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Modulation of Majority Charge Carrier from Hole to Electron by Incorporation of Cyano Groups in Diketopyrrolopyrrole-Based Polymers

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Supporting Information

ABSTRACT: A thienylene-vinylene-thienylene (TVT) derivative with cyano groups in the 3- and 3'-positions was synthesized as a building block of semiconducting polymers for high mobility organic field effect transistors (OFETs). (*E*)-1,2-Di-(3-cyanothiophen-2-yl)ethene (2CNTVT) was copolymerized with diketopyrrolopyrrole (DPP) units via Stille coupling reaction to give 2DPP-2CNTVT and 7DPP-2CNTVT. The properties of these two polymers were compared with those of the corresponding polymers without cyano groups in TVT (2DPP-TVT and 7DPP-TVT). The effects of CN groups and branched alkyl position were found to have a significant influence on the optical, electrochemical, morphological, and



charge transporting properties of the polymers. The average hole mobilities of OFETs fabricated with 2DPP-TVT and 7DPP-TVT OFETs were 1.63 and 2.2 cm² V⁻¹ s⁻¹, respectively, and the average electron mobility for both 2DPP-2CNTVT and 7DPP-2CNTVT OFETs was 1.2 cm² V⁻¹ s⁻¹.

INTRODUCTION

Since the first organic field effect transistor (OFET) based on polythiophene was reported in 1986, conjugated polymers have attracted a lot of attention from academia and industry owing to their tremendous potential in flexible and large-area electronic circuits, such as organic light-emitting diodes (OLEDs), radio-frequency identification tags (RFIDs), smart cards, and sensors.¹⁻⁵ Recently, the performance of conjugated polymer-based OFETs has been significantly improved by proper molecular design and optimized device processing techniques. Furthermore, several conjugated polymers have been synthesized with diketopyrrolopyrrole (DPP) and isoindigo (IID) derivatives, which exhibit hole mobilities (μ_h) exceeding 10 cm² V⁻¹ s⁻¹, surpassing those of amorphous silicon-based transistors ($\mu_{\rm h} \sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^{6,7} Compared to the performance of p-type conjugated polymer-based OFETs, the performance of the n-type analogues lags behind because of a lack of n-type conjugated polymers with appropriate lowest unoccupied molecular orbital (LUMO) energy level and high electron transporting properties.^{8,9} Electron-transport materials are required to have LUMO energy level below -4.0 eV for better air stability.^{10–12} In addition, it is necessary to develop both p-type and n-type conjugated polymers that exhibit high performances for applications in complementary integrated circuits (ICs).¹³

Incorporation of cyano and fluorine groups in a polymer backbone is a widely used strategy to prepare polymers with electron transport properties as these groups have a strong electron withdrawing ability.^{14,15} Such strong electron withdrawing groups (EWGs) can enhance the n-type characteristics by diffusing the electron density in the conjugated backbone and lowering the frontier energy levels. Recently, Yun et al. reported the synthesis of n-type conjugated polymers with high electron mobility ($\mu_e = 7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) by introducing a cyano group in the vinyl linkage.¹⁶ Park et al. have also reported a high electron mobility of 2.36 cm² V⁻¹ s⁻¹ in conjugated polymers with a backbone consisting of fluorine substituents on a phenyl unit.¹⁷

In this study, we designed and synthesized a new type of conjugated building block, (E)-1,2-bis(3-cyanothiophene-2-yl)ethene (2CNTVT), where cyano (CN) groups were introduced to the 3-position of the thiophene ring in (E)-2-(2-(thiophen-2-yl)vinyl)thiophene (TVT). It was expected that the introduction of CN groups would enhance the n-type characteristics because of a low-lying LUMO level and impart good electron transporting ability. 2CNTVT was polymerized

Received: July 18, 2017 Revised: September 13, 2017 Scheme 1^a



^aReagents and conditions: (i) Zn, TiCl₄, THF, 70 °C, 16 h; (ii) CuCN, DMF, 150 °C, 12 h; (iii) LDA, trimethyltin chloride, –78 °C, 12 h; (iv) 13-(6-bromohexyl)heptacosane, K₂CO₃, DMF, 120 °C, overnight; (v) NBS, chloroform, 0 °C, RT.

