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Communication

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Record High Hole Mobility in Polymer Semiconductors via Side-Chain Engineering

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Ⓢ *Supporting Information*

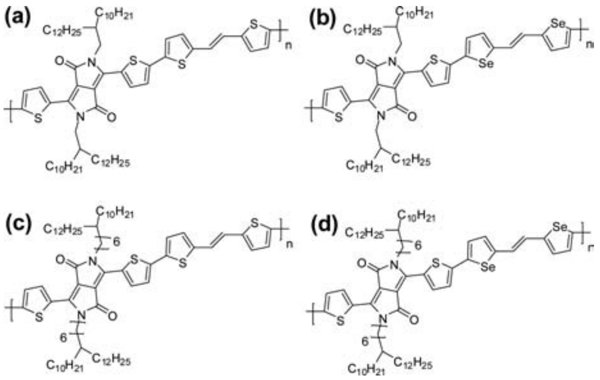
ABSTRACT: Charge carrier mobility is still the most challenging issue that should be overcome to realize everyday organic electronics in the near future. In this Communication, we show that introducing smart side-chain engineering to polymer semiconductors can facilitate intermolecular electronic communication. Two new polymers, P-29-DPPDBTE and P-29-DPPDTSE, which consist of a highly conductive diketopyrrolopyrrole backbone and an extended branching-position-adjusted side chain, showed unprecedented record high hole mobility of 12 cm^2/(V·s). From photophysical and structural studies, we found that moving the branching position of the side chain away from the backbone of these polymers resulted in increased intermolecular interactions with extremely short $\pi-\pi$ stacking distances, without compromising solubility of the polymers. As a result, high hole mobility could be achieved even in devices fabricated using the polymers at room temperature.

Polymer semiconductors have great potential for use in flexible and low-cost electronic devices that are processable with printing technologies, owing to their solution processability and superior mechanical properties.[1−3] Traditionally, polythiophene derivatives, which possess preferentially an edge-on structure with a well-developed microcrystalline domain on the substrate, have been regarded as the most suitable polymer semiconductors exhibiting high charge-carrier mobilities.[4−7] However, it has recently been demonstrated that diketopyrrolopyrrole (DPP)-based donor−acceptor (D-A) polymers are able to afford higher charge-carrier mobilities despite their relatively low crystalline nature.[3,8−16] Hole mobilities exceeding 3 cm^2/(V·s) have been reported via smart molecular design for both the polymer backbone and side chain of such DPP derivatives. The success of these DPP-based D-A backbones can be attributed to the highly polar nature of DPP, which allows for strong charge transfer (CT) between the donor and acceptor units.[17] This strong CT seems to enhance not only intramolecular charge transport but also intermolecular charge transport, which is driven by the more planar backbone.

Although long-branched alkyl side chains obviously improve polymer solubility, they have traditionally been considered to hamper charge transport in polymer films because they are insulating and bulky enough to hinder efficient intermolecular interactions. However, recent reports by Lei et al.[16] and Zhang et al.[18] have demonstrated that these bulky, long-branched side chains can result in a dramatic increase in the charge-carrier mobilities of polymers if branching position is adjusted. In particular, Lei and co-workers systematically elucidated the effect of the branching position on the microcrystalline structure of an indigo-based copolymer and concluded that the greater the distance of the branching position from the polymer backbone, the smaller the intermolecular $\pi-\pi$ stacking distances, leading to high charge-carrier mobility.

Recently, Guo and co-workers as well as our group have reported a DPP-based highly π-extended polymer, namely, poly[2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4-(2*H*,5*H*)-dione-(*E*)-1,2-di(2,2′-bithiophen-5-yl)ethene] (P-24-DPPDBTE),[7,19] and its selenophene analogue, namely, poly-[2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4-(2*H*,5*H*)-dione-(*E*)-(1,2-bis(5-(thiophen-2-yl)selenophen-2-yl)ethene] (P-24-DPPDTSE) (Chart 1).[9] These polymers exhibit exceptionally high charge-carrier mobilities, with the mobilities of both polymers exceeding 5 cm^2/(V·s). Inspired by recent works on side-chain engineering, here we have tried to adjust the branching position of the previously reported polymers P-24DPPDBTE and P-24-DPPDTSE (P-24s). Two new polymers, P-29-DPPDBTE and P-29-DPPDTSE (P-29s)

