

A High-Mobility Electron-Transport Polymer with Broad Absorption and Its Use in Field-Effect Transistors and All-Polymer Solar Cells

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Since the discovery of photoinduced charge transfer in composites of conjugated polymers and C₆₀,¹ polymer solar cells (PSCs) have attracted considerable attention because of their potential for use in low-cost, lightweight, solution-processable, and flexible large-area panels.² Fullerenes, particularly the solution-processable derivative known as PCBM, are commonly used acceptors owing to their good electron-accepting and electron-transporting properties;³ however, PCBM has only weak absorption in the visible and near-IR. Use of acceptor polymers with improved light absorption in PSCs has met with limited success.^{4,5} Here we report the synthesis and application in organic field-effect transistors (OFETs) and all-polymer PSCs of a new solution-processable conjugated polymer (**1**, Chart 1), based on alternating dithienothiophene and perylene diimide (PDI) units, which exhibits high electron mobility, excellent thermal stability, high electron affinity, and which appears almost black because of strong absorption throughout the visible and extending into the near-IR. PDI is an attractive component since small-molecule PDIs have been found to possess high electron affinities (EAs) and high electron mobilities⁶ and have been successfully used in organic solar cells,⁷ while the planarity of fused thiophenes has been found to promote highly ordered π -stacked structures and high hole mobilities.⁸ Moreover, the donor–acceptor character of the polymer suggested the possibility of low-energy charge-transfer transitions, potentially leading to increasing coverage of the solar spectrum.

Polymer **1** was synthesized by Stille coupling of *N,N'*-dialkyl-1,7-dibromo-3,4,9,10-perylene diimide with a distannyl derivative of dithienothiophene (see Supporting Information). The polymer is soluble in chloroform, THF, and chlorobenzene and can readily be processed from solution. The weight-average molecular weight and polydispersity index were estimated as 15000 and 1.5, respectively, using GPC (polystyrene standards). DSC showed a glass-transition temperature of 215 °C, while TGA suggested excellent thermal stability with an onset decomposition temperature under nitrogen of 410 °C.

The charge carrier mobilities of **1** were characterized in an OFET⁹ geometry under nitrogen (See Figure 1 and Supporting Information). In a top-contact geometry, using aluminum as source and drain electrodes, electron mobilities in the saturation regime were found to be as high as $1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (channel width of 1000 μm and length of 100 μm). A low threshold voltage of ca. 4.4 V

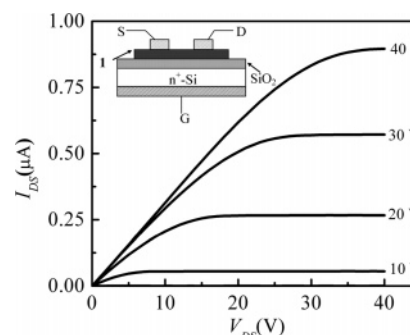
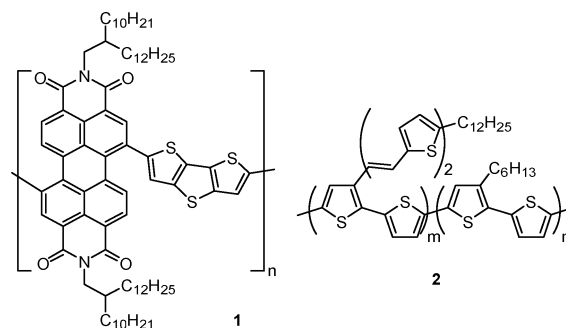


Figure 1. Current–voltage characteristics (I_{DS} vs V_{DS}) at several values of the gate voltage (V_{GS}) for a top contact device with $W = 2000 \mu\text{m}$, $L = 200 \mu\text{m}$, and 100 nm of **1**.

