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Benzodipyrrolidones and Their Polymers

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S Supporting Information

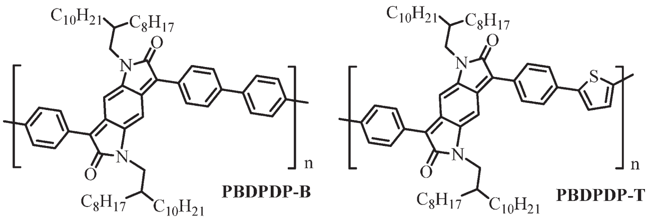
INTRODUCTION

Conjugated polymers have received more and more attention due to their intriguing electronic and optoelectronic properties for application in a variety of optoelectronic devices, such as polymeric light-emitting diodes (PLEDs),[1] organic thin film transistors (OTFTs),[2] and organic photovoltaics (OPVs).[3] Such applications, *inter alia*, encourage the incessant exploration of conjugated polymers with new structures. In recent years, several organic colorants with specialized behavior in properties such as fluorescence, photoconduction, broad range absorption, and reversible redox have been employed in organic electronics. One of the most successfully applied pigments is diketopyrrolopyrrole (DPP) with the underlying pyrolo[3,4-*c*]pyrrole-1,4-dione chromophoric system;[4] DPP has a planar, highly conjugated, lactam structure, resulting in strong $\pi-\pi$ interactions and electron-withdrawing effects. During the past decade, it was shown that incorporation of DPP in polymers,[5−12] oligomers,[13,14] and dendrimers[15] resulted in emerging materials for optoelectronic applications, especially in organic thin film transistors (OTFTs)[6−10] and organic photovoltaic (OPVs).[11−14] Hole mobility as high as 1.95 $cm^2\ V^{-1}\ s^{-1}$ for a DPP and theno[3,2-*b*]thiophene copolymer[10c] and power conversion efficiency (PCE) up to 5.5% for a DPP and phenylene copolymer[12a] have been reported.

Benzodipyrrolidone is a molecule originally prepared as a colorant[16] and is similar in structure to DPP but has the additional twist of being a quinodimethane derivative, as shown in Chart 1. Another similar colorant benzodifuranone has been successfully used to construct low-band-gap polymers.[17] However, examination of the literature revealed that benzodipyrrolidone has not been further pursued. Benzodipyrrolidone can also be envisioned as a “stretched” DPP. It was expected that introduction of alkyl chains to enhance the solubility and adjust the performance of devices would be facile. Moreover, the quinodimethane moiety, in analogy to tetracyanoquinodimethane (TCNQ)[18] and DPP, was expected to exhibit enhanced $\pi-\pi$ stacking. In summary, benzodipyrrolidone and its derivatives should be considered as another interesting building block for donor−acceptor conjugated polymers with promising optoelectronic applications.

In this work, some soluble benzodipyrrolidone-based small molecules were synthesized, and the first two benzodipyrrolidone-based polymers were prepared by means of Suzuki coupling reactions. The packing structure, thermal properties, and photophysical and electrochemical properties are presented. Finally, TFT devices were subsequently fabricated to demonstrate the charge carrier mobility of the polymers.

Chart 1. Structures of Benzodipyrrolidone-Based Polymers



RESULTS AND DISCUSSION

Synthesis. Scheme 1 shows the synthetic route to benzodipyrrolidones (BDPDPs).[16] *p*-Phenylenediamine was condensated with mandelic acid or 4-bromomandelic acid to give amides **2a** and **2b** in yields of 80% and 85%, respectively. Ring-closure reaction of **2a** or **2b** was performed in concentrated H_2SO_4 in high yield, followed by oxidation with potassium persulfate; **3a** and **3b** were converted to **4a** and **4b**. Finally, the alkylation reaction was realized by treating **4a** or **4b** with alkyl bromide or alkyl iodide in the presence of *t*-BuOK to give **5a-1**, **5a-2**, and **5b**.

Two bezodipyrrolidone-based polymers PBDPDP-B and PBDPDP-T were synthesized by coupling of dibromo monomer **5b** with the boronic acid ester of phenylene and thiophene in a yield of 79% and 75%, respectively (Scheme 2). The polymers PBDPDP-B and PBDPDP-T are easily soluble in common solvents such as chloroform and chlorobenzene and were characterized by ^1H NMR and gel permeation chromatography (GPC) with PS (polystyrene) as standard and chloroform as eluent. The number-average molecular weight and (PDI) of PBDPDP-B and PBDPDP-T were found to be 20 kDa (2.08) and 8 kDa (2.29), respectively.

