New TIPS-substituted benzo[1,2-\(b\):4,5-\(b\)]dithiophene-based copolymers for application in polymer solar cells†

Chinna Bathula,\(^a\)† Chang Eun Song,\(^b\)† Sachin Badgujar,\(^a\) Seong-Jin Hong,\(^a\)† In-Nam Kang,\(^d\) Sang-Jin Moon,\(^a\) Jaemin Lee,\(^a\) Shinuk Cho,\(^a\) Hong-Ku Shim\(^a\) and Sang Kyu Lee\(^a\)

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Novel triisopropylsilylethynyl (TIPS)-substituted benzodithiophene-based copolymers, poly[4,8-bis(triisopropylsilylethynyl)benzo[1,2-b:4,5-\(b\)]dithiophene-2,6-diyld-alt-4,6-(2-ethylhexyl-thieno[3,4-b]thiophene-2-carboxylate)] (P1), poly[4,8-bis(triisopropylsilylethynyl)benzo[1,2-b:4,5-\(b\)]thiophene-2,6-diyld-alt-4,6-(1-thieno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one] (P2), and poly[4,8-bis(triisopropylsilylethynyl)benzo[1,2-b:4,5-\(b\)]dithiophene-2,6-diyld-alt-4,6-(2-ethylhexyl(3-fluorothieno[3,4-b]thiophene)-2-carboxylate)] (P3), were designed and synthesized for use in polymer solar cells (PSCs). We describe the effects of the different acceptor segment side groups on the optical, electrochemical, field-effect hole mobility, and photovoltaic characteristics of the resulting TIPS-based copolymers. The side groups in the copolymers were found to significantly influence the carrier mobilities and photovoltaic properties of the copolymers. The field-effect mobilities of the holes varied from 9 \(\times\) 10\(^{-5}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in P2 to 3 \(\times\) 10\(^{-3}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in P1. Under optimized conditions, the TIPS-based polymers showed power conversion efficiencies (PCEs) for the PSCs in the range of 3.16–5.76%.

Among the TIPS-based copolymers studied here, P1 showed the best photovoltaic performance, with an open-circuit voltage (\(V_{oc}\)) of 0.82 V, a short-circuit current density (\(J_{sc}\)) of 12.75 mA cm\(^{-2}\), a fill factor (FF) of 0.55, and a power-conversion efficiency of 5.76% using a P1:PC\(_{71}\)BM blend film as the active layer under AM 1.5G irradiation (100 mW cm\(^{-2}\)).

Introduction

Recently, polymer solar cells (PSCs) based on blends of conjugated polymers and fullerene derivatives have gained considerable attention as a means for harvesting renewable clean solar energy because of their unique advantages, including their low cost, light weight, solution processability, and flexibility.\(^{1-10}\)

Significant efforts have been applied toward improving the power conversion efficiencies (PCEs) of PSCs. The PCEs of PSCs have reached 7–8%, primarily due to the development of new low band gap polymers and better control over the nanoscale morphologies of the interpenetrating electron donor–acceptor networks.\(^{11,12}\)

The decisive parameters that determine the PSC efficiency are the open-circuit voltage (\(V_{oc}\)), short-circuit current (\(J_{sc}\)), fill factor (FF), \(V_{oc}\) is limited by the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor.\(^{13,14}\) \(J_{sc}\) and FF are directly limited by the charge carrier mobility. Higher charge carrier mobilities enable better carrier transport within an active layer without significant photocurrent loss due to recombination of opposite charges.\(^{15,16}\)

Maximization of the short-circuit current requires a planar structure to encourage the crystallinity of the polymer.\(^{17,18}\) The introduction of more rigid planar structural moieties in conjugated polymers has been shown to be an effective approach to minimize the phase separation because the coplanar structures benefit from improved \(\pi-\pi\) stacking of the copolymers in the solid state.\(^{19-21}\)

