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High-Mobility n-Type Conjugated Polymers Based on Electron-Deficient Tetraazabenzodifluoranthene Diimide for Organic Electronics

Haiyan Li, Felix Sunjoo Kim,† Guoqiang Ren, and Samson A. Jenekhe*

Department of Chemical Engineering and Department of Chemistry, University of Washington, Seattle, Washington 98195-1750, United States

Supporting Information

ABSTRACT: High-mobility p-type and ambipolar conjugated polymers have been widely reported. However, high-mobility n-type conjugated polymers are still rare. Herein we present poly(tetraazabenzodifluoranthene diimide)s, PBFI-T and PBFI-BT, which exhibit a novel two-dimensional (2D) π-conjugation along the main chain and in the lateral direction, leading to high-mobility unipolar n-channel transport in field-effect transistors. The n-type polymers exhibit electron mobilities of up to 0.30 $cm^2/(V\ s)$, which is among the highest values for unipolar n-type conjugated polymers. Complementary inverters incorporating n-channel PBFI-T transistors produced nearly perfect switching characteristics with a high gain of 107.

Conjugated polymers are ideal semiconductors for next generation low-cost electronics in part because they combine interesting tunable electronic and optical properties with excellent solution processing and mechanical flexibility.[1] Facile injection and transport of charge carriers, both electrons and holes, in semiconducting polymers are critical factors that determine the achievable performance of organic electronics.[1] Envisioned low power complementary circuits composed of n-channel organic field-effect transistors (OFETs) and p-channel OFETs are necessarily made from two different types of semiconducting polymers, electron-transport (n-type) and hole-transport (p-type) materials.[1,2] Compared to the plethora of solution processable p-type conjugated polymers now available with high hole mobility,[2a,3] very few high-mobility n-type polymer semiconductors have been reported.[4] The development of solution processable high-mobility n-type semiconducting polymers remains a major obstacle to further advances in organic electronics.[1,2b,e,g]

High-mobility n-type semiconducting polymers are scarce because of several scientific challenges. Suitable electron-deficient building blocks or monomers, which can yield polymers with high electron affinity or a low-lying lowest unoccupied molecular orbital (LUMO) energy level essential to facile injection of electrons, are few.[1b,c,2d,e,g] Such n-type conjugated polymers also require high ionization energy or a low-lying highest occupied molecular orbital (HOMO) energy level to suppress facile injection of holes and thus ambipolar charge transport.[1a,2a,5] Electron-deficient monomers are more difficult to controllably polymerize to high molecular weights than well-studied electron-rich monomers used for p-type polymers.[4e,f] Copolymerization of electron-deficient monomers with an electron-rich one frequently results in p-type or ambipolar polymers.[5] Highly planar chain segments, strong intermolecular interactions, and ordered molecular packing necessary for efficient charge transport are often incompatible with requirements for solubility and solution processability.[4a]

In this paper, we report a novel π-conjugated macromolecular architecture composed of an 11-ring polycyclic chromophore, *N*,*N*′-bis(2-decyltetradecyl)-tetraazabenzodifluoranthene diimide (BFI),[6] as the key building block. Our recent study of the monomeric BFI system showed that it was planar, had a 2.0 nm long π-conjugated framework, had a high electron affinity, and exhibited strong intermolecular interactions.[6] We herein demonstrate that embedding of the rigid BFI building block into a polymer main chain creates a well-defined lateral extension of π-electron delocalization in addition to the π-conjugated main-chain spine. The resulting poly(tetraazabenzodifluoranthene diimide)s (PBFIs) are found to exhibit high-mobility electron transport in n-channel transistors and to facilitate the creation of complementary electronic circuits with nearly ideal switching characteristics.

