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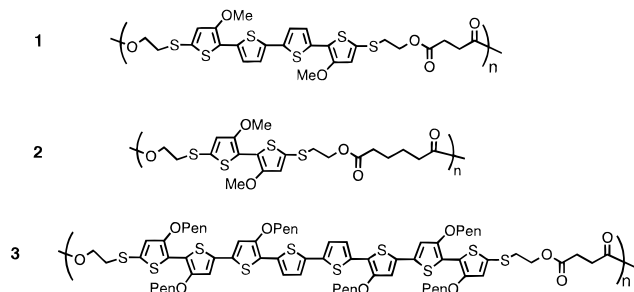
Photodiodes Utilizing Polyesters That Contain Different Colored Oligothiophenes in the Main Chain

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We have recently reported¹ the synthesis and characterization of a polyester, **1**, which has dimethoxyquaterthiophene units in the main chain, isolated from one another by flexible, electrically insulating, aliphatic segments. When oxidized as a cast film, the polymer was electrically conductive. It was also used to form a light-emitting diode.² We now report on the use of **1** and of two similar polymers for formation of photodiodes. Devices were developed that were effective at three different wavelengths with electron/photon efficiencies comparable to the best polymer photodiodes reported.



This study was suggested by previous work on photodiodes that employed either poly(alkylthiophenes)³⁻⁵ or poly(phenylenevinylenes)^{4,6} and other studies that used oligothiophenes.^{7,8} Most pertinently, Heeger and

co-workers sandwiched poly(3-octylthiophene)⁴ between ITO (indium–tin oxide) and gold electrodes and found that with a reverse bias of 15 V (the efficiencies are strongly sensitive to the bias voltage) the photocurrent at 540 nm reached 0.35 A W⁻¹, corresponding to an electron/photon efficiency of about 80%. They indicate that the qualities of such polymeric devices make them competitive in certain ways with commercial silicon photodiodes. Oligothiophenes, especially α -sexithiophene,⁷ but also α -octithiophene,⁸ have been used to prepare photodiodes in various configurations, including organic heterojunction devices. In all cases, the thiophene polymers or oligomers act as electron donors and hole carriers.

The three polyesters used in the present study have either dimethoxybithiophene (**2**), dimethoxyquaterthiophene (**1**), or hexapentaoxyoctithiophene (**3**) units separated by aliphatic ester segments. The synthesis and characterization of **1** have been reported.¹ The sample used here had MW 106 000 estimated by SEC. **2** and **3** were prepared similarly and characterized by NMR, IR, and SEC. The molecular weights of **2** and **3** were rather low (6 000 and 19 000, respectively), and their solubility was limited. Devices, 4 mm in diameter, were formed by vapor deposition of aluminum (100 Å) onto glass, spin coating of the polymer films (1500 Å) from 2 wt % chloroform solutions, and vapor deposition of a gold layer (150 Å). Each metal layer gave about 20% transmission in the visible region of interest. The data reported refer to the transmitted light, and not to the incident light. A calibrated silicon photodiode was used to measure light intensities. For photocurrent action spectra a 450 W Xe lamp was used, and the

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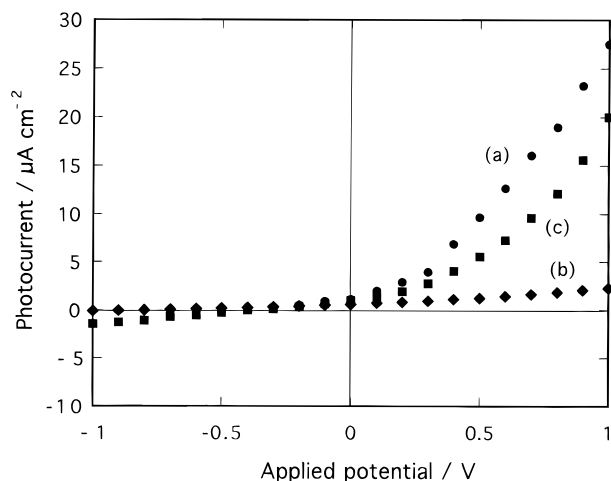


Figure 1. Photocurrents at various bias potentials. (a) Al/1/Au, 0.46 mW cm^{-2} at 430 nm, (b) Al/2/Au, 0.54 mW cm^{-2} at 365 nm, (c) Al/3/Au, 0.25 mW cm^{-2} at 535 nm. Positive potentials refer to a reverse bias (aluminum positive of gold).

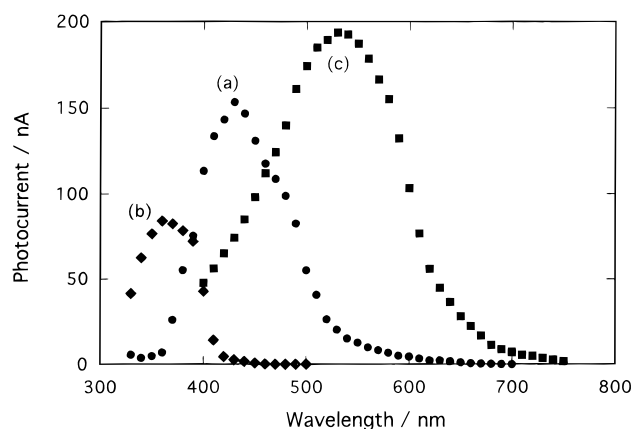


Figure 2. Photoaction spectra for devices employing polymers 1 (a), 2 (b), and 3 (c).

current was normalized to account for the variation of lamp output with wavelength.