with DPP comonomers having a long dodecylhexadecyl side chain with two different branching points in order to enhance the solubility and to control the morphology of the resulting polymers. Properties of the synthesized copolymers were compared with those of the corresponding copolymer analogues without CN groups. The four polymers, 2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT, were evaluated by UV-vis absorption, cyclic voltammetry (CV), theoretical calculations (density functional theory, DFT), two-dimensional grazing incidence X-ray diffraction (2D-GIXD), atomic force microscopy (AFM), and OFET characteristics. The attachment of the CN group on the TVT moiety results in lower LUMO energy levels and enhanced electron mobility. The longer branching position of the alkyl chain contributes to strong intermolecular $\pi - \pi$ interactions in the polymers, according to their optical and 2D-GIXD analysis, because of the alleviated steric effect of the alkyl side chains on the polymer conjugated backbone. It was found that the fabricated devices of 2CNTVT-based polymers showed high electron mobility, while those of corresponding TVT-based polymers exhibited high hole mobility.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic routes for preparing 2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT are shown in Scheme 1, and the detailed procedures of the transformation of the monomers to the corresponding polymers are described in the Experimental Section. The polymers were successfully synthesized via Stille coupling reactions. They were found to be soluble in common organic solvents such as chloroform, toluene, tetrahydrofuran, chlorobenzene, and 1,2-dichlorobenzene. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using polystyrene as the standard. The number-average molecular weights (M_n) of 2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT are 127 kg mol⁻¹ (polydispersity index (PDI) = 2.4), 37 kg mol⁻¹ (PDI = 1.4), 314 kg mol⁻¹ (PDI = 2.6), and 53 kDa (PDI = 1.3), respectively. The thermal decomposition temperatures (T_{dr}) at 5% weight loss) of 2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT are 398, 401, 397, and 405 °C, respectively, as evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. These results reveal

that the CN substitution in these polymer systems slightly enhanced their thermal stability (Figure S1).

Optical and Electrochemical Properties. The absorption spectra of the polymers in chloroform and as thin films are shown in Figure 1a,b. All polymers showed the typical absorption bands from 600 to 950 nm which arise due to the intramolecular charge transfer (ICT) in the D–A conjugated



Figure 1. Normalized absorption spectra of the polymers (a) in their chloroform solution and (b) as thin films.

				$\lambda_{\mathrm{max,abs}} \; (\mathrm{nm})$	λ_{\max} (nm)	$\lambda_{\mathrm{edge}} \ (\mathrm{nm})$			
polymers	M_n^a (kg/mol)	PDI	$T_{\rm d}^{\ b}$ (°C)	solution	film ^c	film ^c	optical $E_{g}^{opt d}$ (eV)	$HOMO^{e}$ (eV)	$LUMO^{f}(eV)$
2DPP-TVT	127	2.4	398.7	779	786	916	1.35	-5.13	-3.78
2DPP-2CNTVT	37	1.4	400.8	776	796	942	1.31	-5.49	-4.18
7DPP-TVT	314	2.6	396.9	790	791	958	1.29	-5.05	-3.76
7DPP-2CNTVT	53	1.3	405.0	797	810	950	1.30	-5.40	-4.10

 ${}^{a}M_{n}$ and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in CHCl₃. b Temperature at 5% weight loss at a heating rate of 10 °C min⁻¹ under nitrogen. ^cPolymer film on a quartz plate by spin-casting from chloroform solution at 1500 rpm for 30 s. d Calculated from the absorption band edge of the copolymer films, $E_{g} = 1240/\lambda_{edge}$. ^cHOMO energy levels were determined from the $E_{ox/onset}$ of the first oxidation potential of ferrocene, -4.8 eV. ^fLUMO = HOMO - E_{g}^{opt} .



Figure 2. Transfer and output characteristics of (a) 2DPP-TVT and (b) 7DPP-TVT.

backbone structure. Compared to polymer solutions, the absorption spectra of the polymer films were red-shifted, and two distinguished peaks were observed because of the aggregation of the polymer main chains and interchain interactions in the thin films.¹⁸ The absorption spectra of the 7DPP-based polymers are red-shifted compared to those of the 2DPP-based polymers. This indicates that the polymers with alkyl side chains branched at the 7-position possessed enhanced intermolecular $\pi - \pi$ interactions compared to the corresponding polymers with the side chains branched at the 2-position, possibly due to favorable molecular packing. The optical band gap energies ($E_{\rm g}^{\rm opt}$) of $\approx 1.29 - 1.35$ eV were estimated from the absorption edge in the absorption spectrum of the polymer film.

The highest occupied molecular orbital (HOMO) energy levels of the polymers in thin films were characterized by CV. These energy levels of the polymers were determined by measuring the oxidation onset potentials (E_{ox}) of the polymer films by cyclic voltammetry and calculated using the following

equation: HOMO (eV) = $-(E_{onset}^{ox} + 4.71)$. The HOMO energy levels of 2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT were -5.13, -5.49, -5.05, and -5.40 eV, respectively (Figure S2). These results demonstrated that the introduction of a CN group in the thiophene moiety effectively lowered the HOMO energy level of the polymers because of its strong electron withdrawing ability. The lowest unoccupied molecular orbital (LUMO) energy levels of the polymers were determined from the HOMO energy levels obtained from the CV experiments and the E_{g}^{opt} values obtained from the onset point of the UV-vis absorption spectra of the films. Thus, the LUMO energy levels of 2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT were evaluated as -3.78, -4.18, -3.76, and -4.10 eV, respectively. These results imply that the 2CNTVT-based polymers would likely show better electron injection property from the Au electrode compared to the TVT-based polymers because of their low-lying LUMO energy levels. The UV-vis absorption measurements, E_{g}^{opt} values, and



Figure 3. Transfer and output characteristics of (a) 2DPP-2CNTVT and (b) 7DPP-2CNTVT.

electrochemical properties of the polymers are summarized in Table 1.

