Organic Electronics 37 (2016) 366–370

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

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

ARTICLE INFO

Article history:
Received 26 June 2016
Received in revised form
7 July 2016
Accepted 11 July 2016

Keywords:
Field-effect transistors
Conjugated polymer
Diketopyrrolopyrrole
Crystalline

ABSTRACT

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.

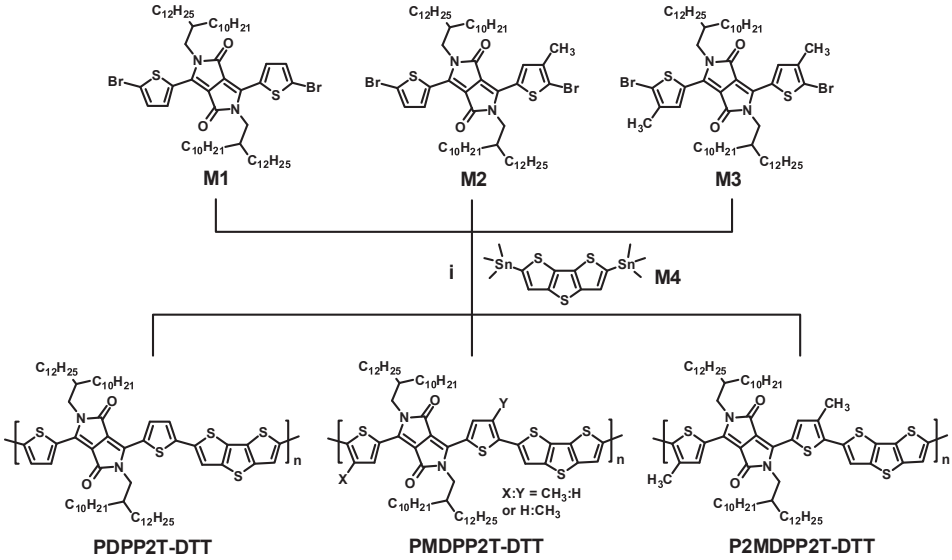
Organic field-effect transistors (OFETs) fabricated from conjugated polymers have shown great potential for industry application due to their flexibility, light weight and low cost. A huge number of conjugated polymers with varied chemical structures have been developed, resulting in high carrier mobilities 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 dithienothiophene (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

* Corresponding author.
** Corresponding author.
E-mail addresses: licheng1987@iccas.ac.cn (C. Li), liweiwei@iccas.ac.cn (W. Li).

http://dx.doi.org/10.1016/j.orgel.2016.07.012
1566-1199/



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-tetrachloroethane-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).

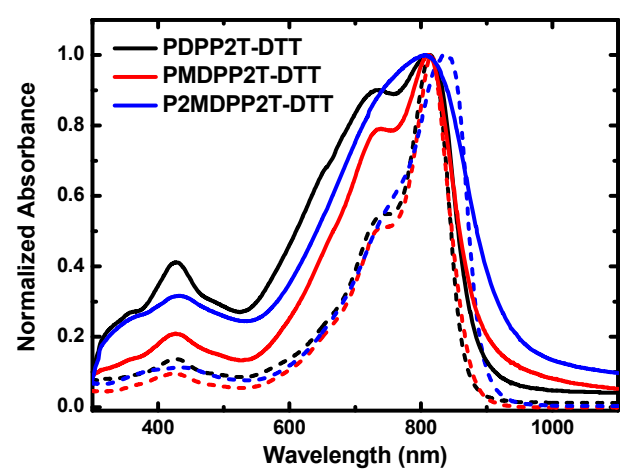


Fig. 1. (a) Absorption spectra of the DPP polymers in $CHCl_3$ solution (dashed lines) and in solid state films (solid lines).

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 $E_{HOMO} + E_g^{film}$.

