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Quinacridone-quinoxaline-based copolymer for organic field-effect transistors and its high-voltage logic circuit operations

Jongwook Jeon[a], Heesauk Jhon[b], Myounggon Kang[c,**], Ho Jun Song[d,***], Tae Kyu An[e,*]

[a] Department of Electronics Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul, 05029, Republic of Korea
[b] Department of Information and Electronic Engineering, MOKPO National University, Jeonnam, 58554, Republic of Korea
[c] Department of Electronics Engineering, Korea National University of Transportation, 50 Daehak-Ro, Chungju, Chungbuk, 27469, Republic of Korea
[d] Research Institute of Sustainable Manufacturing System Intelligent Sustainable Materials R&D Group, Korea Institute of Industrial Technology, 89 Yangdaegiro-gil, Ipjang-myeon, Seobuk-gu, Cheonan-si, Chungcheongnam-do, 31056, Republic of Korea
[e] Department of Polymer Science & Engineering and Department of IT Convergence, Korea National University of Transportation, 50 Daehak-Ro, Chungju, 27469, Republic of Korea

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A B S T R A C T

Poly(quinacridone-quinoxaline) (PQCQx) was synthesized to investigate the potential of quinacridone derivatives as organic semiconductors in organic field-effect transistors (OFETs) and circuits. The device showed a field-effect mobility value of 1.4×10^{-3} $cm^2/(Vs)$ at optimal conditions. The morphologies of the deposited films were characterized by performing X-ray diffraction and atomic force microscopy. And, to confirm the feasibility of using PQCQx OFETs in a high-voltage logic circuit operation, a compact model library to describe the electrical behaviors of PQCQx OFETs was developed. By implementing the developed compact model library into a circuit simulator, we successfully evaluated the high-voltage-logic operation of a p-type organic inverter with a frequency of 45.5 kHz in an 80 V supply condition.

1. Introduction

Several conjugated small organic molecule semiconductors as well as conjugated polymeric semiconductors have been developed to replace their higher-cost inorganic counterparts and have led to considerable improvements in the electrical performances of organic field-effect transistors (OFETs). Current investigations are aiming to apply these improved OFETs to practical applications such as large-area flexible displays and drivers for radio-frequency identification tags, and should also lead to lower costs for various devices [1–3]. Considerable progress has been made in molecular design and device architecture, enough to produce OFETs showing performance levels comparable to or even exceeding those of amorphous silicon-based transistors [4–6]. However, the commercialization of high-performance OFETs still requires several problems to be overcome, including their insufficiently high levels of field-effect mobility, operational stability, and performance reproducibility [7–11].

A variety of developed small organic molecules and conjugated polymers have been shown to be chemically stable conjugated systems and hence to display good electrical performances [12–15]. Polymeric semiconductors offer considerable advantages including good mechanical flexibility and large-area solution processability when using printing technologies such as ink-jet, aerosol-jet and gravure printing, and have hence been used successfully in OFETs [15–18]. Their potential success in OFETs originates from the development of a molecular design strategy involving favorable molecular ordering of the polymeric molecules that endow them with high crystallinity and that enhances their intramolecular charge transport [6,15]. Such enhancements can be achieved by optimizing $\pi-\pi$ stacking to occur over a large area with a large overlap between the component π groups, which in turn requires careful consideration of the orientations of these groups and the planarity of the polymeric chains, as well as of the intra- and intermolecular interactions [19]. To improve interchain orientation for overlap over a large area of $\pi-\pi$ stacking, polymeric chain planarity, curvature, intra- and intermolecular interactions should be considered carefully.

Among the variety of polymeric semiconductors developed, quinacridone (QC)-based polymers have emerged as promising candidates for polymeric semiconductors because they have an ordered structure and can molecular self-assemble, so they have attracted considerable

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: mgkang@ut.ac.kr (M. Kang), song3026@kitech.re.kr (H.J. Song), taekyu1985@ut.ac.kr (T.K. An).

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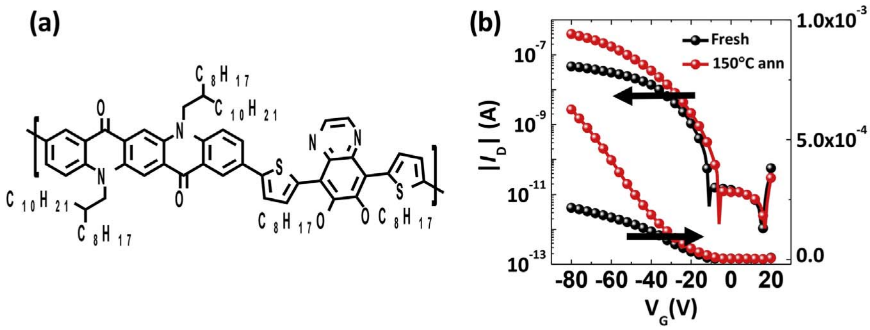

Fig. 1. (a) Molecular structure of PQCQx and (b) transfer curves from pristine and annealed films based on PQCQx.

attention for use in OFETs [20,21]. The Moon group recently reported the synthesis of poly(quinacridone-quinoxaline) (PQCQx) (Fig. 1(a)), a conjugated copolymer consisting of quinacridone (a commonly known red–violet pigment) and quinoxaline [22]. The quinacridone and quinoxaline components can both be easily structurally modified because of their high solubility, and their electronic properties can be tuned with various substituents. PQCQx was thus deployed as an active material for bulk heterojunction-type organic photovoltaic (OPV) cells [22].