Theoretical Calculations. DFT calculations were performed by using the B3LYP functional and 6-31G(d) basis set in order to understand the effect of CN substitution on the frontier molecular orbitals, dihedral angles, dipole moments, and the charge distributions along the conjugated backbone. Calculations were performed on two repeating units (D-A-D-A) with simplified alkyl chains of the TVT (DPP-TVT)and 2CNTVT (DPP-2CNTVT)-based polymers for reducing the calculation time. These calculations were carried out using the Gaussian 09 software package. The HOMO and LUMO energy levels calculated by the simulation are consistent with the experimental results, and it was possible to confirm that the strong electron withdrawing property of the CN group lowered the energy levels. Furthermore, both the molecular orbital distributions in the HOMO and LUMO levels are spread over the entire conjugated backbone (Figure S3). These isosurfaces differ from the general D-A conjugated polymers in which the LUMOs are localized on the electron-withdrawing units.^{19,20} Furthermore, it was found that the HOMO in the DPP-2CNTVT copolymer was slightly localized on the DPP units and the LUMO was more delocalized along the conjugated backbone as compared to DPP-TVT. Therefore, it can be expected that the DPP-2CNTVT polymer would have better electron transporting properties than DPP-TVT. In order to investigate the effects of CN substitution on the conjugated backbone geometries, the dihedral angles A1, A2, A3, and A4 were calculated (Table S1). Both DPP-TVT and DPP-2CNTVT exhibit highly planar molecular backbone structure with very small dihedral angles ($\approx 1^{\circ}$). Furthermore, the dipole moment and direction of the repeating unit of the polymers

were also calculated. It was found that DPP-TVT has a higher dipole moment (1.507 D) than DPP-2CNTVT (1.3635 D), which is expected to enhance molecular ordering as described in a previous report.²¹ Interestingly, the direction of the dipole moment in DPP-2CNTVT was opposite to that of DPP-TVT, which indicated that the 2CNTVT unit is a stronger electron withdrawing moiety than the DPP unit. It is assumed that the conjugated backbone changes from donor–acceptor type to acceptor–acceptor type. These results are shown in Figures S4 and S5.

OFET Characteristics. In order to study the structureactivity relationships, top-gate bottom-contact (TG/BC) OFETs were fabricated with a very thin gold source and drain electrodes (13 nm Au on 3 nm Ni pads) prepatterned by conventional photolithography. Figures 2 and 3 illustrate the typical transfer and output characteristics of the OFETs fabricated with 2DPP-TVT, 7DPP-TVT, 2DPP-2CNTVT, and 7DPP-2CNTVT. A dramatic shift of the nature of the majority carriers from holes to electrons was observed in these fabricated devices. The OFETs fabricated using 2DPP-TVT and 7DPP-TVT exhibited typical p-channel characteristics, while those fabricated using 2DPP-2CNTVT and 7DPP-2CNTVT showed n-channel characteristics. The OFETs fabricated using 2DPP-TVT and 7DPP-TVT showed fairly good average hole field-effect mobilities (μ_{FET}) of 1.63 and 2.2 cm² V⁻¹ s⁻¹, respectively. On the other hand, the OFETs fabricated using 2DPP-2CNTVT and 7DPP-2CNTVT showed average electron μ_{FET} of 1.2 cm² V⁻¹ s⁻¹ after thermal annealing at 200 and 250 °C, respectively. The values of μ_{FET} of the polymer OFETs depend on the annealing temperatures of the active polymer films. The optimum annealing temperatures of the polymer films are in the range 200-250 °C. The detailed

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Table 2. Calculated Device Parameters