The energy levels of the DPP polymers were determined using cyclic voltammetry in thin films (Fig. S3 and Table 1). PDPP2T-DTT has the highest occupied molecular orbital (HOMO) level of −5.27 eV and lowest unoccupied molecular orbital (LUMO) level of −3.88 eV. When introducing methyl units into the polymers, PMDPP2T-DTT and P2MDPP2T-DTT perform slightly low-lying HOMO levels of −5.25 eV and −5.19 eV, but show similar LUMO levels of −3.87 eV and −3.85 eV. This indicates that methyl units have the impact on the HOMO levels of the polymers. The overall effect is the reduced band gap of methylated DPP polymers, which is consistent with their red-shift absorption spectra.

The influence of methyl units on the physical properties of the polymers are further analyzed by density function theory (DFT) calculations at the B3LYP/6-31G level for extended oligomers. In the DFT calculations DT side chains were replaced by methyl units in order to reduce the calculation time. As shown in Fig. S4, the PDPP2T-DTT segment has HOMO and LUMO levels of −4.74 eV and −3.02 eV, while the HOMO and LUMO levels are increased to −4.68 eV and −2.97 eV for PMDPP2T-DTT and −4.65 eV and −2.94 eV for P2MDPP2T-DTT segment. The calculations confirm that methyl units as electron-donating groups can provide high-lying energy levels. The dihedral angle between DTT and T or MT units are also included in Fig. S4, in which only 0.2° is found between DTT and T units. The dihedral angle is increased to 9.38° and 6.01° between DTT and MT units in the methylated polymers, which originates from slightly steric hindrance between the methyl units and hydrogen from thiophene. However, the steric hindrance here has little impact on the conjugation of polymers, as confirmed by the red-shift absorption of methylated polymers.

Charge carrier mobilities of these polymers were determined in a bottom gate-bottom contact (BGBC) FET configuration. The detailed fabrication process and the calculation for hole mobility was provided in the experimental section in SI. DPP polymers dissolved in $CHCl_3$ with 10% *ortho*-dichlorobenzene (*o*-DCB) as additive were spin-coated on the substrates and moved into the N_2-filled glovebox. After annealing at the corresponding temperature for 10 min, the devices were measured at room temperature. Representative transfer and output curves are shown in Fig. 2. The three polymers present the optimized hole mobilities after the polymer thin films were thermal annealed at 180 °C (Table S1). The hole mobilties of the DPP polymers were summarized at Table 2, in which the average values were calculated from eight devices.

All devices exhibit similar on/off ratios of 10^3–10^4 and V_T is around −0.11–8.59 V PDPP2T-DTT exhibits a average hole mobility of 2.88 $cm^2\ V^{-1}\ s^{-1}$, while the hole mobilties of PMDPP2T-DTT and P2MDPP2T-DTT are enhanced to 5.07 $cm^2\ V^{-1}\ s^{-1}$ and 4.63 $cm^2\ V^{-1}\ s^{-1}$. The asymmetric polymer PMDPP2T-DTT shows the maximum mobility of 5.32 $cm^2\ V^{-1}\ s^{-1}$. The hole mobilities in these DPP-DTT-based polymers are much higher than those reported polymers with similar conjugated backbone [22], which might be due to the longer side chains of the new polymers with improved crystalline properties. We also calculated the hole mobilities over the high gate voltage regime (−30 V to −80 V) as suggested in the literature [30]. PDPP2T-DTT was found to provide a