Recently, we reported a new class of triisopropylsilylethynyl (TIPS) group-substituted anthracene-based copolymers, PAT2 and PAT4, that displayed an extended \(\pi\)-conjugation length and yielded improved charge transport properties.\(^{22}\) The hole mobility of PAT4 was high, up to 0.037 cm\(^2\) V\(^{-1}\) s\(^{-1}\). PAT4 displayed a very good absorbance and a promising PCE of 1.7%;
However, the pendant chains on the thiophene unit of PAT2 gave rise to steric interactions and a coplanar polymer backbone, resulting in a poor molecular weight and altered optical and electrochemical properties relative to the TIPS-anthracene-based copolymers. Zhan et al. reported TIPS substituted benzodithiophene-based copolymers containing thiazolothiazole acceptor units with a power conversion efficiency of 4.33%. A new polymer backbone was needed to overcome the solubility, steric hindrance, and band gap problems.

In this study, poly[4,8-bis(triisopropylsilyl)ethynyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-4,6-(2-ethylhexyl-thieno[3,4-b]thiophene-2-carboxylate)] (P1), poly[4,8-bis(triisopropylsilyl)ethynyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-[4,6-((1-thieno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one)] (P2), and poly[4,8-bis(triisopropylsilyl)ethynyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-4,6-(2-ethylhexyl[3-fluorothieno[3,4-b]thiophene]-2-carboxylate)] (P3), which have the same polymer backbone but different side chains, were designed and synthesized to achieve a higher PCE. The steric hindrance and solubility problems of PAT2 were ameliorated here by replacing the thiophene units of the thieno[3,4-b]thiophene derivatives with various electron-withdrawing functional groups, which acted as a donor–acceptor system. We also replaced the anthracene groups with benzo[1,2-b:4,5-b']dithiophene (BDT) units. We attempted to synthesize a TIPS group-substituted anthracene-based copolymer by polycondensation of 2,6-bis(trimethyltin)-9,10-bis(triisopropyldiene-ethyl)anthracene and the corresponding dibrominated thieno[3,4-b]thiophene derivatives for the purpose of using the reference; however, the TIPS group-substituted anthracene-based copolymer was obtained as a sticky liquid that was difficult to purify. We expected that the introduction of BDT units would improve the optical properties, including the band gap and the hole mobility. We systematically investigated the synthesis, thermal stability, optical, and electrochemical properties, field-effect carrier mobilities, and photovoltaic characteristics of the resulting polymers. Bulk heterojunction PSCs prepared from P1 produced a PCE of 5.76% under 100 mW cm⁻² AM 1.5 G irradiation in ambient air.

Results and discussion

Synthesis and characterization of the polymers

The synthetic routes for preparing the TIPS-BDT-based polymers are shown in Scheme 1. Three types of BDT-based copolymers were synthesized by polycondensation of 2,6-bis(trimethyltin)-4,8-bis(triisopropylsilyl)ethynyl]-benzo[1,2-b:4,5-b']dithiophene and the corresponding dibrominated thieno[3,4-b]thiophene derivatives through the palladium-catalyzed Stille reaction. The crude polymers were extracted with chloroform, collected by precipitating them in methanol, and extracted with methanol and acetone, successively, using a Soxhlet apparatus to remove byproducts and oligomers. The molecular weights were determined by gel permeation chromatography (GPC) against polystyrene standards in a chloroform eluent and were found to be in the range of 11–19 kDa with a polydispersity index of 1.7–2.2 (Table 1).

The thermal properties of the copolymers under a nitrogen atmosphere, characterized by thermogravimetric analysis (TGA) at a heating rate of 10 °C min⁻¹, yielded decomposition temperatures (T_d) in the range of 360–420 °C. The physical properties of the polymers are summarized in Table 1.