semiconductor	spin-coating rate	annealing temp (°C)	av mobility $(cm^2/(V s))$	threshold voltage (V)	$R_{\rm c} (\Omega \cdot {\rm cm})$	$I_{\rm on/off}$
2DPP-TVT	1000 rpm/30 s	100	0.20	-47.7	7.4×10^{4}	10 ³
		150	0.32	-21.8	2.3×10^{3}	10^{4}
		200	0.85	-35.8	1.7×10^{3}	10 ³
		250	1.54	-40.5	7.7×10^{4}	10 ³
		300	0.15	-29.9	3.8×10^{3}	$\sim 10^{2}$
	1500 rpm/60 s	250	1.63	-36.5	4.0×10^{3}	$\sim 10^{3}$
	2000 rpm/60 s		1.12	-37.1	9.5×10^{3}	$\sim 10^{3}$
2DPP-2CNTVT	1000 rpm/30 s	100	0.10	56.4	5.5×10^{7}	$\sim 10^{3}$
		150	0.20	27.8	3.9×10^{5}	10 ³
		200	0.50	28.6	9.2×10^{4}	10 ³
		250	0.34	36.1	6.3×10^{5}	10 ³
		300	0.53	43.2	1.1×10^{6}	10 ³
	1500 rpm/60 s	200	1.20	30.0	3.3×10^{4}	$\sim 10^4$
	2000 rpm/60 s		0.52	22.3	3.4×10^{4}	10 ³
7DPP-TVT	1000 rpm/30 s	100	0.40	-13.9	7.8×10^4	10 ⁴
		150	1.24	-25.2	5.7×10^{2}	10 ³
		200	2.20	-38.7	7.1×10^{3}	10 ³
		250	1.20	-40.3	3.1×10^{3}	$\sim 10^{3}$
		300	1.55	-45.0	2.2×10^{4}	$\sim 10^{3}$
	1500 rpm/60 s	200	1.44	-22.4	3.8×10^{3}	$\sim 10^{3}$
	2000 rpm/60 s		1.50	-18.7	2.0×10^{2}	$\sim 10^{3}$
7DPP-2CNTVT	1000 rpm/30 s	100	0.10	-1.0	8.2×10^{9}	$\sim 10^{3}$
		150	0.09	34.9	1.2×10^{8}	10 ²
		200	0.30	33.0	7.4×10^{7}	10 ²
		250	1.20	35.7	2.3×10^{4}	10 ³
		300	0.62	36.0	1.5×10^{5}	10 ³
	1500 rpm/60 s	250	1.11	30.6	1.7×10^{4}	10 ³
	2000 rpm/60 s		1.13	18.9	2.0×10^{4}	10 ³



Figure 4. Two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) images (a-d) and (f) out-of-plane and (e) in-plane XRD diffractogram profiles of the polymer thin films (200 °C for 7DPP-TVT and 2DPP-2CNTVT, 250 °C for 2DPP-TVT and 7DPP-2CNTVT).

device characteristics of the fabricated OFETs including their annealing temperatures are summarized in Table 2. The fabricated OFETs exhibited reasonably low contact resistances $(10^{-3}-10^{-4}~\Omega\cdot cm)$ for either hole or electron injection from the Au electrode.

The operational stabilities of OFETs were also tested. The transfer characteristics of the four OFETs under gate-bias stress and long-term storage in air are given in Figure S6. All OFETs showed good operational stability even after application of continuous bias for 6 h. Electrical properties of p-type 2DPP-

TVT and 7DPP-TVT OFETs slightly degraded even after 7 days storage in the ambient environment. For 2DPP-2CNTVT and 7DPP-2CNTVT OFETs, the degradation of electron transport was much noticeable, although the devices still operated (Figure S7). The poor air stability of n-type 2DPP-2CNTVT and 7DPP-2CNTVT OFETs is likely to the generation of trap sites by reaction with hydrogenated oxygen.²²

Thin-Film Microstructural Analyses. In order to clarify the crystallinity and molecular packing of the polymers, 2D-GIXD was performed on the polymer thin films at their optimum annealing temperature (200 °C for 7DPP-TVT and 2DPP-2CNTVT, 250 °C for 2DPP-TVT and 7DPP-2CNTVT). Figure 4 shows the 2D-GIXD images and the corresponding diffractogram profiles of the polymer thin films. The bare TVT-based polymers (2DPP-TVT and 7DPP-TVT) exhibited an edge-on dominant orientation with distinct lamellar peaks up to the fourth order, which is consistent with the previous reports on the crystal structures of DPP-TVT-based polymers.⁷ Interestingly, unlike the known TVTbased polymers, the 2CNTVT-based polymers (2DPP-2CNTVT and 7DPP-2CNTVT) exhibited a bimodal orientation in which the edge-on and face-on orientations coexist. In order to gain a deeper insight into this orientation, we performed azimuthal angle scans of the (100) reflection (Figure S8). The integrated intensity with azimuthal angle (γ) in the range $0-45^{\circ}$ (or 0 to -45°) was defined as A_{2} , and that ranging from 45° to 90° (or -45° to -90°) was designated as A_{xy} corresponding to the fractions of edge-on and face-on orientations, respectively. The area ratio of A_{xy} to $A_z (A_{xy}/A_z)$ for 2DPP-TVT, 7DPP-TVT, 2-DPP-2CNTVT, and 7DPP-2CNTVT was found to be 0.054, 0.048, 0.102, and 0.219, respectively. The face-on portions of the 2CNTVT-based polymers are more than those of the corresponding TVT-based polymers. These face-on portions of the 2CNTVT based polymers can form 3D charge-conduction channels which would be beneficial for electron charge transport.^{6,23} The lamellar and $\pi - \pi$ spacings of the 2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT thin films were 23.2, 24.9, 30.5, 30.5 Å and 3.748, 3.627, 3.605, 3.590 Å, respectively. Although the lamellar spacing of the 7DPP-based polymers increased because of the change in the bridging point of the alkyl spacer, the $\pi - \pi$ spacing decreased, leading to increased mobility due to a better orbital overlap between the neighboring polymer main chains. 7DPP-2CNTVT and 2DPP-2CNTVT showed comparable $\pi - \pi$ spacing and thus possessed similar electron mobilities. Further details of the crystal structure of the polymers are summarized in Table S2.