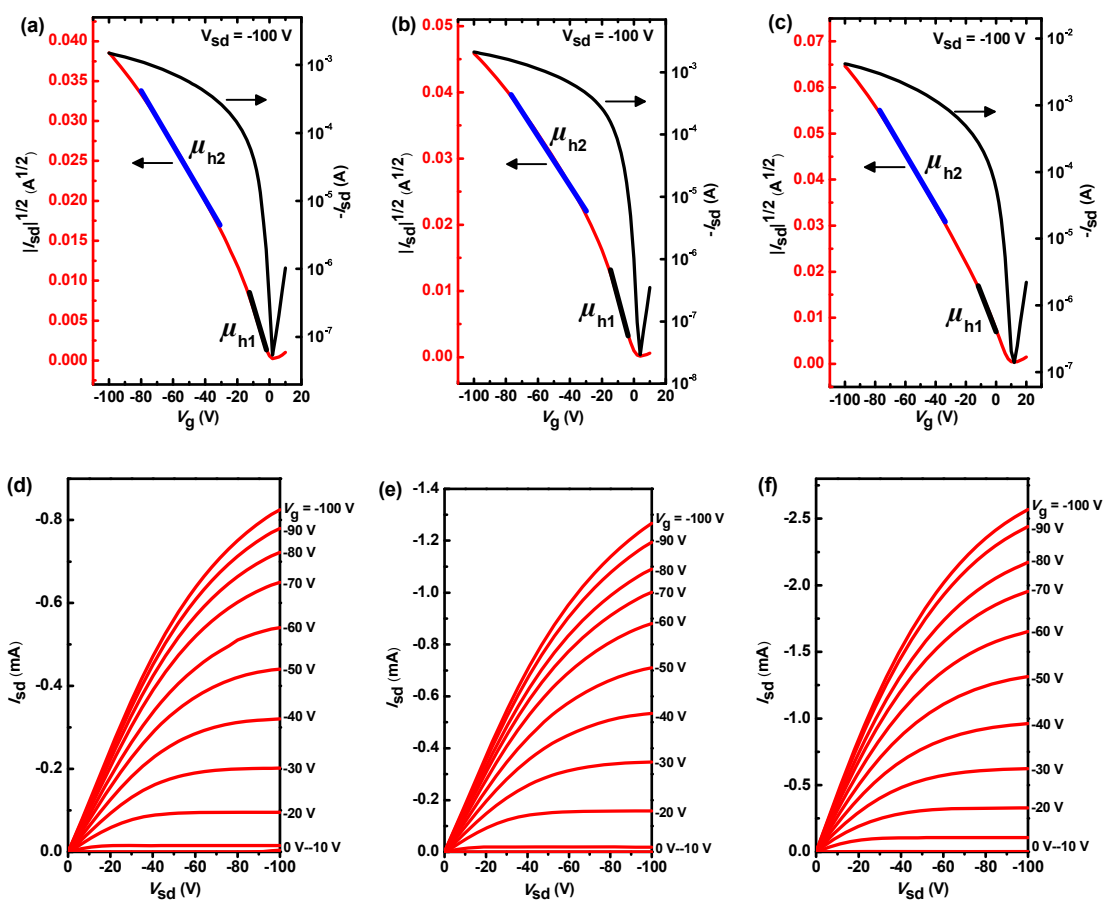


Fig. 2. (a)–(c) Transfer (fitting from different gate voltage region, μ_{h1}: −5 to −15 V and μ_{h2}: −30 to −80 V) and (d)–(f) output curves obtained from BGBC FET devices with the DPP polymer thin films spin cast from $CHCl_3$/*o*-DCB (10%) and annealed at 180 °C: (a, d) for PDPP2T-DTT; (b, e) for PMDPP2T-DTT; (c, f) for P2MDPP2T-DTT. The black lines in (a)–(c) are used for mobility calculations.

