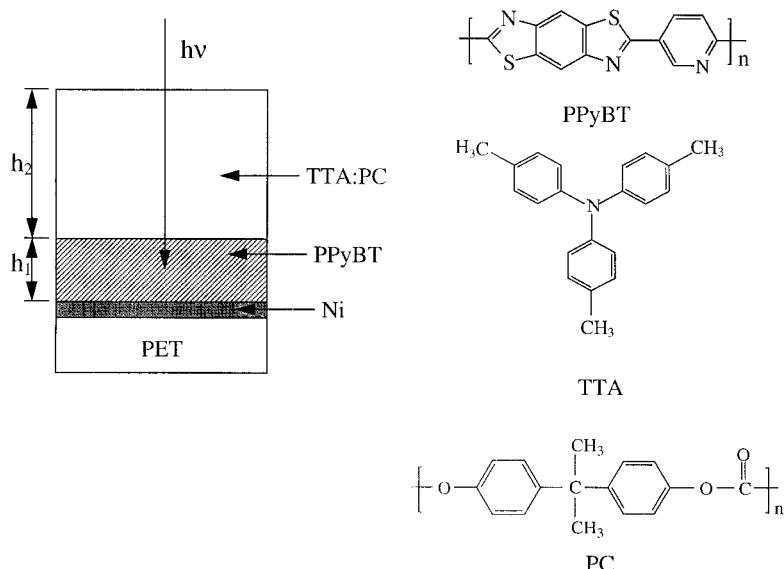


Figure 1. Schematic of the bilayer photoreceptor device and chemical structures of PPyBT, TTA, and PC.

ing aluminum or gallium trichloride (AlCl_3 or GaCl_3)¹⁸ onto a Ni/PET substrate. The resulting PPyBT films were washed in deionized water and vacuum dried at 80 °C overnight. The TTA:PC (40:60 by weight) layers were deposited onto the PPyBT films by blade coating of dichloromethane solutions (10–22 wt % total solids). Single- and double-layer films for optical absorption spectra measurements were similarly prepared except that silica or glass substrates were used. The film thickness was measured by an Alpha-step profilometer and by optical technique based on the known absorption coefficient of PPyBT at 470 nm ($\alpha = 1.5 \times 10^5 \text{ cm}^{-1}$). Details of the equipment and technique of photoinduced discharge measurements in our laboratory have previously been described.⁷ The quantum efficiency for charge photogeneration was determined from the initial rate of discharge of the device:¹⁹

$$\phi = \frac{\epsilon \epsilon_0 (dV)}{eI} \Big|_{t=0} \quad (1)$$

where ϵ is the dielectric constant, ϵ_0 the permittivity of free space, e the electronic charge, I the bilayer film thickness ($I = h_1 + h_2$), I light intensity absorbed, V the surface potential, and t the time. The field across the device was taken as V/I , and the exposure time was set to be 1.2 s. All measurements were made at room temperature (~22 °C).

Figure 2 shows the optical absorption spectra of films of a single-layer PPyBT, a single-layer TTA:PC, and a bilayer PPyBT/TTA:PC on silica substrates. The spectrum of PPyBT is similar to that of poly(*p*-phenylenebenzobisthiazole) (PBZT), and PPyBT has a λ_{\max} at ~440 nm which is the same as that of PBZT.^{7,8} This similarity suggests that the solid-state properties of PBZT and PPyBT may be similar. The optical absorption spectrum of PPyBT/TTA:PC bilayer is essentially a superposition of those of PPyBT and TTA:PC, showing no new absorption band from 200 to 3200 nm. This indicates that PPyBT and TTA do not form observable charge-transfer complexes in their ground states. It is

