

High Open Circuit Voltage in Regioregular Narrow Band Gap Polymer Solar Cells

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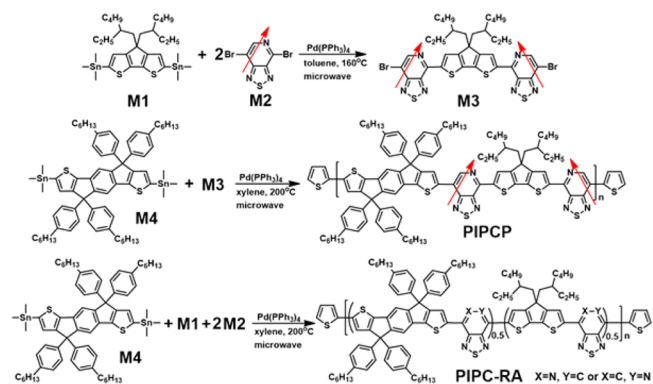
S Supporting Information

ABSTRACT: The regioregular narrow band gap ($E_g \sim 1.5$ eV) conjugated polymer PIPCP was designed and synthesized. PIPCP contains a backbone comprised of CPDT-PT-IDT-PT repeat units (CPDT = cyclopentadithiophene, PT = pyridyl[2,1,3]thiadiazole, IDT = indacenodithiophene) and strictly organized PT orientations, such that the pyridyl N-atoms point toward the CPDT fragment. Comparison of PIPCP with the regiorandom counterpart PIPC-RA illustrates that the higher level of molecular order translates to higher power conversion efficiencies (PCEs) when incorporated into bulk heterojunction (BHJ) organic solar cells. Examination of thin films via absorption spectroscopy and grazing incidence wide-angle X-ray diffraction (GIWAXS) experiments provides evidence of higher order within thin films obtained by spin coating. Most significantly, we find that PIPCP:PC₆₁BM blends yield devices with an open circuit voltage (V_{oc}) of 0.86 V, while maintaining a PCE of $\sim 6\%$. Comparison against a wide range of analogous narrow band gap conjugated polymers reveals that this V_{oc} value is particularly high for a BHJ system with band gaps in the 1.4–1.5 eV range thereby indicating a very low $E_g - eV_{oc}$ loss.

Similarly, the regioregular conjugated polymer PIPT-RG, which contains alternating PT and indacenodithiophene (IDT) units, provides BHJ solar cells with a larger power conversion efficiency (PCE).⁵ Regiochemistry control also improves intermolecular π -stacking and thereby PCE values.⁶

In this contribution, we report the regioregular polymer PIPCP (Scheme 1) which combines two different D fragments

Scheme 1. Polymer Chemical Structures and Preparations^a



^aThe red arrows highlight the orientations of the asymmetric PT unit.

Narrow band gap organic semiconductors are under study due to their application in solution-deposited bulk heterojunction (BHJ) solar cells.¹ The most widely used molecular design strategy centers on conjugated polymers containing electron-rich fragments (donor, D) and electron-deficient fragments (acceptor, A) in an alternating fashion so that backbone excitations are characterized by intramolecular charge transfer (ICT) states with narrow optical band gaps.² Situations may be encountered where either the D or A units are asymmetric relative to the backbone vector. Under these circumstances one needs to consider the possible influence of regiochemistry on relevant optoelectronic and morphological properties.³

Indeed, recent reports highlight the benefit of controlling D–A copolymer regioregularity. For example, a regioregular polymer with a precisely controlled orientation of the pyridyl-[2,1,3]thiadiazole (PT) A unit exhibits 2 orders of magnitude higher mobility than that of the regiorandom counterpart.⁴

(IDT and cyclopentadithiophene, namely, CPDT) with the PT unit and is characterized by an optical band gap (E_g) of ~ 1.47 eV. This material provides an improved performance when compared to a less structurally precise counterpart. More importantly, and quite unexpectedly, we find that despite the narrow E_g of PIPCP, it is possible to fabricate solar cell devices with high open circuit voltages (V_{oc}).

