An Acetylene-Containing Perylene Diimide Copolymer for High Mobility n-Channel Transistor in Air

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ABSTRACT: A new solution-processable conjugated copolymer (P1) of perylene diimide (PDI) and dithienothiophene (DTT) incorporating acetylene spacers was synthesized by palladium(0)-catalyzed Sonogashira coupling reaction. Theory calculation reveals that introduction of rod-like ethynylene spacer in the polymer main chain promotes planarity and π-conjugation of the polymer main chain. Relative to the conjugated copolymer (P2) of PDI and DTT without acetylene spacers, polymer P1 exhibits 0.1 eV down shift of LUMO level and 89 nm red shift of low-energy absorption band. Polymer P1 in top-contact bottom-gate organic field-effect transistors (OFETs) exhibits a saturation electron mobility of 0.06 cm² V⁻¹ s⁻¹ in air, while P2 does not function in the same device in air. Additionally, a saturation electron mobility of 0.075 cm² V⁻¹ s⁻¹ in air, and after six days storage in air, an electron mobility of 0.034 cm² V⁻¹ s⁻¹ were observed for P1 in bottom-contact bottom-gate OFETs; while a saturation electron mobility of 0.038 cm² V⁻¹ s⁻¹ in air, and after six days storage in air, an electron mobility of 0.013 cm² V⁻¹ s⁻¹ were observed for P2 in the same device. The better air stability and higher electron mobility of P1 are attributed to densely ordered packing of the polymer chains excluding oxygen or water and the lower LUMO level of P1.

