Solution-Processed Organic Field-Effect Transistors Based on Polythiophene Derivatives with Conjugated Bridges as Linking Chains

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Organic field-effect transistors (OFETs), the critical components of future organic electronics, attract much interest because of their attractive applications, such as radio frequency identification tags, displays, and large-area sensors.[1] One of the most important aspects for OFETs is that they can be fabricated by easy patterning techniques at low cost and have good compatibility with flexible plastic substrates.[2] Thus the solution processable polymers are preferable to low molecular weight materials, which do not allow efficient patterning and show great device sensitivity to structure defects.[3] Although considerable efforts have been taken in the development of new polymer semiconductors, to date the known polymer semiconductors are still limited and only a few can truly realize the high mobilities required for organic circuits that have adequate performance for application such as active matrix displays or low-cost intelligent labels when deposited in air.[4] Therefore, design and synthesis of new conjugated polymer semiconductors are highly desirable.

Scheme 1. Synthetic Route of the Polymers of PT-VTVTV2 and PT-VTVTV4

x=2% PT-VTVTV2

x=4% PT-VTVTV4
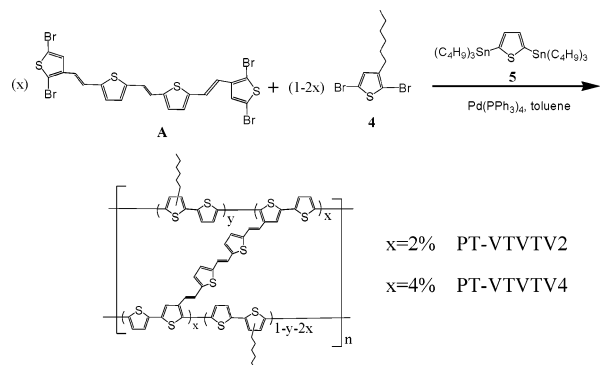
Several methods have been used to obtain the polymers with high hole mobility, including increasing molecular weight, decreasing polydispersity of polymers, and structural design.[5] Among them, structural design is more desirable and many functionally capable semiconductor polymers were reported to give mobilities of higher than 0.1 cm^2 V^{-1} s^{-1}.[6] Recently, Weder et al. found that the network structure of cross-linked conjugated polymers can have significant benefits for the carrier communication between chains[7] and the polythiophene derivatives (PTs) with conjugated bridges as linking chains have been used to improve charge transport in polymer solar cells.[8] However, these cross-linking polymers used as the semiconductors of OFETs have not been reported yet. Longer conjugated bridges, which avoids the distortion of the polymer main chains and possesses better conjugation, could lead to higher mobility of the polymers with conjugated bridges as linking chains. Moreover, we found that the PTs with bi(thienylene vinylene) as conjugated side chains showed the best photovoltaic properties among the PTs with conjugated side chains.[9] Thus, in the current paper, we have synthesized two novel PTs, PT-VTVTV2 and PT-VTVTV4 (see Scheme 1), with vinylene−thienylene−vinylene−thieneylene−vinylene (VTVTV) with con-

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**Table 1. Optical and Electrochemical Properties of the PT-VTVTV2 and PT-VTVTV4**

	UV−vis absorption spectra		CV		
polymer	solution λ_{max} (nm)	film λ_{max} (nm)	HOMO (eV)	LUMO (eV)	E_g^{EC} (eV)
PT-VTVTV2	460	493	−5.01	−2.77	2.24
PT-VTVTV4	457	473	−5.09	−2.88	2.21

jugated bridges as linking chains. Their optical properties, thermal properties, and field-effect characteristics are studied.

The syntheses of PT-VTVTV2 and PT-VTVTV4 were achieved by Stille coupling reaction by adding different ratios of the monomer A (2%, 4%) as seed as outlined in Scheme 1 (for details of the synthesis, see Supporting information). The monomer A was synthesized by Wittig−Hornor reaction (Scheme S1 in Supporting Information). The regioregularities of PT-VTVTV2 and PT-VTVTV4 are 70% and 69%, respectively, which are calculated from the ratio of the integral area of the two peaks at 2.5−2.8 ppm in the ^{1}H NMR spectra (Figure S2 in Supporting Information). Gel-permeation chromatography (GPC) analysis exhibited a number-average molecular weight (M_n) of 37 000 with a polydispersity of 1.98 and 26 000 with a polydispersity of 2.25 against polystyrene standards for PT-VTVTV2 and PT-VTVTV4, respectively.