Our design strategy for the PIPCP backbone includes flanking each PT unit on one side with the CPDT D unit and the opposite side with an IDT fragment, which is less electron-rich relative to CPDT.⁷ Phenomenologically, we anticipated the strong donor characteristics of CPDT would accentuate the ICT characteristics of the excited state,² while the IDT would contribute toward keeping a relatively deep highest occupied molecular

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orbital (HOMO) energy level so to promote high V_{oc} values when blended with a fullerene electron acceptor.⁸

To achieve the regioregularity of PIPCP, the symmetrical monomer **M3** was first synthesized via Stille cross-coupling reaction of **M1** and **M2** with a yield of 80%; see Scheme 1. Postpurification, the regioselectivity of **M3** is >99%.⁹ **M3** and **M4** were subsequently polymerized together under microwave heating at ~ 200 °C to yield the desired product. Proton nuclear magnetic resonance (^1H NMR) spectroscopy of PIPCP in CDCl_3 reveals sharp peaks in the aromatic region, which indicate that each building block in the polymer chain is in a similar chemical environment, consistent with the proposed regioregularity. Nuclear Overhauser effect spectroscopy (NOESY) was also carried out and shows that the PT proton is in close proximity to a proton in the IDT fragment (Figure S1, SI).

In order to provide a comparison from a structurally related polymer structure, i.e. containing units of [IDT-PT] and [CPDT-PT] fragments in a presumably random organization, PIPC-RA was prepared by the direct reaction of **M1**, **M2**, and **M4** in the appropriate ratios, as shown in Scheme 1. Peaks in the ^1H NMR spectrum of PIPC-RA are broader relative to those of PIPCP (Figure S2 in the SI). The number-average molecular weight (M_n) and polydispersity index (PDI) were determined by gel permeation chromatography (GPC). For PIPCP one obtains an M_n of 86 kDa and a PDI of 1.6, while PIPC-RA is characterized by an M_n = 33 kDa and a PDI = 2.4. Both polymers are soluble in chloroform and chlorobenzene at rt in concentrations higher than 10 mg/mL. No thermal transitions were observed for either material by differential scanning calorimetry (DSC) in the range 30–280 °C (Figure S3, SI).

Absorption spectra in the 350–1000 nm region of PIPCP and PIPC-RA thin films are shown in Figure 1. Solution absorption is

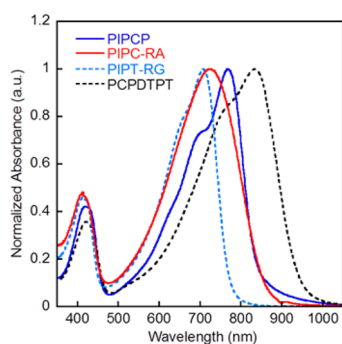
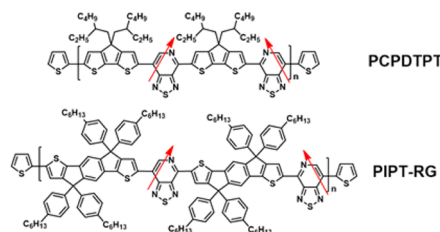


Figure 1. Absorption spectra in the 350–1000 nm range of different polymer thin films. Films were spun-cast at 1000 rpm from 5 mg/mL solutions in chlorobenzene on glass substrates.

provided in Figure S4 of the SI. Both polymers exhibit bands centered at ~ 410 nm, which are attributed to π – π^* transitions.¹⁰ Broader and further red-shifted bands arise from ICT transitions. Relative to PIPC-RA, one observes that the band from PIPCP is further red-shifted, is narrower in width, and exhibits vibronic-like features. The latter is consistent with a greater degree of structural order, both within the polymer backbone and in the multichain aggregates. We recognize, however, that the lower average molecular weight of PIPC-RA may also influence its blue-shifted absorption. To further understand the influence of the structural units on the properties of PIPCP and PIPC-RA, the absorption of the binary D–A regioregular polymers PIPT-RG and PCPDTPT (Scheme 2) are also provided in Figure 1. One observes that the absorption edges of PIPCP and PIPT-RA are

located at intermediate values relative to PIPT-RG and PCPDTPT, which indicates an “averaging” of the band gaps according to the D and A ratio.¹¹

Scheme 2. Polymer Chemical Structures of PCPDTPT and PIPT-RG



Cyclic voltammetry measurements were used to estimate HOMO energy levels by using the onset of oxidation.¹² Lowest unoccupied molecular orbital (LUMO) energy levels were deduced by addition of E_g to the HOMO energies. For the two reference polymers, PCPDTPT has a higher HOMO (-5.10 eV) than PIPT-RG (-5.27 eV) in accordance with CPDT being a stronger donor IDT. As in the case of the absorption spectra, the HOMO levels have shown a combined effect of CPDT and IDT. Particularly, PIPCP shows a HOMO of -5.21 eV, slightly deeper than that of PIPC-RA (-5.15 eV) (Figure S6, SI). The results suggest that devices built with PIPCP:PC₆₁BM blends should reasonably provide higher V_{oc} values than analogous cells fabricated using PIPC-RA:PC₆₁BM blends.