Solid-State Structure of BDPP. Single crystals of **5a-1** were prepared from chloroform solution. The crystal structure and the packing are depicted in Figure 1. The bond lengths from C1 to C2 to C3 to C4 were found to be 1.365, 1.463, and 1.343 Å, respectively. The alternating bond length pattern firmly verifies the quinodimethane structure of the core. Moreover, just as in DPP, the core of **5a-1** is fully coplanar, which ensured full conjugation. There is a 38° dihedral angle between the side

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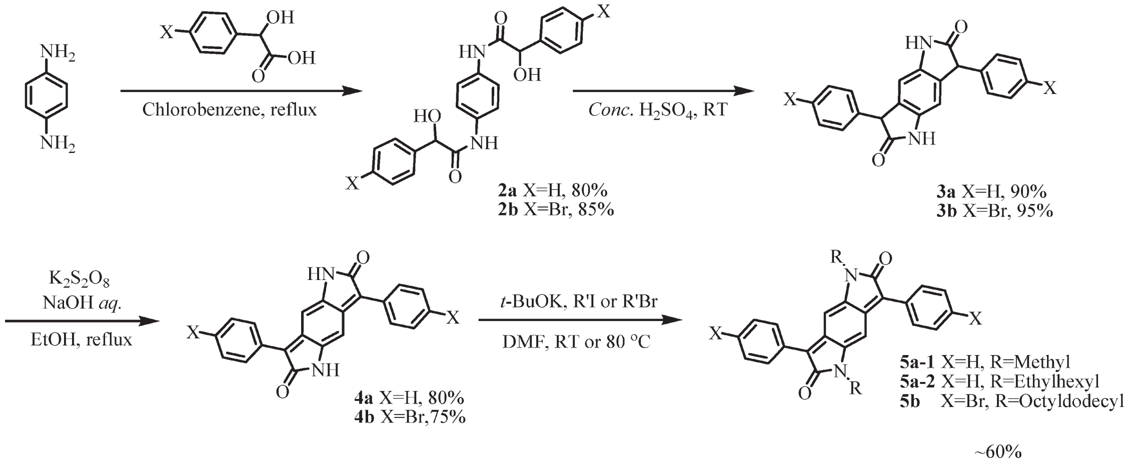
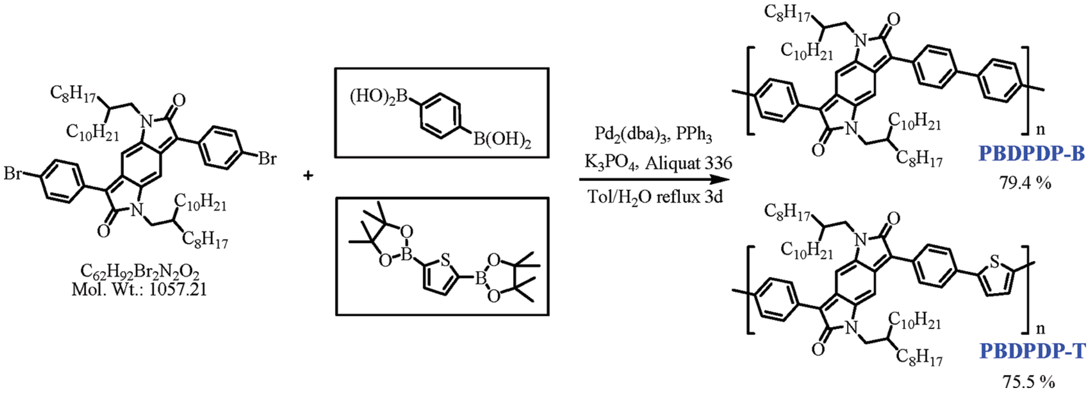
Scheme 1. Synthetic Route of the BDPDPs