Chart 1. Chemical Structures of (a) P-24-DPPDBTE (M_n = 31 900, M_w = 54 230, PDI = 1.7), (b) P-24-DPPDTSE (M_n = 33 530, M_w = 59 820, PDI = 1.78), (c) P-29-DPPDBTE (M_n= 33 369, M_w = 60 781, PDI = 1.82), and (d) P-29-DPPDTSE (M_n = 35 826, M_w = 58 038, PDI = 1.62)



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(Chart 1), in which the branched alkyl chain has a relatively longer alkyl spacer (C6) between the branching point and the backbone, were synthesized and used as semiconductors for high-performance field-effect transistors (FETs).[20] By optimizing device geometry and using heat treatments, the maximum hole mobility could be increased to as much as 12 $cm^2/(V{\cdot}s)$. In addition, these polymer-based transistors exhibited an exceedingly high hole mobility of 5 $cm^2/(V{\cdot}s)$ even when not subjected to a heat treatment. On the basis of the results of photophysical and structural analyses of the devices, the high mobility of the P-29s was attributed to their excellent self-organizing properties during the solution process; these properties originated from side-chain modification with an extended linear alkyl spacer. The $\pi-\pi$ stacking distance for P-29-DPPDTSE, which showed the highest mobility, was as short as 3.58 Å.

The UV–vis absorption spectra of the P-24s and P-29s were measured both in solution and in thin-film form, as shown in Figure 1. All polymers exhibit dual-band absorptions (with absorption maxima near 450 and 800 nm, respectively); this is a general feature of D-A copolymers.[13] Compared to the P-24s, the P-29s exhibit a distinctly red-shifted absorption maximum and absorption onset by approximately 20 nm in both film and solution forms. This red shift can be attributed to their backbone being planarized to a greater extent. The effect of thermal annealing on the absorption spectra of the P-29s was not very pronounced, while a slight growth of the shoulder peaks (0-1 vibrational peaks) was noticed in the absorption spectra of the P-24s after thermal annealing. This implies that the P-29s preferentially form a highly ordered crystalline structure even in pristine film form.

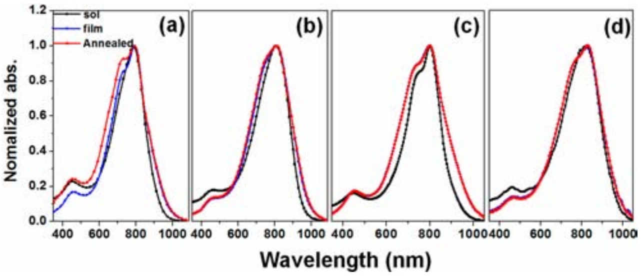

Figure 1. UV–vis absorption spectra of (a) P-24-DPPDBTE, (b) P-24-DPPDTSE, (c) P-29-DPPDBTE, and (d) P-29-DPPDTSE in solution in chloroform, as an unannealed film, and as a film annealed at 200 °C.

The molecular orbital energy levels of the polymers were calculated using cyclic voltammetry (CV). It was found that inserting an alkyl spacer (C6) between the branching point and the polymer backbone led to an increase in the highest occupied molecular orbital (HOMO) levels from −5.31 eV (P-24-DPPDBTE) and −5.33 eV (P-24-DPPDTSE) to −5.25 eV (P-29-DPPDBTE) and −5.27 eV (P-29-DPPDTSE). Together with UV–vis absorption spectra, these observations suggest that the backbones of the polymers with the alkyl spacer have a more planar structure, possibly originating from the lower steric hindrance offered by the branched alkyl chain to the polymer backbone and/or from more extended intermolecular $\pi-\pi$ interactions.