The new n-type conjugated polymers, including the thiophene-linked (PBFI-T) and the bithiophene-linked (PBFI-BT) derivatives, were synthesized by Stille cross-coupling polymerization (Scheme 1).[7] PBFI-T had excellent solubility in organic solvents (e.g., chloroform, toluene, and chlorobenzene) whereas PBFI-BT was not very soluble in these solvents. The number- and weight-average molecular weights (M_n, M_w) of PBFI-T, determined by gel chromatography against polystyrene standards, were 48 and 175 kDa with a polydispersity index (M_w/M_n) of 3.68. Both polymers had excellent thermal stability with an onset thermal decomposition temperature of 450 °C and 43−48% weight remaining at 800 °C in nitrogen under thermogravimetric analysis (Figure S1). Melting or glass transition was not observed in the 20−400 °C range of differential scanning calorimetry scans. These rugged thermal stability characteristics of the PBFIs are reminiscent of those of ladder polymers.[4a]

Optical absorption spectroscopy provides insight into the electronic structure of the new conjugated polymers. The monomeric chromophore BFI thin film has a main absorption

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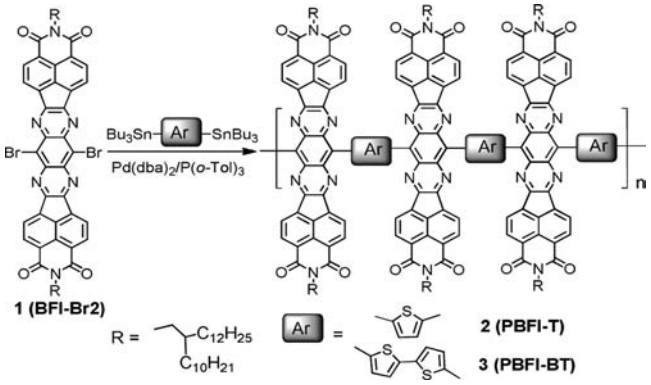
Scheme 1. Synthesis of PBFIs including PBFI-T and PBFI-BT



band centered at 360 nm due to the $\pi-\pi^*$ transition.[6] In contrast, both polymers retain this high energy band with a peak at ~380 nm while exhibiting a new, broad, lower energy band at 500−950 nm for PBFI-T and 600−1300 nm for PBFI-BT, respectively (Figure 1). Emergence of the new lower

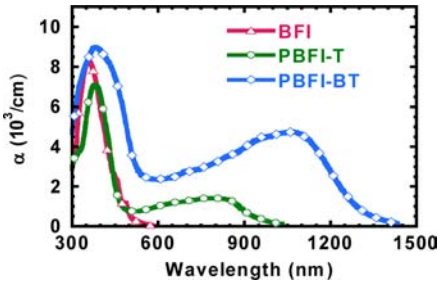


Figure 1. Optical absorption spectra of BFI, PBFI-T, and PBFI-BT thin films on glass substrates.

energy absorption band in PBFI-T and PBFI-BT confirms electronic delocalization along the chain axis, which is enhanced by intramolecular charge transfer (ICT) between the electron-deficient BFI unit and the electron-donating thiophene or bithiophene ring.[7,8] The ICT character of this absorption band also explains why it is red-shifted and its oscillator strength is larger in PBFI-BT compared to PBFI-T since bithiophene is a stronger electron-donating unit than thiophene. Optical absorption edge band gaps of 1.29 and 0.94 eV were obtained for PBFI-T and PBFI-BT, respectively, from the thin film absorption spectra (Figure 1). Reduction and oxidation cyclic voltammetry of the polymer thin films provided additional characterization of the electronic structure (Figure S3), yielding LUMO/HOMO energy levels of −3.80/−5.45 eV and −3.74/−5.14 eV for PBFI-T and PBFI-BT, respectively (Table S1).