INTRODUCTION

Compared with traditional inorganic materials based micro-electronics, optoelectronic devices based on conjugated polymers are a promising candidate which has advantages of low cost, lightweight, solution processability and flexibility.¹⁻⁴ Conjugated polymers can be classified as hole (p-type) or electron (n-type) transporting materials according to the type of orderly migrating charge carriers under a given set of conditions. Hole transporting conjugated semiconductor have seen a revolutionary rise in performance over the past two decades; some p-type polymers show extremely high hole mobility (>1 cm² V⁻¹ s⁻¹),⁵⁻⁸ approximate to that of amorphous silicon. However, the electron mobilities of n-type semiconducting polymers have lagged behind those of their p-type counterparts. In particular, air stable, high-mobility n-type polymer semiconductors remain very rare.⁹⁻¹⁴ Considering the importance of n-type organic materials in the fabrication of organic p–n junctions, solar cells, n-channel organic field-effect transistors (OFET) and complementary logic circuits, the development of high-performance electron-transport semiconductors is one of the biggest challenges in organic electronics.¹⁵⁻¹⁷ Rylene diimides combine highly planar π-conjugated cores (naphthalene, perylene etc.) with electron-withdrawing tetracarboxydiimide; substituents on imide nitrogen can manipulate solubility, morphology, and solid-state packing without disrupting backbone electronic conjugation.¹⁸ Rylene diimides are a robust, versatile class of n-type materials with excellent stability, low LUMOs and, in some cases, high electron mobilities; they are, therefore, promising candidates for a variety of organic electronics applications.¹⁹⁻²⁰ Several n-type conjugated polymers based on perylene diimides (PDIs)²¹⁻²³ and naphthalene diimides (NDIs)¹¹,²⁴⁻²⁷ have been synthesized and used in n-channel OFETs. For example, Zhan et al. reported the synthesis of the first soluble rylene diimide-based fully conjugated copolymer; this PDI-dithienothiophene (DTT) copolymer (P2, Chart 1) in bottom-gate top-contact OFETs exhibited a saturation electron mobility of 0.013 cm² V⁻¹ s⁻¹ and a low threshold voltage of 4 V in nitrogen.²¹ Later, Facchetti and co-workers reported a copolymer of NDI and bithiophene; OFETs in top-gate bottom-contact on polymeric
dielectrics device configuration exhibited electron mobilities of 0.10–0.85 cm² V⁻¹ s⁻¹ under ambient conditions with on/off ratios >10⁶. ¹¹ Poly(arylene ethynylene)s with triple bonds in main chains have attracted increasing interest during the past few decades as a promising class of semiconductors. The incorporation of ethynylene π-spacers offers a viable approach to induce planarity, enhance π-conjugation along the polymer chain and thus charge carrier mobility. ²⁸,²⁹ Furthermore, LUMO levels may be lowered by the presence of electron-withdrawing triple bond spacers. ³⁰,³¹ Recently, a paucity of PDI or NDI oligomers and copolymers incorporating ethynylene spacers has been reported. ³²–³⁴ These semiconductors exhibited the highest electron mobility of 0.1 ± 0.05 cm² V⁻¹ s⁻¹ in nanowire OFETs. ³⁵ Here, we report a new soluble n-type PDI copolymer (P₁, Chart 1) by introducing ethynylene spacers between the electron acceptor PDI units and the electron donor DTT units in P₂ in order to reduce the steric hindrance between PDI and DTT units, promote planarity and enhance the π-conjugation along the polymer main chain. Relative to P₂, P₁ exhibits lower LUMO level, higher electron mobility and better ambient stability. Bottom-gate top-contact OFETs based on P₁ exhibits a saturation electron mobility of 0.06 cm² V⁻¹ s⁻¹ in air, while P₂ does not function in the same device in air. To the best of our knowledge, electron mobility of 0.075 cm² V⁻¹ s⁻¹ is among the highest reported for bottom-gate OFETs based on n-type conjugated polymers in air.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. It is well-known that the PDI bromination procedure gives a mixture of 1,7 and 1,6 regioisomers. ¹⁹,³⁶ The ratio of 1,7- to 1,6-regioisomer in our PDI dibromide is 84%: 16%, determined by ¹H NMR (600 MHz) spectroscopy. We did not separate 1,7- and 1,6-regioisomers and used their mixture for next polymerization since it is very hard to get isomer pure monomer. In view of 1,7-isomer is the major product, the isomer mixture was simplified as 1,7-isomer. The synthetic route for polymer P₁ is shown in Scheme 1. P₁ was synthesized in 84% yield through a Sonogashira coupling polymerization of N,N’-bis(2-decyl-tetradecyl)-1,7-dibromo-3,4:9,10-perylene diimide with 2,6-diethynyldithieno[3,2-b:2′,3′-d]thiophene in the presence of Pd(PPh₃)₄ catalyst. Polymer P₁ is soluble in common organic solvents such as chlorobenzene, chloroform, and THF and can readily be processed from solution. The number-average molecular weight (Mₙ), weight-average molecular weight (Mₚ), and polydispersity index (Mₚ/Mₙ) of P₁, measured by gel permeation chromatography versus polystyrene standards, were 15 000, 17 000, and 1.1, respectively, similar to those of P₂. Since we purified polymer P₁ and only collected the first part by size exclusion column chromatography, the molecular weight distribution is pretty narrow. The thermal stability of P₁...
was determined using thermogravimetric analysis (Figure S1, Supporting Information); the decomposition temperature, defined as that at which initial 5% of weight loss, is higher than 300 °C under nitrogen. Differential scanning calorimetry (DSC) traces (Figure S2, Supporting Information) of P1 show no evidence for any phase transitions or other processes up to 250 °C.

**Calculation.** To explore the molecular architecture of the polymers, density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level 

