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Communications to the Editor

Spectral Broadening in MEH-PPV:PCBM-Based Photovoltaic Devices via Blending with a Narrow Band Gap Cyanovinylene−Dioxythiophene Polymer

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Recent interest in the development of conjugated polymer-based photovoltaic devices stems from the promise of achieving lightweight, flexible solar cells.[1] Narrow band gap conjugated polymers[2] can exhibit multiple accessible redox states, which give rise to dual p- and n-type dopable polymers.[3] As such, these narrow band gap polymers are useful for electrochromic devices[4] and show potential for application in LEDs and TFTs. To develop polymer solar cells to a point of utility, efficiencies must be improved, as the best reported devices in the literature are only able to achieve 2.5−4% power conversion efficiencies.[5] In the field of polymer solar cells, much effort is devoted to improving the efficiency of the devices. One of the most promising avenues to this end is to develop narrow band gap polymers (E_g < 1.8 eV) that are capable of strongly absorbing sunlight (visible and near-infrared) near the peak of photon flux from the sun.[6] Relatively few reports of polymers with band gaps of less than 1.8 eV are reported for use in solar cells. Importantly, to the best of our knowledge, no systematic design of an "ideal" donor polymer for use in solar cells has been presented. Here, we report on a new narrow band gap polymer and illustrate the design principles for developing an ideal donor polymer with the proper electronic band structure requirements in a comprehensive manner.

As a primary route to improving device efficiencies, many groups have relied on the polymeric-electron-donor C_{60}-electron-acceptor platform and attempted to increase the number of absorbed photons by more closely matching the donor absorption spectrum to the solar spectrum. This has been achieved by using narrow band gap polymers,[7] by using a blend of a conjugated polymer and sensitizing dye,[8] or by using blends of several polymers of varying band gap.[9] While these approaches have led to devices exhibiting efficiencies on the order of 1−2%, no improvement over the best MDMO-PPV:PCBM or P3HT:PCBM devices has been achieved.

As an effort to develop a robust polymer that strongly absorbs sunlight and that can be blended with higher band gap polymers in order to fully blanket the solar spectrum, here we present the synthesis of a new soluble, narrow band gap polymer (Scheme 1) based on cyanovinylene and 3,4-propylenedioxythiophene-dihexyl (ProDOT-Hx_2)[10] linkages, along with electrochemical, spectroscopic, and initial photovoltaic device characterization. This work serves as an extension of our previous work on insoluble donor−acceptor cyanovinylene polymers.[11]

Structurally, PProDOT-Hx_2:CN-PPV is designed to be a PPV analogue modified in order to access several desired properties of an "ideal" donor polymer (see Figure 1) in fullerene-based photovoltaic devices. Focusing on the electronic band structure, such an ideal donor has the minimal band gap as allowed by frontier orbital requirements for air stability and photoinduced charge transfer to a fullerene acceptor. For PProDOT-Hx_2:CN-PPV, incorporating alternating donor and acceptor groups in the backbone targets a narrow band gap.[2] Second, it is desired that the polymer be air stable (i.e., resistant to oxidation) in order to allow ease of handling and processing by having a fairly low-lying HOMO (~5.2 eV or lower,[12] assuming that the energy level of SCE is 4.7 eV below the vacuum level[13]). Notice in Figure 1 that homopolymers of dioxythiophenes (i.e., PProDOT-Hx_2) are unstable to air oxidation with HOMO energies of ~5.1 eV, while alkoxy-substituted PPVs (MEH-PPV) have HOMO energies low enough to ensure air stability (5.4 eV). To convert MEH-PPV into an ideal donor, the LUMO must be lowered while minimizing any effect on the HOMO energy as the band gap is compressed. The replacement of vinylene linkages with cyanovinylene linkages is known to lower both the LUMO and the HOMO by ~0.5 eV while having little effect on the magnitude of the band gap as seen for CN-PPV.[14] In the case of this new CN-PPV analogue PProDOT-Hx_2:CN-PPV, one dialkoxybenzene per repeat unit is replaced with an electron-rich dioxythiophene in order to raise the HOMO relative to CN-PPV and minimize the band gap based on the stronger donor−acceptor interaction. As a final concern, a donor polymer intended for use with a soluble fullerene acceptor should have a LUMO offset of approximately 0.3−0.4 eV[8,15] relative to PCBM (4.2 eV) in order to ensure effective charge transfer. While cyanovinylene is typically a structural motif used in electron-accepting polymers, cyanovinylene polymers have been used as donors in PCBM-based photovoltaic devices, albeit with limited success.[16] It should be noted that the cyanovinylene linkage may serve as a Michael acceptor and be susceptible to hydrolytic degradation, making device encapsulation important when device stability is to be considered. The determination of the PProDOT-Hx_2:CN-PPV band structure, as depicted in Figure 1, is discussed below.