Optical properties

The UV-vis absorption spectra of the polymers in chloroform and in the spin-coated films are shown in Fig. 1 and 2, respectively, and the corresponding absorption properties are summarized in Table 2. In the chloroform solvent, all polymers exhibited similar absorption spectra. The UV-vis absorption maxima of P1, P2, and P3 occurred at 641, 648, and 628 nm, respectively, in solution, and at 678, 677, and 669 nm, respectively, in the film state. The absorption maxima of the polymer films were red-shifted by 29–41 nm compared with the maxima of the polymers in solution. The red shift indicated a higher polymer coplanarity and/or enhanced intermolecular electronic interactions in the solid state. The red shift observed for P1 and P3 was larger than that of P2 due to the structural changes in the side chain induced by the ketone group (P2) and the ester group (P1). These effects were investigated by performing theoretical calculations using density functional theory (DFT) with the DMol 3 software. The computational study was conducted by selecting several repeating units as simplified models (two repeating units). Fig. 3 depicts the electron state density distribution of the HOMO and LUMO of the geometry-optimized structures of the polymers. The results predicted that the HOMO was delocalized over the polymer backbone, whereas the LUMO was almost localized at the electron-acceptor site. This configuration is generally observed for low band gap polymers with push–pull units. The dihedral angles between the BDT units and the thieno[3,4-b]thiophene units were significant, as can be seen from the calculated structures (Fig. 3). The torsional angles of P1 and P3 were smaller than those of P2. The resulting red shift observed for P1 and P3, compared with P2, arose from the minimal coplanarity of the polymer backbone with the ester group substitution.

The absorption maxima of the fluorinated polymer, P3, were blue shifted by 10 nm relative to the maxima of the unfluorinated polymer, P1. As previously reported, the introduction of more electron-withdrawing fluorene groups to the polymer backbone blue-shifted the polymer absorption maxima. The optical band gap obtained from the extrapolation of the absorption edges of the film followed the ordering P2 (1.67 eV) < P1 (1.69 eV) < P3 (1.71 eV).

Electrochemical properties

The energy levels of the HOMO and LUMO were determined by measuring the electrochemical properties of the polymers using cyclic voltammetry (CV). A platinum (Pt) electrode was modified with a polymer film by means of dip-coating, and was used as the working electrode. A Pt wire was used as the counter electrode, and Ag/AgNO₃ (0.10 M) served as the reference electrode. The CV measurements were carried out in a tetraethylammonium tetrafluoroborate (TBABF₄, 0.1 M)/acetonitrile electrolyte at room temperature under a nitrogen atmosphere at a scan rate of 50 mV s⁻¹. Fig. 4 shows the oxidation cyclic voltammograms of the polymers. The HOMO level of the polymers was deduced...
based on the oxidation onsets under the assumption that the energy level of ferrocene (Fc) was 4.8 eV below the vacuum level. In the anodic scan, the onset of oxidation for P1, P2, and P3 occurred at 0.80, 0.81, and 0.80 V, corresponding to ionization potential values of −5.60, −5.61, and −5.60 eV, respectively. As expected from the structures of the polymers, polymers with identical backbone structures had similar HOMO energy values.

**Scheme 1** Synthetic scheme for the monomer and copolymers.
The LUMO energies of the copolymers were estimated based on the optical band gaps (determined from the absorption onsets in the UV-vis spectra of the polymers films) and the HOMO energies. The energies of the LUMO levels of P1, P2, and P3 are listed in Table 2. No fluorine effects were observed in the electrochemical properties. Any inter- or intra-chain interaction may also influence the HOMO level. The dihedral angle between the bulky TIPS-BDT units and the thienothiophene units is significant, as can be seen from the calculated structures (Fig. 3). The dihedral angle for P1 without the fluorine unit is very similar to that for P3 with the fluorine unit. We guess that steric hindrance between the bulky TIPS-BDT units and the thienothiophene units significantly affects the coplanar structure of the polymers. For this reason, we think that not the fluorine effect but the interaction between the bulky TIPS-BDT units and the thienothiophene units exerted an important effect on optical properties as well as electrochemical properties.