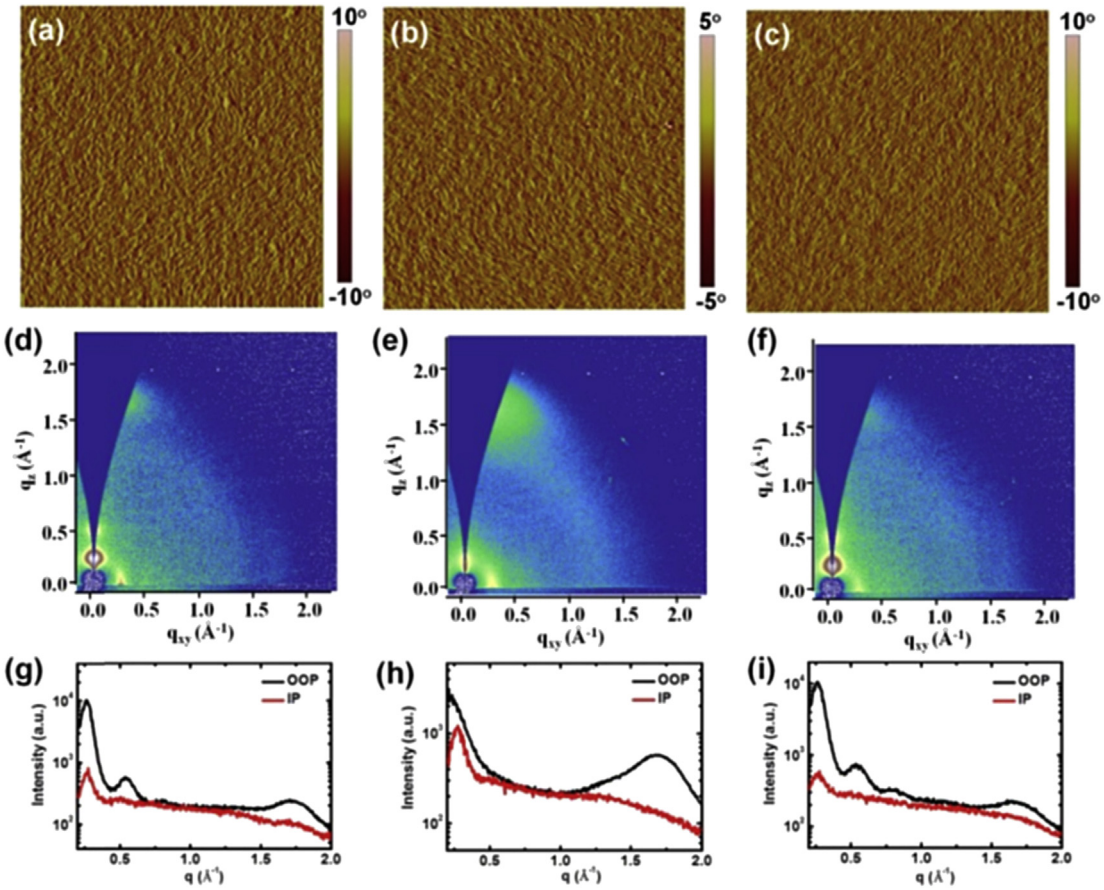


Fig. 3. Characteristics of the polymer thin films spin coated from $CHCl_3$/*o*-DCB and annealed at 180 °C. (a)–(c) AFM phase images (3 × 3 μm^2). (d)–(f) 2D-GIWAXS patterns and (g)–(i) the out-of-plane (OOP) and in-plane (IP) cuts of the corresponding 2D-GIWAXS patterns. (a), (d), (g) PDPP2T-TTT. (b), (e), (h) PMDPP2T-TTT. (c), (f), (i) P2MDPP2T-TTT.

Table 2
Field effect hole mobilities of the DPP polymers in a BGBC configuration. The thin films were thermal annealed at 180 °C for 10 min before measurement.

Polymer	μ_{h1}[a] (cm^2 V^{-1} s^{-1})		V_T (V)	μ_{h2}[b] (cm^2 V^{-1} s^{-1})	I_{on}/I_{off}	d_{100} (Å)	d_{010} (Å)
	Ave[c]	Max					
PDPP2T-DTT	2.88	3.16	−0.11	0.85	3 × 10^4	24.2	3.67
PMDPP2T-DTT	5.07	5.32	0.17	1.01	7 × 10^4	23.3	3.70
P2MDPP2T-DTT	4.63	5.27	8.59	2.22	4 × 10^3	24.2	3.79

[a] Fitting from gate voltage region of −5 to −15 V.
[b] Fitting from gate voltage region of −30 to −80 V.
[c] From eight devices.

hole mobility of 0.85 cm^2 V^{-1} s^{-1}, while the methylated polymers present increased mobilities of 1.01 cm^2 V^{-1} s^{-1} and 2.22 cm^2 V^{-1} s^{-1} (Table 1).