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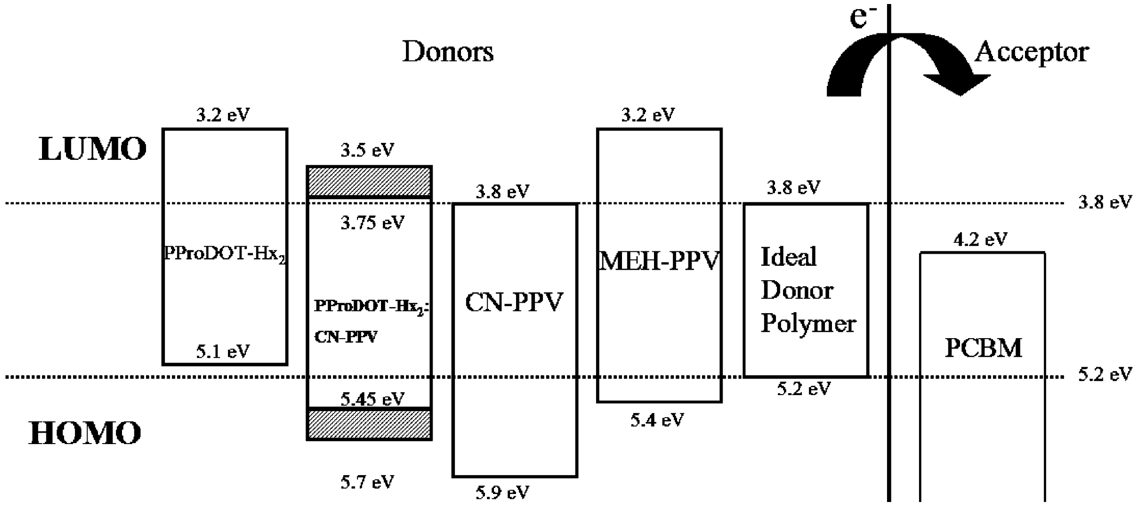
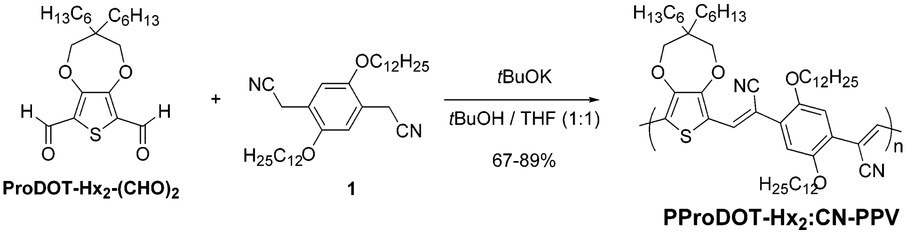


Figure 1. Band diagram for an ideal donor polymer for PCBM along with donors MEH-PPV,[14c] CN-PPV,[14c] PProDOT-Hx$_2$:CN-PPV, and PProDOT-Hx$_2$.[10] Dashed lines indicate the thresholds for air stability (5.2 eV) and effective charge transfer to PCBM (3.8 eV). Note that these values are all approximate, as some values come from the literature and the method of determining HOMO−LUMO energies varies from sample to sample. In all cases orbital energies are given based on the assumption that the energy of SCE is 4.7 eV vs vacuum,[13] and Fc/Fc$^+$ is +0.380 V vs SCE[17] (i.e., 5.1 eV relative to vacuum). Shaded areas in the band structure of PProDOT-Hx$_2$:CN-PPV represent the difference between the optical gap (1.7 eV) and the electrochemical gap (2.2 eV).