37,38 with the Gaussian 09 program package 39 were performed for oligomer models (PDI–ethynylene–DTT–ethynylene–PDI and PDI–DTT–PDI, with N-methyl groups replacing N-2-decyltetradecyl) of P1 and P2. The dihedral angles between PDI and DTT (θ₁ and θ₂, Figure 1, Table 1) in P2 are 56.81° and 52.85°, much larger than those (9.45° and 8.47°) in P1. Steric interaction between DTT and the bay-position neighboring hydrogen atom leads to a more twisted main chain in P2. The introduction of ethynylene spacer between PDI and DTT in P1 reduces the steric hindrance between PDI and DTT units in P2, and induces coplanarity and rigidity of the main chain. The more planar conformation of the main chain leads to stronger interchain interaction in P1 compared to P2. The calculated molecular orbital geometry and energy levels of the polymers is shown in Figure 2. The LUMO of P1 is delocalized over the polymer backbone, while the LUMO of P2 is located on the PDI units. Thus, P1 exhibits lower LUMO, higher HOMO and smaller bandgap as a result of promoted planarity and enhanced π-conjugation along the polymer main chain relative to P2.

**Absorption.** The normalized UV–vis absorption spectra of P1 and P2 in dilute CHCl₃ solution and in thin film are illustrated in Figure 3. Introduction of ethynylene spacer between PDI and DTT in P1 results in a considerable red shift of the low-energy maximum absorption in solution from 625 to 714 nm, stemmed from promoted planarity and enhanced π-conjugation along the polymer main chain. Additionally, the appearance of vibronic fine structure in the low-energy absorption band of P1 in solution and film reveals greater backbone rigidity of P1 induced by the rod-like ethynylene spacer relative to P2. The band at ca. 487 nm in P2 is 56.81° and 52.85°, much larger than those (9.45° and 8.47°) in P1. Steric interaction between DTT and the bay-position neighboring hydrogen atom leads to a more twisted main chain in P2. The introduction of ethynylene spacer between PDI and DTT in P1 reduces the steric hindrance between PDI and DTT units in P2, and induces coplanarity and rigidity of the main chain. The more planar conformation of the main chain leads to stronger interchain interaction in P1 compared to P2. The calculated molecular orbital geometry and energy levels of the polymers is shown in Figure 2. The LUMO of P1 is delocalized over the polymer backbone, while the LUMO of P2 is located on the PDI units. Thus, P1 exhibits lower LUMO, higher HOMO and smaller bandgap as a result of promoted planarity and enhanced π-conjugation along the polymer main chain relative to P2.

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onset oxidation and reduction potentials, respectively. The HOMO is 0.10 eV higher but the LUMO is 0.10 eV lower than that of P2 due to introduction of ethynylene units, showing the same trend as the computational prediction. The combination of deeper LUMO and more coplanarity of the polymer main chain caused by the presence of electron-withdrawing ethynylene units will be favorable to increase the ambient stability and electron mobility of P1.

Field-Effect Transistors. The electron mobilities of n-channel OFETs based on P1 and P2 were measured in top contact, bottom gate (TCBG) and bottom contact, bottom gate (BCBG) transistor configuration. OFET devices of P1 and P2 based on TCBG geometry were fabricated on octadecyltri-chlorosilane (OTS)-modified SiO₂ (300 nm)/Si substrate by spin-coating a 10 mg/mL CHCl₃ solution. Gold (Au) was used as drain and source electrodes. The drain-source channel length (L) is 80 μm and width (W) is 8.8 mm. All the FET measurements were determined in ambient atmosphere (around 30% of humidity). Typical characteristic curves of P1 in TCBG transistor are depicted in Figure 5. After annealing at 170 °C, an electron mobility of 0.06 cm² V⁻¹ s⁻¹, on/off current ratio of 10⁶ and low threshold voltage of 4 V in the saturation regime were obtained. In contrast, polymer P2 in TCBG OFETs exhibited an electron mobility of 0.017 cm² V⁻¹ s⁻¹, on/off current ratio of 10⁶ and threshold voltage of 13 V in N₂ atmosphere, but showed complete inactivity in air. TCBG OFETs based on P1 exhibit moderate air stability (Figure S3, Supporting Information). The electron mobilities of P1 in TCBG OFETs have a sharp drop after 2 days storage in air, which is 9.2% of the initial value. However, there was almost no obvious variation in the following four days, and the on/off current ratio still kept at 10⁵–10⁶. Higher electron mobilities and enhanced air stability could be expected for isomer pure 1,7-linked P1 due to a more π-conjugated structure and stronger assembly of a regioregular polymer backbone relative to the regioirregular (1,6- + 1,7-linked) P1.⁴³