Illuminated through aluminum with 430 nm light (0.46 mW cm^{-2}) the photocurrent for the device using **1** increased with increasing bias voltage (aluminum biased positive of gold) from 1.1 μA cm^{-2} at 0 V to 27.5 μA cm^{-2} at 1 V (Figure 1). The open-circuit photovoltage was 0.74 V, and the fill factor was 0.14. Illuminated through aluminum, the photocurrent action spectrum (Figure 2) followed the absorption spectrum of the polymer, which has λ_{max} 430 nm. Illuminated through gold only small currents were observed and the spectrum did not resemble the absorption spectrum. This suggests that a Schottky barrier is formed at the Al/1 interface and that the polymer absorbs light and gives charge separation near this interface. As expected the polymer acts as a donor and hole carrier and the reverse bias increases the efficiency substantially. Figure 3 shows the efficiency as a function of light-intensity at 1 V bias. At low flux the efficiency (electrons/photon of absorbed light) reached 40%. Run in an argon atmosphere, the photocurrent decayed over 1 h to a steady value approximately 40% of the initial value. It is expected that oligothiophenes (and polythiophenes) will be sensitive to oxygen and light. In air the photocurrent decayed by 90% in 1 h.

Devices formed from bithiophene polymer **2** and octithiophene polymer **3** performed similarly (Figure 1–3). Irradiated at 365 nm (λ_{max} of **2**) through alumi-

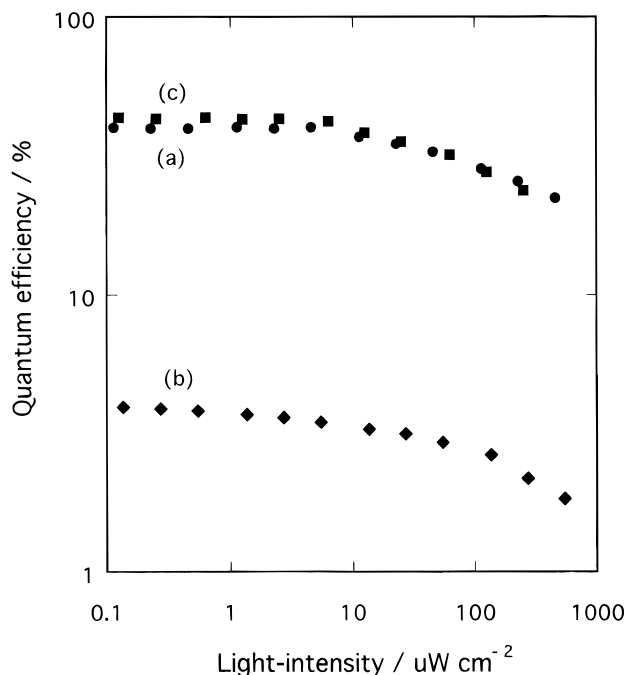


Figure 3. Electron/photon efficiencies for devices at a reverse bias of 1 V. (a) Al/1/Au at 430 nm; (b) Al/2/Au at 365 nm; (c) Al/3/Au at 535 nm.

num, Al/2/Au gave an open-circuit photovoltage of 0.82 V. At 0.1 mW cm^{-2} the efficiency was about 1% at open circuit and 3% at a reverse bias of 1 V. Al/3/Au devices were irradiated at 535 nm (λ_{max} of **3**) giving a smaller open-circuit photovoltage of 0.4 V. The response of the photocurrent to bias voltage was similar to that of Al/1/Au. Using a low intensity of 0.1 μW cm^{-2} , the open-circuit efficiency was 14%. At a reverse bias of 1 V, 0.1 μW cm^{-2} gave 43% and 0.1 mW gave 29% efficiency. For both Al/2/Au and Al/3/Au the photoaction spectra followed the absorption spectrum of the polymers when the irradiation was through aluminum but not through gold. Thus, the three polymers give a similar device behavior, but at three different wavelengths. Perhaps expectedly, the bithiophene polymer **2** gives the highest open-circuit photovoltage but the lowest efficiencies.

The results reported here demonstrate that these polyesters can be formed into efficient photodiodes that are selective for various spectral regions. It is quite surprising that polyester **2**, which has only small bithiophene units as the active entities, can function so effectively, and generally surprising that these devices compare well with the best devices reported. For example, ITO/poly(3-octylthiophene)/Au photodiodes at 1 V bias and 1 mW of 633 nm incident light generate about 1 μA cm^{-2} .^{4b} Al/3/Au with 1.35 mW of 535 nm light incident on the aluminum surface (0.25 mW on the polymer) and 1 V bias gives 20 μA cm^{-2} . Although the instability of the polyester devices poses practical problems, the initial results suggest many possibilities for fundamental studies of the phenomena responsible and reveal a new structural avenue for device formulation. Since both the aromatic and aliphatic portions of these polymers can be varied in a simple and well-defined manner, many structural variations are possible.

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