Scheme 2. Preparation of the BDPDP Copolymers



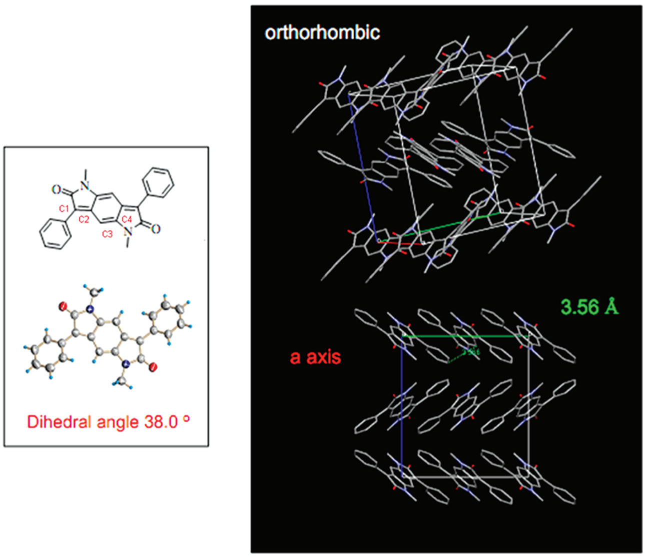


Figure 1. Single crystal structure of **5a-1**.

benzene ring and the core. Molecule **5a-1** exhibits an orthorhombic packing structure. The nearest interaction is between the middle six-membered ring and the side benzene ring with a distance of 3.56 Å, indicative of $\pi-\pi$ interaction.

Thermal Properties. The thermal behaviors of the compounds were evaluated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). For the small molecules **5a-1** and **5a-2**, 5% weight loss occurred at 290 and 301 °C, respectively (Figure S1). The polymers PBDPDP-B and PBDPDP-T showed rather high thermal stability (Figure 2). There was no weight loss until 400 °C for both polymers. DSC results show that **5a-2** has a melting point at 138 °C and another transition at 91.6 °C (Figure S2). No transition was detected during the scan of both polymers.

Optical Properties. The UV−vis absorption and spectra of benzodipyrrolidone-based small molecules and polymers were recorded in chloroform at a concentration of 10^{-5} M and in spin-coated thin film (Figure 3). As depicted, in solution **5a-1** and **5a-2** reach a maximum absorption wavelength at 458 nm. In solid state, **5a-2** shows broadened absorption, and the maximum absorption wavelength red-shifted to 523 nm, indicating strong intermolecular interaction, which will facilitate charge transport. The maximum absorption wavelengths of PBDPDP-B and PBDPDP-T are located at 524 and 579 nm, respectively. The large absorption red shift compared with the monomer (**5a-1** or **5a-2**) is symptomatic of the extended conjugation

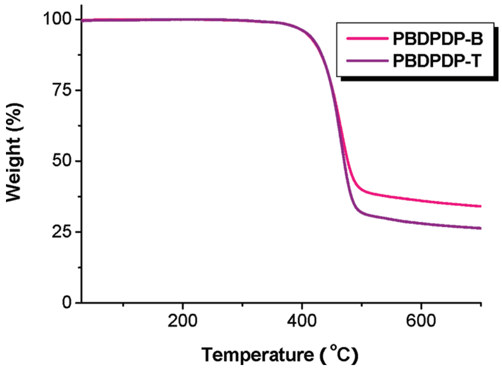


Figure 2. TGA curves of bezodipyrrolidone-based polymers (N_2 atmosphere with a heating rate of 10 °C min^{-1}).

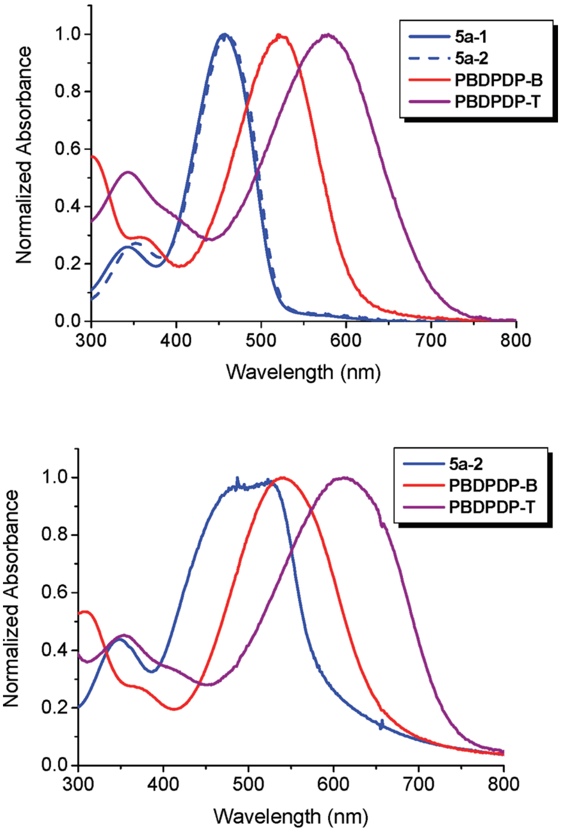


Figure 3. Normalized UV−vis absorption spectra of benzdipyrrolidone-based small molecules and polymers (top: solution, 10^{-5} M in chloroform; bottom: film, spin-coating from chloroform solution).