BCBG transistor configuration was also employed to measure the electron mobility of P1 and P2. BCBG OFETs based on P1 and P2 were fabricated on OTS-treated SiO₂/Si substrates. The polymer activity layer was spin-coated from CHCl₃ solution (10 mg/mL). Gold/Ti was used as the source and drain electrodes. The channel length (L) was 38 μm; and the channel width (W) was 1400 μm. Typical characteristic curves of P1 and P2 in BCBG transistor are depicted in Figure S4 and S5 in Supporting Information. An electron mobility of 0.075 cm² V⁻¹ s⁻¹ and threshold voltage of 14 V were achieved for P1 in this device geometry in ambient atmosphere after annealing at 170 °C; the electron mobility is slightly higher than that of P1 in TCBG configuration. In contrast, P2 in BCBG OFETs exhibited an electron mobility of 0.038 cm² V⁻¹ s⁻¹, on/off current ratio of 10⁶ and threshold voltage of 11 V in air after annealing at 170 °C. The mobility of 0.038 cm² V⁻¹ s⁻¹ for P2 is only half of that for P1 in the same device configuration.

BCBG OFETs based on P1 and P2 exhibited good air stability (Figure S6, Supporting Information). The electron mobilities of P1 in BCBG OFETs have a sharp drop after one day storage in air, which is 68% of the initial value. However, there was almost no obvious variation in the following three days, and finally high electron mobility of 0.034 cm² V⁻¹ s⁻¹ and high on/off current ratio of ca. 10⁶ were still observed after six days storage in ambient atmosphere. The evolution of the electron mobilities of P2 over the time exposing to air showed the same trend as that of P1. Surprisingly, after exposure to air for six days, a BCBG transistor based on P2 still maintained a high electron mobility of 0.013 cm² V⁻¹ s⁻¹, which is ca. one-third of that for P1 in the same condition. Obviously, BCBG OFETs based on P1 and P2 showed higher electron mobilities and better air stability than those with TCBG configuration. It is speculated that, for BCBG OFETs, the conducting channel (ca. a few nanometers) could be encapsulated by ca. 100 nm active organic semiconductor.
thin film spin-coated on the top of the devices against penetration of H₂O and O₂.

**Film Morphology.** Grazing incidence X-ray diffraction (GIXRD) (Figure 6) and atomic force microscopy (AFM) (Figure 7) of P1 and P2 films annealed at 170 °C were employed to characterize the microstructure and surface morphology of the active layer. In the out-of-plane scattering profile from the GIXRD, strong first diffraction peak (100) at 2θ = 2.96° was observed for P1 (Figure 6b), corresponding to a d-spacing (the lamellar repeating distance between the polymer chains) of 2.94 nm. The weak second diffraction peak (200) at 2θ = 5.98° was also observed for P1 (Figure 6c). Additionally, lacking of significant diffraction intensity in the in-plane scattering profiles suggests that P1 had predominantly edge-on packing in film relative to the substrates. However, no diffraction peaks were observed in the out-of-plane (Figure 6a) and in-plane scattering profiles of P2. Thus, polymer P1 has ordered crystalline structure while P2 has amorphous structure lacking of order. The stronger intermolecular interactions and more ordered packing are attributed to the coplanarity of the P1 polymer main chain with rod-like ethynylene units.

As illustrated in the AFM images of annealed P1 films, an entangled nodule-like morphology with a broad distribution of aggregate domains ranging from ca. 80 to 400 nm was observed, stemmed from the strong intermolecular interaction between the more planar P1 polymer main chains. Compared to annealed P2 films without obvious crystalline domains, the P1 film showed more and larger interconnecting domains, which is consistent with the GIXRD results. The densely ordered packing can exclude oxygen or water in P1 film and enhance mobilities and air stability.

