



Effect of side chain position and conformation of quinacridone–quinoxaline based conjugated polymers on photovoltaic properties



Kyu Hyo Hwang, Doo Hun Kim, Min Hee Choi, Jae Pil Han, Doo Kyung Moon*

Department of Materials Chemistry and Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

ARTICLE INFO

Article history:

Received 31 July 2015

Received in revised form 8 October 2015

Accepted 24 October 2015

Available online 30 October 2015

Keywords:

Quinacridone

Quinoxaline

Side-chain

Suzuki coupling reaction

Bulk heterojunction polymer solar cells

ABSTRACT

Poly[quinacridone-*alt*-dithienylquinoxaline](PQCDTQx)s series with alkoxy chains at different anchoring positions (*meta*- or *para*-) in quinoxaline were synthesized via Suzuki coupling reaction. The ICT effects were stronger at the *meta* than *para*. *Meta*-polymers had enhanced π – π stacking of the polymer main chains and showed a lower HOMO energy level than those of the *para*, from -5.26 to -5.16 eV, because of the greater electron-withdrawing effects of the alkoxy groups. As a result, the photovoltaic device comprising a PQCDTQx-mEH/PC₇₁BM (1:4) blend system exhibited performance, with a PCE, J_{sc} , V_{oc} , and FF of 2.1%, 4.8 mA/cm², 0.73 V, and 59.3%, respectively.

© 2015 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Introduction

Polymer solar cells (PSCs) have recently received much attention, because they use an unlimited amount of photovoltaic energy, which is reproducible. And they offer many advantages, such as low production costs, lightweight, flexibility and suitability to large-scale production. Bulk heterojunction (BHJ) systems, combining conjugated polymers as the electron donors and fullerene derivatives as the electron acceptors, have played a significant role in enhancing the photovoltaic performance of PSCs. Therefore, BHJ PSCs have been the subject of diverse studies [1–5]. The formation of a donor–acceptor (D–A) system by the alternate copolymerization of an electron-donating unit (D) and electron-accepting unit (A) is a typical method for designing the molecular structures of conjugated polymers for high-efficiency BHJ PSCs. An appropriate selection of these D and A building blocks can be used to effectively tune the energy levels of PSCs [6].

The use of quinacridone (QC) as an electron-donating unit is well known, because of its red–violet pigments, ordered structure, self-assembly characteristics, and high hole mobility. It has been increasingly used in organic thin-film transistors (OTFTs) [7,8]. The Takimiya group reported the use of a polymer composed of QC derivatives with a high hole mobility (0.2 cm²/V s) in OTFTs [9].

Quinoxaline (Qx) derivatives are widely used as the electron-accepting units owing to their superior electron-withdrawing properties, caused by the presence of two imine nitrogens. The structural modification of Qx derivatives has been readily achieved by using a variety of substituents to change their solubility and electronic properties [10–12].

An understanding of the correlation between the molecular structure and the device performance is also important for the production of high-efficiency PSCs. The open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) play important roles in determining the power conversion efficiency (PCE) of PSCs. V_{oc} is determined from the difference between the lowest unoccupied molecular orbital (LUMO) of the electron acceptor and the highest occupied molecular orbital (HOMO) of the electron donor, i.e., the difference in their electron affinities. Therefore, the HOMO level of the polymer donor is an important factor in determining the PCE [13]. A previous study reported the tuning of the HOMO and LUMO levels of conjugated polymers by changing their electron affinities according to the positions of the side chains introduced, while retaining the same polymer backbone repeating unit [14]. Takimiya et al. reported an enhancement in the photovoltaic properties by determining its exciton diffusion, charge separation, and charge transport properties by using the effect of the type of side chain used on a polymer's crystallinity and backbone orientation [15]. Moreover, Wang et al. demonstrated a maximum PCE of 5% using a thiophene–quinoxaline (TQ)-based alternating copolymer to

* Corresponding author. Tel.: +82 2 450 3498; fax: +82 2 444 0765.
E-mail address: dkmoon@konkuk.ac.kr (D.K. Moon).

study its aggregation, orientation, and phase behavior as a function of side chain type [16].

