Highly Soluble Heteroheptacene: A New Building Block for p-Type Semiconducting Polymers

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ABSTRACT
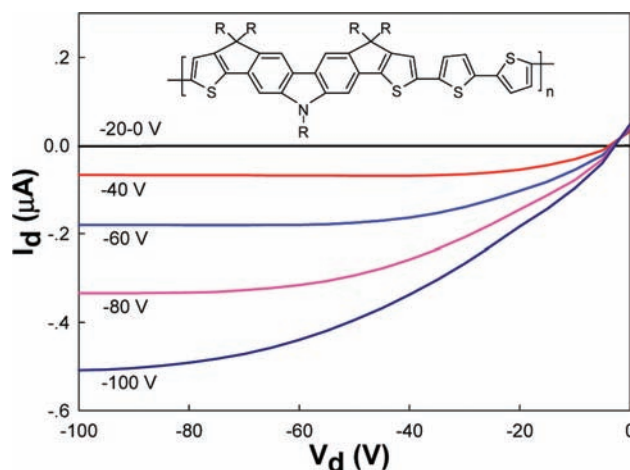
A facial synthetic route to a new heteroheptacene with the inclusion of carbazole and thiophene units is described. The synthesis of two new semiconducting copolymers with use of the heteroheptacene unit is also reported. The introduction of heteroatoms (sulfur, nitrogen) in the fused-ring system leads to small optical band-gaps of these polymers. The charge carrier mobilities for these polymers are measured in ambient conditions which are sufficient for photovoltaic applications.
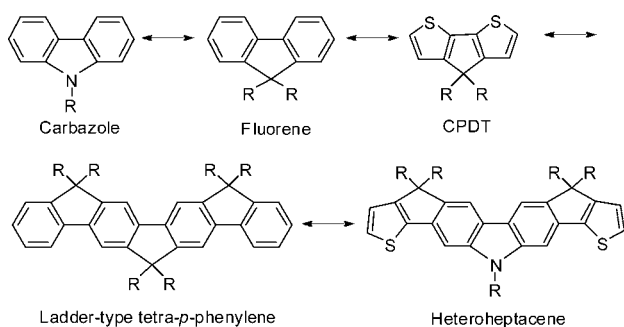
In the past decade, π-conjugated polymers as semiconducting materials have received increasing attention due to their various electronic applications such as printed thin-film transistors,[1] photovoltaic cells,[2] and light-emitting displays.[3] Compared to inorganic semiconducting materials, one salient characteristic of these organic semiconducting materials is the possibility of using solution casting or roll-to-roll

manufacturing for the film and device fabrication that would enable inexpensive, large-area, and flexible electronics.[4] Recently, ladder-type oligo-*p*-phenylene units were introduced into donor−acceptor structures to obtain low-band gap polymers with modulated electronic properties for photovoltaic applications.[2n] In organic electronics, thiophene, carbazole, fluorene, cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT), and ladder-type oligo-*p*-phenylenes (or heptacenes) are popular building blocks for polymeric semiconducting

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materials (Scheme 1).[2n,5] The structure of ladder-type tetra-*p*-phenylenes consists of three "linearly overlapping" fluorenes, and it has an extended π-conjugation that leads to a broader, more intense absorption band. As we know, the introduction of heteroatoms (e.g., sulfur, nitrogen) in the fused-ring system (namely heteroacenes) could be a good approach to further modify the physical and chemical properties of ladder-type tetra-*p*-phenylenes molecules. Thus, the polymers for bulk heterojunction (BHJ) solar cells can be rationally designed to exhibit not only a relative low band gap to maximize sunlight absorption property (a high short-circuit current) but also a suitable highest occupied molecular orbital (HOMO) energy level to ensure a high open-circuit voltage (V_{oc}). These considerations prompted us to seek new heteroheptacene, which includes both carbazole and thiophene

units as well as the ladder-type structural configuration. At the same time, the solubilizing alkyl chains will provide a better solution processability of the target polymers. Interesting, heteroheptacenes are seldom studied due to the lack of efficient synthetic methods.

Herein, we present the facile synthesis and properties of a new heteroheptacene as a buliding block for p-type polymers in photovoltaic applications.