**Field-effect transistor characteristics**

The effects of the side chain substitutions on the electrical transport properties of the resulting materials were examined by measuring the mobilities of each of the three copolymers. The

### Table 1 Physical properties of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ [kg mol$^{-1}$]</th>
<th>PDI</th>
<th>Yield (%)</th>
<th>$T_d$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>11</td>
<td>1.9</td>
<td>85</td>
<td>372</td>
</tr>
<tr>
<td>P2</td>
<td>19</td>
<td>2.2</td>
<td>84</td>
<td>420</td>
</tr>
<tr>
<td>P3</td>
<td>11</td>
<td>1.7</td>
<td>87</td>
<td>360</td>
</tr>
</tbody>
</table>

*The molecular weights were determined by using gel permeation chromatography (GPC) against polystyrene standards in chloroform eluent. $^b$ Temperature resulting in 5% weight loss based on initial weight.*

### Table 2 Optical and electrochemical properties of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max, sol}}$ (nm)</th>
<th>$\lambda_{\text{max, film}}$ (nm)</th>
<th>HOMO$^b$ (eV)</th>
<th>LUMO$^c$ (eV)</th>
<th>$E_{g, \text{opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>641</td>
<td>678</td>
<td>$-5.60$</td>
<td>$-3.91$</td>
<td>$1.69$</td>
</tr>
<tr>
<td>P2</td>
<td>648</td>
<td>677</td>
<td>$-5.61$</td>
<td>$-3.94$</td>
<td>$1.67$</td>
</tr>
<tr>
<td>P3</td>
<td>628</td>
<td>669</td>
<td>$-5.60$</td>
<td>$-3.89$</td>
<td>$1.71$</td>
</tr>
</tbody>
</table>

*The UV-Vis absorption spectra of the polymers were measured in chloroform solution and thin film. $^b$ HOMO levels of the polymer were determined from onset voltage of the first oxidation potential with reference to ferrocene at $-4.8$ eV. $^c$ LUMO levels of the polymer were estimated from the optical band gaps and the HOMO energies. $^d$ Optical band gap calculated from the UV-Vis absorption onset in film.
field-effect carrier mobilities of the polymers were investigated by fabricating thin film transistors (TFTs) with a bottom-contact geometry using Au electrodes. The device fabrication process is described in detail in the Experimental section. A high charge-carrier mobility (comparable to or exceeding $10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$) was necessary to reduce the photocurrent loss and obtain high-performance PSC devices.

Fig. 5 shows the transfer curves for the polymers. The TFTs of the polymers were found to exhibit typical p-channel TFT characteristics. The TFT mobilities were calculated in the saturation region using the following equation:

$$I_{ds} = \frac{(WC)}{2L} \mu (V_G - V_T)^2,$$

where $I_{ds}$ is the drain-source current in the saturated region, $W$ and $L$ are the channel width (120 $\mu$m) and length (12 $\mu$m), respectively, $\mu$ is the field-effect mobility, $C_G$ is the capacitance per unit area of the insulating layer ($\text{SiO}_2$, 300 nm), and $V_G$ and $V_T$ are the gate and threshold voltages, respectively.

The field-effect mobilities of P1, P2, and P3 were determined to be $3 \times 10^{-3}$, $9 \times 10^{-5}$, and $7 \times 10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. The hole mobilities of the ester-substituted thienothiophene-based P1 were 2 orders of magnitude higher than those of the ketone-substituted thienothiophene-based P2. The higher mobility measured for P1 compared with P2 was understood in terms of better solubility and $\pi-\pi^*$ stacking, which corresponded well to the UV-vis results. The hole mobility of P1 was within the desired range for PSC materials (comparable to or exceeding $10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$), allowing for efficient charge extraction and a good FF. Previous reports indicated that the hole mobilities of fluorinated polymers are higher than those of unfluorinated polymers due to a higher intermolecular packing among fluorinated backbones.

In our study, no fluorine effects were observed in the field-effect carrier mobilities of the acceptor.

The hole mobility by TFTs is a “horizontal” measurement rather than the “vertical” charge transport. A method to measure the hole mobility in the vertical direction is space charge limited current (SCLC) to reveal the vertical transport in OPV device structures. To obtain the SCLC curves, the hole only devices were fabricated with the structure ITO/PEDOT:PSS/polymer/PC71BM/Ca/Al. As shown in the ESI, the trend of hole mobility by SCLC is similar to that by TFTs.

