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Diketopyrrolopyrrole-based three-armed conjugated small molecule and their charge transport property

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ABSTRACT

We synthesized three-armed conjugated small molecule, PTD bearing diketopyrrolopyrrole (DPP) moieties and investigated the fundamental properties such as physical, photophysical and electronic properties. Also, field-effect transistor (FET) based on the micro-patterned film was fabricated by using template-guided solution-shearing (TGSS) method and displayed higher hole mobility than the thin film transistor made of spin-coated film.

KEYWORDS

diketopyrrolopyrrole; conjugated small molecule; field-effect transistor; micro-patterning.

Introduction

Conjugated small molecules have considerable attention in electronic devices due to their favorable merits such as perfect purification, reproducibility, high crystallinity, and fine-tuned energy levels [1–3]. Until now, many researchers have investigated in molecular packing or alignment of conjugated small molecules in the solid state for high-performance thin film transistors (TFTs). Thermally annealing process is the simplest method to enhance the degree of crystallinity in thin film states [4, 5]. However, this method is difficult to control their own molecular packing and ordering in the solid state efficiently. As an ideal method for small molecules, fabrication of single crystalline objects having perfect crystalline structure with high charge carrier mobility is mostly desired [6–9], but it has a disadvantage that it is difficult to fabricate large single crystalline objects suitable for electronic devices. In addition, the single crystalline objects are almost impossible to prepare with larger molecular weight molecules such as linear oligomers and star-shape molecules. Therefore, solution sheared or precisely patterned film can be employed as a way for preparing highly crystalline semiconducting objects. Thus, a number of micro-/nano-sized patterning methods using conjugated small molecules have been proposed in several literatures for high-performance field-effect transistors [10–12]. Recently, template-guided solution-shearing (TGSS) method was suggested to induce an alignment of the polymer chains in our previous literature [13]. Corresponding FET devices showed highly enhanced hole mobilities and anisotropic charge transport behavior. However, this useful method has not been applied to conjugated small molecules to date.

In this study, to verify the universal applicability of TGSS method, we newly synthesized a disc-type small molecule, PTD containing DPP moiety with a benzene core. The optical and

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electrochemical properties of PTD was investigated and its electronic property was also characterized in terms of device fabrication. In addition, the TGSS method was applied to elaborate micro-patterns of PTD molecule for preparing high-performance field effect transistors. As a result, TFT made with a thermally annealed film of PTD showed larger hole mobility ($\mu = 9.15\times10^{-5}$ cm^2 V^{-1} s^{-1}) than TFT with pristine film, ($\mu = 7.91\times10^{-4}$ cm^2 V^{-1} s^{-1}). In contrast, FET made with micro-patterns fabricated by TGSS method exhibited much higher hole mobility of 2.90×10^{-3} cm^2 V^{-1} s^{-1}, which is 30 times higher than TFT with pristine film and 3 times higher than TFT with thermally annealed film.

Experimental section

Materials

All reagents were purchased from Acros, TCI, and Sigma-Aldrich Co. and used without further purification unless stated otherwise. Intermediate 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1**) and 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**2**) were prepared according to literatures [14, 15].

6,6′,6″-(5,5′,5″-(Benzene-1,3,5-triyl)tris(thiophene-5,2-diyl))tris(2,5-bis(2-ethylhexyl)-3-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione) (3, PTD)

3-(5-Bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4 -c]pyrrole-1, 4(2H,5H)-dione (**1**) (0.53g, 0.88 mmol), 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**2**) (0.1 g, 0.22 mmol), and anhydrous toluene (30 mL) deoxygenated with nitrogen were added to three-necked round-bottom flask. $Pd(PPh_3)_4$ (0.01 g, 0.009 mmol), 2M K_2CO_3 (10mL), and a few drops of Aliquat 336 were added to the mixture and it was allowed to stir at 100°C for 12 h. After cooling down the mixture to room temperature, it was poured into water and extracted with dichloromethane. The organic phase was dried over $MgSO_4$. It was purified by silica-gel column chromatography (eluent: MC only) to yield 0.25 g (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.96–8.92 (t, 6H), 7.90 – 7.85 (s, 3H), 7.67 – 7.63 (d, J = 5.08 Hz, 3H), 7.60 – 7.56 (d, J = 4.32 Hz, 3H), 7.30 – 7.28 (m, 3H), 4.15 – 4.00 (m, 12H), 2.00 – 1.85 (m, 6H), 1.50 – 1.15 (m, 48H), 1.00 – 0.80 (m, 36H), Anal. Calcd. for $C_{96}H_{120}N_6O_6S_6$: C, 70.03; H, 7.35; N, 5.10; O, 5.83; S, 11.69, found : C, 69.82; H, 7.29; N, 4.98; S, 12.15.

