

## Plastic Near-Infrared Photodetectors Utilizing Low Band Gap Polymer\*\*

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Organic photodetectors (PDs) have been the subject of extensive research in the past decade due to several inherent advantages: large-area detection, wide selection of materials, and low-cost fabrication on flexible substrates. High external quantum efficiency (EQE)<sup>[1,2]</sup>, full-color<sup>[3,4]</sup>, fast-response<sup>[5,6]</sup>, and position-sensitive<sup>[7]</sup> PDs have been reported in the past. However, there are few reports on organic near-infrared photodetectors (NIR-PDs) in spite of their tremendous potential in industrial and scientific applications, such as remote control, chemical/biological sensing, optical communication, and spectroscopic and medical instruments.<sup>[8]</sup> S. Meskers and co-workers reported an infrared PD in which doped poly(2, 4-ethylenedioxythiophene)/poly(styrene sulfonic acid) (PEDOT/PSS) was used as the active material.<sup>[9]</sup> More recently, G. Konstantatos and coworkers fabricated NIR-PDs by spin-coating colloidal quantum dots from solution onto gold interdigitated electrodes.<sup>[10]</sup> The device showed a large photoconductive gain and high detectivity at 1.3 µm. However, 3-dB bandwidth was only about 18 Hz and the working voltage was as high as 40 V. These characteristics strongly restrict their applications in the fields of imaging and communication where high-speed and low-power PDs are desired. Thus, there is a strong need for the development of fast response and low working voltage NIR-PDs while simultaneously maintaining the benefit of low-cost solution process. Here we report an organic near-infrared photodetector using a new low band gap polymer. By utilizing an ester group mod-

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Dr. V. Shrotriya Solarmer Energy, Inc. El Monte, CA 91731 (USA) ified polythieno[3,4-*b*]thiophene, we have successfully lowered the highest occupied molecular orbital (HOMO) energy level of the low band gap (LBG) polymer, so that it can match the energy level of (6,6)-phenyl  $C_{61}$ -butyric acid methyl ester (PCBM), and has good solubility and easy processing ability. In this communication, we report a device which has a donoracceptor type energy structure whose operation shows excellent NIR detection capability.

Reports on LBG polymers for solar energy conversion have emerged recently.<sup>[11-16]</sup> The preparation of LBG, high mobility, solution-processable polymers is not trivial and requires judicious design.<sup>[16]</sup> Among several band gap tuning strategies for conjugated polymers, polymerization of fused heterocyclic rings has been known to yield polymers with very low band gaps.<sup>[17,18]</sup> Polythieno[3,4-b]thiophene (PTT) is one kind of LBG polymers in which the fused thiophene moieties can stabilize the quinoid structure of the backbone, thereby reducing the band gap of the conjugated system.<sup>[19,20]</sup> Several PTTs without side chains have been reported previously, but the poor solubility makes them difficult to process and limits their use in electro-optical and electronic devices.<sup>[21-23]</sup> Synthesis of alkyl chains substituted thieno[3,4-b]thiophenes monomers have been reported and the resulting polymers exhibit better solubility, but poor oxidative stability.<sup>[19]</sup> It was found that the HOMO levels of these polymers are too high to match the energy levels of the commonly used electron acceptor, PCBM.

We report a new type of ester group modified PTT polymer (Scheme 1). The introduction of an ester group at the 2-position of thieno[3,4-*b*]thiophene has two effects. First, the electron withdrawing ester group can stabilize the electron-rich thienothiophene and lower the HOMO energy level of the polymer to match the energy level of PCBM. Second, a long tertiary alkyl side chain from the ester group can increase the solubility of the polymer. Polymer was synthesized by Stille polycondensation reaction between the bisbrominated thieno[3,4-*b*]thiophene and bis-stannylated thiophene. (Scheme 1; see Supporting Information for details) The resulting polymer has good solubility in chloroform and chlorobenzene.