**CONCLUSION**

A new solution-processable PDI copolymer incorporating acetylene spacers was synthesized. Introduction of rod-like ethynylene spacers in the polymer main chain reduces the steric hindrance between PDI and DTT units, promotes planarity and enhances the π-conjugation along the polymer main chain. As a result, the low-energy maximum absorption of P1 in solution red shifts 89 nm and LUMO down shifted by 0.10 eV relative to those of P2. GIXRD and AFM reveal that annealed P1 films exhibit an entangled nodule-like crystalline morphology with densely ordered packing, while annealed P2 films exhibit an amorphous morphology lacking of order. Combination of low-lying LUMO energy level and the dense packing in the solid state could improve mobilities and air stability. As a result, P1 in top-contact bottom-gate OFETs exhibited a saturation electron mobility of 0.06 cm² V⁻¹ s⁻¹ in air. In contrast to P1, P2 did not function in the same devices in air although it exhibited electron mobilities of 0.017 cm² V⁻¹ s⁻¹ in nitrogen. Electron mobilities of 0.075 and 0.038 cm² V⁻¹ s⁻¹ were achieved in P1 and P2-based bottom contact, bottom gate OFETs in ambient atmosphere, respectively. The electron mobilities of P1 are among the highest reported for bottom-gate OFETs based on n-type conjugated polymers in air. BCBG OFETs based on P1 and P2 exhibited better air stability than TCBG devices. After 6 days storage in air, an electron mobility of 0.034 cm² V⁻¹ s⁻¹ and high on/off current ratio of ca. 10⁶ were still observed for P1 in BCBG OFETs, while an electron mobility of 0.013 cm² V⁻¹ s⁻¹ was observed for P2 in the same device.
EXPERIMENTAL SECTION

Materials. Unless stated otherwise, starting materials were obtained commercially and were used without further purification. Triethylamine was distilled from calcium hydride and toluene was distilled from sodium-benzophene under nitrogen prior to use. 2,6-Diethynylidithieno[3,2-b:2′,3′-d]thiophene45 and N,N′-bis(2-decyl-tetradecyl)-1,7-dibromo-3,4-9,10-perylene diimide31 were synthesized according to our published procedures.

Characterization. The 1H NMR spectra was recorded on a Bruker DMX 300 MHz or Bruker AVANCE 600 MHz spectrometer. Elemental analysis was carried out using a FLASH EA1112 elemental analyzer. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed using a METTLER differential scanning calorimeter (DSC822e) under a nitrogen atmosphere with a heating and cooling rate of 10 °C/min. Solution (chloroform) and thin-film (on quartz substrate) UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen in a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in acetonitrile using a computer-controlled CHI 660D electrochemical workstation, a thin film of the sample coated on glassy-carbon working electrode, a platinum-wire pseudoreference electrode. The gel permeation chromatography sample was loaded on Bio-Rad Bio-Beads S-X1 eluting with THF as eluent and polystyrene standards as calibrants; three Waters columns (HT2, 3, 4) connected in series were used. X-ray diffraction (XRD) measurements of thin films were performed in reflection mode using a D/MAX-TTR III Rigaku X-ray diffractometer. Grazing incidence X-ray diffraction pattern of organic thin films were obtained at a constant incidence angle of 0.2° (λ = 2θ, sin θ = 1.54 Å). AFM images of organic thin films were obtained on a NanoMan VS microscope (Digital Instruments) in tapping mode.