Instrumentation

^{1}H-NMR spectra were recorded on Varian Mercury NMR spectrometer (400 MHz). Elemental analyses of new compounds were measured using an EA1112 (Thermo Electron Corp.). Thermal properties were performed in nitrogen atmosphere using a Mettler DSC 821e instrument. The electronic properties of the molecules were analyzed using cyclic voltammetry (CV, Model: EA161 eDAQ, scan rate = 50 mV s^{-1}). The electrolyte solution was a 0.10 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes. Atomic force microscopy (AFM, Advanced Scanning Probe Microscope, XE-100,

PSIA, tapping mode with a silicon cantilever) was used to characterize the surface morphologies of the thin films. The films were fabricated by spin-coating a chloroform solution of sample (5 mg mL^{-1}) on a n-octyltrichlorosilane (OTS)-treated silicon wafer followed by drying at 60°C under vacuum. In order to study optical absorption behavior, thin films were fabricated on glass substrates. The films were dried at 60°C for 6 h under vacuum. Absorption spectra of the samples as a thin film and in solution (1 mM in chloroform) were obtained using a UV-Vis absorption spectrometer (Agilent 8453, photodiode array type) in the wavelength range of 190–1100 nm. Grazing incidence wide-angle X-ray diffraction (GIXD) measurements were performed at the 9A (U-SAXS) beamline (energy = 11.105 keV, pixel size = 79.6 mm, λ = 1.12 Å, $2\theta = 0°\sim20°$) at the Pohang Accelerator Laboratory (PAL). The film samples were fabricated by spin-casting on OTS−SiO_2/Si substrate, followed by drying at 60°C under vacuum. (solvent: chloroform, concentration: 5 mg mL^{-1}).

Fabrication of thin film transistor

To fabricate TFT devices, bottom gate top contact device geometry was employed. On the heavily n-doped Si/SiO_2 substrate the spin-coated films (thickness ~ 40–50 nm) were prepared for surface modification as OTS-treated silicon wafer. Source and drain electrodes were then thermally evaporated (thickness = 100 nm) through shadow mask with the channel width and length of 1500 μm and 100 μm for the TFT devices respectively. All field effect mobilities were determined using this following equation, $\mu_{sat} = (2I_{DS}L)/(WC_i(V_G - V_{th})^2)$. ($I_{DS}$ = saturation drain current, C_i = capacitance of SiO_2 dielectric, V_G = gate bias, V_{th} = threshold voltage) The device performance was measured in air using 4200-SCS semiconductor characterization system.

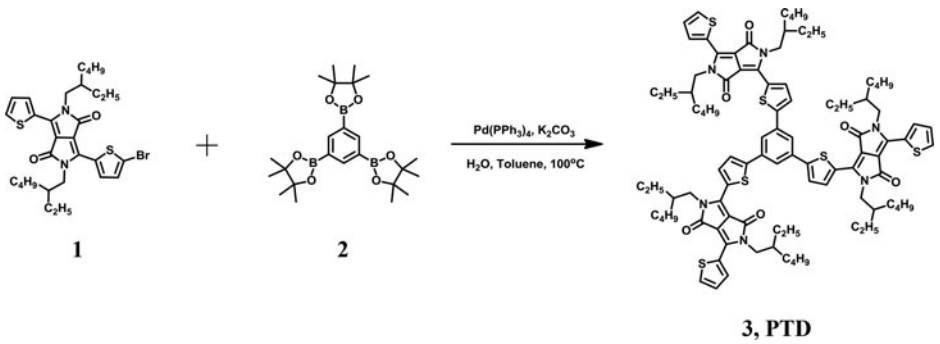
Fabrication of field effect transistor made through TGSS method