Scheme 1. Synthesis of PProDOT-Hx$_2$:CN-PPV



On the basis of the above design principles, polymer synthesis for PProDOT-Hx$_2$:CN-PPV proceeded via the Knoevenagel polycondensation of the 2,5-dialdehyde of 3,4-propylenedioxythiophene-dihexyl (PProDOT-Hx$_2$-(CHO)$_2$) and 1,4-didodecyloxy-2,5-phenylene-diacetonitrile (**1**) to yield PProDOT-Hx$_2$:CN-PPV in 67−89% yield. The polymer was isolated by precipitation into methanol and purified by reprecipitation from chloroform into methanol. Analogous polymers based on alkylthiophenes (as opposed to dioxythiophenes) have been reported for use in LEDs.[18] Also, similar soluble dioxythiophene polymers have been reported,[19] although oxidative polymerization using FeCl$_3$ was employed which often leads to trapped charged sites in the polymer as the as-made polymer does not fully dedope easily. The molecular weight (M_n) of PProDOT-Hx$_2$:CN-PPV was found to be 14 000−17 000 g/mol (PDI = 1.5) as determined by GPC in THF vs polystyrene. MALDI−TOF MS has confirmed molecular weights over 25 000 g/mol. Characterization results from ^{1}H NMR, IR, and elemental analysis are found to be consistent with the expected structure, and PProDOT-Hx$_2$:CN-PPV is soluble in THF, chloroform, toluene, and dichlorobenzene. In toluene, PProDOT-Hx$_2$:CN-PPV gives a deeply colored blue solution with a molar absorptivity of 1.9×10^4 L mol^{-1} cm^{-1} at λ_{max} (628 nm). As a comparison, the absorptivity of MEH-PPV in toluene is 1.3×10^4 L mol^{-1} cm^{-1} (496 nm).

Spectroscopic evaluation of thin films of PProDOT-Hx$_2$:CN-PPV reveals the potential utility of this polymer for photovoltaic applications. In Figure 2a the thin film absorption spectra of PProDOT-Hx$_2$:CN-PPV and MEH-PPV are shown relative to the solar spectrum. It can be seen from the onset of the thin film $\pi-\pi^*$ transition that the band gap of PProDOT-Hx$_2$:CN-PPV is ~1.7 eV. It is apparent that while PProDOT-Hx$_2$:CN-PPV absorbs strongly near the peak of photon flux from the sun (700 nm), a blend of PProDOT-Hx$_2$:CN-PPV with MEH-PPV is capable of absorbing over the entire range of 400−750 nm. However, this spectral broadening approach is only useful if both donor polymers are able to ultimately transfer an electron to PCBM upon photoexcitation. As a means of qualitatively establishing photoinduced charge transfer from PProDOT-Hx$_2$:CN-PPV to PCBM, Figure 2b shows the absorption and emission spectra of a pristine film of PProDOT-Hx$_2$:CN-PPV and the absorption and emission spectra of a film consisting of 1:4 PProDOT-Hx$_2$:CN-PPV:PCBM. It can be seen that upon excitation of the pristine polymer at 570 nm strong emission is observed with a maximum at 700 nm. Upon excitation of the polymer−PCBM blend at 570 nm, the intensity of the emission at 700 nm is reduced by 95%. This photoluminescence quenching is indicative of either photoinduced charge transfer or possibly energy transfer.

