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Significantly increasing open-circuit voltage of the benzo[1,2-*b*:4,5-b′]dithiophene-*alt*-5,8-dithienyl-quinoxaline copolymers based PSCs by appending dioctyloxy chains at 6,7-positions of quinoxaline

Wenyan Su, Manjun Xiao, Qunping Fan, Juan Zhong, Jianhua Chen, Dongfeng Dang, Junwei Shi, Wenjin Xiong, Xongwei Duan, Hua Tan *, Yu Liu, Weiguo Zhu *

College of Chemistry, Xiangtan University, Key Lab of Environment-Friendly Chemistry and Application in Ministry of Education, Xiangtan 411105, China

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ABSTRACT

Two novel 5,8-disubstituted benzo[1,2-*b*:4,5-*b*′]dithiophene-*alt*-2,3-di(4-methoxylphenyl)-6,7-dioctyloxy-5,8-dithienyl-quinoxaline copolymers of PBDTDT-(Qx-2)-O and PBDTDT(Qx-2)-T were designed and synthesized, in which the substituents are branch dioctyloxy and di(octylthienyl), respectively. Their optical, thermal, electro-chemical and photovoltaic properties were investigated. Compared to the reported analogues, both one- and two-dimensional (1D and 2D) copolymers exhibited outstandingly increasing open-circuit voltages (V_{oc}) about 0.91–0.95 V in their bulk hetero-junction polymer solar cells (PSCs) with [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) acceptor. The maximum power conversion efficiency (PCE) of 6.31% with V_{oc} of 0.95 V, short-circuit current of 10.82 mA cm^{-2} and fill factor of 61.4% was obtained in the 2D-conjugated polymer of PBDTDT(Qx-2)-T/$PC_{71}BM$-based device. The PCE value is 1.42 times higher than that of the 1D-conjugated polymer of PBDTD(Qx-2)-O/$PC_{71}BM$-based device. Our work demonstrates that V_{oc} values of the quinoxaline-type copolymers based PSCs can remarkably be increased by appending dioctyloxy chains at 6,7-positions of quinoxaline.

1. Introduction

Driven by the urgent need for a renewable energy supply, bulk hetero-junction (BHJ) polymer solar cells (PSCs) have been developed extensively in recent years because of their potential for low cost, light weight, and applications in flexible and large-area devices [1–4]. As important components in PSCs, solution processable π-conjugated polymers used as donor materials have specially drawn great attention [5–7]. In order to obtain high-performance donor polymers, most of polymers with donor–acceptor (D–A) framework in the main chain were developed as this class of polymers has broad absorption spectra and high absorption coefficients in visible region resulting from intramolecular charge transfer (ICT) transitions [8–12]. To further decrease the highest occupied molecular orbit (HOMO) energy levels and fine-tune the intermolecular interaction, some two-dimensional (2D) conjugated polymers were recently presented, which contain conjugated side-chain in D–A backbone [13–15]. Researches have showed that these 2D copolymers exhibited much broader optical absorption, lower HOMO energy levels and higher hole mobility, as well as better photovoltaic performance

* Corresponding authors. Tel.: +86 731 58293377; fax: +86 731 58292251.
E-mail addresses: tanhua815@126.com (H. Tan), zhuwg18@126.com (W. Zhu).

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in comparison with their corresponding alkoxy-substituted one-dimensional (1D) conjugated counterparts [16–18].

For instance, Hou et al. reported a class of copolymers of PBDTDTQx-T and PBDTDTQx-O with an alternating D–A backbone of benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) and 2,3-di(3-alkyloxyphenyl)quinoxaline (Qx). The 2D copolymer of PBDTDTQx-T with di(alkylthiophene)-substituted BDT was found to exhibit the maximum power conversion efficiency (PCE) of 5.0% with an open-circuit voltage (V_{oc}) of 0.76 V in BHJ-PSCs, which is 1.67 times high value of the devices using its 1D-conjugated counterpart of PBDTDTQx-O with dialkyloxy-substituted BDT as donor materials [18]. In order to further study the effect of various substituted groups on photovoltaic properties of these BDT-*alt*-Qx copolymers, Chou et al. exhibited another 1D copolymer of PBDT-TFQ with 6,7-difluoro-2,3-di(3-(hexyloxy)phenyl)quinoxaline unit and its high-performance PSCs with the maximum PCE of 7.8% and V_{oc} of 0.76 V [19]. Hwang et al. displayed a novel 1D copolymer of PTIPSBDT-DTQx containing another alternating D–A backbone of ditriisopropylsilylethynyl-substituted BDT and 2,3-di(4-octyloxyphenyl)quinoxaline. The maximum PCE of 1.6% with V_{oc} of 0.81 V was obtained in the PTIPSBDT-DTQx based BHJ-PSCs [8]. The significant influence of various substituted groups on PCE of these copolymers based devices was observed. However, V_{oc} values only took little variation in these devices although these copolymers have various substituted groups, such as alkoxy at meta-(or para-)position of phenyl, fluorine (or hydrogen) at 6,7-positions of quinoxaline and alkyloxy (or alkylthienyl or triisopropylsilylethynyl) at 7,8-positions of BDT unit. Furthermore, it is still unknown how do alkyloxy groups at 6,7-positions of quinoxaline influence photovoltaic properties of their D−A copolymers.