In contrast to inorganic semiconductors, photoexcitation of organic semiconductors generates strong bound excitons rather than free charge carriers. To dissociate excitons efficiently, the donor/acceptor bulk heterojunction approach is typically used. The active layer in our PD comprises of PTT and PCBM (Fig. 1a), forming interpenetrating donor/acceptor networks. Details of the device fabrication process are given in the Experimental section. Figure 1b shows the absorption spectra of PTT and PTT: PCBM films. Pure PTT thin film ab-



<sup>[\*\*]</sup> Y. Yao and Y. Liang contributed equally to this work. Y. Yang and Y. Yao acknowledge financial support from the Solarmer Energy Inc. (grant number 20061880), and the University of California Discovery matching grant (grant number GCP05-10208). Y. L., S. X., and L. Y. gratefully acknowledge the financial supports of the National Science Foundation and the NSF MRSEC program at the University of Chicago. Supporting Information is available online from Wiley InterScience or from the authors.





Scheme 1. Synthesis of ester-functionalized polythieno[3,4-b]thiophene.

sorbs in NIR range with a peak at 750 nm and a shoulder at 850 nm. The absorption onset is at 970 nm with an optical band gap ( $E_g$ ) of 1.3 eV, which is about 0.6 eV lower than that of regioregular poly(3-hexylthiophene) (P3HT,  $E_g = 1.9$  eV). PTT shows excellent electrochemical stability both in oxidation (p-doping) and reduction (n-doping) processes in Figure 1c, which is a good sign for high structural stability in charged states. The onsets of oxidation potential ( $\varphi_{ox}$ ) and reduction potential ( $\varphi_{ox}$ ) and reduction potential ( $\varphi_{red}$ ) are 0.05 V and -1.45 V vs. Ag/Ag<sup>+</sup>. As a result, the HOMO and lowest unoccupied molecular orbital (LUMO) energy levels are -4.76 and -3.26 eV. Figure 1d shows the energy level diagram of the difference between PLT

and PCBM is  $\sim 0.4 \text{ eV}$ , which ensures just sufficient driving force for charge separation.<sup>[24]</sup>

To check the response of PD, we used a NIR laser diode working in continuous mode as a monochromatic light source. Figure 2a shows the currentvoltage (*I–V*) characteristics measured in the dark and under illumination with  $\lambda = 850$  nm. Device shows good rectification ratio of  $10^4$  ( $\pm 2$  V) in the dark. Under illumination, photovoltaic effect was observed with an overall power conversion efficiency (PCE) of 1 %. To get responsivity (*R*), the ratio

of photocurrent to incident-light power, we measured the EQE under short-circuit and reverse bias using lock-in technique and the data is presented in Figure 2b. Similar profiles of absorption and EQE of PTT (Figs. 1b and 2b) indicate that photons absorbed in IR range by PTT do contribute to the photocurrent. At the working wavelength of infrared laser diode (850 nm), the EQE is 19 % and increases by a factor of 2 to 38 % at –5 V. Accordingly, *R* is calculated to be 0.13 and 0.26 A W<sup>-1</sup>. We note that recently several novel LBG polymers are reported to have efficient photovoltaic activity in IR spectral region.<sup>[25–27]</sup> For example, Wienk et al. showed spectral response extended to 1  $\mu$ m with EQE exceeding 15 % at 850 nm.<sup>[25]</sup> Mühlbacher et al. showed highest PCE so far



**Figure 1.** Materials structure and properties. a) Chemical structures of PTT and PCBM. b) UV-visible absorption spectra of PTT and PTT:PCBM thin films. c) Cyclic voltammetry of PTT film on a Pt electrode in 0.1 M  $Bu_4NBF_6$ -acetonitrile solution with scan rate 100 mV s<sup>-1</sup>. d) Energy diagram of the photodector (ITO/PEDOT/PTT:PCBM blend/Ca/Al).