Photovoltaic characteristics

Bulk-heterojunction PSCs were fabricated with the structure ITO/PEDOT:PSS/polymer:PC$_{71}$BM/Ca/Al. The device-fabrication process is described in detail in the Experimental section. The performance of PSCs was strongly affected by the processing parameters, such as the choice of solvent, blend ratio of the polymer and PC$_{71}$BM, and the additive effects. We investigated the performance of the PSC materials under a variety of conditions (see the ESI). Optimal fabrication conditions were obtained from a 8 mg mL$^{-1}$ solution, at a spin-coating rate of 1300 rpm, and with a polymer:PC$_{71}$BM ratio of 1 : 1.5 (w/w). The layer thicknesses were PEDOT:PSS (40 nm), active layer (90 nm), and Ca/Al (100 nm). In agreement with the TFT properties described earlier, P1 was found to be a suitable material for PSC applications.

Fig. 6 shows the current–voltage curves of the optimized devices based on blends of the BDT-based polymer and fullerene. The output characteristics of the resulting polymer-based devices are summarized in Table 3. Previous studies reported that the solar cell performances of benzo[1,2-b:4,5-b’]dithiophene-based polymers could be improved using a 3% 1,8-diodooctane (DIO) to form an active layer. We repeated the solar cell tests using P1 either with or without the 3% DIO additive. The performance of P1 improved in both $J_{sc}$ and FF, yielding a maximum efficiency of 5.76% (see the ESI). Fig. 7 shows the UV-vis absorption spectra of the P1:PC$_{71}$BM films with and without the 3% DIO additive. The UV-vis spectrum of P1 with DIO displayed well-defined sharp vibronic features compared to the
lower energy absorption peaks are associated with a transition if the films are processed with additives. The red shift indicates that the local structural order is higher than that in films processed from pure chlorobenzene. Under optimized conditions (97% CB/3% DIO solvent), the BDT-based polymers showed PCEs for the PSCs in the range of 3.16–5.76%. The best PSC performance was observed for P1:PC71BM devices, which reached a PCE of 5.76%, with a $J_{sc}$ of 12.75 mA cm$^{-2}$, a $V_{oc}$ of 0.82 V, and a FF of 0.55 under AM 1.5 G irradiation (100 mW cm$^{-2}$).

The $V_{oc}$ value was closely related to the energy difference between the HOMO of the polymer and the LUMO of the electron acceptor, PC71BM. As expected from the HOMO energy levels of the polymers, all polymers exhibited similar $V_{oc}$ values. $J_{sc}$ of a PSC is affected by many factors, including the absorption strength of the active layer and the charge-carrier mobilities. The values of $J_{sc}$ measured for P1, P2, and P3 were 12.75, 8.38, and 9.47 mA cm$^{-2}$, respectively. These results agree well with the OFET measurements. As expected from the hole mobilities of the polymers (3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} for P1, 9 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} for P2, and 7 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} for P3), the unfluorinated ester-substituted thiophene-based P1 exhibited a higher $J_{sc}$ than the other polymers.

Fig. 8 shows the external quantum efficiency (EQE) spectra of the optimized PSC devices prepared with 3% DIO under monochromatic light illumination. The EQE spectra agreed well with the optical absorption curves, indicating that excitons were mainly generated in the polymer phase. The spectral responses of the PSC devices showed that photons within the range of 350–800 nm contributed significantly to the EQE. With monochromatic light illumination, the EQE spectra agreed well with the EQE results and the photon flux under AM 1.5 G. The spectral responses of the PSC devices showed that photons within the range of 350–800 nm contributed significantly to the EQE. With monochromatic light illumination, the EQE spectra agreed well with the EQE results and the photon flux under AM 1.5 G. The spectral responses of the PSC devices showed that photons within the range of 350–800 nm contributed significantly to the EQE. With monochromatic light illumination, the EQE spectra agreed well with the EQE results and the photon flux under AM 1.5 G.