To study the charge transport behavior of the polymers, we fabricated FETs based on the P-24s and P-29s. First, thin films of the polymers were prepared on conventional octadecyltrichlorosilane (OTS)-modified SiO_2/Si substrates via spin coating. We employed relatively short channels (50 μm in length) because we had previously found that channels 160 μm in length resulted in unusual transfer characteristics.[9] In addition to our group, a number of other groups have also noticed that the $(I_{DS})^{1/2}-V_G$ plot (transfer plot in the saturation regime) for DPP-based FETs very often exhibited significant nonlinearity in the high-V_G regime. Li et al. have shown that this unusual phenomenon can be partially rectified by applying a high electric field along the channel direction.[3] Even though we used a rather short channel length and high voltage, resulting in an electric field of $\sim 2 \times 10^4$ V/cm, some degree of nonlinearity was still observed in the transfer characteristics of all the organic field-effect transistors (OFETs) (Figure 2a,b and Supporting Information) Therefore, we also fabricated FETs based on the P-24s and P-29s on Cytop-modified substrates. It is well known that Cytop surfaces are most suited for upper-deposited semiconductors, especially for Cytop-modified surfaces which are themselves hydroxyl-group free and hydrophobic.[21] Figure 2 compares the typical transfer and output characteristics of the FETs based on P-29s fabricated on the OTS and Cytop-modified SiO_2/Si substrates. (FET data for P-24s are in Supporting Information.) The most important difference noticed in the transfer characteristics with Cytop was that the unusual, i.e., nonlinear, transfer behavior was not noticed any more. All the FETs exhibited ideal, hysteresis-free transfer and output characteristics. Therefore, it can be argued the polymers form defect-free interfaces with Cytop, and the resulting charge transport characteristics fully reflect the intrinsic electrical properties of the polymers. The calculated field-effect mobilities of the FETs based on the P-24s and P-29s are listed in Table 1. In both cases, OTS-modified and Cytop-modified OFETs, it can be seen that the mobilities of the FETs based on the P-29s are two or three times higher than those of the FETs based on the P-24s, regardless of the annealing conditions. It is also worth noting that the effect of thermal annealing on the field-effect mobilities was not as

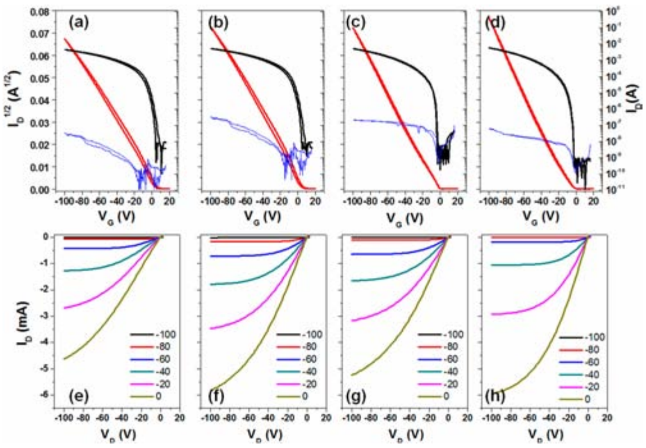

Figure 2. (Top) Transfer characteristics of FETs based on (a) P-29-DPPDBTE and (b) P-29-DPPDTSE fabricated with OTS-modified SiO_2/Si substrate. (c) and (d) correspond to Cytop-modified substrate for P-29-DPPDBTE and P-29-DPPDTSE, respectively. In each figure, blue curve represents leakage current. (Bottom) Output characteristics of FETs based on (e) P-29-DPPDBTE and (f) P-29-DPPDTSE fabricated with OTS-modified SiO_2/Si substrate. (g) and (h) correspond to Cytop-modified substrate for P-29-DPPDBTE and P-29-DPPDTSE, respectively.

Table 1. Device Performances of the Various OFETs Fabricated and Tested[a]

dielectric layer	heat treatment temp (°c)	μ [cm^2/(V·s)] ave	μ [cm^2/(V·s)] max	I_{on}/I_{off}
	P-24-DPPDBTE			
OTS/SiO$_2$	rt	0.13	0.2	>10^6
	200	2.1	2.8	>10^6
Cytop/SiO$_2$	rt	0.19	0.31	>10^6
	200	0.94	1.4	>10^6
	P-24-DPPDTSE			
OTS/SiO$_2$	rt	0.35	0.47	>10^6
	200	3.1	4.4	>10^6
Cytop/SiO$_2$	rt	0.29	0.47	>10^5
	200	1.4	1.8	>10^7
	P-29-DPPDBTE			
OTS/SiO$_2$	rt	3.6	5.1	>10^6
	200	8.5	10.54	>10^6
Cytop/SiO$_2$	rt	2.9	3.72	>10^6
	200	4.8	6.17	>10^6
	P-29-DPPDTSE			
OTS/SiO$_2$	rt	3.7	5.8	>10^6
	200	9.8	12.04	>10^6
Cytop/SiO$_2$	rt	3.3	4.57	>10^6
	200	6.9	8.11	>10^7

[a] Mobility values were summarized from more than 10 devices for each fabrication condition.

dramatic in the case of the FETs based on the P-29s as it was for the devices based on the P-24s; one can see a distinct increase of an order of magnitude in the mobilities in the latter case. Also, we can see that polymers with selenophene have higher mobility compared to those with thiophene when the side chain is remained same. This result can be attributed to selenium-oriented stronger intermolecular interaction, leading to denser chain packing as well as higher charge carrier mobility of polymers.[9] In total, we observed five devices whose mobilities were in excess of 8 cm^2/(V·s).