Chart 1



was obtained and the on/off current ratio was $> 10^4$. The polymer did not function as a p-type material under these experimental conditions. The electron mobility obtained for **1** is among the highest obtained for a solution-processed OFET,^{10,11} exceeding that of many other conjugated polymers.¹²

Another factor in PSC device efficiency is the overlap of the absorption spectra of the materials with the visible and near-IR solar spectrum. A thin film of **1** (Figure 2) shows significant absorption throughout the visible and extending into the near-IR region (to ca. 850 nm), that is, to considerably lower energy than those of cyano-substituted poly(*p*-phenylenevinylene)s (CN-PPVs, less than ca. 600 nm), which have been widely used as polymer electron acceptors in photovoltaics.^{4,5}

The ionization potential and EA of **1** were estimated at 5.9 and 3.9 eV, respectively, from onset redox potentials, assuming the absolute energy level of $\text{FeCp}_2^{+/0}$ to be 4.8 eV below vacuum.¹³ The EA of **1** is a little higher than that estimated in the same way

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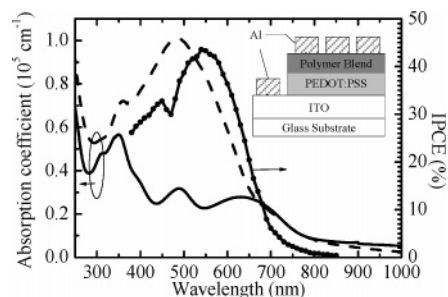


Figure 2. Absorption spectra of films of **1** (plain line), and of a **1:2** (1:1, w/w) blend (dashed line) spin-coated from chlorobenzene, and plot of incident photon to current conversion efficiency (IPCE) as a function of wavelength.

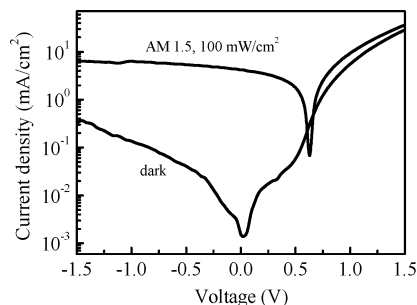


Figure 3. Current density–voltage characteristics of a device with the structure ITO/PEDOT/PSS/**1:2** (1:1, w/w)/Al in the dark and under the illumination of an AM 1.5 solar simulator, 100 mW/cm².

for PCBM (3.7 eV)^{5c} and somewhat higher than that estimated for CN–PPV (3.20 eV) using a similar method.¹²

To investigate the potential of **1** for photovoltaic applications, we used **1** as an electron acceptor and a bi(thienylenevinylene)-substituted polythiophene, **2** (Chart 1), the synthesis and photovoltaic properties of which have been previously reported,¹⁴ as an electron donor, and fabricated all-polymer PSCs with a structure of ITO/PEDOT/PSS/**1:2** (1:1, w/w)/Al. As shown in Figure 2, the blend exhibits a very broad absorption between 250 and 850 nm and a broad incident photon-to-current conversion efficiency spectrum up to 850 nm with a maximum of 44% at 540 nm. The *J*–*V* characteristics of the device are plotted in Figure 3. Under white-light illumination (AM 1.5 solar simulator, 100 mW/cm²), the bulk heterojunction device exhibits an open circuit voltage (*V*_{oc}) of 0.63 V, a short-circuit current density (*J*_{sc}) of 4.2 mA/cm², and a fill factor (FF) of 0.39. The average power conversion efficiency (PCE) is over 1%, among the highest achieved to date in all-polymer blend PSCs.^{4,15} It is worth noting that the convolution of the IPCE spectrum with a true AM 1.5 spectrum leads to a PCE of 1.5%. Optimization of the device structures can be expected to substantially increase the PCE of the PSCs.

In summary, we have described a solution-processable, narrow band gap, high-mobility, alternating copolymer of perylene diimide and dithienothiophene building blocks that exhibits broad absorption through the visible and into the near-IR. Device measurements show that alternating donor–acceptor polymers of this type are promising electron-transport materials for n-channel OFETs and promising sensitizers and electron-transport materials for all-polymer solar cells.

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Supporting Information Available: Complete synthetic procedures and characterizing data for new compounds; fabrication and characterization of polymer solar cells and field-effect transistors; TGA, DSC, and CV curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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