after polymerization. Moreover, a higher degree of conjugation can be achieved by coupling with thiophene units. In thin film, the same as **5a-2**, a broadened and red-shifted absorption can be obtained, i.e., PBDPDP-B, 538 nm, and PBDPDP-T, 579 nm. The absorption edges of the film were 650 nm for PBDPDP-B and 737 nm for PBDPDP-T. The optical bandgaps (ΔE_g^{opt}) were calculated to be 1.9 eV for PBDPDP-B and 1.68 eV for PBDPDP-T. The low band gaps indicate benzodipyrrolidone should be an effective unit for constructing low-bandgap polymers. The photoluminescence spectra of the small molecules and the polymers were also recorded in chloroform

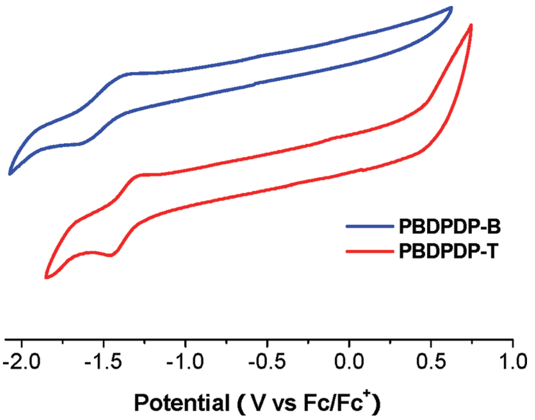


Figure 4. Cyclic voltammograms of benzodipyrrolidone-based polymers PBDPDP-B and PBDPDP-T in *o*-dichlorobenzene.

at a concentration of 10^{-5} M. There is essentially no fluorescence that can be observed.

Electrochemical Properties. The electrochemical properties of benzodipyrrolidone-based small molecules and polymers were investigated by cyclic voltammetry (CV) in a three-electrode electrochemical cell with Bu_4NPF_6 (0.1 M) and Ag/Ag$^+$ as the electrolyte and reference electrodes, respectively. The potentials were calibrated with ferrocene/ferrocenium redox couple (Fc/Fc$^+$). The cyclic voltammetry of **5a-1** and **5a-2** were performed in methylene chloride (Figure S3). These two molecules have two reversible redox processes at negative potential and quasi-reversible oxidation processes at positive scan. The lowest unoccupied molecular orbital (LUMO) energy levels of **5a-1** and **5a-2**, estimated from the reduction onset, are −3.63 and −3.53 eV, respectively. The highest occupied molecular orbital (HOMO) levels are −5.83 and −5.90 eV, calculated from oxidation onset. As to DPP, even with electron-withdrawing Cl substituents, the reduction occurred at more negative potential ($E_{1/2} = -1.62$ V vs Fc$^+$/Fc), whose LUMO was estimated to be −3.18 eV.[19] The deeper LUMOs of benzodipyrrolidones show stronger electron affinity properties. CV of polymers PBDPDP-B and PBDPDP-T were recorded in *o*-dichlorobenzene, and they exhibited only one reversible reduction. The LUMO levels are −3.35 and −3.50 eV, respectively. The HOMO levels, calculated from the optical band gaps (solution), were −5.39 eV for PBDPDP-B and −5.25 eV for PBDPDP-T.

Charge Carrier Transport. Bottom gate/bottom contact FET devices were fabricated by spin-coating from polymer solution (10 mg/mL in chloroform) on to DTS-treated SiO_2 (200 nm)/n^{++}-Si substrate. The devices were then dried at 60 °C for 0.5 h and annealed at the desired temperature for 10 min in a glovebox. The output and transfer characteristics of the transistors based on the polymers are depicted in Figure 5. PBDPDP-B shows strong n-type behavior with an electron mobility estimated to be 2.4×10^{-3} cm^2/(V s), comparable to PCBM (∼10^{-3} cm^2/(V s)). The highest mobility can be achieved after annealing at 240 °C (Figure S4). PBDPDP-T exhibits ambipolar properties with a hole mobility 3.5×10^{-3} cm^2/(V s) of and electron mobility of 6.4×10^{-3} cm^2/(V s) from devices annealed at 240 °C (Figure S5). The value of the charge mobility is sufficient for charge carrier transport to the electrode in potential photovoltaic devices. The data presented above indicates that benzodipyrrolidone can be a new unit for the construction of n-type materials with various electronic properties.