In order to gain further insight into the polymer structures, film morphologies of the polymers were investigated by AFM, using tapping mode under ambient conditions. For the roughness measurements, the polymer films (2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT) were annealed at temperatures for their best device performances (200 °C for 7DPP-TVT and 2DPP-2CNTVT, 250 °C for 2DPP-TVT and 7DPP-2CNTVT) for 30 min (Figure S9). As revealed in the images, the 2DPP-TVT, 2DPP-2CNTVT, 7DPP-TVT, and 7DPP-2CNTVT films have a crystalline morphology and exhibit smooth surfaces with root-meansquare (rms) roughness of 0.802, 0.644, 1.12, and 0.913 nm, respectively. Compared to 2DPP-based polymers, the 7DPPbased polymers exhibit more developed fibrillar networks with higher rms roughness values because of their high crystallinity. The data obtained from AFM measurements is in good agreement with the 2D-GIXD results and the observed charge transporting properties.

CONCLUSION

In summary, we successfully synthesized novel n-type conjugated polymers consisting of DPP and TVT monomers with cyano groups, and the effect of the cyano group on the frontier orbital energy levels, crystal orientation, and charge transporting properties of the synthesized polymers was also investigated. The CNTVT-based polymers showed lower HOMO/LUMO energy levels compared to the TVT-based polymers, which was more favorable for electron injection from the Au electrode. Moreover, the polymers exhibited bimodal orientation with good crystallinity such that the fabricated OFETs using CNTVT-based polymers showed high electron mobility. This work demonstrates that the newly synthesized 2CNTVT unit could be used as a good electron accepting building block for high performance n-type conjugated polymers for OFETs.

EXPERIMENTAL SECTION

Materials. All reagents were purchased from Aldrich, Alfa Aesar, or TCI Korea and used without further purification. Tris(dibenzylidene-acetone)dipalladium(0) and tri(o-tolyl)phosphine were purchased from Strem. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere. Column chromatography was performed using silica gel (Electronic Materials Index, SL-60-60A). 3-Bromothiophene-2-carbaldehyde, (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene, 3,6-bis-(5-bromothiophene-2-yl)-2,5-bis(2-dodecylhexadecyl)pyrrolo[3,4-c]-pyrrole-1,4-(2H,5H)-dione, 13-(6-bromohexyl)heptacosane were synthesized following previously reported procedures.^{24–26}

Measurements. ¹H and ¹³C NMR spectra were measured on a Varian Mercury Plus 300 MHz spectrometer. High-resolution mass spectra (HRMS) were acquired on high-resolution mass spectrometers: Q-TOF (ionization mode: ESI) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) was performed on Voyager DE-STR (Applied Biosystems). Thermal analyses were carried out on a TA Instruments Q600 (PH407 PUSAN, Korea Basic Science Institute (KBSI)) under an inert N_2 atmosphere, with heating and cooling rates of 10 °C min⁻¹. The UVvis absorption spectra were measured on a JASCO JP/V-570 model spectrophotometer. The number-average (M_n) and weight-average (M_w) molecular weights were determined by gel permeation chromatography (GPC) (Waters model M590) using polystyrene as a standard. Cyclic voltammetry experiments were performed with a CH Instruments electrochemical analyzer in acetonitrile solutions containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) as the supporting electrolyte, with Ag/AgNO3 as the reference electrode, a platinum wire as the counter electrode, and a platinum working electrode. Density functional theory (DFT) calculations were performed using the Gaussian 09W package with the Becke threeparameter Lee-Yang-Parr (B3LYP) function and the 6-31G(d) basis set to elucidate the HOMO and LUMO energy levels and backbone planarity. 2D-GIXD experiments were performed at the 3C beamlines of the Pohang Accelerator Laboratory (PAL), Korea. X-rays with a wavelength of 1.2096 Å (9.9899 keV) were used. The incidence angle (0.13°) was chosen to allow for complete penetration of the X-rays into the polymer film. The surface morphologies of the polymer thin films were characterized by using an AFM (SPM System) operated in the tapping mode. The polymers were spin-coated on the SiO₂/Si substrates and postannealed at the optimum temperatures for the 2D GIXD measurements and AFM analysis.