In this study, the deep HOMO levels and backbone orientations of polymers were observed according to the position and form of the Qx side chain and the morphological changes caused by the miscibility of Qx with 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C71(PC₇₁BM). In order to accomplish these characteristics, different QC-Qx-based conjugated polymers, poly[quinacridone-*alt*-dithienyl-(3-octyloxy phenyl)quinoxaline] (PQCDTQx-m8), poly[quinacridone-*alt*-dithienyl-(3-(2-ethylhexyloxy phenyl)quinoxaline] (PQCDTQx-mEH), poly[quinacridone-*alt*-dithienyl-(4-octyloxy phenyl)quinoxaline] (PQCDTQx-p8), and poly[quinacridone-*alt*-dithienyl-(4-(2-ethylhexyl)phenyl)quinoxaline] (PQCDTQx-pEH), were synthesized by introducing two types of side chains (linear octyl or branched 2-ethylhexyl) at two different phenyl ring positions (*meta*- or *para*-) on Qx. By UV–visible (UV–vis) spectroscopy, an absorption shoulder peak (λ_{sh}) was identified at the *meta* position of the polymer in both the solution and thin-film states. Moreover, the HOMO and LUMO energy levels of the resulting polymers were regulated according to the differences in the electron-donating abilities caused by the position of the alkoxy side chain. The backbone orientations of the polymers, according to the positions and conformations of the side chains, were confirmed by X-ray diffraction (XRD) measurements. When PQCDTQx-mEH was used as the donor polymer, the best photovoltaic performance (PCE = 2.1%) was achieved at PQCDTQx-mEH:PC₇₁BM (1:4, w/w).

Results and discussion

Synthesis and characterization of polymers

Scheme 1 shows the chemical structures of the monomers and polymers used, along with their synthetic processes. The relevant monomers (Qx derivatives) used in this study were synthesized by introducing two types of side chains (linear octyl or branched 2-ethylhexyl) onto the *meta*- and *para*-positions of the phenyl ring according to the previously reported procedures [27–29]. Thiophene was introduced as the conjugated linker on the acceptor unit to synthesize 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxaline (M2), 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(3-(2-ethylhexyloxy)phenyl)quinoxaline (M3), 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline (M4), and 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy)phenyl)quinoxaline (M5) according to the procedures as described in Scheme 1. As shown in Scheme 1, poly[quinacridone-*alt*-dithienyl-quinoxaline] (PQCDTQx-m8, PQCDTQx-mEH, PQCDTQx-p8, and PQCDTQx-pEH) was synthesized via the Suzuki coupling reaction of 2,9-diboronester-*N,N'*-di (2-octyl-dodecyl)quinacridone (M1) and M2 through M5. The polymerization of the three polymers, PQCDTQx-m8, PQCDTQx-p8, and PQCDTQx-pEH, was performed for 24 h at 90–95 °C using toluene, Pd(PPh₃)₄(O), a 2 M aqueous potassium carbonate solution, and Aliquat 336 as the solvent, catalyst, base, and surfactant, respectively. However, because of its low solubility, PQCDTQx-mEH was polymerized for 48 h using toluene/DMF (9:1) as the solvent. After polymerization was completed, the polymers were end-capped with bromothiophene. The polymers were then recovered by precipitation in methanol. Purification was performed using a Soxhlet extraction, sequentially with methanol, acetone, and chloroform. Finally, the polymers were recovered by precipitating the chloroform fraction in methanol. As a result, the yields of PQCDTQx-m8, PQCDTQx-mEH, PQCDTQx-p8, and PQCDTQx-pEH were 89, 88, 51, and 91%, respectively. The derived polymers dissolved easily in common organic solvents such as tetrahydrofuran (THF), chloroform, chlorobenzene, and *o*-dichlorobenzene, forming homogeneous violet semitransparent films after spin coating. The structures of

the synthesized polymers were confirmed via ¹H NMR spectroscopy (see the electronic Supplemental information (ESI), Fig. S1) and elemental analysis (EA).

