Letter

Methylated conjugated polymers based on diketopyrrolopyrrole and dithienothiophene for high performance field-effect transistors

Fan Yang [a], Cheng Li [a, **], Jianqi Zhang [b], Guitao Feng [a], Zhixiang Wei [b], Weiwei Li [a, *]

[a] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 10090, China
[b] National Center for Nanoscience and Technology, Chinese Academy of Sciences, Beijing, 100190, China

A B S T R A C T

In this work, a series of conjugated polymers based on diketopyrrolopyrrole (DPP) and dithienothiophene were designed for application in field-effect transistors (FETs). Owing to the synthetic nature of DPP units, the DPP polymers here contain different aromatic linkers with thiophene and methylthiophene, resulting in non-methylated and methylated DPP polymers. Methylated DPP polymers were found to show good crystalline properties and provide high hole mobilties up to 5.32 cm^2 V^{-1} s^{-1} in FETs, while non-methylated polymer exhibits a hole mobility of 3.16 cm^2 V^{-1} s^{-1}. Especially, the polymer containing asymmetric linkers presents "face-on" orientation in thin films but provides the highest mobility. Our results reveal that the polymers incorporating methyl units as side chains can be used to realize high carrier mobility in FETs.

© 2016 Elsevier B.V. All rights reserved.

Organic field-effect transistors (OFETs) fabricated from conjugated polymers have shown great potential for industry application due to their flexibility, light weight and low cost. A huge number of conjugated polymers with varied chemical structures have been developed, resulting in high carrier mobilities above 10 cm^2 V^{-1} s^{-1} in FET devices [1–4]. Nowadays, "donor-acceptor" conjugated polymers consisting of electron-donating and electron-deficient units in the backbone are well-studied, due to the advantage of tunable optical band gaps (E_g), energy levels, crystalline and charge transport properties [5]. In order to realize solution processes for large-area fabrication, alkyl side chains are introduced, which also influences the microstructure of conjugated polymers and the charge transport properties in thin film OFETs [6].

Besides conjugated backbone and flexible side chains, the minor modification of the chemical structures of conjugated polymers can also have great influence on the device performance. For instance, conjugated polymers bearing fluorine atoms show high crystalline properties and preferential orientation of polymer backbone, consequently providing high carrier mobilities in FETs.[7–11] Similar effect on the charge transport is observed when introducing other heteroatoms such as N [12], Si [13], Se [14], and Ge

[15,16] into the conjugated backbone. The physical and chemical properties of conjugated polymers can also be tailored by using bulky substitutions, such as cyano [17], methyl [4,18], and thienyl units [19]. In most case, these bulky units cause steric hindrance in the conjugated backbone, which might greatly reduce the inter- and intra-molecular interaction, resulting in low carrier mobilities in transistors. Therefore, the design strategy by using bulky units as side groups is less studied compared to the simple methods by applying heteroatoms into conjugated polymers for FETs.

In this work, we are interested with the influence of methyl units on the charge transport properties of conjugated polymers. In our previous studies, a methylated conjugated polymer was developed to show a high power conversion efficiency of 7.0% in polymer solar cells [20]. We also designed an asymmetrically methylated polymer that exhibit a high hole mobility of 12.5 cm^2 V^{-1} s^{-1} [4]. These results encourage us to explore more methylated conjugated polymers for application in OFETs. The new conjugated polymers are designed by using electron-deficient diketopyrrolopyrrole (DPP) unit and electron-donating dithieno-thiophene (DTT) unit, as shown in Scheme 1. It has been reported that DPP-DTT-based polymers had good crystalline properties and provided hole mobilities up to 0.6 cm^2 V^{-1} s^{-1} [21–23]. In this study, methylated conjugated polymers are developed by using methylthiophene (MT) as bridges to connect DPP and DTT building blocks. The new methylated polymers were found to provide high
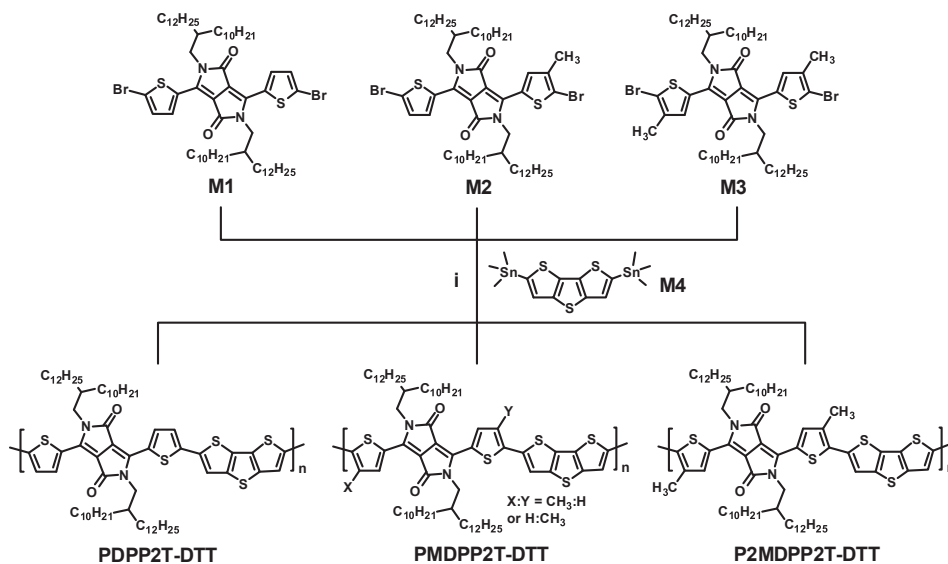
Scheme 1. Chemical structures of the DPP polymers PDPP2T-TTT, PMDPP2T-TTT and P2MDPP2T-TTT and their synthetic routes. (i) Stille polymerization by using $Pd_2(dba)_3$/PPh$_3$ in toluene/DMF (10:1, v/v) at 115 °C.