Device Fabrication and Characterization. Top-gate bottomcontact configuration was adopted for device fabrication. Glass substrates with prepatterned Ni/Au (3 nm/13 nm) source and drain Scheme 2. Synthesis and Chemical Structures of the Polymers



electrodes were cleaned ultrasonically in deionized water, acetone, and isopropyl alcohol for 10 min each, blown dry by nitrogen gas, and then baked at 110 °C to remove residual water. The spacing (channel length) between the contacts ranged from 10 to 50 μ m, and the channel width was 1000 μ m. The polymers were dissolved in 1,2,4trichlorobenzene to form solutions at a concentration of 5 mg mL $^{-1}$. The polymer solutions were heated on a hot plate at 80 °C for complete dissolution for more than 24 h and then spin-coated at different spin coating rates of 1000, 1500, and 2000 rpm for 30 s (in the case of 1000 rpm) and 60 s to form films with different thicknesses. All four solutions were filtered before film deposition and annealed at different temperatures ranging from 100 to 300 °C for 30 min to remove residual solvent and promote molecular packing. PMMA (6.2 nF cm⁻²) was used as the gate dielectric. It was spincoated using the 80 mg mL⁻¹ butyl acetate solution and spin-coated at 2000 rpm for 60 s to form a 500 nm thick dielectric layer and annealed at 80 °C for 2 h. Al gate electrodes of 50 nm thickness were deposited by thermal evaporation through shadow masks to complete the devices. All of the above-mentioned fabrication procedures were carried out under a nitrogen atmosphere.

Electrical properties of the OFETs were characterized by using a Keithley 4200-SCS parameter analyzer in a nitrogen-filled glovebox at room temperature. The device parameters such as the mobility and threshold voltage values were extracted in the saturation region by the classic method using the formula $I_{d,sat} = \frac{W}{2L}C_{i}\mu(V_{g} - V_{th})^{2}$, where I_{d} is drain-to-source current, W and L are the channel width and length, respectively, C_{i} is the gate dielectric capacitance per unit area, μ is the field effect mobility in the saturation regime, and V_{g} and V_{th} are gate-to-source and threshold voltages, respectively.

Monomer and Copolymer Syntheses. Synthesis of (E)-1,2-Bis(3-bromothiophen-2-yl)ethene (1). TiCl₄ (12.07 mL, 109.8 mmol) was added dropwise to a slurry of 3-bromothiophene-2-carbaldehyde (14 g, 73.2 mmol) in THF (200 mL) with stirring over a period of 30 min at -18 °C. After stirring at this temperature for 30 min, Zn powder (15 g, 219.6 mmol) was added in small portions over a period of 30 min. The mixture was stirred at -18 °C for another 30 min, warmed to room temperature, and then refluxed for 4 h. The reaction was quenched by adding ice-cold H₂O (100 mL). The mixture was extracted with dichloromethane several times and dried over MgSO4. The solvent was removed and purified by silica gel column chromatography using hexane as the eluent to obtain the desired product as a yellow solid. Yield: 39% (10 g) of the pure (E) isomer. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.20 (d, J = 5.4 Hz, 2H), 7.12 (s, 2H), 6.98 (d, J = 5.4 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 136.5, 130.9, 124.4, 121.4, 111.5. HRMS (ESI) *m/z*: 348.86 [M + H]⁺, calcd 348.83.

Synthesis of (E)-1,2-Bis(3-cyanothiophene-2-yl)ethene (2). The mixture of compound 1 (2.5 g, 7.14 mmol) and CuCN (3.19 g, 35.7 mmol) in anhydrous DMF (100 mL) was stirred for 12 h at 150 °C.

Subsequently, it was allowed to cool to room temperature. To this mixture, FeCl₃·6H₂O (7.75 g, 28.56 mmol) in 2 M aqueous HCl (15 mL) was added and stirred at 70 °C for 1 h. Then the mixture was extracted with dichloromethane several times and dried over MgSO₄. The solvent was removed and purified by silica gel column chromatography using dichloromethane:hexane (2:1 v/v) to obtain the desired compound as a yellow solid. Yield: 74% (1.28 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.39 (s, 2H), 7.35 (d, *J* = 5.1 Hz, 2H), 7.22 (d, *J* = 5.1 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 150.0, 129.3, 126.5, 122.3, 114.4, 110.0. Elem Anal. Calcd for C₁₂H₆N₂S₂: C, 59.5; H, 2.5; N,11.5; S, 26.5. Found: C, 59.2; H, 2.4; N,11.5; S, 26.5. HRMS (ESI) *m/z*: 243.00 [M + H]⁺, calcd 243.00.