The synthesis of dibromoheteroheptacene **6** is shown in Scheme 2. Beginning with 2,7-dibromocarbazole,[5e] a solubilizing group was attached by *N*-alkylation with 2-ethylbromohexane in the presence of potassium carbonate to give 2,7-dibromo-*N*-(2-ethylhexyl)carbazole with a yield of 80%. With the aid of the electron-donating effects of the nitrogen atom in the carbazole, a 2-fold Friedel−Crafts acylation with

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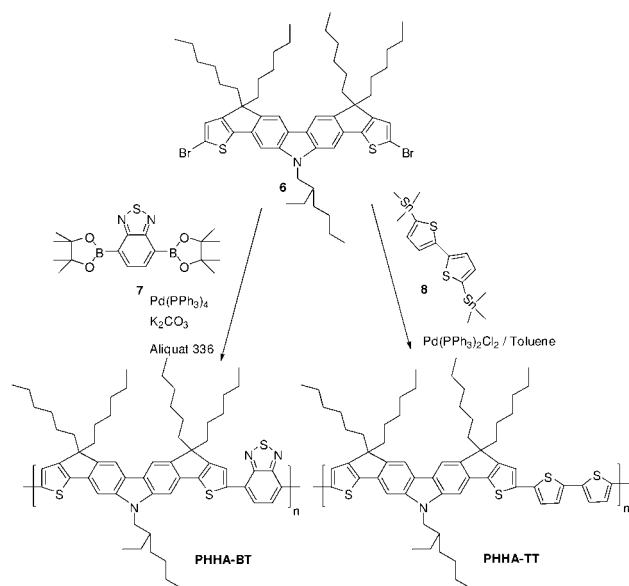
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Scheme 3. Synthesis of Copolymers **PHHA-BT** and **PHHA-TT**

Figure 1. Linear absorption and emission spectra for the polymers in chloroform (a) and in the solid state (b).

heptanoyl chloride and AlCl₃ in dichloromethane proceeded smoothly to afford the diheptan-1-one **3** in 85% yield. The Stille coupling reaction between **3** and 2-(tributylstannyl)thiophene was carried out in the presence of Pd(PPh₃)₄ with DMF as the solvent to afford compound **4** with a yield of 75%. Then compound **4** was transformed into the dialcohol derivative with *n*-hexyllithium immediately followed by the ring-closure reaction with boron trifluoride etherate via a double intramolecular Friedel−Crafts alkylation to afford heteroheptacene **5** (17% yield from **4**). The relatively low yield in this step could be due to the steric effects imparted by the hexyl substituents. Optimization of this reaction yield is possible by introducing different side chains. After the addition of boron trifluoride, a strong blue fluorescent solution is obtained, indicating the formation of the heteroheptacene. The heteroheptacene was directly brominated with NBS in CHCl₃/CH₃COOH to afford compound **6** in a yield of 83%. Using the synthetic route described in Scheme 2, other heteroheptacenes with different heteroatoms or different solubilizing alkyl chains can also be made as good building blocks for materials in electronic applications.

Copolymers **PHHA-BT** and **PHHA-TT** were synthesized as shown in Scheme 3 (and the Supporting Information) by a Suzuki coupling reaction and a Stille reaction, respectively. Both synthetic routes provide polymers with good yields and sufficiently high molecular weights. At the same time, both polymers have good solubility in common organic solvents such as chloroform, THF, and chlorobenzene, due to the five solubilizing alkyl on the heteroheptacene core. For an example, the solubility of **PHHA-TT** in chloroform is as high as 100 mg/mL at room temperature, which may provide an advantage in the solution processing of the polymer.

The optical absorption and emission spectra of the two polymers were measured in solutions (in chloroform) and as drop-cast thin films as shown in Figure 1. Furthermore,
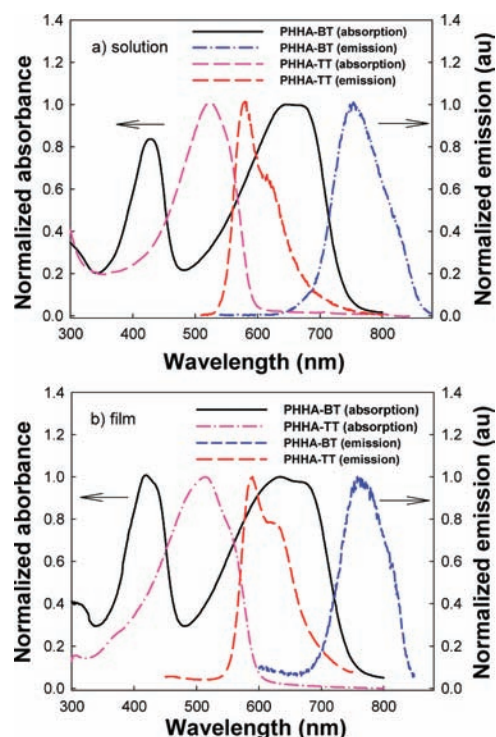
PHHA-BT shows a more red-shifted linear absorption compared to **PHHA-TT**. The long wavelength absorption found for **PHHA-BT** is due to the charge transfer from the heteroheptacene donor to the benzothiadiazole acceptor within the polymer chains. As shown in Figure 1, **PHHA-BT** shows a broad absorption band from 400 to 730 nm, with the main absorption peak at ∼650 nm, and the shoulder peak at ∼426 nm. The optical band gap obtained from the onset of the linear absorption spectrum of the film was estimated to be 1.68 eV. The relatively low bandgap for **PHHA-BT** will lead to a higher short-circuit current due to the improved sunlight harvesting ability. The HOMO level of the **PHHA-BT** determined electrochemically by cyclic voltammetry (CV) was −5.07 eV. As shown in Scheme 3, **PHHA-BT** has a donor−acceptor configuration, while **PHHA-TT** has a donor−donor configuration since benzothiadiazole is an electron acceptor and bithiophene is an electron donor. Therefore, we could not find the charge transfer band for **PHHA-TT**. Similarly, the optical band gap and the HOMO level of **PHHA-TT** were estimated to be 2.08 and −5.16 eV, respectively. The optical and eletrochemical properties of the polymers are listed in Table 1. The LUMO and HOMO energy levels of these polymers are suitable for acting as donors to fullerenes in BHJ solar cells, and they are not so high that they will be extremely air-sensitive.