Synthesis and Characterization of P1. To a 50 mL three-necked round-bottomed flask were added N,N′-bis(2-decyl-tetradecyl)-1,7-dibromo-3,4-9,10-perylene diimide (0.2 mmol, 245 mg), and the mixture was deoxygenated with nitrogen for 30 min. Pol(PPh3)2 (20 mmol, 23 mg) and Cul (0.04 mmol, 7.6 mg) were added under nitrogen. Dry toluene (10 mL) and triethylamine (5 mL) were added by syringe and purged by nitrogen for 15 min. The dark red solution was stirred at 60 °C for 3 d under nitrogen atmosphere. The resulting dark green sticky solution was cooled down to room temperature. The mixture was extracted with CH2Cl2 (2 × 100 mL), washed with water (2 × 100 mL), and the extracts were dried over anhydrous MgSO4. The solution was concentrated to 15 mL, then dropped into 200 mL of methanol. The dark green precipitate was filtered, and washed with methanol. Finally, the polymer was purified by size exclusion column chromatography over Bio-Rad Bio-Beads S-X1 eluting with THF. Polymer P1 was dissolved in chloroform and filtered through a 0.22 μm Nylon-6 filter to remove the insoluble impurities. After removal of the solvent to afford a dark green solid (219 mg, 84%). GPC: Mw = 15 000, Mn = 17 000, Mw/Mn = 1.1. 1H NMR (300 MHz, CDCl3, 25 °C): δ 8.68 (br, 2H), 8.12 (br, 2H), 7.62 (br, 2H), 7.53 (br, 2H), 4.28 (br, 4H), 2.08 (br, 2H), 1.35 (br, 80H), 0.94 (br, 12H). Anal. Calcd for (C39H111N2O4S3)2: C, 77.43; H, 8.46; N, 2.10. Found: C, 76.62; H, 8.35; N, 1.92.

OFET Device Fabrication and Characterization. OFETs based on P1 and P2 films were fabricated in a top contact, bottom gate configuration. OFETs based on P1 films were also fabricated in a bottom contact, bottom gate configuration. Fabrication of Top Contact Bottom Gate Transistors. Heavily doped n-type Si wafers were used as substrates for the devices. SiO2 layers of a capacitance of 11.5 nF/cm2 as gate dielectrics were thermally grown on the Si substrates to a thickness of 300 nm. The substrates were cleaned sequentially with pure water, hot concentrated sulfuric acid-hydrogen peroxide solution (concentrated sulfuric acid/hydrogen peroxide water = 2:1), pure water, and isopropyl alcohol. Octadecltrichlorosilane (OTS) was used as a self-assembled surface modifier for SiO2. A 100 nm-thick (±10 nm) semiconductor film was spin-coated on top of the OTS-treated SiO2 from 10 mg/mL chloroform solution of P1 or P2. Then the as-spun thin film was annealed in vacuum oven at 170 °C for an hour. The channel length (L) and width (W) were 80 μm and 8.8 mm, respectively. Gold source and drain contacts (50 nm) were deposited on the organic layer through a shadow mask under high vacuum.

Fabrication of Bottom Contact Bottom Gate Transistors. Gold/Ti source and drain electrodes were patterned by photolithography and lift-off techniques on silicon/silica substrate. Before deposition of the semiconducting polymer, the substrate was modified using OTS monolayer. The polymer semiconductor layer was spin-coated from chloroform solution (10 mg/mL). The channel length (L) was 38 μm; and the channel width (W) was 1400 μm. Then the as-spun thin film was annealed in vacuum oven at 170 °C for an hour. All OFETs were characterized with a Keithley 4200 semiconductor characterization system in air or in a N2-filled glovebox. The mobility in the saturated regime was extracted from the following equation: 0.5 DS = μT(W/2L) · (VGS − V1/2), where 0.5 DS is the drain current, C is the capacitance per unit area of the gate dielectric layer, and VGS and V1/2 are the gate voltage and threshold voltage, respectively.

ASSOCIATED CONTENT

Supporting Information

TGA and DSC curves of P1, μe/μe_initial vs time plot of P1-based top-contact bottom-gate devices, typical current–voltage characteristics for a bottom-contact bottom-gate device based on P1, typical current–voltage characteristics for a bottom-contact bottom-gate device based on P2, and μe vs time plot of bottom-contact bottom-gate devices based on P1 and P2. 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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