Fig. 8 External quantum efficiency of P1:PC71BM (black), P2:PC71BM (red), and P3:PC71BM (green).
active layer surface leads to an increase in the photovoltaic performances of \( \text{P1} \).

Considering that the \( V_{oc} \) values of PSCs fabricated using the previously reported BDT-based copolymers with alkyl chains were found to be in the range of 0.62–0.76 V, the TIPS-substituted benzodithiophene-based copolymers showed a high \( V_{oc} \) of 0.82 V. The performance of the PSCs could potentially be greatly improved by enhancing the FF and \( J_{sc} \). Further modifications of the polymer structure are currently underway toward achieving an even better performance.

Conclusions

In summary, a series of novel TIPS-substituted benzodithiophene-based copolymers with the same polymer backbone and different side chains were synthesized via Stille coupling polymerization. Although all polymers displayed similar optical and electrochemical properties, \( \text{P1} \) exhibited a higher hole mobility and PSC performance than the other polymers. Under optimized conditions, bulk-heterojunction solar cells fabricated from blends containing \( \text{P1} \) and PC\(_{71}\)BM exhibited PCEs of 5.76%, with a \( J_{sc} \) of 12.75 mA cm\(^{-2}\), a \( V_{oc} \) of 0.82 V, and a FF of 0.55. In light of the field-effect carrier mobility and photovoltaic properties of \( \text{P1} \), TIPS-substituted benzodithiophene-based copolymers are promising candidates as next-generation solar cell materials. In our study, no fluorine effects were observed in the TIPS-substituted benzodithiophene-based copolymers. Also the ester-substituted thienothiophene-based \( \text{P1} \) exhibited higher field-effect carrier mobility and photovoltaic properties than the ketone-substituted thienothiophene-based \( \text{P2} \). A preliminary experimental study of the photovoltaic performances of the TIPS-substituted BDT-based polymer was performed, and modifications of the polymer structure are in progress in an effort to achieve even better performances.

Experimental section

General

The synthesized compounds were characterized with \(^1\)H NMR spectra obtained using a Bruker DPX-300 NMR Spectrometer. UV-visible analysis was performed with a Lambda 20 (Perkin Elmer) diode array spectrophotometer. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC; Viscotek) equipped with a TDA 302 detector and a PL-gel (Varian) column, using chloroform as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C min\(^{-1}\) with a Dupont 9900 analyzer.

Fabrication of the organic thin film transistors (OTFTs)

OTFT devices were fabricated in a bottom-contact geometry (channel length = 12 \( \mu \)m, width = 120 \( \mu \)m). The source and drain contacts consisted of gold (100 nm), and the dielectric was silicon oxide (SiO\(_2\)) with a thickness of 300 nm. The SiO\(_2\) surface was cleaned, dried, and pretreated with a solution of 1.0 mM octyl-trichlorosilane (OTS-8) in toluene at room temperature for 2 h under nitrogen to produce apolar and smooth surfaces onto which the polymers could be spin-coated. The polymers were dissolved to a concentration of 0.5 wt\% in chloroform. Films of the organic semiconductors were spin-coated at 1500 rpm for 50 s to a thickness of 50 nm, followed by an annealing process. All device fabrication procedures and measurements were carried out in air at room temperature.

Fabrication of the polymer solar cells (PSCs)

In this study, the devices were fabricated with the structure ITO/PEDOT:PSS/polymer:PC\(_{71}\)BM/Ca/Al. The procedure for cleaning the ITO surface included sonication and rinsing in...
deionized water, methanol, and acetone. The hole-transporting PEDOT:PSS layer was spin-coated onto each ITO anode from a solution purchased from Heraeus (Clevios™ P). Each polymer:PC71BM solution was then spin-coated onto the PEDOT:PSS layer. PC71BM was purchased from Nano-C Inc. The polymer solution for spin-coating was prepared by dissolving the polymer (8 mg mL\(^{-1}\)) in 97% CB/3% 1,8-diiodooctane (DIO). Calcium and aluminum contacts were formed by vacuum deposition at pressures below 3 \times 10^{-6} \text{Torr}, providing an active area of 0.09 cm\(^2\). Solar cell efficiencies were characterized under simulated 100 mW cm\(^{-2}\) AM 1.5G irradiation from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated silicon photodiode, and the illumination intensity was set using an NREL-certified silicon diode with an integrated KG1 optical filter. The EQE was measured by underfilling the device area using a reflective microscope objective to focus the light output from a 100 W halogen lamp outfitted with a monochromator and an optical chopper; the absolute photon flux was determined using a calibrated silicon photodiode. All device fabrication procedures and measurements were carried out in air at room temperature.