X-ray diffraction (XRD) analysis of drop cast PBFI-T and PBFI-BT films on glass substrates provided ordering and molecular packing information on the polymers in the solid state. The reflections of PBFI-T at 3.3° and 6.5° indexed as the (100) plane and its weak second order (200) reflection, respectively, suggested a lamellar crystalline ordering with a *d*-spacing of 2.6 nm (Figure 2a). A weak reflection at 11.3°, which intensified by tilting the substrate from 90° to 54.5° (Figure S4) corresponds to a *d*-spacing of ~0.8 nm due to the diffraction of the repeating unit along the polymer chain. A broad weak peak at 20.9° with a *d*-spacing of 0.4 nm arises from weak $\pi-\pi$ stacking of the polymer. The (100) and

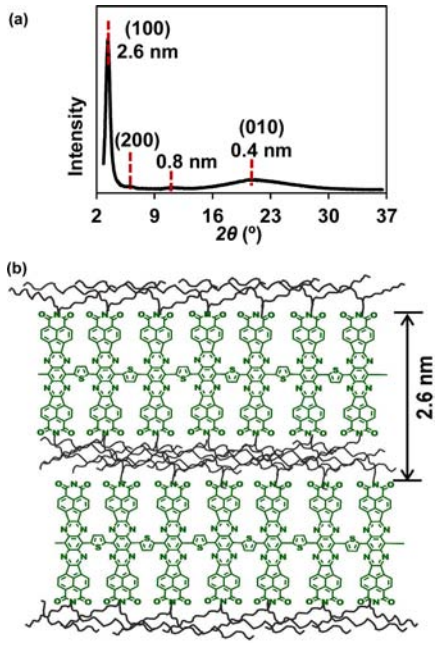


Figure 2. (a) XRD patterns of drop-cast PBFI-T film on a glass substrate after annealing at 250 °C. (b) Schematic illustration of the lamellar ordered structure of PBFI-T deduced from the XRD patterns.

corresponding (200) reflections of PBFI-BT were found at 2.88° and 5.62°, respectively, corresponding to a larger lamellar *d*-spacing of 3.1 nm than that of PBFI-T (Figure S5). Weak broad diffraction at 26.1° due to $\pi-\pi$ stacking corresponds to a distance of 0.35 nm, which is significantly shorter than that of PBFI-T as a result of better coplanarity of PBFI-BT. An unusual feature of the observed lamellar crystalline structure is the very small space occupied by the insulating and solubilizing alkyl side chains between the rigid π-conjugated framework (Figure 2b),[9] an important consequence of the large lateral π-conjugation length (~2.0 nm)[6] of this class of conjugated polymers.

The unusual lamellar structure of PBFI-T and PBFI-BT chains was further investigated by high resolution transmission electron microscopy (HRTEM). One- and few-monolayer thin film samples of PBFI-T and PBFI-BT on 300 mesh lacey-carbon-coated copper grids were imaged at 200 kV (Figures S6 and S7). HRTEM images revealed widths of 1.5−2.0 nm, which corresponds to the conjugated width of the nanoribbon-like polymer chains (Figures S6b, 6c and S7b); longer polymer chains could not be observed likely because of overlapping chains, molecular mobility, and resolution limitations of the instrument. Selected area electron diffraction (SAED) revealed a lamellar crystalline ordering of the few-monolayer PBFI-T films (Figure S6 inset), from which the (200) and (010) electron diffractions corresponding to *d*-spacings of 2.4 and 0.87 nm were observed in close agreement with the above X-ray diffraction results (Figure S9).

We fabricated and evaluated thin film OFETs in nitrogen to study the charge transport properties of PBFI-T and PBFI-BT. The bottom-gate and top-contact transistors were fabricated on silicon/silicon dioxide substrates, and the surface of the SiO_2 gate dielectric was hydrophobically modified by either a monolayer of octyltrichlorosilane (OTS8) or a polymer dielectric thin film such as the fluoropolymer CYTOP or cross-linked benzocyclobutene (BCB). Figure 3a and 3b show