Recently, Moon et al. reported a class of quinacridone-*alt*-2,3-diphenyl-quinoxaline copolymers of PQCDTQ-a with octyloxy chains around the backbone at 6,7-positions of quinoxaline and PQCDTQ-b with octyloxy chains far away the backbone at 4-positions of phenyl. It was found that both polymers exhibited different ICT effect and HOMO energy levels depending on the octyloxy chain position. Wherein, PQCDTQ-a exhibited a weaker ICT and lower HOMO energy level, as well as better photovoltaic properties with PCE of 4.0% and V_{oc} of 0.85 V, than the PQCDTQ-b in PSCs [20]. In addition, some 5,6-dioctyloxy-benzo[*c*][1,2,5]thiadiazole-based polymers were further found to exhibit a weaker ICT and lower HOMO energy level than those copolymers without 5,6-dioctyloxy chains [21,22]. Therefore, it is very interesting in studying the effect of alkyloxy chain position on photovoltaic properties of their resulting D−A copolymers. In this wok, for this reason, a novel class of 5,8-disubstituted benzo[1,2-*b*:4,5-*b*′]dithiophene-*alt*-2,3-di(4-methoxylphenyl)-6,7-dioctyloxy-5,8-dithienyl-quinoxaline copolymers of PBDTDT(Qx-2)-O and PBDTDT(Qx-2)-T were designed and synthesized, in which substituents are branch dioctyloxy and di(octylthienyl) groups, respectively. As shown in Chart 1, compared to the reported analogic copolymers [8,18,19], both copolymers here were appended with methoxyl groups at 4-position of phenyl and octyloxy groups at 6,7-positions in the 2,3-diphenyl-quinoxaline building unit. As long branched side chains can weaken intermolecular interactions, leading to an increasing V_{oc} but a lower J_{sc}, in contrast, short straight side chains can promote intermolecular interactions, rendering an enhanced J_{sc} value [21–26], we expected that two short-chain methoxyl units at para-positions of phenyl and two long-chain octyloxyl groups instead of fluorine and hydrogen atoms at 6,7-positions of quinoxaline are able to improve photovoltaic property with a high V_{oc} value for their copolymers in PSCs due to the above corporate effect.

The synthetic routes for PBDTDT(Qx-2)-O and PBDTDT(Qx-2)-T are shown in Scheme 1. Their optical, thermal, electrochemical, charge-transporting and photovoltaic properties were investigated. As expected, the 2D-conjugated PBDTDT(Qx-2)-T with a branch di(octylthienyl)-substituted BDT unit shows a smaller optical band gap, broader absorption range and lower HOMO energy level than the 1D-conjugated PBDTDT(Qx-2)-O with a branch octyloxy-substituted BDT unit. Hole mobility of the PBDTDT(Qx-2)-T/$PC_{71}BM$ blend (1:4, *w/w*) is 1.41×10^{-4} cm^2 V^{-1} s^{-1}, which is three times high value of the PBDTDT(Qx-2)-O/$PC_{71}BM$ blend (1:4, *w/w*). More importantly, both copolymers exhibited a high V_{oc} value of 0.91–0.95 V in their BHJ-PSCs using [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as acceptor. The maximum PCE of 6.31% with V_{oc} of 0.95 V was obtained in the PBDTDT(Qx-2)-T/$PC_{71}BM$ based device. To our best knowledge, the recorded maximum V_{oc} value here is highest than those for the previous benzo[1,2-*b*:4,5-*b*′]dithiophene-*alt*-5,8-dithienylquinoxaline copolymeric derivatives in BHJ-PSCs. The V_{oc} values in both copolymers-based devices were remarkably increased by appending dioctyloxy chains at 6,7-positions of quinoxaline.

2. Results and discussion

2.1. Synthesis and thermal property

The synthetic route to monomer and polymer is outline in Scheme 1. Compound **2** was prepared through a ring-opening reaction and used immediately to synthesize compound **3** via the condensation reaction. The compound **3** then reacted with 2-thienyl tributyltin via the classic Stille coupling reaction to get DT(Qx-2) at the present of tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) with a high yield of 82.3%. DT(Qx-2) was brominated with *N*-bromosuccininide (NBS) in tetrahydrofunan (THF) to afford the monomer DT(Qx-2)Br_2 with a high yield of 92.7%. The D–A copolymers of PBDTDT(Qx-2)-O and PBDTDT(Qx-2)-T were obtained by palladium-catalyzed Stille-coupling polymerization between DT(Qx-2)Br_2 and the corresponding organotin reagents with a moderate yield. The chemical structures of compounds **3**, DT(Qx-2) and DT(Qx-2)Br_2 were confirmed by ^1H NMR, ^{13}C NMR, MALDI-TOF mass spectroscopy. The molecular weights of polymers were determined with gel permeation chromatography (GPC) relative to polystyrene standards. The number average molecular weights (M_n) of 11.9×10^4 and 11.6×10^4 g mol^{-1} were observed for PBDTDT(Qx-2)-O