Synthesis of (E)-1,2-Bis(5-(trimethylstannyl)-3-cyanothiophene-2-yl)ethene (3). A solution of compound 2 (0.24 g, 1 mmol) in anhydrous THF (30 mL) was added dropwise at -78 °C to 2.0 M lithium diisopropylamine (LDA, 1.05 mL, 2.1 mmol). After stirring for 1 h at -78 °C, trimethyltin chloride (3 mL, 3 mmol, 1 M in hexanes) was added dropwise to the reaction mixture. Subsequently, the reaction flask was warmed to room temperature and stirred overnight. The reaction mixture was quenched with distilled water and extracted with ethyl acetate. The organic layer was washed twice with brine and dried over MgSO₄. After drying the extracts, the obtained residue was purified by recrystallization from ethanol to give a yellow product. Yield: 74% (0.42 g). ¹H NMR (300 MHz, $CDCl_3$, ppm): δ 7.37 (s, 2H), 7.21 (s, 2H), 0.37 (s, 18H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 155.5, 141.5, 136.5, 121.8, 115.0, 110.9, - 8.1. Elem Anal. Calcd for C₁₈H₂₂N₂S₂: C, 38.0; H, 3.9; N, 4.9; S, 11.3. Found: C, 36.8; H, 4.0; N, 4.7; S, 11.4. MS (MALDI-TOF) m/z: 569.12 [M⁺], calcd 569.93.

Synthesis of 2,5-Bis(7-dodecylhenicosyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4). A mixture of 3,6-di-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione (3.00 g, 0.1 mol) and potassium carbonate (8.25 g, 0.6 mol) was dissolved in 100 mL of anhydrous N,N-dimethylformamide (DMF) and heated to 120 °C under nitrogen for 1 h. Subsequently, 13-(6-bromohexyl)heptacosane (15.54 g, 0.3 mol) was added dropwise, and the mixture was stirred overnight at 120 °C. The mixture was allowed to cool down to room temperature and quenched with distilled water. The organic layer was then extracted with chloroform and dried over MgSO₄. The crude product was purified by silica column chromatography with dichloromethane/hexane (1:1) to obtain a purple compound 2-a. Yield: 26% (3.2 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.95 (d, 2H), 7.65 (d, 2H), 7.30 (t, 2H), 4.07 (t, 4H), 1.75 (m, 4H), 1.25 (m, 114H), 0.88 (t, 12H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 161.34, 140.06, 135.25, 130.59, 129.81, 128.58, 107.71, 42.31, 37.35, 33.31, 31.93, 30.17, 29.72, 29.69, 29.68, 29.42, 29.38,26.45, 24.08, 22.71, 14.15. MS (MALDI-TOF) m/z: 1225.06 [M⁺], calcd 1225.04.

Synthesis of 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(7-dodecylhenicosyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5). Compound 3 (3.2 g, 2.6 mmol) was dissolved in 50 mL of CHCl₃, and the reaction flask was covered with aluminum foil. *N*-Bromosuccinimide (1.12 g, 5.98 mmol) was added to the flask at 0 °C, and the mixture was stirred at room temperature overnight. Subsequently, the reaction was quenched with distilled water. The organic layer was extracted with chloroform and dried over MgSO₄. The crude product obtained after evaporating the solvent was recrystallized with CHCl₃/MeOH to obtain a deep purple solid. Yield: 87% (3.2 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.67 (d, 2H), 7.25 (d, 2H), 3.96 (t, 4H), 1.70 (m, 2H), 1.25 (m, 114H), 0.87 (t, 12H). ¹³C NMR (75 MHz, CDCl₃, ppm): 161.75, 140.44, 135.62, 130.91, 130.20, 128.99, 108.18, 42.67, 37.85, 34.55, 32.23, 30.51, 30.35, 30.12, 29.73, 29.67, 27.30, 27,31, 27.05, 23.60, 14.51. MS (MALDI-TOF) *m*/*z*: 1381.02 [M⁺], calcd 1380.86.

General Polymerization Procedure. The four copolymers were synthesized via Stille coupling polymerization, as shown in Scheme 2. (E)-1,2-Bis(5-(trimethylstannyl)thiophen-2-yl)ethene (TVT-Tin), (E)-1,2-bis(5-(trimethylstannyl)-3-cyanothiophene-2-yl)ethene (2CNTVT-Tin), 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-dodecylhexadecyl)pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione (2DPP), and 3,6bis(5-bromothiophen-2-yl)-2,5-bis(7-dodecylhenicosyl)pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione (7DPP) were synthesized using previously reported procedures. Tris(dibenzylideneacetone)dipalladium(0) and tri(o-tolyl)phosphine were dissolved in anhydrous chlorobenzene (CB) and stirred at 120 °C for 2 days. Subsequently, a solution of excess 2-bromothiophene and tributyl(thiophen-2-yl)stannane (the end-capper) in 1 mL of anhydrous toluene was added to the reaction mixture and after 12 h of stirring, it was cooled to \sim 50 $^{\circ}$ C and 200 mL of methanol was added slowly with vigorous stirring. The crude polymer was collected by filtration and purified by Soxhlet extraction using methanol, acetone, hexane, and chloroform, successively. The polymers were obtained by reprecipitation of the chloroform solution into methanol.

