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Low band gap polymer consisting of quinacridone and diketopyrrolopyrrole and isoindigo units: correlation of ordered structure and intramolecular charge transfer properties

Doo Hun Kim[a], Ho Jun Song[b], Eui Jin Lee[a], Eui Jin Ko[a], Doo Kyung Moon[a,*]

[a] Department of Material Chemistry and Engineering, Konkuk University, Seoul 143-701, Republic of Korea
[b] Cungcheong Regional Division IT Convergence Material R&D Group, Korea Institute of Industrial Technology, 89 Yangdaegiro-gil, Ipjang-myeon, Seobuk-gu, Cheonan-si, Chungcheongnam-do 331-822, Republic of Korea

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ABSTRACT

Demand for low band gap polymer materials is driven by the fast growing organic photovoltaic industry. In the present study, to develop highly functional conjugated polymers, poly[quinacridone-diketopyrrolopyrrole] (PQCDPP) and poly[quinacridone-isoindigo] (PQCDIG) were synthesized via the Suzuki coupling reaction. While these two polymers provided high absorption in the region of over 700 nm, PQCIDG had broader absorption across the visible spectrum (300–600 nm) than PQCDPP because a greater intramolecular charge transfer occurs between the quincaridone and isoindigo units. Based on X-ray diffraction (XRD) results, large factions of the two polymers exhibited a face-on orientation with respect to the substrate, and the orientation distributions of 24.5° were more dominant in PQCIDG, compared with PQCDPP. In this study, we fabricated enhanced-polymer-based bulk-heterojunction (BHJ) solar cells using a normal structure of ITO/PEDOT:PSS/active-layer/Al and assessed its performance in terms of photovoltaic characteristics. The PQCIDG-based devices (polymer/$PC_{71}BM = 1:3$) showed power conversion efficiency (PCE) of 2.7% with open circuit voltage (V_{oc}) of 0.83 V, short circuit current (J_{sc}) of 7.4 mA/cm^2 and fill factor (FF) of 43.1%.

1. Introduction

Semiconducting polymers are used in a wider range of applications, including organic light emitting diodes(OLEDs), [1–3] organic photovoltaic cells (OPVs) [4–9], organic thin film transistors (OTFTs) [10–12]. In particular, polymer application in photovoltaic cells (OPV) draws international attention for promising results, associated with its environment-friendly and cost-effectiveness advantages. Bulk heterojunction (BHJ) polymer solar cells (PSC) hold great promise because of low-cost fabrication, roll-to-roll processing and large area coverage, and the optimization of molecular structure of polymers is a crucial step in achieving the desired photovoltaic performance of PSC. Conjugated polymers are considered ideal when they meet the following criteria: (1) low band gap for wide absorption spectrum (2) crystallite structure to achieve good charge transport (3) low highest occupied molecular orbital (HOMO) energy level to achieve high V_{oc} and (4) appropriate lowest unoccupied molecular orbital (LUMO) energy levels required for effective electron transfer to fullerene.

As a way of reducing the band gap, electron withdrawing properties of the acceptor can be incorporated into the main chain of the polymer to construct a donor (D)–acceptor (A) (D–A) type. The D–A type low band gap polymers provide great potential because it is easy to improve their electron properties for a wider absorption spectrum by modifying unique D–A characteristics [13].

Diketopyrrolopyrrole (DPP) and isoindigo (IDG) pigments are widely used as a strong acceptor of D–A conjugated polymers [14–16].

All DPP compounds are flat in an ordered structure, and strong π–π interaction of polymer chains becomes possible, enabling charge delocalization and intramolecular charge hopping for effective carrier mobility [17]. Yang et al. claimed a very high hole mobility of 12.25 cm^2 V^{-1} s^{-1} by applying DPP derivatives (ε-chain) as an acceptor to OFET and modifying intramolecular π–π interactions [18].

The IDG-based polymers reportedly have a wide absorption spectrum, low-lying HOMO (−5.30 to −5.90 V) and LUMO (−3.70 to −4.00 V), indicating a low band gap ranging from 1.3 to 1.8 [16]. Peng et al. introduced a new D–A type polymer by synthesizing fluorinated isoindigo after inserting fluorine atoms into IDG. They claimed the D–A type polymers had a band-gap of

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[*] Corresponding author. Fax: +82 2 444 0765.
E-mail address: dkmoon@konkuk.ac.kr (D.K. Moon).

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1.6 and UV absorption spectrum of 300–800. Also, they found a shoulder peak resulted from fluorine-induced aggregation between polymer backbones [19].

Quinacridone(QC) derivatives, which are known as red-violet pigments, are also used as OTFTs material because their high crystallinity and unique self-assembly increase hole mobility. However, small molecules and oligomer forms of QC derivatives limit their use for polymers. Recently, Takimiya et al. unveiled novel QC derivative-based polymers that have high hole mobility of 0.2 $cm^2 V^{-1} s^{-1}$ and are designed for use in OTFTs [20].

In this study, we employed DPP, IDG derivatives and QC derivatives to synthesize two novel polymers of poly[quinacridone-diketopyrrolopyrrole](PQCDPP) and poly[quinacridone-isoindigo](PQCIDG). These synthetic polymers are characterized by strong electron-withdrawing, wide absorption spectrum and strong intramolecular charge transfer. The structure and properties of the synthetic polymers were characterized and compared. The efficiency of BHJ devices fabricated using these polymers and $PC_{71}BM$ (3′H-cyclopropa[8,25][5,6]fullerene-C70-D5h(6)-3′-butanoic acid, 3′-phenyl-, methyl ester) was also assessed.

