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Correlation of intramolecular charge transfer and orientation properties among quinacridone and acceptor units

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ABSTRACT

This study synthesized a highly soluble quinacridone-acceptor series (PQCDTB, PQCDTQ-a, PQCDTQ-b) through the Suzuki coupling reaction by introducing planar quinacridone and a highly soluble acceptor unit. The polymers largely dissolved organic solvents, and the M_n ranged from 40.5 to 63.1 kg/mol. The intermolecular charge transfer (ICT) effects were much stronger in PQCDTQ-b than in PQCDTB and PQCDTQ due to the position of the oxygen atom. The HOMO and LUMO levels of the polymers were -5.18 to -5.37 eV and -3.28 to -3.40 eV, respectively. According to XRD measurements, PQCDTB exhibited the formation of an ordered lamellar structure and conventional edge-on π -stacking, whereas PQCDTQ-a and PQCDTQ-b exhibited face-on formation relative to the substrate. The open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) were 0.85 V, 7.6 mA/cm², 61.5%, and 4.0%, respectively, for PQCDTQ-a with a 1:2 ratio of PC₇₁BM.

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1. Introduction

Semiconducting polymers have been used in diverse applications, such as organic light emitting diodes (OLEDs) [1–3], organic photovoltaic cells (OPVs) [4–11], and organic thin film transistors (OTFTs) [12,13], for several decades. OPVs have received significant attention in these applications due to the global technology trend toward economic feasibility and continuous development coupled with preservation of the environment. However, the low power conversion efficiency (PCE) of these materials has been the greatest obstacle in developing OPVs [6]. The donor–acceptor (D–A)-type low-band gap polymer has received considerable attention in recent years because its electronic properties can easily be changed based on the unique combination of the D–A unit. This polymer can also increase the absorption spectra with long wavelengths [6]. Nevertheless, the low PCE has remained the largest obstacle in D–A-type polymers.

The following idealistic conditions are required in D–A-type polymers to improve the PCE [14]: (1) a low band gap with a wide absorption area, (2) ordered orientation to produce good charge transport characteristics, (3) a low highest occupied molecular orbital (HOMO) energy level with which a high open-circuit voltage (V_{oc}) can be produced, and (4) an appropriate lowest

unoccupied molecular orbital (LUMO) energy level for effective electron charge transfer to fullerene.

To acquire good charge transport characteristics, the close packing between polymers must be increased through the reduction of energetic disorder by increasing the coplanarity and interchain π – π interaction. A quinacridone (QC) derivative is an appropriate candidate for this process. A QC derivative, which is known as a red-violet pigment, has an ordered structure and self-assembled characteristics and has received significant attention as an OTFT because of its high mobility [15,16]. The Takimiya group has recently reported on a polymer composed of QC derivatives with a high hole mobility ($0.2 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$) for use in OTFTs [17]. We have synthesized polymers by introducing QC, benzothiadiazole, and a quinoxaline derivative and reported on the optical, electrochemical, and photovoltaic properties [18,19].

As observed in Chart 1, the polymer structure with oxygen around the backbone exhibits a weak intramolecular charge transfer (ICT) effect due to the electro-deficient property of the oxygen atom, which will exhibit a wide band gap and high LUMO level [20]. In addition, for the quinoxaline derivative, a polymer with quinoxaline exhibits various electrochemical and morphology properties depending on the position of the alkoxy chain [21]. Thus, if the oxygen position is far away around the polymer backbone, the polymer will exhibit an effective ICT effect and a broader absorption.

In this study, we synthesized D–A-type polymers based on a QC derivative depending on the oxygen position, and the resulting optical, electrochemical, and morphology properties were investigated. In

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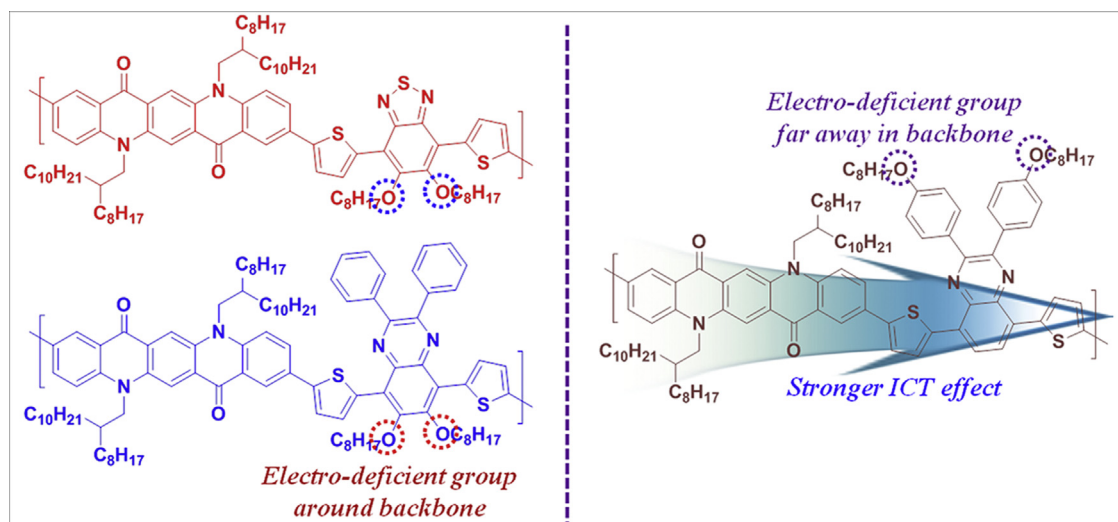


Chart 1. Schematic representation of effective intramolecular charge transfer.

addition, polymers based on a QC derivative reported by our group revealed improved efficiency through optimized device structure (additive, solvent) compared with the previously reported efficiency.

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°), 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. Theoretical study was performed by using density functional theory (DFT), as approximated by the B3LYP functional and employing the 6–31 G^* basis set in Gaussian09.

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 ($10 \Omega/\square$)] 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 $0.45 \mu\text{m}$ 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). The concentration was controlled adequately in the 0.5 wt% range, and the solutions were then filtered through a $0.45 \mu\text{m}$ PTFE filter and then spin-coated (500–2000 rpm, 30 s) on top of the PEDOT:PSS layer. The PFN solution in methanol and acetic acid was spin-coated on the top of the obtained active layer at 4000 rpm for 30 s to form a thin interlayer of 5 nm. The device fabrication was completed by depositing thin layers of BaF_2 (1 nm), Ba (2 nm), and Al (200 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).

The illumination intensity was calibrated using a standard a Si photodiode detector that was equipped with a KG-5 filter. The output photocurrent was adjusted to match the photocurrent of the Si reference cell in order to obtain a power density of $100 \text{ mW}/\text{cm}^2$. 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 Pcell solar simulator under an illumination of AM 1.5 G ($100 \text{ mW}/\text{cm}^2$). Thicknesses of the thin films were measured using a KLA Tencor Alpha-step 500 surface profilometer with an accuracy of 1 nm.

2.3. Materials

All reagents were purchased from Aldrich, Acros or TCI companies. All chemicals were used without further purification. The following compounds were synthesized following modified literature procedures: poly[quinacridone-*alt*-benzothiadiazole] (PQCDTB) [18], poly[quinacridone-*alt*-6,7-bis(octyloxy)quinoxaline] (PQCDTQ-a) [19], 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(octyloxy)phenyl)quinoxaline M4 [6].

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