The absorption spectral data of the two polymers are summarized in Table 1. The UV−vis absorption spectra (Figure S3 in Supporting Information) of PT-VTVTV2 and PT-VTVTV4 in diluted chloroform solution exhibited a main absorption with λ_{max} at 460 and 457 nm, respectively, while their thin films showed a strong absorption with λ_{max} at 493 and 473 nm, respectively. The two polymers showed a small red-shift in absorption from solution to thin film (33 nm for PT-VTVTV2 and 16 nm for PT-VTVTV4), and the small red-shifts are in sharp contrast to those of regioregular polythiophenes such as head-to-tail poly(3-hexythiophene) (P3HT about 100 nm) and poly(didodecylquarterthiophene) (PQT about 75 nm), suggesting that PT-VTVTV2 and PT-VTVTV4 might have a conformation with twisted thienylene units in the solid state.[6d,10] In addition, the thin-film spectrum of PT-VTVTV2 showed larger bathochromic shifts over its solution spectrum than that of PT-VTVTV4, revealing its higher molecular orders in the solid state and different chain conformaton from PT-VTVTV4 due to fewer linking bridges. The optical band gaps of the polymers were determined from the absorption onset. The optical band gaps of PT-VTVTV2 and PT-VTVTV4 were found to be 2.0 and 1.99 eV, respectively. The band gaps of these polymer films were found to decrease a little as the fraction of bridges increased.

The electronic states of the films on the Pt electrode were investigated by cyclic voltammetry (CV) to better understand charge injection processes in the new polymer semiconductors and devices made from them. The two polymers showed similar reversible oxidation and reduction peaks (Figure S4 in Supporting Information). All the electrochemical data are also summarized in Table 1. The highest occupied molecular orbital (HOMO) levels of PT-VTVTV2 and PT-VTVTV4 were −5.01 and −5.09 eV, respectively, which are similar

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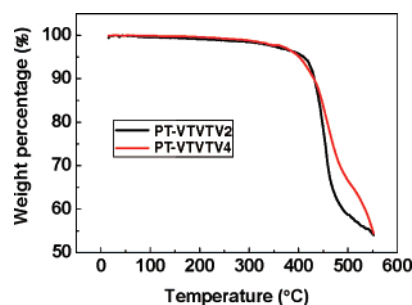
Figure 1. TGA of PT-VTVTV2 and PT-VTVTV4.

to those of most regioregular polythiophenes such as −5.0 eV of P3HT and −5.1 eV of PQT.[4a] The HOMO levels of the polymers are comparable with the work function of Au, indicating better carrier injection from the contact to the semiconductors of OFETs.[11] The HOMO−lowest unoccupied molecular orbital (LUMO) gaps of PT-VTVTV2 and PT-VTVTV4 were obtained to be 2.24 and 2.21 eV, respectively, which is consistent with the result obtained from UV−vis spectra measurement.

The thermal property of PT-VTVTV2 and PT-VTVTV4 was evaluated by thermalgravimetric analysis (TGA, Figure 1) and differential scanning calorimetry (DSC). The DSC of PT-VTVTV2 and PT-VTVTV4 showed broad peaks at ∼215 and 225 °C, respectively (Figure S5 in Supporting Information), which are attributed to the melting of polymer backbones. The high rigidity of the backbone of PT-VTVTV4 due to more conjugated bridges was responsible for its higher meltng points than that of PT-VTVTV2.[6a] Excellent thermal stability of PT-VTVTV2 and PT-VTVTV4 was manifested in their TGA profile with decomposition temperatures of 419 and 410 °C, respectively, demonstrating its thermal stability approaching that of poly(4,8-didodecyl-benzo[1,2-b:4,5-b′]dithiophene).[6a,12]

The structure order and crystallization of PT-VTVTV2 and PT-VTVTV4 were investigated by film X-ray diffraction (XRD) and atomic force microscopy (AFM). The XRD measurements were carried out for the thin films, which were prepared on *n*-octadecyltrichlorosilane (OTS)-modified SiO$_2$/Si substrates by drop-coating and then annealing at 150 °C for 30 min (Figure S6 in Supporting Information). The XRD pattern of the PT-VTVTV2 film exhibited highly crystalline patterns with a strong primary diffraction peak at $2\theta = 5.0°$, which arises from the ordered interlayer stacking of the polymers and corresponds to a interlayer *d*-spacing of 17.3 Å.[13] The XRD pattern of PT-VTVTV4 films exhibited several sharp peaks from 20° to 25° with concomitant disappearance of interlayer stacking peaks. The sharp peaks in the XRD spectrum, which arise from $\pi−\pi$ stacking order, supported the good crystalliity of PT-VTVTV4. Figure 2 shows the AFM topographic image of PT-VTVTV2 and PT-VTVTV4 thin films on OTS-modified SiO$_2$/Si substrates.