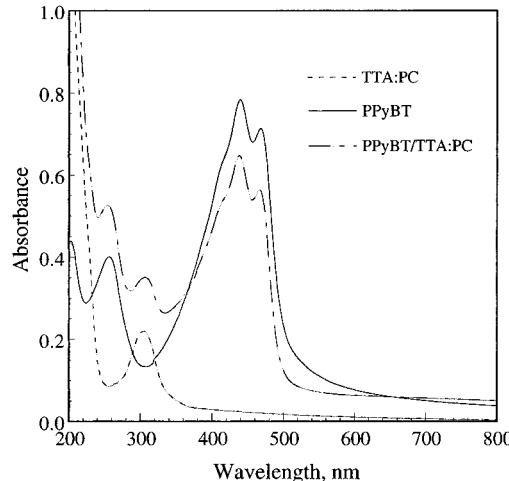


Figure 2. Optical absorption spectra of (1) a single-layer TTA:PC (the absorption coefficient for TTA:PC is $3.57 \times 10^4 \text{ cm}^{-1}$, from ref 8), (2) a single layer PPyBT, and (3) a bilayer PPyBT/TTA:PC (the thicknesses of PPyBT layer and TTA:PC layer are 43 and 63 nm, respectively).

interesting to note that the strong absorption band of PPyBT in the visible range meets the spectral requirement for photoreceptors in copier applications.⁶

Figure 3 shows a typical photoinduced discharge curve (PIDC) for a PPyBT/TTA bilayer device (with a 43-nm PPyBT layer) which was initially charged to a surface potential of -480 V. The device was illuminated at 470 nm, the absorption maximum of PPyBT. Three important parameters, including photosensitivity, dark decay, and residual potential, can be obtained from the PIDC. The *photosensitivity* is defined as the exposure (erg/cm²) where the surface potential drops to half its original value before illumination.⁶ For this particular bilayer device, the photosensitivity was ~7 erg/cm², the dark decay was ~10 V/s, and the residual potential was ~20 V. The photosensitivities varied from 6.4 to 9.0 erg/cm² as the PPyBT layer thickness varied from 9 to 97 nm. These properties are comparable to those reported for organic photoconductive materials.⁶

Figure 4 shows the measured electric-field-dependent quantum efficiency $\phi(E)$ for charge photogeneration in three PPyBT/TTA:PC bilayers photoexcited at the ab-

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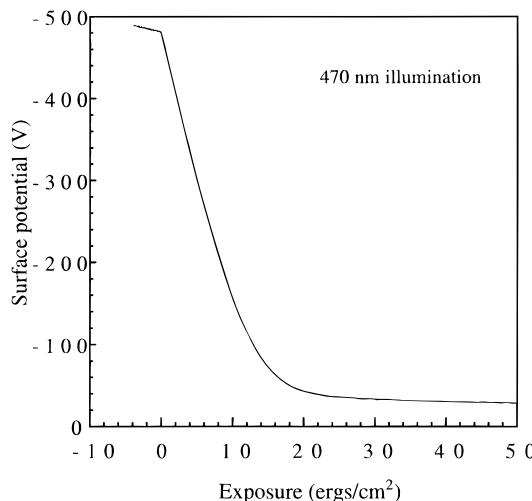


Figure 3. Photodischarge curve for a PPyBT/TTA:PC bilayer device (with a 43 nm thick PPyBT layer) under 470 nm illumination.

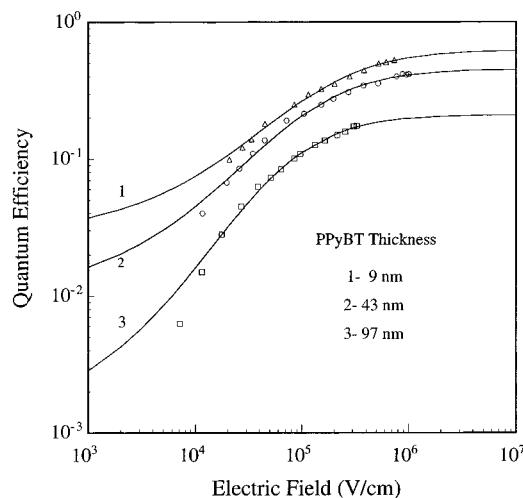


Figure 4. Field dependence of quantum efficiency for photogeneration in PPyBT/TTA:PC bilayer devices with varying PPyBT thickness under 470 nm illumination: (1) 9; (2) 43; (3) 97 nm. The points are data, and the lines are theoretical model fits.

sorption maximum (470 nm) of PPyBT. A remarkable variation of $\phi(E)$ with nanometer-sized film thickness ($h_1 = 9\text{--}97\text{ nm}$) of the light absorbing PPyBT is observed. In contrast, variation of the TTA:PC layer thickness ($h_2 = 10\text{--}22\text{ }\mu\text{m}$) while maintaining the PPyBT layer thickness does not change the photogeneration quantum efficiency as expected for a trap-free hole-transporting material.¹⁷ The mechanism of charge photogeneration in the bilayers and the possible origins of the observed nanometer size effects on photoconductivity of PPyBT films are discussed in the following paragraphs.