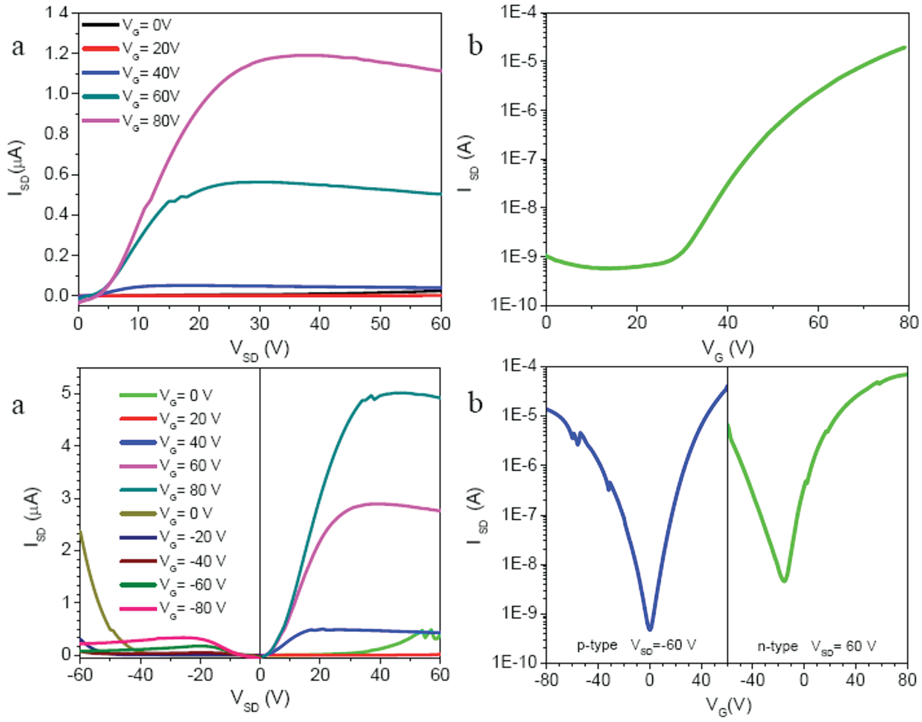


Figure 5. Output (a) and transfer (b) characteristics of transistors based on PBDPDP-B (top) and PBDPDP-T (bottom).

CONCLUSIONS

In summary, several benzodipyrrolidone-based small molecules were synthesized. The basic properties such as packing structure, UV absorption, and electrochemical oxidation and reduction were demonstrated. Moreover, two benzodipyrrolidone-based low-band-gap conjugated polymers were prepared by means of Suzuki coupling polymerization. The band gaps were estimated to be 1.9 eV of PBDPDP-B and 1.68 eV of PBDPDP-T. They showed reversible reduction behavior under negative potential. The LUMO levels were calculated to be −3.35 eV (PBDPDP-B) and −3.50 eV (PBDPDP-T), respectively. FET devices showed n-type behavior of PBDPDP-B with electron mobility of 10^{-3} $cm^2/(V\ s)$. While PBDPDP-T gave ambipolar properties with hole mobility of 10^{-3} $cm^2/(V\ s)$ and electron mobility of 10^{-3} $cm^2/(V\ s)$. The charge carrier mobility value ensured effective charge transporting for OPV device applications. The investigation of organic photovoltaic devices is on the way. While the benzodipyrrolidones described here are not an exact analogue of DPP (phenyl interspersed between the dipyrrole and thiophene), we are aware that direct binding to the thiophenes will red-shift their absorption beyond that of DPP. Work in that direction is in progress and will be reported in due course. Based on the above, benzodipyrrolidone will become a unit for construction of new series of n-type and donor−acceptor materials for applications in organic electronics.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Information regarding experimental procedures, characterizations for all compounds, and single crystal X-ray diffraction data of **5a-1**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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