The polydimethylsiloxane (PDMS) mold having uniaxially aligned microgrooves (width: 5 μm, depth: 1 μm) was prepared by following the literature method. PTD was dissolved in chlorobenzene (CB) and chloroform (CF) (1:1, *v*/*v*) at a concentration of 5 mg mL^{-1}. The PDMS mold was fixed to a shearing plate, and the OTS-treated n-doped Si/SiO_2 substrate was placed on a stage heated at 90°C. After the polymer solution was applied to the substrate, the PDMS mold was placed in contact with the substrate, and the mold was moved across the substrate at a shearing speed of 0.1 mm s^{-1}. The resulting PTD micro-patterned prisms were heated for a few minutes at 90°C to remove residual solvent. Finally, gold electrodes (150 nm) were deposited to finish the fabrication of the bottom-gate top-contact devices through a shadow mask.

Results and discussion

Synthesis and characterization

The synthetic procedure of new semiconducting small molecule with three DPP unit was shown in Scheme 1. PTD is composed of benzene as a core unit and DPP units as peripheral arms. 2-Ethylhexyl group was substituted in the *N*-positions of DPP unit to promote solubility. Suzuki coupling reaction was employed to prepare the PTD, **3** using compounds **1** and **2** in a high yield over 60%



Scheme 1. Synthetic procedure for DPP-based three-armed conjugated small molecule, PTD.

The normalized UV-vis absorption spectra of PTD in solution and thin film are shown in Figure 1(a). The maximum absorption wavelengths (λ_{max}s) of PTD were observed at 581 nm in solution and 611 nm in thin film. The thin films displayed red-shifted absorption behavior compare to solution state and it is attributed to strong intermolecular $\pi-\pi$ interaction in the solid state. The optical bandgap energy (E_g^{opt}) was determined from the absorption edge ($\lambda_{cut\text{-}off}$) to be 1.87 eV for PTD.

Cyclic voltammetry (CV) was used to investigate the molecular energy levels of PTD. The results were displayed in the Figure 1(b). The highest occupied molecular orbital (HOMO) energy level of PTD is determined to be −5.47 eV. The lowest unoccupied molecular orbital (LUMO) energy level is calculated to be −3.60 eV using optical bandgap and HOMO level.

In order to investigate the thermal property of PTD, DSC measured under a nitrogen atmosphere. The three-armed PTD exhibited a crystallization temperature at 156°C and melting temperature 220°C as shown in Figure 2. Although PTD has bulky DPP-based three peripheral arms, it displayed obvious crystalline melting temperature, implying the possible existence of molecular arrangement under specific conditions.

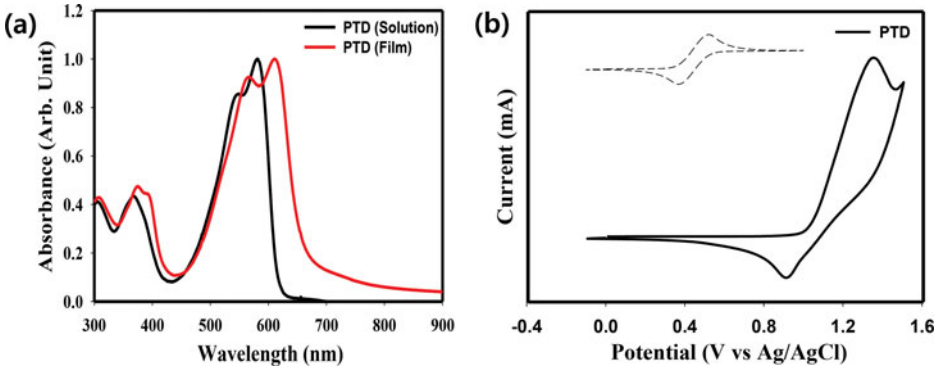


Figure 1. (a) UV-vis absorption spectra of PTD in $CHCl_3$ solution and thin film. (b) Cyclic voltammograms of PTD. *Sample : thin film on Pt wire.

In order to investigate the crystallinity and molecular packing behavior of PTD, two dimensional X-ray diffraction (2D GI-XRD) was measured. Figure 3 shows the 2D GI-XRD patterns of pristine film and thermally annealed film of PTD. Clear diffraction peak was not observed in pristine film, but highly ordered *(h00)* peaks appeared in thermally annealed film due to their periodically ordered lamellar crystalline structure. This indicates that the crystallinity of PTD was greatly increased when the film was thermally annealed at 200°C.