In prior studies of charge photogeneration in bilayers of conjugated polymers ($h_1 \sim 100\text{--}1000\text{ nm}$) and trap-free TTA:PC, we established that photoinduced charge transfer and exciplex formation at the conjugated polymer/TTA:PC interface were central to the charge carrier generation.^{7\text{--}9} This conclusion was based on a number of experimental observations on bilayer assemblies, including steady-state and picosecond time-resolved photoluminescence (PL), picosecond photoinduced absorption, and excitation-wavelength-dependent photogeneration quantum efficiency at constant electric

field.⁸ Similar observations on PPyBT/TTA:PC bilayers with nanoscale (9\text{--}195 nm) PPyBT films in the present study confirm the interfacial nature of the photogeneration process. For example, the steady-state PL spectroscopy on PPyBT/TTA:PC bilayers showed that the photoluminescence was significantly quenched compared to the PPyBT single layer, as expected from photoinduced electron transfer between PPyBT and TTA. We propose that the observed nanometer size effects on photoconductivity of PPyBT (Figure 4), i.e., a large enhancement of $\phi(E)$ with reduced PPyBT film thickness, partly originate from the interfacial nature of the charge-carrier generation process in PPyBT/TTA:PC bilayers. The ratio of PPyBT molecules at the interface of the bilayer to the PPyBT molecules in the PPyBT volume increases dramatically with decreasing layer thickness in the 9\text{--}97 nm range. Since it is only those PPyBT molecules at or near the interface that can be expected to interact with the donor TTA molecules to form the ion-pair species that are eventually dissociated by electric field [e.g., $(\text{A}-\text{D})^* \rightarrow \text{A}^- + \text{D}^+$], enhancement of $\phi(E)$ in ultrathin PPyBT films can thus be expected.

Electric-field-dependent photogeneration quantum efficiency data for organic photoreceptors^{20,21} have sometimes been analyzed in terms of Onsager's 1938 theory.²² This theory, however, predicts thermalized separation distances of 20\text{--}30 Å. Also, the theory in most cases does not predict the temperature dependence of the quantum efficiency $\phi(E)$. Theoretical kinetic models^{23\text{--}25} relating to Onsager's 1934 theory²⁶ have been shown to give improved predictions of field and temperature dependent ϕ . We have recently developed a version of the kinetic model of charge photogeneration for application to exciplex-mediated carrier photogeneration in conjugated polymer bilayers where ion-pair separation distances are expected to be significantly less than 20\text{--}30 Å. In the theoretical model, the field-dependent quantum efficiency $\phi(E)$ is written as the product of the initial exciplex (D\text{--}A ion pair) quantum yield ϕ_0 which is assumed to be field-independent and the field-dependent probability for geminate ion-pair dissociation $P(E,r)$.²⁷

$$\phi(E) = \phi_0 P(E,r) \quad (2)$$

Analysis of the $\phi(E)$ data with such a theoretical model furnishes two important parameters which give insights into the mechanism of charge photogeneration and the possible origin of the observed confinement size effects: ϕ_0 , the initial ion-pair yield, and r_0 the thermalized ion-pair separation distance.

Figure 4 shows a theoretical fit of the $\phi(E)$ data, indicating an excellent agreement. The observed similarity of the field dependence of quantum efficiency data for the three different film thicknesses of PPyBT sug-

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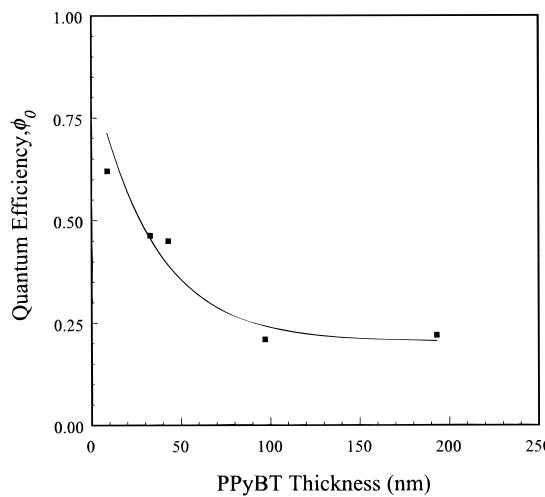