To establish a complete picture of the band structure of PProDOT-Hx$_2$:CN-PPV, HOMO and LUMO energies were investigated using cyclic voltammetry (CV) on solution-cast polymer films in 0.1 M TBAPF$_6$/acetonitrile. PProDOT-Hx$_2$:CN-PPV is found to have a CV determined onset of oxidation of +0.6 V and an onset of reduction of −1.6 V, both measured vs Fc/Fc$^+$. Considering that the estimated energy level of Fc/Fc$^+$ is 5.1 eV below the vacuum level, these onsets cor-

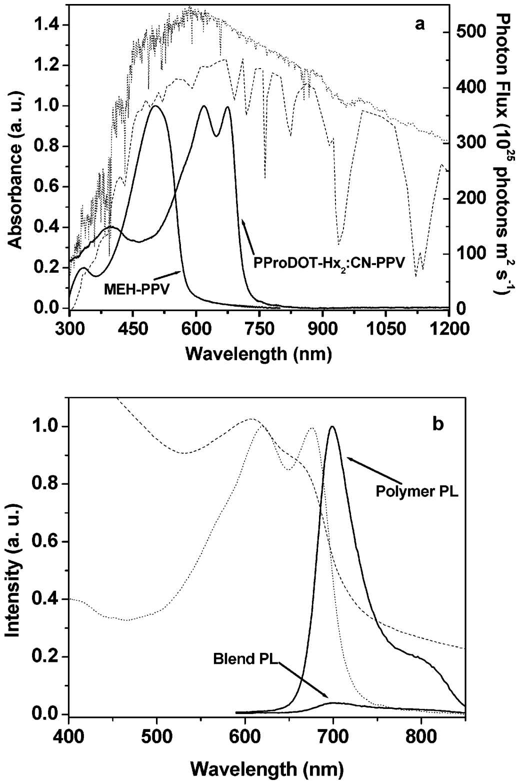


Figure 2. (a) Normalized UV−vis absorbance of thin films of PProDOT-Hx$_2$:CN-PPV (solid line as labeled) and MEH-PPV (solid line as labeled) superimposed on the solar spectrum (dotted line = AM0 and dashed line = AM1.5). (b) Normalized UV−vis absorbance of a PProODOT-Hx$_2$:CN-PPV thin film (dotted line) and the corresponding emission (solid line, polymer PL) upon excitation at 570 nm. Also shown is the absorption (dashed line) of a thin film of 4:1 PCBM:PProDOT-Hx$_2$:CN-PPV along with the corresponding emission (solid line, blend PL) upon excitation at 570 nm.

respond to a HOMO energy of 5.7 eV and a LUMO energy of 3.5 eV for an electrochemical band gap of 2.2 eV. To account for this discrepancy between the electrochemical and optical band gaps, the band edges for PProDOT-Hx$_2$:CN-PPV in Figure 1 are determined by CV, and the optical band gap (unshaded region) is superimposed about the baricenter of the electrochemical band gap. Importantly, the band structure reveals a HOMO energy of 5.45−5.7 eV, which is well below the cutoff for ambient stability to oxidation. Note that this value alone does not guarantee that the polymer will give rise to highly stable solar cells. Such stability can only be assessed by long-term testing, as reported by others.[20]

Photovoltaic devices were constructed using PProDOT-Hx$_2$:CN-PPV and PCBM as well as several tricomponent blends consisting of MEH-PPV, PCBM, and PProDOT-Hx$_2$:CN-PPV as a means of broadening the spectral range over which solar energy could be absorbed. In all these devices the content of PCBM was held constant (80 wt %) while the relative proportions of PProDOT-Hx$_2$:CN-PPV and MEH-PPV were varied. In all cases, the active layer was spin-coated from dichlorobenzene solutions with a concentration of 30 mg/mL to yield films 70−140 nm in thickness. In this initial study, film thicknesses were not optimized to enhance device performance, and indeed the devices presented are unoptimized with respect to solvent choice, blend concentration, and blend composition and are meant to serve as a proof-of-concept. Figure 3 shows the photocurrent action spectra for several representative devices. For the device consisting of PProDOT-Hx$_2$:CN-PPV and PCBM, the maximum in the IPCE (incident photon to current efficiency) is observed at 600 nm with an efficiency of ~11%. The photocurrent matches well with the polymer absorption spectra, showing photocurrent out to 700 nm and establishing charge transfer from photoexcited PProDOT-Hx$_2$:CN-PPV as the primary source of photocurrent in the device. The IPCE data are also shown for a device consisting of only MEH-PPV and PCBM. In this case, the photocurrent spectrum matches well the combined absorption of MEH-PPV and PCBM and shows a maximum of ~26% at 490 nm. Figure 3 also shows that in tricomponent blend devices both polymers are observed to contribute to the photocurrent in the device. In the case of the device with a 1:1 polymer blend composition, a general enhancement in the photocurrent is observed from 350 to 750 nm.