Although PQCQx has been investigated for use in OPV cells, we are not aware of any attempts to apply it as an active material in OFETs. Copolymers based on the quinacridone unit may show promise for use as active materials in OFETs because of the relatively simple, compact, and planar structure of this unit [20]. In this work, we characterized PQCQx for applications in OFETs and carried out a numerical circuit simulation to determine how well it would perform in a high-voltage logic circuit application. The PQCQx shows the feasibility of the logic circuit application in a high-voltage and 45.5 kHz operating frequency. To investigate the properties of PQCQx OFETs, specifically to study the morphological and microstructural properties of their films, we performed atomic force microscopy (AFM) and X-ray diffraction (XRD) experiments.

2. Experiments

2.1. Materials, device fabrication and measurements

The PQCQx polymer was synthesized by carrying out a Suzuki coupling reaction, as described previously [22]. The synthesized PQCQx polymer was determined to have a number-average molecular weight (M_n) of 15.6 kg/mol, and a polydispersity index (PDI) of 2.60, by using gel permeation chromatography with tetrahydrofuran at 40 °C. The electrical properties of the PQCQx film were characterized with the film in a top-contact OFET configuration using a 300-nm-thick SiO_2 dielectric on a highly doped n-Si substrate, which served as the gate electrode. The SiO_2 dielectric was treated with an octadecyltrichlorosilane (ODTS) monolayer and with toluene for 90 min at room temperature. Solutions of the organic semiconductors were prepared at a concentration of 0.2 wt% in chloroform and heated at 50 °C for 30 min before being filtered using a 0.2-μm-pore-sized polytetrafluoroethylene (PTFE) membrane syringe filter. The polymer film was deposited by carrying out spin-coating for 60 s at 2000 rpm. Gold source and drain electrodes were evaporated on top of the semiconductor layers (100 nm) using a shadow mask over the active layer. In all measurements, the channel lengths (L) were 50 μm and the channel widths (W) were 1000 μm. The electrical characteristics of the FETs were measured at room temperature under a nitrogen atmosphere using a Keithley 4200 SCS. Field-effect mobilities were extracted in the saturation regime from the slope of a line fitted to a plot of the square root of the source–drain current (I_{DS}) versus the gate voltage (V_G); the fitting was based on the equation $I_{DS} = (WC_i/2L)\mu(V_G - V_{th})^2$, where C_i is the capacitance per unit area of the dielectric, μ is the field-effect mobility, and V_{th} is the threshold voltage.

2.2. Morphological characterization

XRD experiments were performed using X-rays with an energy level of 11.57 keV at the 5 A beamline at the Pohang Accelerator Laboratory (PAL), Pohang, Korea. AFM experiments were conducted using a Multimode Illa (Veeco Inc.) operating in tapping mode with a silicon cantilever. The thin-film samples used in the XRD and AFM studies were fabricated by spin-coating at 2000 rpm with the 0.2% chloroform solution on an ODTS-modified silicon wafer to mimic the device fabrication process, followed by drying under vacuum at room temperature. After film deposition, the samples were annealed at 150 °C to observe the effect of thermal annealing.

2.3. Computational simulations

To observe the high-voltage logic circuit performance, we simulated inverter with the synthesized PQCQx OFET with post-annealing process step. In order to verify the circuit characteristics, Synopsys' HSPICE was used to simulate dynamic circuit characteristics in conjunction with an industry standard compact model of the Berkeley Short-Channel IGFET Model-4 (BSIM4) that describes electrical device characteristics [23]. About 40 BSIM4 parameters are used to model the electrical characteristics of I-V and C-V in all operating domains of the fabricated OFET, and the process of extracting parameters has been described in detail in our previous work [23]. Note that BSIM4 model cannot capture all physics of OFETs such as carrier hopping, and low mobility induced by grain-boundary scattering and so on since BSIM4 model has been developed for silicon-based planar MOS transistor. However, we used BSIM4 model as a behavioral model to fit the measured I-V and C-V characteristics of single W/L OFET to run circuit simulator at only room temperature [23].

3. Results and discussion

The transfer characteristics of OFETs based on PQCQx are shown in Fig. 1(b). The devices showed the typical p-channel transfer characteristics, and the annealing treatments improved the field-effect mobility (Table 1). The saturation field-effect mobility of the as-cast PQCQx film was calculated from the slope of the corresponding plot in Fig. 1(b) to be 9.2×10^{-5} cm^2/(Vs) with an on/off ratio of 1.0×10^4. In the annealed film, the field-effect mobility was found to be 1.4×10^{-3} cm^2/(Vs) with an on/off ratio of 2.7×10^5. Structural

Table 1
Performance properties of PQCQx-based OFET devices.

Conditions	Mobility (cm^2/Vs)	On/Off	Threshold voltage (V)	Subthreshold swing (V/dec)
Fresh film	9.2×10^{-5}	1.0×10^4	–2.1	0.92
Annealed film	1.4×10^{-3}	2.7×10^5	–24	0.69