To further investigate the crystallinities and molecular orientations of the thin films of the polymers, out-of-plane and in-plane XRD analyses were performed; the results of these are shown in Figures 3 and S8 and Table S1. The presence of highly ordered (00l) reflection peaks of P-29s ranging up to (004) suggested that these polymers have a long-range-ordered, edge-on lamellar crystalline structure when coated on the substrate, even in the absence of thermal annealing. Figure 3 shows the out-of-plane and in-plane XRD spectra for the polymers after they had been thermally annealed under optimal conditions (at 200 °C for 10 min). Compared with the P-29s, the P-24s exhibited fewer diffraction peaks, and these peaks were remarkably broad (i.e., they had large full widths at half-maximum). Together, these facts implied that the polymers without an alkyl spacer, i.e., P-24s, had a short-range-ordered crystalline structure.[22] A strong out-of-plane diffraction at 2θ of 2.32° noticed in the case of both the P-29 polymers corresponded to a d-spacing of 26.9 Å, ~5 Å longer than that for the P-24s, for which the (001) diffraction appeared at 2θ of 2.86°, corresponding to a d-spacing of 21.5 Å. The in-plane XRD spectra showed that the (010) reflection peaks were distinctly observable in the case of the films of both the P-29 polymers. These results suggested clearly that the films of the P-29 polymers formed preferentially with an edge-on orientation on the substrate, thus facilitating efficient charge-carrier hopping transport. The corresponding $\pi-\pi$ stacking distance was 3.62 Å for P-29-DPPDBTE and 3.58 Å for P-29-DPPDTSE. In addition, diffraction halos were also observed with the corresponding distance being ~4 Å, implying the occurrence of close interactions between the alkyl chains. In contrast, the $\pi-\pi$ stacking distance observed in case of the P-24s was far longer (>3.7 Å) and the (010) reflection peak itself was much less pronounced. The remarkably small $\pi-\pi$ stacking distance of 3.58 Å for P-29-DPPDTSE is one of the shortest for reported polymers with high charge-carrier mobilities.[13,16] Interestingly, P-29-DPPDTSE showed very well developed crystalline structure even in as-cast condition, in good agreement with mobility analysis (Figures S10 and S11)

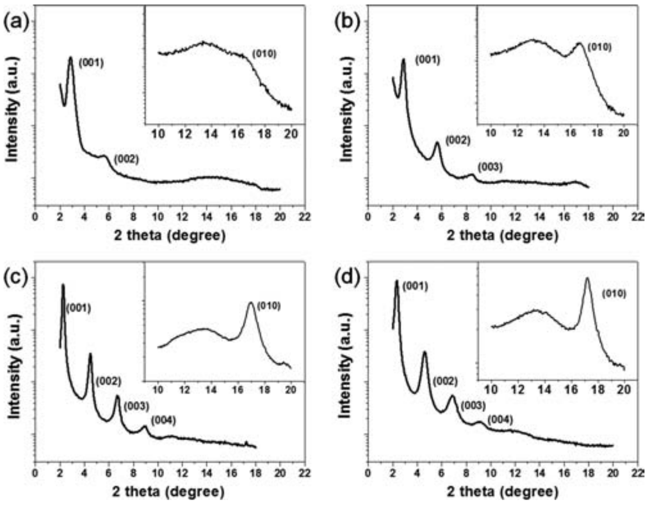

Figure 3. Out-of-plane and in-plane XRD spectra of (a) P-24-DPPDBTE, (b) P-24-DPPDTSE, (c) P-29-DPPDBTE, and (d) P-29-DPPDTSE. In each figure, the inset shows the corresponding in-plane diffractogram.

In conclusion, we have demonstrated that the polymers P-29s, which consist of a highly conductive polymer backbone and a branching-position-adjusted side chain, are high-mobility polymeric semiconductors suitable for OFETs. Moving the branching position of the side chain away from the backbone of the DPP-based polymers resulted in enhanced intermolecular interactions with exceptionally short $\pi-\pi$ stacking distances with the good solubility of the polymers being maintained. As a result, a high hole mobility of 5 cm^2/(V·s) could be achieved even in devices fabricated using the polymers at room temperature. In addition, an unprecedentedly high hole mobility of 12 cm^2/(V·s) was obtained after thermal annealing under optimized conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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Notes

The authors declare no competing financial interest.

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