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed to investigate relevant structural features.¹³ The results of these studies are provided in Figure 2. A

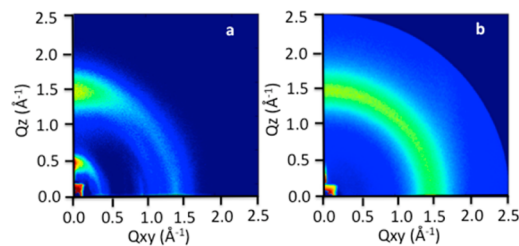


Figure 2. GIWAXS patterns of PIPCP (a) and PIPC-RA (b) thin films. Films were spun-cast from 5 mg/mL solutions in chlorobenzene on silicon wafers.

strong reflection peak in the out-of-plane direction at $q = 1.47$ \AA^{-1} is observed for PIPCP that corresponds to a real space distance of 0.43 nm, a value typically attributed to π – π stacking. There is another intense reflection peak at $q = 0.24$ \AA^{-1} , which presumably is due to alkyl chains with a lamella distance of 2.6 nm (q values are obtained from the out-of-plane line cut profile in Figure S7 of the SI). Both signals extend to the in-plane direction. This analysis suggests that both face-on and edge-on orientations exist in the thin film. For the regiorregular PIPC-RA, instead of clear reflection peaks one observes an amorphous hump on either the out-of-plane or in-plane direction. This comparative set of data indicates that the molecular precision of PIPCP translates into films of greater morphological order.

Hole mobilities were measured using hole-only diodes. Device fabrication details and current density–voltage (J – V) characteristics are provided in the SI (Figure S8). Using the space-charge-limited-current (SCLC) model,¹⁴ PIPCP exhibits a hole mobility

of $1.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas the mobility of PIPC-RA is $1.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The higher mobility for PIPCP is consistent with the greater degree of molecular order inferred from optical absorption and GIWAXS measurement.

Single-junction solar cells were made using the inverted device structure ITO/ZnO/(PIPCP or PIPC-RA):PC₆₁BM/MoO₃/Ag. Specifically, ~40 nm of zinc oxide was deposited atop indium tin oxide (ITO) coated glass substrates.¹⁵ Polymer:PC₆₁BM blends were spin-coated, followed by the evaporation of 6 nm of molybdenum oxide and 40 nm of silver. A preliminary screening of BHJ compositions and deposition conditions was carried out. The following polymer:PC₆₁BM weight ratios were tested: 1:1.4, 1:2, and 1:3; the 1:2 combination was found to be the best among these conditions. Solutions were also prepared using different solvents, and the mixed solvent of chlorobenzene/chloroform (1/9, v/v) at a solid concentration of 12 mg/mL was found to be optimal (see SI). These conditions provided an active layer thickness of ~90 nm.

J - V curves of optimal devices obtained with PIPCP:PC₆₁BM and PIPC-RA:PC₆₁BM are shown in Figure 3. Measurements

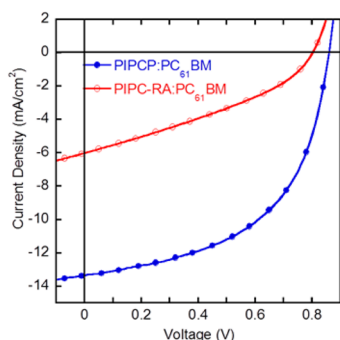


Figure 3. J - V curves of PIPCP:PC₆₁BM and PIPC-RA:PC₆₁BM devices.

were carried out under AM1.5G illumination ($100 \text{ mW}/\text{cm}^2$). PIPCP exhibits a V_{oc} of 0.86 V, a J_{sc} of $13.4 \text{ mA}/\text{cm}^2$, and a fill factor (FF) of 0.53, which together give rise to a PCE of 6.13%. The average PCE is $5.86 \pm 0.19\%$, based on the evaluation of 14 devices. Cells fabricated with regiorandom PCPT-RA are not as effective: $J_{sc} = 6.0 \text{ mA}/\text{cm}^2$, $V_{oc} = 0.80 \text{ V}$, FF = 0.35, and PCE = 1.67%. External quantum efficiency (EQE) curves are shown in Figure 4. Both polymers show a broad EQE response from 300 to 900 nm, but PIPCP exhibits a higher EQE value than the PIPC-RA across nearly the entire absorption range and the maximum is ~60% in the absorption range 690–790 nm. The J_{sc} values