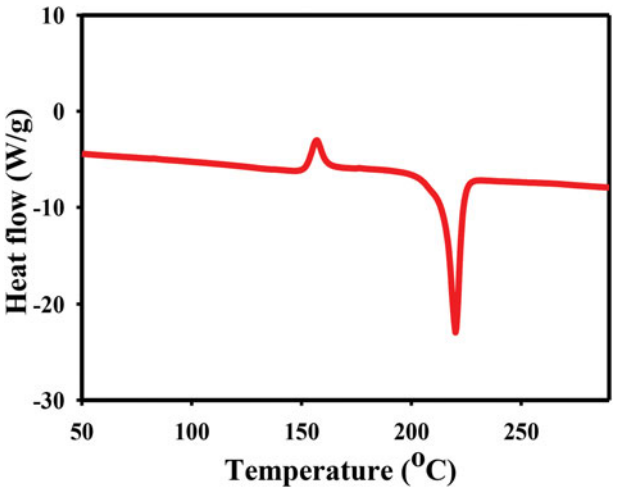


Figure 2. Differential scanning calorimetry (DSC) curves of PTD.

Figure 4 shows the AFM topographic images of the PTD pristine film and thermally annealed films at 200°C. The surface morphology of the thermally annealed film changed significantly compare to pristine film. In thermally annealed film, highly crystalline domains were found and thermally annealed film-based TFT is expected to exhibit more favorable charge transport properties.

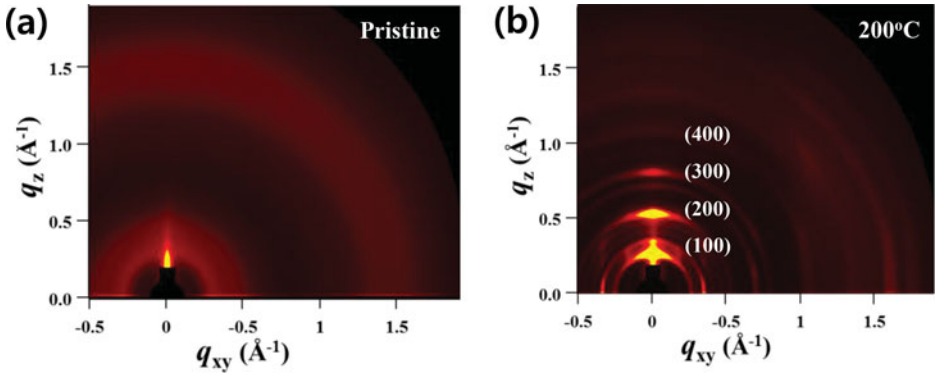


Figure 3. 2D GI-XRD patterns of PTD for (a) pristine film and (b) thermally annealed film.

Performance of PTD-based TFTs

To evaluate charge transport properties of PTD in film state, we fabricated top-contact FET devices in pristine, thermally annealed films, and micro-patterned prism. Their performances were characterized precisely. The saturated hole mobility of the PTD was measured to be 9.15×10^{-5} cm^2 V^{-1} s^{-1} ($I_{on/off} = 10^4$, $V_{th} = -10$ V) in pristine film and 7.91×10^{-4} cm^2 V^{-1} s^{-1} ($I_{on/off} = 10^5$, $V_{th} = -3$ V) in thermally annealed film at 200°C as shown in Figure 5a and 5b. TFT device bearing thermally annealed film showed the increase of hole mobility, which is about 10 times higher than that of TFT made of pristine film.

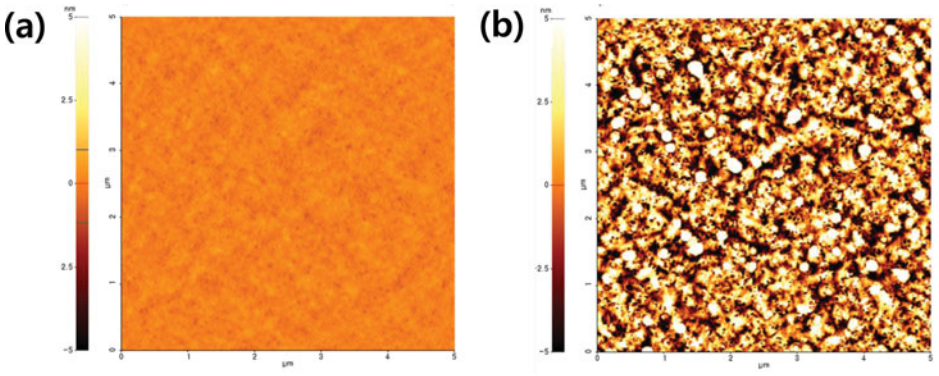


Figure 4. Atomic force microscopy (AFM) images of PTD thin films. (a) pristine and (b) thermally annealed film ($T_{annealing} = 200°C$).