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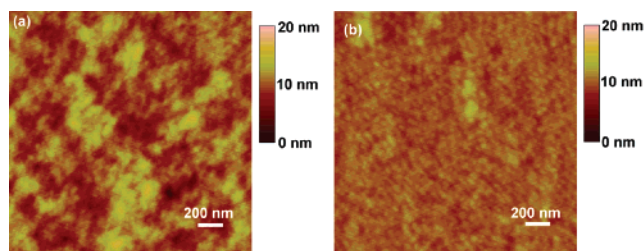(13) Chen, T. A.; Wu, X. M.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

Figure 2. AFM images of films spin-coated onto OTS-modified SiO$_2$/Si substrates: (a) for PT-VTVTV2 and (b) for PT-VTVTV4.
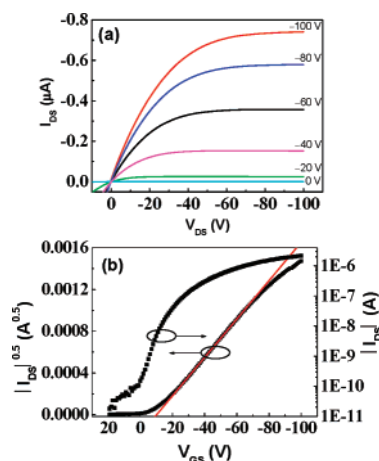

Figure 3. FET characteristics of an exemplary OFET with PT-VTVTV2 on OTS-modified substrate (channel length = 60 μm, channel width = 3000 μm): (a) output curves at different gate voltages and (b) transfer curve in saturated regime at constant source−drain voltage of −100 V and square root of the absolute value of current as a function of gate voltage.

Films of both PT-VTVTV2 and PT-VTVTV4 show homogeneous morphology with small granule crystallite. The crystallite of the PT-VTVTV4 film exhibits a more ordered arrangement than that of the PT-VTVTV2 film, resulting in more defined grain boundaries and smoother surface and facilitating the fabrication of high performance OFETs.

To characterize the FET performance of PT-VTVTV2 and PT-VTVTV4, OFETs were constructed on OTS-modified SiO$_2$/Si substrates with top-contact configuration. The transistors based on PT-VTVTV2 and PT-VTVTV4 were found to exhibit typical *p*-type FETs characteristics. The output and transfer characteristics of typical OFETs are shown in Figure 3. The output behaviors conform well to the conventional metal oxide semiconductor FET gradual-channel models in both the linear and the saturated regime, and no contact resistance can be observed, which is consistent with the results above. The devices based on PT-VTVTV2 afforded a best hole mobility of about 1.1 × 10^{-3} cm^2 V^{-1} s^{-1} with an on/off ratio of 10^5 and threshold voltage of about −10 V in saturation regime, much larger than that of the polymer without the conjugated bridge.[14] With the increase of the conjugated bridges, the devices based on PT-VTVTV4 showed higher mobility, affording a best hole mobility of about 3.8 × 10^{-3} cm^2 V^{-1} s^{-1} with an on/off ratio of 10^4 and threshold voltage of about 24 V. These data indicate that the conjugated bridges can strongly increase the carrier mobility of the polymers with conjugated bridges as linking chains, which is consistent with the results in literature.[7] Though the carrier mobilities of PT-VTVTV2 and PT-VTVTV4 are not as good as those of the best devices previously reported, they are among the best performance of the copolymers with low regioregularity for OFETs reported. To improve their mobility, many ways, such as the modification of the structure of PT-VTVTV2 and PT-VTVTV4 by introducing different alkyl group end-cappers and improving their regioregularity, are underway.

In summary, we have synthesized a new class of PTs with conjugated bridges as linking chains, PT-VTVTV2 and PT-VTVTV4. OFETs based on them provide better FET performance in spite of their low regioregularity, affording a hole mobility of about 3.8 × 10^{-3} cm^2 V^{-1} s^{-1} with an on/off ratio of 10^4. These polymer semiconductors therefore represent a useful class of solution-processable semiconductors for fabrication of OFET circuits for printed electronics.

Supporting Information Available: The synthesis, DSC, UV/vis absorption spectra, and CV of PT-VTVTV2 and PT-VTVTV4, the fabrication and characterization of OFETs based on the films of PT-VTVTV2 and PT-VTVTV4, and XRD of the thin films (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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