Poly{2,5-bis(2-dodecylhexadecyl)-3,6-di(thiophen-2-yl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-(E)-1,2-bis(thiophen-2-yl)ethene} (2DPP-TVT). (E)-1,2-Bis(5-(trimethylstannyl)thiophen-2-yl)ethene (83.3 mg, 0.145 mmol) was mixed with 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-dodecylhenicosyl)pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione (200 mg, 1.0 equiv), tris(dibenzylideneacetone)dipalladium(0) (2.94 mg, 2.91 µmol), tri(*o*-tolyl)phosphine (3.91 mg, 11.6 µmol), and CB (3 mL). Polymer yield = 91%. Elem Anal. Calcd for C₈₀H₁₂₄N₂O₂S₄: C, 75.4; H, 9.8; N, 2.2; S, 10.1. Found: C, 75.3; H, 10.0; N, 2.1; S, 10.3. $M_n = 127$ kg mol⁻¹, PDI = 2.4, and $T_d =$ 398 °C.

Poly{2,5-bis(2-dodecylhexadecyl)-3,6-di(thiophen-2-yl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-(E)-1,2-bis(3-cyanothiophen-2yl)ethene} (2DPP-2CNTVT). (E)-1,2-Bis(5-(trimethylstannyl)-3-cyanothiophene-2-yl)ethene (137 mg, 0.241 mmol) was mixed with 3,6bis(5-bromothiophen-2-yl)-2,5-bis(7-dodecylhenicosyl)pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione (300 mg, 1.0 equiv), tris(dibenzylideneacetone)dipalladium(0) (4.42 mg, 4.82 μmol), tri(*o*-tolyl)phosphine (5.87 mg, 19.3 μmol), and CB (4.5 mL). Polymer yield = 90%. Elem Anal. Calcd for C₈₂H1₂₂N₄O₂S₄: C, 74.4; H, 9.3; N, 4.2; S, 9.7. Found: C, 74.2; H, 9.4; N, 4.1; S, 9.8. M_n = 37 kg mol⁻¹, PDI = 1.4, and T_d = 401 °C.

Poly{2,5-bis(7-dodecylhenicosyl)-3,6-di(thiophen-2-yl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-(E)-1,2-bis(thiophen-2-yl)ethene} (7DPP-TVT). (E)-1,2-Bis(5-(trimethylstannyl)thiophen-2-yl)ethene (74.85 mg, 0.144 mmol) was mixed with 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-dodecylhenicosyl)pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione (200 mg, 1.0 equiv), tris(dibenzylideneacetone)dipalladium(0) (2.64 mg, 2.89 µmol), tri(*o*-tolyl)phosphine (3.51 mg, 11.5 µmol), and CB (3 mL). Polymer yield = 93%. Elem Anal. Calcd for C₉₂H₁₄₂N₄O₂S₄: C, 76.4; H, 10.3; N,2.0; S, 9.1. Found: C, 76.2; H, 10.5; N, 1.9; S, 8.7. M_n = 314 kg mol⁻¹, PDI = 2.6, and T_d = 397 °C.

Poly{2,5-bis(7-dodecylhenicosyl)-3,6-di(thiophen-2-yl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-(E)-1,2-bis(3-cyanothiophen-2yl)ethene (7DPP-2CNTVT). (E)-1,2-Bis(5-(trimethylstannyl)-3-cyanothiophene-2-yl)ethene (123.11 mg, 0.216 mmol) was mixed with 3,6bis(5-bromothiophen-2-yl)-2,5-bis(7-dodecylhenicosyl)pyrrolo[3,4-c]- pyrrole-1,4-(2*H*,5*H*) -dione (300 mg, 1.0 equiv), tris(dibenzylideneacetone)dipalladium(0) (3.97 mg, 4.33 μ mol), tri(*o*-tolyl)phosphine (5.28 mg, 17.3 μ mol), and CB (4.5 mL). The polymer yield was 90%. Elem Anal. Calcd for C₉₂H₁₄₂N₄O₂S₄: C, 75.5; H, 9.8; N,3.8; S, 8.7. Found: C, 75.3; H, 10.1; N, 3.4; S, 8.2. M_n = 53 kg mol⁻¹, PDI = 1.3, and T_d = 405 °C.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.7b01524.

¹H and ¹³C NMR spectra, TGA and CV results, DFT calculations, OFET data, 2D-GIXD and AFM data (PDF)

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Notes

The authors declare no competing financial interest.

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