**Figure 2.** a) *I*–V characteristics of the PD in the dark and under 850 nm monochromatic illumination. b) EQE vs. wavelength at various biases. c) Transient response of a PD under 1 MHz modulated 850 nm monochromatic illumination. d) *I*–V characteristics of hole-only devices (ITO/PEDOT: PSS/PTT/Au) with different PTT thickness (70, 100, and 180 nm). The applied bias voltage is corrected for the built-in potential so that  $V = V_{APP} - V_{BI}$ . The current is given by  $J = 9\epsilon_0\epsilon_{\mu}W^2/8L^3$ , where  $\epsilon_0\epsilon_{\nu}$  is the permittivity of the polymer,  $\mu$  is the carrier mobility, and *L* is the device thickness. e) Frequency response of PDs with different device areas of 1 mm<sup>2</sup> and 12 mm<sup>2</sup>. f) Capacitance-voltage measurements at the frequency of 10 KHz.

obtained for LBG polymers of 3.2 %, 38 % EQE around 700 nm and 13 % at 850 nm.  $^{[27]}$ 

Speed measurement is performed by turning the 850 nm laser diode on and off periodically while measuring the photocurrent response. Fast response is strongly desired in highspeed applications. For example, image generation demands periodic read-out of a detector signal, hence the frame rate for image generation is dependent on the speed of PD.<sup>[2]</sup> Figure 2c shows the photocurrent response when illumination is modulated at 1 MHz. The rise and fall times are both around 100 ns and are attributed to the slow and dispersive transport of holes in the polymer PTT.<sup>[28]</sup> We measured the hole mobility of  $10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for pure PTT hole-only devices by fitting dark *J*–*V* curves to the space-charge limited current model<sup>[29]</sup>



as shown in Figure 2d. We also studied the speed dependence on the device area and reverse bias on the detector. Figure 2e shows that the 3-dB bandwidth decreases from 4 MHz to 1 MHz when the device area is increased from 1 mm<sup>2</sup> to 12 mm<sup>2</sup>, suggesting that the speed is mostly limited by *RC* constant of the circuit and the intrinsic speed could be faster. Capacitance-voltage measurements in Figure 2f reveal the capacitance of PD is almost independent of the reverse bias in contrast to the p-i-n or Schottky-barrier PDs made of inorganic semiconductors. Thus, fast response can be achieved even at zero or low biasing voltage.<sup>[4]</sup>

Noise equivalent power (NEP), the minimum impinging optical power that a detector can distinguish from noise, is an important figure of merit for PD.<sup>[10]</sup> NEP is given by  $i_{\mu}/R\Delta f^{1/2}$ where  $i_n$  is the noise current in A, R the responsivity in AW<sup>-1</sup>,  $\Delta f$  the electrical bandwidth in Hz. The noise characteristics of the NIR-PD are measured using a low noise current preamplifier and a fast Fourier transform dynamic signal analyzer. The noise floor of the measurement setup, limited by the noise parameters of the preamplifier, is  $10^{-25} \text{ A}^2 \text{ Hz}^{-1}$ . The experimental results of noise spectra at various biases are presented in Figure 3a. At higher values of reverse bias, the appearance of 1/f noise is observed. We also plot in Figure 3b the measured noise current versus the dark current at the frequency of 4 kHz. We found the noise current approaches the shot noise limit within 3 dB. To calculate NEP of NIR-PD at 850 nm at 4 kHz, the measured noise currents are  $5 \times 10^{-13}$  A Hz<sup>-1/2</sup> (at 0 V) and  $3.5 \times 10^{-12}$  A Hz<sup>-1/2</sup> (at -5 V). Knowing the values of R, the corresponding NEP is  $3.85 \times 10^{-12}$  W Hz<sup>-1/2</sup> (0 V) and  $1.35 \times 10^{-11} \text{ W Hz}^{-1/2}$  (-5V).

Former studies indicate that charge carrier transport and recombination could be strongly influenced by polymer film morphology.<sup>[30]</sup> Recently we have achieved solar cell efficiency close to 5 % by controlling the morphology of the active layer.<sup>[31]</sup> At the same time, higher carrier mobility and a much balanced charge transport was achieved.<sup>[32]</sup> Here we studied the surface morphology of PTT:PCBM blend films using atomic force microscopy. Figure 4 shows that the surface is very rough with root-mean-square roughness of 15 nm. This is probably a result of limited solubility of PTT in dichlorobenzene and its incompatibility with PCBM when solvent is removed during the spin coating process. The unfavorable morphology of the polymer/fullerene blend leads to charge recombination at 0 V as indicated in the field-dependent EQE measurements (Fig. 2a)<sup>[27]</sup> and an increase in the dark current and noise characteristics. By optimizing the effect of solvent selection, film coating parameters and phase separation, we believe recombination and dark current can be further minimized, and accordingly higher EQE and lower NEP values could be achieved.