Figure 5. Film thickness dependence of quantum efficiency for photogeneration ϕ_0 , showing spatial confinement effect.

gests similar $P(E,r)$ and the differences in the magnitude of $\phi(E)$ with varying film thickness can be accounted for by variation in the initial ion-pair (exciplex) quantum yield ϕ_0 . Indeed, the initial ion-pair quantum yield ϕ_0 obtained from the theoretical fitting of the $\phi(E)$ data in Figure 4 is 0.21, 0.45, and 0.62 for PPyBT thickness of 97, 43, and 9 nm, respectively. In contrast, the average ion-pair separation distance between the donor (TTA) and acceptor (PPyBT) molecules obtained from the fitting was constant at about 6 Å (5.9 Å for 9 nm, 5.8 Å for 43 nm, and 6.0 Å for 97 nm) regardless of the PPyBT film thickness. The estimated ion-pair separation distance of 6 Å is very realistic and is in the range of what to expect for donor–acceptor separation distances in intermolecular exciplexes.²⁸ The finding that the ion-pair separation distance r_0 is constant with PPyBT film thickness clearly confirms the central role of the conjugated polymer/TTA:PC interface in the photogeneration. The average donor (TTA) and acceptor (PPyBT) separation at the interface and hence r_0 should not change with film thickness of the acceptor layer.

Figure 5 shows the film thickness dependence of ϕ_0 . The quantum efficiency is independent of film thickness above 100 nm. The finding that ϕ_0 increases by a factor of 3 when the PPyBT film thickness is reduced from 97 to 9 nm is the most dramatic confinement size effect to be explained. Absorption of photons by PPyBT leads to the production of excitons throughout the film thickness; however, only a fraction ϕ_0 of excitons created diffuses to the interface region and results in the formation of the ion-pair species (exciplex). An impor-

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tant factor that would influence the ϕ_0 value is the exciton diffusion length which has been estimated to be 10–18 nm for films of PBZT,⁸ about 5 nm for films of poly(*p*-phenylenevinylene),²⁹ ~20 nm for poor-quality crystals of anthracene,³⁰ and ~40–60 nm for good-quality crystals of anthracene.³⁰ The absorption depth ($1/\alpha$) of PPyBT is about 67 nm. Exciton diffusion lengths (L) of conjugated polymers are much less than their absorption depths.^{8,29} Therefore, we expect the exciton diffusion length (L) for PPyBT films to be about the same order of magnitude as PBZT, i.e., ~10–18 nm. Such a small exciton diffusion length in PPyBT would inhibit the formation of ion pairs, the severity of which would depend on the film thickness of PPyBT relative to L . Thus, the closer the semiconducting polymer layer thickness is to L , the larger the expected ϕ_0 . The generally small exciton diffusion lengths in conjugated polymers are related to electronic, chemical, and morphological defects as well as the overall supramolecular structure and morphology in the materials. Thus, emerging methods such as the layer-by-layer molecular self-assembly of electroactive and photoactive polymers should allow improvement of exciton diffusion lengths in these materials.³¹

In summary, nanoscale confinement size effects in semiconducting polymers were investigated by means of photoconductivity experiments on bilayer photo-receptors consisting of a conjugated poly(2,5-pyridylenebenzobisthiazole) charge-generation layer and a trap-free tri-*p*-tolylamine-doped polycarbonate charge-transporting layer. A 3-fold increase in quantum efficiency for photogeneration and an enhancement of photosensitivity were observed when the semiconducting polymer layer thickness was reduced from ~100 to ~10 nm. The observed confinement effects on photoconductivity are related to the generally small exciton diffusion lengths (5–20 nm) in semiconducting polymers and the interfacial nature of the charge photogeneration process in the bilayers. Ongoing studies are trying to understand better nanoscale size effects on photoconductivity as well as on other electroactive and optical properties of various conjugated polymers.

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