Table 1 shows the measured molecular weights of the polymers; As shown in Table 1, PQCDTQx-m8, PQCDTQx-mEH, PQCDTQx-p8, and PQCDTQx-pEH exhibited number average molecular weights (M_n) of 112, 113, 197, and 129 kDa, respectively, and polydispersity indices (PDIs) of 2.10, 2.01, 2.32, and 2.53, respectively. Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the polymers, and the TGA results are shown in the ESI (Fig. S2). According to the TGA results, the temperature at which a 5% thermal weight loss occurred in N₂ atmosphere was >340 °C for all the polymers. All the synthesized polymers exhibited good thermal stability, and their suitability for device fabrication and application was verified.

Optical properties

To examine the effects of side chain position on the optoelectronic properties of QC-Qx-based polymers, normalized UV–vis absorption spectra of the polymers in both the solution and thin-film states are shown in Fig. 1, and the results are summarized in Table 2. As indicated in Fig. 1, all the polymers displayed two absorption peaks between 300 and 800 nm. The peak in the high-energy region (300–450 nm) was owing to the π - π^* transitions of the donor segments (QC group), whereas the peak in the low-energy region (450–700 nm) was caused by an intramolecular charge transfer (ICT) transition between the donor and acceptor [17,18]. The maximum absorption peaks of PQCDTQx-m8 and PQCDTQx-mEH in solution were 399 and 555 nm (λ_{sh} = 600 nm), and 402 and 555 nm (λ_{sh} = 600 nm), respectively, while those for PQCDTQx-p8 and PQCDTQx-pEH appeared at 393 and 544 nm, and 393 and 545 nm, respectively. The absorption coefficient calculated from the maximum absorption peak (λ_{max}) of each polymer in the solution was 7.0×10^4 , 7.8×10^4 , 8.2×10^4 , and 6.7×10^4 M⁻¹ cm⁻¹ for PQCDTQx-m8, PQCDTQx-mEH, PQCDTQx-p8, and PQCDTQx-pEH, respectively. The maximum absorption peaks of PQCDTQx-m8 and PQCDTQx-mEH in the thin film were 399, 575 nm (λ_{sh} = 607 nm), and 399, 571 nm (λ_{sh} = 593 nm) respectively and these values red-shifted by 20 and 16 nm, respectively, in comparison to the solution-state results. PQCDTQx-p8 and PQCDTQx-pEH displayed peaks at 393, 541 nm (λ_{sh} = 579 nm), and 393, 551 nm (λ_{sh} = 585 nm), respectively, and were similar to the peaks observed in solution. The occurrence of a red shift in the thin-film state could have been caused by the aggregation and π - π intermolecular interactions of the polymer main chains, which were stronger in the solid state [19,20]. Accordingly, because the polymers in the *meta* position showed a greater red-shift, stronger polymer main chain aggregation and more ordered π - π stacking occurred to induce more effective intermolecular interactions, enabling smaller optical band gaps to be obtained from the absorption occurring in a broader region of the spectrum. Moreover, when the side chain was introduced in the *meta* position (PQCDTQx-m8 and PQCDTQx-mEH), shoulder peaks appeared in both the solution (λ_{sh} = 600 nm) and thin-film (λ_{sh} = 607 and 593 nm) states, because polymers in the *meta* position have strong aggregation and excellent π - π stacking even in dilute solutions [21,22]. When the side chains were introduced in the *para* position (PQCDTQx-p8 and PQCDTQx-pEH), shoulder peaks were not observed in solution; however, absorption shoulder peaks at 579 and 585 nm were observed in the thin-film state, respectively. The position of side chain attachment affected the stacking properties, polymer chain interaction, and UV–vis absorption region. However, no significant difference in the UV–vis spectra was observed by the type of side chain [30]. The calculation of the optical band gaps (E_g^{opt}) of the four polymers

Download English Version:

<https://daneshyari.com/en/article/228231>

Download Persian Version:

<https://daneshyari.com/article/228231>

[Daneshyari.com](https://daneshyari.com)