In summary, we have synthesized a 1.3 eV band gap polymer and demonstrated plastic NIR-PDs with EQE exceeding 38 %, response bandwidth of 4 MHz, and the NEP of  $3.85 \times 10^{-12}$  W/Hz<sup>1/2</sup> at 850 nm. Preliminary studies of device lifetime show that the performance of encapsulated devices stored in the air degrades less than 20 % over six months. Although



**Figure 3**. a) Measured dark current noise spectra at different biases. b) Measured noise current as a function of dark current. The shot noise limit is also plotted for comparison.



Figure 4. AFM topography image of PTT/PCBM thin film spun-cast from the blend solution at 1500 rpm on the PEDOT:PSS coated ITO surface.



these parameters are still inferior to those of commercial inorganic detectors, it must be emphasized that our plastic NIR-PDs have not been fully optimized. In the future, by further optimizing processing conditions and film morphology, we believe there is still plenty of room for better performance.

## Experimental

Device Fabrication: PTT (number-average molecular weight 12000 g mol<sup>-1</sup>, weight-average molecular weight 39000 g mol<sup>-1</sup>, polydispersity 3.3, determined from gel permeation chromatography vs. polystyrene standards) and PCBM (purchase from Solenne B.V.; used as received) were co-dissolved in 1, 2-dichlorobenzene (ODCB) in weight ratio 1:1 (PTT concentration = 13.3 mg ml<sup>-1</sup>) and stirred overnight. ITO (~ 150 nm) coated glass substrates were cleaned by ultrasonic treatment in detergent, de-ionized water, acetone and isopropyl alcohol, sequentially. This was followed by spin-coating a thin layer (~ 30 nm) of PEDOT: PSS (Baytron P VP A1 4083) to modify the ITO surface. Then an active layer was spun-cast from the blend solution at 1500 rpm on the modified ITO surface. The optimum film thickness was 100 nm. Ca (20 nm) and Al (80 nm) were used as top electrode. Then the entire device was transferred into a glove box and encapsulated. The photodiode device area is 1 mm<sup>2</sup>.

Current-Voltage and Transient Measurement: NIR light source is provided by a commercial infrared laser diode with 850 nm (OPV 310, Opteck Inc.) For *J*–*V* measurement of PDs, the laser diode works in continuous mode powered by a Keithley 2400 SMU and laser power was monitored by a calibrated power meter (1830-C, Newport). For transient response measurement, the laser diode is powered by square pulses from a universal waveform generator (Model 195, Waveteck Inc.). Photocurrent from the NIR-PD was amplified using a trans-impedance amplifier (DLPCA-200, Femto Inc.) and the output signal was displayed on a 400 MHz digital oscilloscope (TDS 460A, Tektronix) with 50  $\Omega$  input impedance.

*EQE Measurement*: EQEs under short circuit and reverse biases are determined by illuminating the device with periodic (i.e., "chopped") monochromatic light. The AC photocurrent from the device is converted to an AC voltage and measured with a lock-in amplifier. The dark current at reverse bias is DC signal and therefore excluded by the lock-in amplifier. Incident light from a xenon lamp (50 W) passing through a monochromator (SpectraPro-2150i, Acton Research Corp.) was chopped at 170 Hz and focused on the active area of device. Bigger device (12 mm<sup>2</sup>) was used in the measurement and the light spot area was around 2 mm<sup>2</sup>. The photodiode signal was first amplified using a trans-impedance amplifier (SR570, Stanford Research Systems) and then detected by a lock-in amplifier (SR830, Stanford Research Systems). SR570 can also provide reverse bias directly on the device. A calibrated crystalline silicon diode (818UV, Newport) was used as a reference before each measurement.

*Noise Measurement*: The noise characteristics of IR photodiode was measured in the frequency rang of 1 to 51.2 KHz using preamplifier (SR570) and dynamic signal analyzer (HP 35670A). The bias is varied from 0 to -5 V, and the sample is kept at room temperature.

Received: November 22, 2006

Revised: March 8, 2007

Published online: October 26, 2007

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