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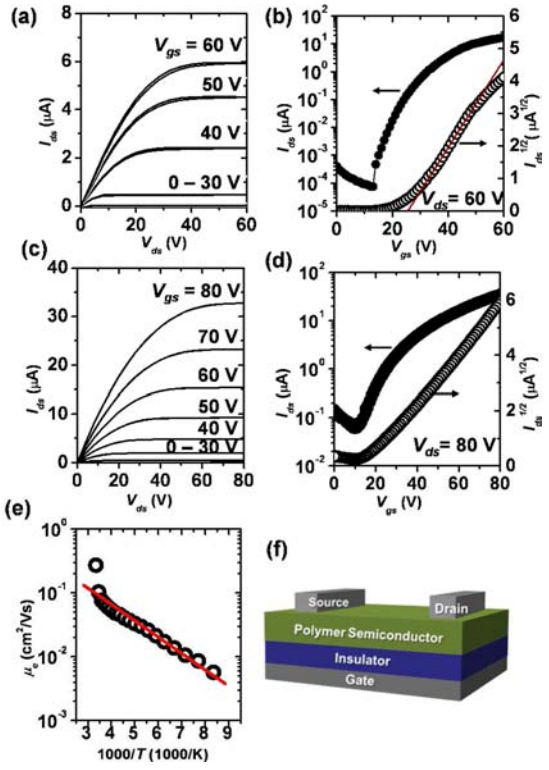

Figure 3. Current–voltage output and transfer curves of (a and b) PBFI-T transistors with Ag source–drain electrodes on an OTS8-treated substrate; (c and d) PBFI-T transistors with Ag source–drain electrodes on a CYTOP-coated substrate; (e) electron mobility versus inverse temperature with least-squares fitting of the data to the Arrhenius equation ($\mu = \mu_0 \exp(-E_A/k_BT)$); (f) Schematic of bottom-gate/top-contact transistors.

the output curves and transfer characteristics, respectively, of n-channel OFETs consisting of PBFI-T thin films on OTS8 and silver (Ag) source–drain electrodes. PBFI-T devices annealed at 200 °C had a high saturation region electron mobility of 0.30 cm^2/(V s) (0.18 cm^2/(V s) average of 16 devices fabricated in 4 batches) with excellent current modulation (10^5–10^6), which is among the highest mobilities for n-type conjugated polymers.[4a−c,f] PBFI-T OFETs with a CYTOP buffer layer (Figure 3c and 3d) also showed ideal linear and saturation characteristics but had a lower electron mobility of 0.11–0.13 cm^2/(V s). In contrast to the PBFI-T OFETs, the best PBFI-BT transistors were on the BCB-modified dielectric (Figure S10) and they gave a saturation electron mobility of 0.09 cm^2/(V s) with moderate on/off current ratios (10^3–10^4). The significantly lower performance of PBFI-BT n-channel OFETs compared to those of PBFI-T is due largely to the poor solubility and poor quality of its spin-coated thin films.

Temperature-dependent charge transport measurements on PBFI-T transistors provided insight into the high electron mobility. The thermally activated nature of electron transport in PBFI-T is confirmed by the temperature dependent I–V curves of the PBFI-T transistor (Figure S11a). A plot of electron mobility as a function of inverse temperature is overlaid with Arrhenius-type fitting to the equation $\mu = \mu_0 \exp(-E_A/k_BT)$ (Figure 3e). The observed Arrhenius-type dependence originates from trapping events of charge carriers in localized states, which are present at the interfacial imperfections and/or at the boundaries of high-mobility domains, in thin films of organic semiconductors.[10] The observed pre-exponential constant μ_0 of 0.7 cm^2/(V s) and low activation energy E_A of 50.9 meV obtained from the fitting imply that the intrinsic electron mobility of PBFI-T is much higher than we obtained from the device. Switching from the OTS8- to CYTOP-modified gate dielectric slightly reduced the parameters to μ_0 = 0.4 cm^2/(V s) and E_A = 43.8 meV (Figure S11b and S11c). The observed activation energy of 44–51 meV is similar to or lower than the 44–85 meV seen in other high-mobility n-type polymer semiconductors, suggesting that the electronic energy levels for charge transport are close to the Fermi level under on-state conditions of the OFETs and that there is a rather low density of deep trapping sites in PBFI-T thin films.[10]