As one knows, good charge carrier mobilites are desirable in materials for organic photovoltaic applications. To ensure the hole transporting properties of the polymers, top-contact bottom-gate transistors were fabricated under ambient conditions by spin-casting chlorobenzene solutions of the synthe-

polymers	M_n/M_w (KDa)	absorption λ_{max} (nm)[a]	emission peak (nm)[a]	film absorption λ_{max} (nm)	film emission peak (nm)	HOMO (eV)	LUMO (eV) [b]	μ (cm²/(V s))	threshold (V)	on/off
PHHA-BT	2.9/6.8	656	754	656	757	−5.07	−3.39	3.1×10^{-5}	−35	10^3
PHHA-TT	3.6/7.8	513	576	514	585	−5.16	−3.08	3.0×10^{-4}	−5	10^3

[a] Solvent: chloroform. [b] Estimated according to the following equation: $E_{LUMO} = E_{HOMO} + E_{bandgap\ (opt)}$.
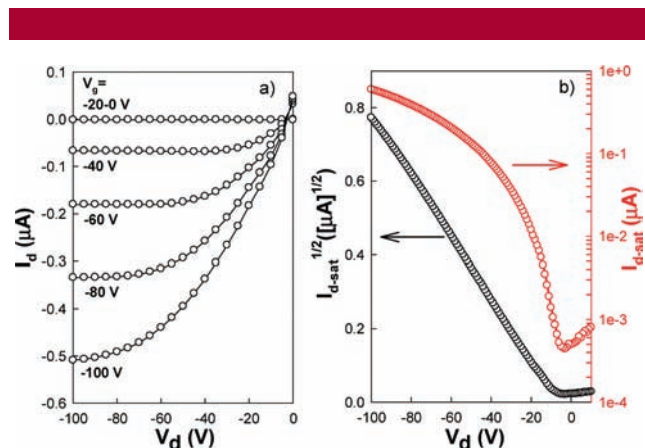
Figure 2. $I_d - V_d$ curves of FET devices as a function of V_g (left), $I_{d\text{-sat}}$, and $I_{d\text{-sat}}^{1/2}$ vs V_g (right) based on spin-cast films for the polymer **PHHA-TT**.

sized polymers on the heavily doped Si(100) substrates treated with hexamethyldisilazane (HMDS). Figure 2 shows the typical current−voltage characteristics of the polymeric field effect transistor (FET) devices with a channel width and length of approximately 6.5 mm and 270 μm, respectively, where I_d, V_d, and V_g represent the source-drain current, source-drain voltage, and gate voltage, respectively. The saturation region mobilities were calculated from the transfer characteristics of the FETs by using the slope derived from the square root of the absolute value of the current as a function of gate voltage between −80 and −40 V. The threshold voltages of the polymeric FETs were derived from the onsets of the transfer curves. Device performance data

of the two polymers are listed in Table 1. The mobilities for **PHHA-BT** and **PHHA-TT** in air were found to be 3.1×10^{-5} and 3.0×10^{-4} cm²/(V s), respectively. While not high by organic electronics standards, they would be sufficient for hole mobility to not be a limiting factor for solar cell effeciency. The on/off current ratios for both polymers are around 10^3, which will minimize leakage currents. The FETs devices fabricated by **PHHA-TT** show almost 10-fold higher mobilities compared to those by **PHHA-BT**, which could be attributed to the more amorphous nature of the **PHHA-BT** thin film considering their structural differences.

In summary, a new highly soluble heteroheptacene has been synthesized through multistep reactions and introduced into a new family of semiconducting copolymer backbone. Solution processed transistors were successfully fabricated from these two copolymers and tested under ambient conditions. The **PHHA-BT** polymer in particular has a quite broad absorption band from 400 to 730 nm, overlapping with the solar spectrum. The fabrication of bulk heterojunction solar cells with use of these new polymers is currently under investigation.

Supporting Information Available: Detailed experimental procedures and full characterization data for **2−6**, **PHHA-BT**, and **PHHA-TT**. This material is available free of charge via the Internet at http://pubs.acs.org.

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