hole mobilities up to 5.32 cm^2 V^{-1} s^{-1} in FETs, while non-methylated polymer showed a hole mobility of 3.16 cm^2 V^{-1} s^{-1}. Interestingly, we found that methylated polymers with high hole mobilities exhibit "face-on" orientation that the π-π stacking direction is perpendicular to the substrate, which were usually found in conjugated polymer thin films with high electron mobilties [24,25].

The chemical structures of the polymers, PDPP2T-DTT, PMDPP2T-DTT and P2MDPP2T-DTT, and their synthetic routes are present in Scheme 1. The detailed synthetic procedures are described in the supporting information (SI). 2-Decyltetradecyl (DT) side chains are used for solubility. The DPP-based monomer M1, asymmetric monomer M2 and dimethylated monomer M3 are synthesized according to the literatures [26,27]. The three polymers were prepared by Stille polymerization, in which the catalyst system $Pd_2(dba)_3$/PPh$_3$ and solvent mixture toluene/DMF were used. The polymerization condition has been widely used to synthesis DPP polymers with high molecular weight [28]. ^{1}H NMR spectrum of the polymers were recorded at 100 °C with 1,1,2,2-tetrachloro-ethane-d$_2$ as the solvent (Fig. S1), but it is difficult to distinguish the peaks due to the strong aggregation of the polymers. The molecular weight of the polymers were determined by GPC measurement, in which a low concentration of 0.1 mg ml^{-1} and a high temperature of 140 °C was used to prevent the aggregation of polymer backbone. Although the polymers were found to form viscous solution in CHCl$_3$ as other high molecular weight DPP polymers, GPC results show that the polymers only provided relatively low molecular weight with the peak (M_p) of 29.3, 34.4 and 29.3 kg mol^{-1} (Table 1 and Fig. S2). Similar phenomenon was also observed in some other DPP polymers when using the same instrument to measure the

molecular weight [29].

The optical absorption spectra of the DPP polymers in CHCl$_3$ and thin films are present in Fig. 1 and the data is summarized at Table 1. The polymers PDPP2T-DTT, PMDPP2T-DTT and P2MDPP2T-DTT in CHCl$_3$ solution have E_g of 1.42, 1.41 and 1.38 eV, while the E_gs are reduced to 1.39, 1.38 and 1.34 eV in thin films. The absorption shoulder around 700 nm for the polymer thin films is also observed, indicating H-aggregation for these polymers. Red-shift absorption is observed in methylated polymers compared to non-methylated polymer, corresponding to the electron-donating ability of methyl unit (see Fig. 1).
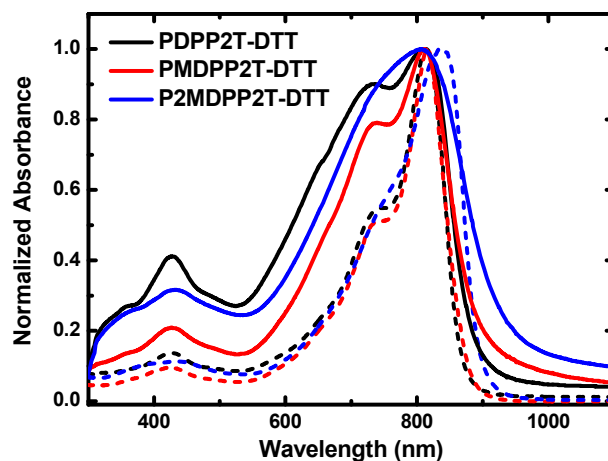
Fig. 1. (a) Absorption spectra of the DPP polymers in CHCl$_3$ solution (dashed lines) and in solid state films (solid lines).

Table 1
Optical and electrochemical properties of the DPP polymers.

Polymer	M_p (kg mol^{-1})	E_g^{sol} (eV)	E_g^{film} (eV)	HOMO[a] (eV)	LUMO[b] (eV)
PDPP2T-DTT	29.3	1.42	1.39	−5.27	−3.88
PMDPP2T-DTT	34.4	1.41	1.38	−5.25	−3.87
P2MDPP2T-DTT	29.3	1.38	1.34	−5.19	−3.85

[a] Determined using a work function value of −4.8 eV for Fc/Fc$^+$.
[b] Determined as $E_{HOMO} + E_g^{film}$.