Complementary inverters based on n-channel PBFI-T OFETs were fabricated and evaluated to explore their potential for developing complementary polymer electronic circuits (Figure 4a).[2c] The needed p-channel OFETs were fabricated

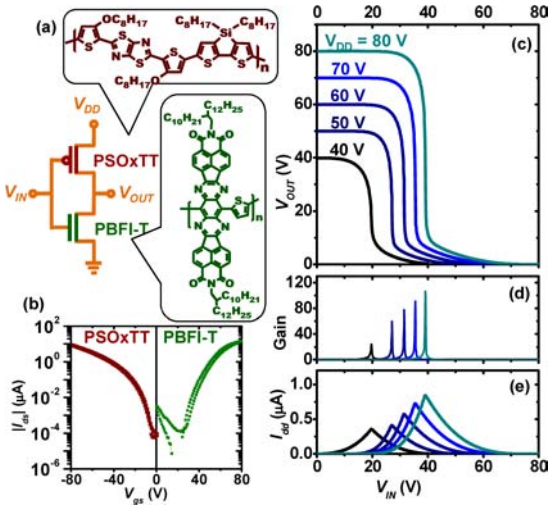

Figure 4. (a) Schematic of a complementary p/n polymer inverter and molecular structures of p-channel polymer PSOxTT and n-channel polymer PBFI-T. (b) Transfer curves of the p-channel and n-channel polymer transistors. Static switching characteristics of the inverter: (c) output voltage, (d) gain, and (e) current as a function of input voltage (V_{IN}) with various power supply voltages (V_{DD}).

from the semiconducting polymer poly[(4,4′-bis(2-octyl)-dithieno[3,2-*b*:2′,3′-*d*]silole)-2,6-diyl-alt-(2,5-bis(3-octyloxy-thiophen-2yl)thiazolo[5,4-d]thiazole) (PSOxTT), which has a reported hole mobility of 0.1 cm^2/(V s).[11] The I–V curves of the constituent PBFI-T and PSOxTT OFETs show comparable on-current and off-current (Figure 4b). Inverters fabricated with the same device architecture (i.e., OTS8-treated 200-nm-thick SiO_2 and gold electrodes with channel width/length = 10) for both OFETs have an ideal switching behavior (Figure 4c, 4d, and 4e). The switching voltage was nearly at half of the supply voltage (V_{IN}–$V_{DD}/2$). The transition of the complementary inverter was also very sharp with the voltage gain ($-dV_{OUT}/dV_{IN}$) as high as 107, resulting in the large noise tolerance of the circuits. The amount of current (I_{DD}) flowing through the complementary inverter, and thus its power consumption, is only high (0.84 μA, or 67 μW, at V_{DD} = 80 V) when the circuit is under active switching. In the static state, I_{DD} was less than 19 nA (i.e., power less than 1.5 μW) when V_{DD} = 80 V. The power consumption could be further significantly

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reduced compared to this value by the use of recently developed low-voltage OFET methodology.[12]

In summary, new n-type π-conjugated polymers with a large lateral extension (2.0 nm) of π-conjugation were realized by embedding a tetraazabenzodifluoranthene diimide building block into a polymer chain and the unusual lamellar ordering was confirmed by XRD. The novel class of π-conjugated polymers provides a new approach to high-mobility electron transport in polymer semiconductors. The observed electron mobilities of up to 0.30 $cm^2/(V\ s)$ for PBFI-T are among the highest to date for n-channel polymer transistors. The temperature-dependent charge transport measurements indicated a low density of deep trapping sites. n-Channel transistors based on PBFI-T enabled the fabrication of high-gain complementary inverters with nearly ideal switching characteristics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jenekhe@u.washington.edu

Present Address

[†]Department of Chemical Engineering and Materials Science, Chung-Ang University, Seoul, Korea.

Notes

The authors declare no competing financial interest.

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