2. Experimental

2.1. Instruments and characterization

Unless otherwise specified, all the reactions were carried out under nitrogen atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230–400 mesh, Merck) as the stationary phase. 1H-NMR spectra were performed in a Bruker ARX 400 spectrometer using solutions in $CDCl_3$ and chemical were recorded in ppm units with TMS as the internal standard. The elemental analyses were measured with EA1112 using a CE Instrument. Electronic absorption spectra were measured in chloroform using a HP Agilent 8453 UV–vis spectrophotometer. The cyclic voltammetric waves were produced using a Zahner IM6eX electrochemical workstation with a 0.1 M acetonitrile (substituted with nitrogen for 20 min) solution containing tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6) as the electrolyte at a constant scan rate of 50 mV/s. ITO, a Pt wire, and silver/silver chloride [Ag in 0.1 M KCl] were used as the working, counter, and reference electrodes, respectively. The electrochemical potential was calibrated against Fc/Fc+. The HOMO levels of the polymers were determined using the oxidation onset value. Onset potentials are values obtained from the intersection of the two tangents drawn at the rising current and the baseline changing current of the CV curves. TGA measurements were performed on NETZSCH TG 209 F3 thermogravimetric analyzer. All GPC analyses were made using THF as eluant and polystyrene standard as reference. X-ray diffraction (XRD) patterns were obtained using SmartLab 3 kW (40 kV 30 mA, Cu target, wavelength: 1.541871 ang), Rigaku, Japan. Topographic images of the active layers were obtained through atomic force microscopy (AFM) in tapping mode under ambient conditions using a XE-100 instrument.

2.2. Fabrication and characterization of polymer solar cells

All of the bulk-heterojunction PV cells were prepared using the following device fabrication procedure. The glass/indium tin oxide (ITO) substrates [Sanyo, Japan (10 Ω/γ)] were sequentially lithographically patterned, cleaned with detergent, and ultrasonicated in deionized water, acetone, and isopropyl alcohol. Then the substrates were dried on a hot-plate at 120 °C for 10 min and treated with oxygen plasma for 10 min in order to improve the contact angle just before the film coating process. Poly(3,4-ethylene-dioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS, Baytron P 4083 Bayer AG) was passed through a 0.45 μm filter before being deposited onto ITO at a thickness of ca. 32 nm by spin-coating at 4000 rpm in air and then it was dried at 120 °C for 20 min inside a glove box. Composite solutions with polymers and PCBM were prepared using 1,2-dichlorobenzene (DCB) or chlorobenzene (CBz). The concentration was controlled adequately in the 0.5 wt% range, and the solutions were then filtered through a 0.45 μm PTFE filter and then spin-coated (500–2000 rpm, 30 s) on top of the PEDOT:PSS layer. The device fabrication was completed by depositing thin layers of Al (100 nm) at pressures of less than 10^{-6} torr. The active area of the device was 4.0 mm^2. Finally, the cell was encapsulated using UV-curing glue (Nagase, Japan). In this study, all of the devices were fabricated with the following structure: ITO glass/PEDOT:PS/polymer:PCBM/Al/encapsulation glass. The illumination intensity was calibrated using a standard a Si photodiode detector that was equipped with a KG-5filter. The output photocurrent was adjusted to match the photocurrent of the Si reference cell in order to obtain a power density of 100 mW/cm^2. After the encapsulation, all of the devices were operated under an ambient atmosphere at 25 °C. The current–voltage (I–V) curves of the photovoltaic devices were measured using a computer-controlled Keithley 2400 source measurement unit (SMU) that was equipped with a Peccell solar simulator under an illumination of AM 1.5G (100 mW/cm^2). Thicknesses of the thin films were measured using a KLA Tencor Alpha-step 500 surface profilometer with an accuracy of 1 nm. Hole-only devices were fabricated with a diode configuration of ITO (170 nm)/PEDOT:PSS (40 nm)/polymer:$PC_{71}BM$ (34–110 nm)/MoO_3 (30 nm)/Al (100 nm). The hole mobilities of the active layers were calculated from the SCLC using the J–V curves of the hole only devices in the dark as follows:

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu_{h(e)} \frac{V^2}{L^3} \exp\left(0.89\sqrt{\frac{V}{E_0 L}}\right)$$

where ε_0 is the permittivity of free space (8.85×10^{-14} C/Vcm); ε_r is the dielectric constant (assumed to be 3, which is a typical value for conjugated polymers) of the polymer; $\mu_{h(e)}$ is the zero-field mobility of holes (electrons); L is the film thickness; and $V = V_{appl} - (V_r + V_{bi})$, where V_{appl} is the voltage applied to the device, V_r is the voltage drop due to series resistance across the electrodes and V_{bi} is the built-in voltage.

2.3. Materials

All reagents were purchased from Aldrich, Acros or TCI companies. All chemcals were used without further purification. The following compound were synthesized following modified literature procedures: *N*,*N*′-di(2-octyldodecyl) quinacridone (QC-1), 2,9-dibromo-*N*,*N*′-di(2-octyldodecyl) quinacridone. (QC-2), 5,12-bis(2-octyldodecyl)-2,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) quinolino[2,3-b]acridine-7,14(5H,12H)-dione (M1) [21], 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (M2) [9], isoindigo (M3) [22].

2.4. Poly[quincaridone- diketopyrrolopyrrole] (PQCDPP)

5,12-Bis(2-octyldodecyl)-2,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) quinolino[2,3-b]acridine-7,14(5H,12H)-dione (M1) (0.23 g, 0.20 mmol), 3,6-bis(5-bromothiophen-2-yl)-2,5-bis (2-hexyldecyl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (M2)

(0.18 g, 0.20 mmol) Pd(PPh3) 4(0) (0.007 g, 0.006 mmol) and aliquat 336 were placed in a Schlenk tube, purged by performing three nitrogen/vacuum cycles and, under a nitrogen atmosphere,