



# Novel fluoride-substituted donor/acceptor polymers containing benzodithiophene and quinoxaline units for use in low-band gap solar cells

Ashutosh Singh, Ravinder Singh, Chein-Min Lin, Murali Krishna Pola, Chiao-Kai Chang, Kung-Hwa Wei\*, Hong-Cheu Lin\*

Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

## ARTICLE INFO

### Article history:

Received 16 December 2015

Received in revised form 15 March 2016

Accepted 19 March 2016

Available online 21 March 2016

### Keywords:

Donor/acceptor polymer

Low-band gap polymer

Fluoride-substituted polymer

Benzodithiophene

Quinoxaline

Stille polycondensation

## ABSTRACT

In this study we used Stille polycondensation to synthesize a series of low-band gap fluoride-substituted conjugated polymers containing electron-donating benzodithiophene (BDT) and electron-accepting quinoxaline (Qx) units, with the latter presenting either two or four fluoride atoms. These donor/acceptor polymers exhibited a broad absorption range (from 300 to 750 nm), with band gap energies of less than 1.20 eV (measured using cyclic voltammetry). Because of their strongly electron-donating thiophene units, the donor/acceptor polymers featuring the more highly fluorinated structures possessed the lowest band gaps (as low as 1.14 eV) and, thus, induced the greatest photovoltaic performance among these tested polymers. The highest power conversion efficiency (2.13%) was obtained from the polymer solar cell featuring an active layer of the polymer **PTF2** blended with PC<sub>70</sub>BM (1:1.5, w/w), with a short-circuit current density, open circuit voltage, and fill factor of 8.7 mA cm<sup>-2</sup>, 0.72 V, and 0.34, respectively.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Research into polymer solar cells (PSCs) has drawn widespread attention from both academia and industry because of their light weight, flexibility, and inexpensive high-throughput production using, for example, roll-to-roll fabrication [1–3]. Nevertheless, one of the crucial factors limiting the performance of PSCs is their low absorption in some regions of the terrestrial solar spectrum. Accordingly, many attempts have been made to tailor the structures of organic electronic materials, including low-band gap conjugated polymers, to match the absorption spectrum of the active layer to the solar spectrum [4]. To date, the most effective approach toward the design of low-band gap polymers has been to copolymerize donor (D) and acceptor (A) structural moieties into the polymer backbones [5–8]. A low-band gap polymer is obtained when copolymerizing an A monomer featuring a low-energy lowest unoccupied molecular orbital (LUMO) with a D monomer having a high-energy highest occupied molecular orbital (HOMO)—the result of intramolecular charge transfer (ICT) from the D units to the A units in the D/A polymer [6].

In the photovoltaic applications of low-band gap D/A copolymers, the D units play several important roles. Among the various established electron-donor units, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) [9–12] has attracted much attention because of its symmetrical and planar conjugated structure, as well as its ability to enhance the photovoltaic performance of PSCs

\* Corresponding authors.

E-mail addresses: [khwei@mail.nctu.edu.tw](mailto:khwei@mail.nctu.edu.tw) (K.-H. Wei), [linhc@mail.nctu.edu.tw](mailto:linhc@mail.nctu.edu.tw) (H.-C. Lin).

incorporating its D/A copolymers. The comparison work summarized by Huo and Huo presented the presence of BTD unit showed the highest PCE (7–8%) compared to other corresponding D units in their polymer design [9]. Furthermore, increase the alkoxy chain lengths in the BDT unit can overcome the issue of poor solubility in post-polymerization [13,14], while also resulting in low-band gap copolymers [15]. In addition, extending the aromatic side chains in the BTD unit can result in greater planarity and conjugation, as well as higher electron donating ability from the D units to the A units.

Furthermore, quinoxaline (Qx) is a typical electron-deficient A unit exhibiting strong electronegativity as a result of the two nitrogen atoms in its electron-deficient N-heterocyclic ring. This n-type building block has been exploited in polymers featuring typical D/A structures, with potential applications in systems requiring high photovoltaic performance [6–24]. Changing the substituents on the Qx units can modify the molecular energy levels [9], as well as impact the optical properties, of corresponding copolymers. Indeed, several groups have studied the effects of slight extensions of the Qx ring with phenyl [4] and thiophene [28] units and flexible chains. The resulting low-band gap materials have provided PSCs displaying quite good performance, including high power conversion efficiencies (PCEs) [25–28]. Xu and coworkers studied the side-chain engineering of fluorinated Qx unit copolymerized with various BTD units containing different alkyl (or alkoxy) pendants to have the highest PCE value of 5% (with the band gap of 2.13 eV) [4], where the branched alkoxy groups induced better lamellar-like ordering but poorer face-to-face packing behavior. However, Pranabesh Dutta and co-workers presented their work on Qx-based copolymers PTNDDT-QX-I and PTNDDTQX-II, where Qx units were extended by *para* and *meta*-octoxyphenyl moieties and copolymerized with thiophene-bridged naphtho[1,2*b*:5,6-*b'*]dithiophene [15], with a narrow band-gap of 1.7 eV and PCE < 1.8%. Therefore, BTD unit was selected as our donor monomer in this study. Furthermore, the incorporation of fluorine (F) [4] atoms into the A unit can enhance the electron withdrawing properties of low-band gap conjugated polymer systems, improving the photovoltaic performance and increasing PCEs. Inspired by such results of analogous D/A copolymers and various conjugated polymers, we have been interested in extending the structure of the Qx unit by adding additional phenyl rings bearing heterocyclic rings and F atoms. Only a few examples [29–32] exist of low-band gap D/A structures (Eg < 1.9 eV), with BDT as the D unit and Qx as the A unit, providing PSCs displaying practically applicable photovoltaic properties (PCE > 5%).