In order to provide the deep sight into the influence of methyl units on the charge transport properties, we investigate the molecular packing and crystalline properties using atom microscopy (AFM) and 2D grazing-incidence wide angle X-ray scattering (2D-GIWAXS) measurements. The thin films were spin-coated from $CHCl_3$ with 10% *o*-DCB on Si/SiO_2 substrates, following by thermal annealing at 180 °C for 10 min. As shown in Fig. 3a–c and Fig. S5, fiber-like structures are present in all DPP polymer thin films surface, indicating the good crystallinity. The thin films were further studied by 2D-GIWAXS measurement, as shown in Fig. 3d–i. PDPP2T-DTT shows a distinct (100) diffraction peak in the out-of-plane (OOP) direction, corresponding to a lamellar packing distance of 24.2 Å of the DT side chains. The (010) diffraction peak in the OOP direction for PDPP2T-DTT is related to the π-π stacking distance of 3.67 Å of the conjugated backbone. The (010) diffraction peaks in the in-plane (IP) is absent, which therefore we tentatively attribute this behaviour to the mixed "edge-on" and "face-on" orientation of the PDPP2T-DTT polymer chains on the surface. The methylated polymer P2MDPP2T-DTT presents similar orientation with strong (100) and (010) diffraction peak in the OOP direction. The π-π stacking distance of P2MDPP2T-DTT is 3.67 Å that is higher than that of PDPP2T-DTT, which should originated from twist backbone induced by methyl units. Interestingly, the asymmetric polymer PMDPP2T-DTT shows strong (100) diffraction peak in the IP direction and strong (010) diffraction peak in the OOP direction, which can attribute to the "face-on" orientation of PMDPP2T-DTT chains on the surface. It has been widely reported that "edge-on" configuration with π-π stacking ordering parallel to the substrate could be beneficial for charge carriers transport in FET devices

[31–33]. Only a few results show that conjugated polymers with "face-on" orientation can offer high electron mobilities [23,24]. Our results present a very good example that conjugated polymers with "face-on" orientation can realize high performance FETs.

It is desired to emphasize that, the reason for improved hole mobility in methylated polymers is still unclear, although we observed their different microstructure. We speculate that in methylated polymers the reduced HOMO levels will be helpful for charge injection between electrode (Au) and polymer thin films [34]. In addition, semi-crystalline conjugated polymers contain ordered and disorder regions in thin films, where some evidences suggest that disorder regions are crucial for charge hopping between different polymer chains [35,36]. Methylated polymers might have better aggregation in disorder region and thus provide better carrier mobilities. Further studies will be required to reveal the high mobilities in these methylated polymers.

In conclusion, three conjugated polymers based on DPP and DTT units without or with methyl groups were designed for FETs. Methylated polymers exhibit high hole mobilities up to 5.36 $cm^2 V^{-1} s^{-1}$ in FETs. Further studies reveal that methylated polymers perform high crystalline properties with "face-on" orientation. Our results demonstrate that methylated conjugated polymers have the great potential to realize high performance FETs.

Acknowledgment

We thank Ralf Bovee and Qiang Wang at Eindhoven University of Technology (TU/e, Netherlands) for GPC analysis. The measurements of NMR were performed at the Center for Physicochemical Analysis and Measurements in ICCAS. The help from Dr. Junfeng Xiang was acknowledged. This work was supported by the Recruitment Program of Global Youth Experts of China. The work was further supported by the National Natural Science Foundation of China (21574138, 91233205) and the Strategic Priority Research Program (XDB12030200) of the Chinese Academy of Sciences.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2016.07.012.