Performance of FET made with TGSS micro-patterns

To control the molecular orientation to the specific direction, it is necessary to induce the predetermined direction pattern for high charge carrier mobility in field-effect transistor. However, small molecules are difficult to fabricate patterned film using spin-coating method because of difficulty to control individual molecular orientation on OTS-treated SiO_2/Si substrate. The mobility of TGSS film based FET was measured to be 2.90×10^{-3} cm^2 V^{-1} s^{-1} ($I_{on/off} = 10^5$, $V_{th} = -2$ V). It was found to show significant improvement of the charge carrier mobility in micro-patterned film of PTD. FET bearing the micro-patterned prism showed the mobility which is 30 times higher than that of pristine film and three times higher than

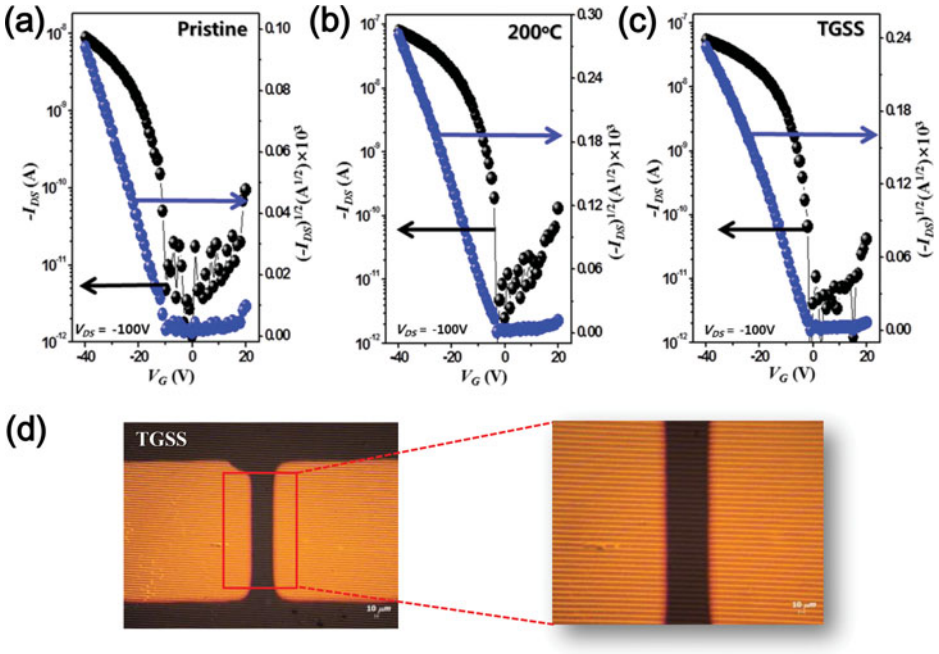


Figure 5. Transfer curves of the FET device fabricated with (a) pristine film, (b) thermally annealed film ($T_{annealing} = 200°C$) and (c) patterned film prepared by template-guided solution-shearing (TGSS) method. (d) Optical microscopy images of patterned film made by TGSS method.

that of thermally annealed film. As a result, TGSS method is a universal technique for small molecules and polymers. It is quite useful to control the molecular orientation for inducing dense packing of three-armed PTD.

Conclusions

We have successfully synthesized and characterized three-armed DPP-based conjugated small molecule, PTD. This molecule exhibited high degree of crystallinity in the solid state after thermally annealing treatment. Furthermore, PTD molecule was applied to interesting TGSS method for improving molecular orientation in active channel of FET device. FET based on micro-patterned prisms provided relatively high hole mobility of 2.90×10^{-3} cm^2 V^{-1} s^{-1} with a high current on/off ratio (10^5), which is three times higher than that of thermally annealed film..

Acknowledgments

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