Materials

Trisopropylacetylene, \(N,N',N'\)-tetramethyl-ethane-1,2-diamine (TMEDA), trimethylchioride, dimethylformamide (DMF), tetrakis(triphenylphosphine)palladium and toluene (99.8%, anhydrous) were purchased from Aldrich. All chemical were used without further purification. The monomers benzo[1,2-b:4,5-b']dithiophene-2,6-dione,\(^{39}\) 2-ethylhexyl-4,6-dibromothieno[3,4-b]thiopheno[4,2-carboxylate],\(^{16}\) 1-[4,6-dibromothieno[3,4-b]thiophen-2-yl]-2-ethylhexan-1-one,\(^{11}\) 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiopheno[2-carboxylate]\(^{12}\) were prepared by previously described methods.

4,8-Bis(trisopropylsilylethynyl)-benzo[1,2-b:4,5-b'][dithiophene (2)

To an oven-dried 500 mL round-bottom flask equipped with a stir bar and cooled to 0 °C under the protection of argon were added tetrahydrofuran (THF) (50 mL) and 6.7 mL of trisopropylsilylethyl acrylene (29.9 mmol), followed by the dropwise addition of 19.3 mL of \(t\)-BuLi (32.7 mmol, 1.7 M solution in pentane). This mixture was stirred for 2 h, then THF (120 mL) and benzo[1,2-b:4,5-b']dithiophene-4,8-dione (5 g, 13.7 mmol) were added. The mixture was stirred at room temperature for 24 hours, and then quenched with water. The resulting mixture was poured into a saturated ammonium chloride solution and extracted with ethyl acetate (EA). The organic layer was washed with brine and dried over anhydrous MgSO\(_4\). After the solvent being evaporated, the residue was dissolved in THF (120 mL), and then SnCl\(_2\)-H\(_2\)O (15.3 g, 68.1 mmol, in 50 mL 50% acetic acid) was added dropwise. The mixture was stirred at room temperature overnight, and poured into water and extracted with EA. The organic layer was washed with sodium bicarbonate and brine, and then dried over anhydrous MgSO\(_4\). Solvent was removed and the crude product was purified with column chromatography on silica with hexane as eluent, to yield 2 (3.6 g, 48%) as a light green solid. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.61 (d, 2H), 7.56 (d, 2H), 1.23 (m, 42H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 140.86, 138.51, 128.28, 123.14, 112.18, 102.63, 101.62, 18.78, 11.33. EI-MS: \(\text{m/z}\): 551. Anal. calcd for C\(_{36}\)H\(_{46}\)S\(_2\)Si\(_2\): C, 69.75; H, 8.41; S, 11.63. Found: C, 69.71; H, 8.40; S, 11.63%.

2,6-Bis(trimethyltin)-4,8-bis(trisopropylsilylethynyl)-benzo[1,2-b:4,5-b'][dithiophene (3)