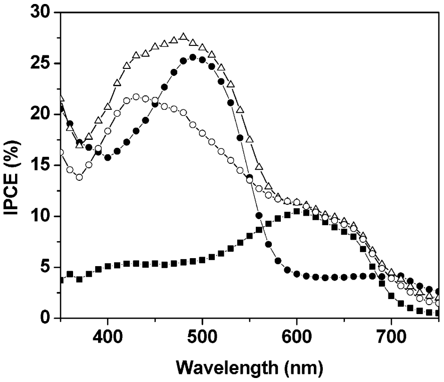


Figure 3. IPCE data for blends consisting of MEH-PPV, PProDOT-Hx$_2$:CN-PPV, and PCBM. PProDOT-Hx$_2$:CN-PPV/PCBM (1/4) (■), MEH-PPV/PCBM (1/4) (●), MEH-PPV/PProDOT-Hx$_2$:CN-PPV/PCBM (0.5/0.5/4) (△), and MEH-PPV/PProDOT-Hx$_2$:CN-PPV/PCBM (0.1/0.9/4) (○).

In a preliminary study, the power conversion efficiencies (η) of several tricomponent devices were also evaluated under AM1.5 conditions. Devices based on 1:4 blends of PProDOT-Hx$_2$:CN-PPV and PCBM were found to give $\eta = 0.1\%$, and efficiencies were found to be ~1.0% with up to a 50/50 blend of PProDOT-HX$_2$:CN-PPV and MEH-PPV in 80% PCBM solar cells. The best literature values reported for MEH−PPV devices range from 1.2 to 2.9%.[21] With an excess of PProDOT-Hx$_2$:CN-PPV relative to MEH-PPV, the device performance drops off to an efficiency of only ~0.3% at 3:1 PProDOT-Hx$_2$:CN-PPV to MEH-PPV. This decrease in device performance is probably due to a change in the film morphology that results when PProDOT-Hx$_2$:CN-PPV becomes the dominant polymer component. Preliminary AFM results indicate that with a 50/50 blend of the two polymers and PCBM a smooth continuous surface is observed. However, upon increasing the amount of PProDOT-Hx$_2$:CN-PPV relative to MEH-PPV, a rough discontinuous surface is generated. Detailed morphological studies will expand on the understanding of this result.

In summary, we have presented a new narrow band gap PPV polymer based on dioxythiophene and cyanovinylene. This polymer is soluble in common organic solvents and can be blended with other donor-type polymers as well as acceptors such as PCBM to yield thin films suitable for use in photovoltaic devices. Photoluminescence quenching measurements coupled with measured IPCE data indicate that PProDOT-Hx$_2$:CN-PPV is functioning as a photoexcited donor in blends with PCBM. While no significant enhancement in overall device performance is observed upon incorporation of PProDOT-Hx_2:CN-PPV into MEH-PPV/PCBM devices, data from photocurrent action spectra indicate that PProDOT-Hx_2:CN-PPV is effectively absorbing low-energy photons and broadening the spectral range over which sunlight is captured.

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Supporting Information Available: Synthesis of PProDOT-Hx_2:CN-PPV and full experimental details concerning electrochemistry, spectroscopy, and photovoltaic device construction. This material is available free of charge via the Internet at http://pubs.acs.org.

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