In this study, we synthesized low-band gap polymers having D/A structures based on BDT and Qx for solar cell applications. With enhanced conjugation of the Qx ring through attachment of a heterocyclic (pyrrole) unit and Schiff base formation for further extension to phenyl rings presenting either one or two F atoms, we synthesized the two Qx-based acceptor units **AM1** and **AM2**. Combining these two **A** monomers with two BTD-based **D** units (**DM1**, **DM2**), we synthesized four polymers (**PTF1**, **POF1**, **PTF2**, and **POF2**) through Stille polycondensation and examined the behavior of PSCs incorporating them.

## 2. Experimental

### 2.1. Materials and instrumentation

All reagent-grade chemicals and solvents were purchased from Aldrich, TCI, Fluka, TEDIA, ACROS, and Lancaster. Tetrahydrofuran (THF) was distilled over sodium/benzophenone prior to use. Chloroform (CHCl<sub>3</sub>) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were purified by refluxing over CaH<sub>2</sub> and then distilling. All other solvents were degassed with N<sub>2</sub> for 1 h prior to use.

UV-Vis absorption spectra were recorded from dilute solutions (10<sup>-5</sup> M) in *o*-dichlorobenzene (ODCB), using a HP G1103A spectrophotometer. Solid films for UV-Vis measurements were spin-coated onto glass plates from CHCl<sub>3</sub> solutions at a concentration of 5 mg mL<sup>-1</sup>. Fourier transform infrared (FTIR) spectra of samples (dispersed in KBr disks) were recorded on a Perkin-Elmer Spectrum 100 Series instrument. <sup>1</sup>H NMR spectra were recorded using a Bruker DX-300 (300 MHz) spectrometer and 500 MHz Varian Inova NMR spectrometer, with CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub> and chlorobenzene-*d*<sub>5</sub> as solvents. Thermogravimetric analyses (TGA) and Thermogravimetric derivative (DTG) were conducted with a TA Instruments Q500 at a heating rate of 20 °C/min under nitrogen. Flash chromatography was performed through Merck silica gel 60 (230–400 mesh) under compression using desired solvents. Elemental analysis (EA) was conducted using a HERAEUS CHN-OS RAPID elemental analyzer. Molecular weights (Mn, Mw) were determined through gel permeation chromatography (GPC) using Waters 1515 (isocratic HPLC pump) and 2414 (reflective index detector) instruments and THF solutions of the copolymers (1 mg mL<sup>-1</sup>). Transition temperatures were determined by differential scanning calorimetry (DSC, Perkin-Elmer Pyris 7) with a heating rate of 10 °C/min. XRD patterns were recorded by powder samples on glass substrates using Bruker D2 Phaser diffractometer. Cyclic voltammetry (CV) of copolymer solutions in 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile was performed using a BAS 100 electrochemical analyzer and a standard three-electrode electrochemical cell at room temperature (scanning rate: 100 mV s<sup>-1</sup>). During CV measurements, the cell featured an ITO glass coated with a thin layer of polymer, a platinum wire as the counter electrode and a silver wire as the quasi-reference electrode; Ag/AgCl (3 M KCl) electrode was used as a reference electrode for all potentials quoted herein. The redox couple of ferrocene/ferrocenium ion (Fc/Fc<sup>+</sup>) was used as an external standard. The HOMO and LUMO energy levels were determined from the values of E<sub>ox</sub>/onset and E<sub>red</sub>/onset for the solid films, which were drop-cast at similar thicknesses from THF (for **PTF2**) and ODCB (for **PTF1**, **POF1**, and **POF2**) solutions (ca. 2 mg mL<sup>-1</sup>). The topologies of the films were investigated using atomic force microscopy (AFM, Veeco dilnnova; scanning rate: 3–4 Hz), performed in the tapping mode in a dry environment

Download English Version:

<https://daneshyari.com/en/article/1399151>

Download Persian Version:

<https://daneshyari.com/article/1399151>

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