Under the protection of argon, 5.1 mL of \(n\)-BuLi (8.1 mmol, 1.6 M solution in hexanes) was added drop-wise via syringe to compound 2 (1.5 g 2.7 mmol) and TMEDA (1.2 mL, 8.1 mmol) in THF (30 mL) which was cooled at \(-78\) °C. After stirring at low temperature for 30 minutes, 10.8 mL of trimethyltrichloro (10.8 mmol, 1 M solution in hexane) was added in one portion. The reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with water then concentrated via rotary evaporation. The residue was diluted with chloroform, washed with brine and water. Organic layer was dried over magnesium sulfate and concentrated via rotary evaporation. Crude compound was recrystallized with isopropyl alcohol to yield a pale yellow solid (1.9 g, 80%). \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.69 (s, 2H), 1.23 (m, 42H), 0.47 (s, 18H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 144.68, 143.51, 139.10, 110.36, 103.33, 100.64, 19.06, 11.39, -8.3. EI-MS: \(\text{m/z}\): 876. Anal. calcd for C\(_{93}\)H\(_{116}\)S\(_2\)Si\(_2\): C, 52.06; H, 7.13; S, 7.32. Found: C, 52.09; H, 7.11; S, 7.29%.

General procedure for the synthesis of polymers with the Stille reaction: the synthesis of poly[4,8-bis(trisopropylsilylethynyl)benzo[1,2-b:4,5-b'][dithiophene-2,6-diyl-alt-4,6-(2-ethylhexyl-thieno-[3,4-b]thiopheno-2-carboxylate)] (P1) is presented in detail as a representative example. 2,6-Bis(trimethyltin)-4,8-bis(trisopropylsilylethynyl)-benzo[1,2-b:4,5-b'][dithiophene (262 mg, 0.3 mmol), 2-ethylhexyl 4,6-dibromothieno[3,4-b]thiopheno-2-carboxylate (136 mg, 0.3 mmol), and Pd(PPh\(_3\))\(_2\) (14 mg, 0.04 eq) were added into a 50 mL round-bottom flask. Then, anhydrous DMF (1 mL) and anhydrous toluene (4 mL) were added. The polymerization was carried out at 105 °C under argon protection. After 24 h, the reaction mixture was cooled to about 50 °C and added slowly to a vigorously stirred mixture consisting of 230 mL methanol and 13 mL 1 N aqueous HCl. The polymer fibers were collected by filtration and reprecipitation from methanol. The polymer was purified by washing for 2 days in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues. The reprecipitation procedure in toluene–methanol was then repeated several times. The final product was obtained after drying in vacuo at 40 °C. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (pm): 8.14 (br, 1H); 7.86 (br, 1H); 7.80 (br, 1H); 4.37 (br, 2H); 1.94–0.84 (m, 57H). Anal. calcd: C, 66.93; H, 7.41; S, 15.21; Found: C, 66.91; H, 7.42; S, 15.26%.

Poly[4,8-bis(trisopropylsilylethynyl)benzo[1,2-b:4,5-b'][dithiophene-2,6-diyl-alt-[4,6-{1-thieno-[3,4-b]thiophen-2-yl}-2-ethylhexan-1-one]] (P2) was synthesized with the procedure described for P1. The copolymerization of the monomers 2,6-bis-(trimethyltin)-4,8-bis(trisopropylsilacycletene)-benzo[1,2-b:4,5-b'][dithiophene (262 mg, 0.3 mmol) and 1-[4,6-dibromothieno[3,4-b]thiophen-2-yl]-2-ethylhexan-1-one (126 mg, 0.3 mmol) gave P2 (84%). \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.98 (br, 1H);
poly[4,8-bis(trimethylsilyl)ethy1en]benzo[1,2-b:4,5-b']dithiophene-2,6-diy-alt-4,6-(2-ethylhexyl)3-fluorothieno[3,4-b]thiophene-2-carboxylate] (P3) was synthesized with the procedure described for P1. The copolymerization of the monomers 2,6-bis(trimethyltin)4,8-bis(trimethylsilyl)acetylene)-benzo[1,2-b:4,5-b']dithiophene (262 mg, 0.3 mmol) and 2-ethylhexyl 4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (140 mg, 0.3 mmol) gave P3 (87%). 1H NMR (300 MHz, CDCl3) δ (ppm): 7.96 (br, 1H); 7.70 (br, 1H); 4.28 (br, 2H); 1.86–0.80 (m, 57H). Anal. calcld: C, 67.92; H, 7.44; S, 15.77. Found: C, 67.87; H, 7.51; S, 15.78%.

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