References

[1] J.Y. Back, H. Yu, I. Song, I. Kang, H. Ahn, T.J. Shin, S.-K. Kwon, J.H. Oh, Y.-H. Kim, Chem. Mater 27 (2015) 1732–1739.
[2] H.-R. Tseng, H. Phan, C. Luo, M. Wang, L.A. Perez, S.N. Patel, L. Ying, E.J. Kramer, T.-Q. Nguyen, G.C. Bazan, A.J. Heeger, Adv. Mater 26 (2014) 2993–2998.
[3] G. Kim, S.-J. Kang, G.K. Dutta, Y.-K. Han, T.J. Shin, Y.-Y. Noh, C. Yang, J. Am. Chem. Soc. 136 (2014) 9477–9483.
[4] Y. Ji, C. Xiao, Q. Wang, J. Zhang, C. Li, Y. Wu, Z. Wei, X. Zhan, W. Hu, Z. Wang, R.A.J. Janssen, W. Li, Adv. Mater 28 (2016) 943–950.
[5] Y.J. Cheng, S.H. Yang, C.S. Hsu, Chem. Rev. 109 (2009) 5868–5923.
[6] T. Lei, J.-Y. Wang, J. Pei, Chem. Mater 26 (2014) 594–603.
[7] Z. Fei, P. Boufflet, S. Wood, J. Wade, J. Moriarty, E. Gann, E.L. Ratcliff, C.R. McNeill, H. Sirringhaus, J.-S. Kim, M. Heeney, J. Am. Chem. Soc. 137 (2015) 6866–6879.
[8] P. Boufflet, Y. Han, Z. Fei, N.D. Treat, R. Li, D.-M. Smilgies, N. Stingelin, T.D. Anthopoulos, M. Heeney, Adv. Funct. Mater 25 (2015) 7038–7048.
[9] X. Wang, Z.-G. Zhang, H. Luo, S. Chen, S. Yu, H. Wang, X. Li, G. Yu, Y. Li, Polym. Chem. 5 (2014) 502–511.
[10] T. Lei, X. Xia, J.-Y. Wang, C.-J. Liu, J. Pei, J. Am. Chem. Soc. 136 (2014) 2135–2141.
[11] T. Lei, J.-H. Dou, Z.-J. Ma, C.-H. Yao, C.-J. Liu, J.-Y. Wang, J. Pei, J. Am. Chem. Soc. 134 (2012) 20025–20028.
[12] W. Li, W.S.C. Roelofs, M. Turbiez, M.M. Wienk, R.A.J. Janssen, Adv. Mater 26 (2014) 3304–3309.
[13] M.C. Scharber, M. Koppe, J. Gao, F. Cordella, M.A. Loi, P. Denk, M. Morana, H.-J. Egelhaaf, K. Forberich, G. Dennler, R. Gaudiana, D. Waller, Z. Zhu, X. Shi, C.J. Brabec, Adv. Mater 22 (2010) 367–370.
[14] J.S. Ha, K.H. Kim, D.H. Choi, J. Am. Chem. Soc. 133 (2011) 10364–10367.
[15] M.C. Scharber, M. Koppe, J. Gao, F. Cordella, M.A. Loi, P. Denk, M. Morana, H.-J. Egelhaaf, K. Forberich, G. Dennler, R. Gaudiana, D. Waller, Z. Zhu, X. Shi, C.J. Brabec, Adv. Mater 22 (2010) 367–370.
[16] Z. Fei, R.S. Ashraf, Z. Huang, J. Smith, R.J. Kline, P. D'Angelo, T.D. Anthopoulos, J.R. Durrant, I. McCulloch, M. Heeney, Chem. Commun. 48 (2012) 2955–2957.
[17] A. Casey, Y. Han, Z. Fei, A.J.P. White, T.D. Anthopoulos, M. Heeney, J. Mater. Chem. C 3 (2015) 265–275.
[18] W. Li, A. Furlan, K.H. Hendriks, M.M. Wienk, R.A.J. Janssen, J. Am. Chem. Soc. 135 (2013) 5529–5532.
[19] J. Hou, Z. Tan, Y. Yan, Y. He, C. Yang, Y. Li, J. Am. Chem. Soc. 128 (2006) 4911–4916.