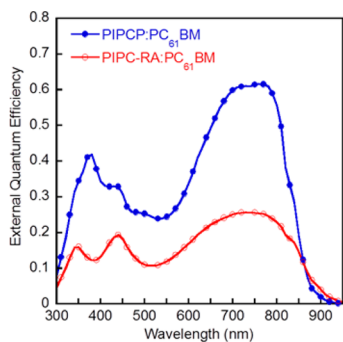


Figure 4. EQE curves of PIPCP:PC₆₁BM and PIPC-RA:PC₆₁BM devices.

calculated from integration of the EQE with the AM1.5G reference spectrum are $12.9 \text{ mA}/\text{cm}^2$ for PIPCP and $5.9 \text{ mA}/\text{cm}^2$ for PIPC-RA, which agree with the J_{sc} obtained from the J - V measurement within 5% error.

It is worth commenting on the high V_{oc} of the PIPCP:PC₆₁BM devices. We begin by noting that similarly high values can be used with PIPCP:PC₇₁BM. As shown in the SI, PIPCP:PC₇₁BM blends perform equally well ($J_{sc} = 12.97 \pm 0.25 \text{ mA}/\text{cm}^2$, $V_{oc} = 0.86 \pm 0.01 \text{ V}$, FF = 0.55 ± 0.00 , and PCE = $6.15 \pm 0.17\%$). To highlight the high V_{oc} feature of PIPCP:PC₆₁BM, we define the donor photon energy loss as $E_g - eV_{oc}$ where E_g is the optical band gap of the donor polymer and V_{oc} is obtained from the corresponding device with either PC₆₁BM or PC₇₁BM. Figure 5

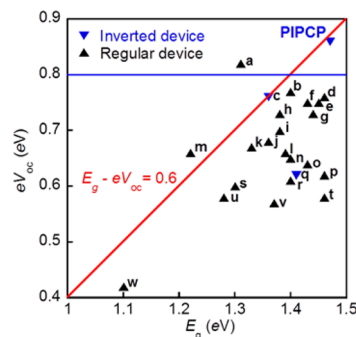


Figure 5. E_g and V_{oc} distributions of recent high performance narrow band gap polymer devices. Blue line is the eV_{oc} of 0.8 eV, and red line is the “ $eV_{oc} = E_g - 0.6$ ”. Letters refer to different works in reference 16.

provides a plot of eV_{oc} vs E_g for a series of polymer combinations reported in the literature for devices with PCE > 5% (see also Table S6, SI).¹⁶ Included in the plot is a line in red corresponding to $E_g - eV_{oc} = 0.6 \text{ eV}$. This quantity is often used in the literature as an approximation to the maximum voltage achievable by a specific BHJ blend.¹⁷

Figure 5 demonstrates that the PIPCP:PC₆₁BM BHJ layer is outstanding in terms of the $E_g - eV_{oc}$ loss. We note that $E_g - eV_{oc}$ disregards the impact of the acceptor and only describes the energy loss from donor absorption. Few narrow band gap polymers can obtain a higher V_{oc} than 0.8 V, and most of the polymers are below the line of $E_g - eV_{oc} = 0.6$. PIPCP has the highest V_{oc} and the energy loss is one of the lowest.

In conclusion, the work here provides the synthesis and characterization of the regioregular polymer PIPCP, which incorporates two different donor units (IDT and CPDT) and the PT acceptor in the backbone. Structural control in PIPCP is also achieved via the precise orientation of the PT fragments relative to the backbone vector. Higher structural order, charge carrier mobilities, and PCEs are achieved relative to the less structurally precise PIPC-RA analog. Of particular relevance is the very low photon energy loss when BHJ blends are prepared with PIPCP and either PC₆₁BM or PC₇₁BM. Indeed, we find that the $E_g - eV_{oc}$ value of the PIPCP blends is very high relative to a wide comparison of literature examples and closely approaches the widely referenced 0.6 V limit. Subsequent optical spectroscopy and device testing studies are required to understand the precise energetic landscape that describes the exciton to charge carrier conversion process in such systems. A further challenge stems from correlating the energy of the different states to specific morphological features responsible for the difference in performance relative to other conjugated polymer BHJ blends. While these questions are the subjects of ongoing studies,

PIPCP:PC₆₁BM blends provide unexpected new opportunities for device engineering optimization given the high V_{oc} values.

■ ASSOCIATED CONTENT

● Supporting Information

The experimental details of synthesis of monomers and polymers, ¹H NMR and NOESY spectra, DSC curves, UV–vis spectra, CV data, SCLC mobility measurements, solar cell device data, and the summary of high performance narrow band gap polymers are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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