[20] W. Li, A. Furlan, K.H. Hendriks, M.M. Wienk, R.A.J. Janssen, J. Am. Chem. Soc. 135 (2013) 5529–5532.
[21] A.V. Patil, W.-H. Lee, K. Kim, H. Park, I.N. Kang, S.-H. Lee, Polym. Chem. 2 (2011) 2907–2916.
[22] J.W. Jung, F. Liu, T.P. Russell, W.H. Jo, Energy Environ. Sci. 5 (2012) 6857–6861.
[23] M. Shahid, R.S. Ashraf, Z. Huang, A.J. Kronemeijer, T. McCarthy-Ward, I. McCulloch, J.R. Durrant, H. Sirringhaus, M. Heeney, Photovoltaic and field effect transistor performance of selenophene and thiophene diketopyrrolopyrrole co-polymers with dithienothiophene, J. Mater. Chem. 22 (2012) 12817–12823.
[24] J. Rivnay, M.F. Toney, Y. Zheng, I.V. Kauvar, Z.H. Chen, V. Wagner, A. Facchetti, A. Salleo, Unconventional face-on texture and exceptional in-plane order of a high mobility n-type polymer, Adv. Mater 22 (2010) 4359–4363.
[25] J.H. Park, E.H. Jung, J.W. Jung, W.H. Jo, A fluorinated phenylene unit as a building block for high-performance n-type semiconducting polymer, Adv. Mater 25 (2013) 2583–2588.
[26] S. Cho, J. Lee, M.H. Tong, J.H. Seo, C. Yang, Adv. Funct. Mater 21 (2011) 1910–1916.
[27] A. Zhang, C. Xiao, Y. Wu, C. Li, Y. Ji, L. Li, W. Hu, Z. Wang, W. Ma and W. Li, 2016, to be published.
[28] W. Li, K.H. Hendriks, A. Furlan, W.S.C. Roelofs, M.M. Wienk, R.A.J. Janssen, J. Am. Chem. Soc. 135 (2013) 18942–18948.
[29] K.H. Hendriks, W. Li, M.M. Wienk, R.A.J. Janssen, J. Am. Chem. Soc. 136 (2014) 12130–12136.
[30] I. McCulloch, A. Salleo, M. Chabinyc, Avoid the kinks when measuring mobility, Science 352 (2016) 1521–1522.
[31] A.R. Han, G.K. Dutta, J. Lee, H.R. Lee, S.M. Lee, H. Ahn, T.J. Shin, J.H. Oh, C. Yang, Adv. Funct. Mater 25 (2015) 247–254.
[32] T. Lei, J.-H. Dou, X.-Y. Cao, J.-Y. Wang, J. Pei, Adv. Mater 25 (2013) 6589–6593.
[33] B. Sun, W. Hong, Z. Yan, H. Aziz, Y. Li, Adv. Mater 26 (2014) 2636–2642.
[34] A. Kumatani, Y. Li, P. Darmawan, T. Minari, K. Tsukagoshi, On practical charge injection at the metal/organic semiconductor interface, Sci. Rep. 3 (2013) 1026.
[35] X. Zhang, H. Bronstein, A.J. Kronemeijer, J. Smith, Y. Kim, R.J. Kline, L.J. Richter, T.D. Anthopoulos, H. Sirringhaus, K. Song, M. Heeney, W. Zhang, I. McCulloch, D.M. DeLongchamp, Nat. Commun. 4 (2013) 2238.
[36] R. Noriega, J. Rivnay, K. Vandewal, F.P.V. Koch, N. Stingelin, P. Smith, M.F. Toney, A. Salleo, Nat. Mater 12 (2013) 1038–1044.