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Tuning the Charge Carrier Polarity of Organic Transistors by Varying the Electron Affinity of the Flanked Units in Diketopyrrolopyrrole-Based Copolymers

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Abstract

Fine-tuning of the charge carrier polarity in organic field effect transistors (OFETs) is an important step towards high-performance organic complementary circuits and related devices. In this study, three new semiconducting polymers, namely, pDPF-DTF2, pDPSe-DTF2, and pDPPy-DTF2, were designed and synthesized using furan, selenophene, and pyridine flanking group-based diketopyrrolopyrrole (DPP) cores, respectively. Upon evaluating electrical
properties of these newly synthesized polymers in OFET devices, a best performance has been achieved for pDPSe-DTF2 polymer with the highest and average hole mobility of 1.51 and 1.22 cm² V⁻¹ s⁻¹, respectively. Most intriguingly, we observed a clear charge-carrier-polarity change when the devices were measured under vacuum. The pDPF-DTF2 polymer exhibited a balanced ambipolar performance with the $\mu_h/\mu_e$ ratio of 1.9 under vacuum, whereas pDPSe-DTF2 exhibited $p$-type dominated charge carrier transport properties with the $\mu_h/\mu_e$ ratio of 26.7. Such a charge carrier transport change is due to the strong electron-donating nature of the selenophene. Furthermore, pDPPy-DTF2 with an electron-withdrawing pyridine flanking unit demonstrated unipolar $n$-type charge transport properties with the electron mobility as high as 0.20 cm² V⁻¹ s⁻¹ under vacuum. Overall, this study demonstrated a simple yet effective approach to switch the charge carrier polarity in OFETs by varying the electron affinity of flanking groups of DPP units.

**Introduction**

Field effect transistors are an attractive class of electronic devices; they are extensively used in integrated circuits and backplane switch for display devices. Recently, organic field effect transistors (OFETs) received significant attention in the organic electronics community owing to their unique advantages compared to their inorganic counterparts in terms of low cost, lightweight, roll-to-roll large-area fabrication, and flexibility. The advantages of using organic semiconducting materials in the active layer are due to their solution processability that enables facile synthesis, easy structural modification, low-temperature and large-scale homogeneous film formation on flexible substrates.

Recently, diketopyrrolopyrrole (DPP) conjugated planar core has proven to be one of the most versatile and widely used building blocks for constructing a wide range of organic semiconducting conjugated small molecules and polymers. The electron-deficient character
of the DPP unit permits designing molecules with outstanding light harvesting properties in the
visible range, and DPP-based materials can deliver excellent photovoltaic performances in
solar cells.\[4\] In addition to the electron deficiency, the high planarity of the DPP unit provides
significant intermolecular $\pi-\pi$ interactions between the conjugated backbones, which in turn
facilitates the charge carrier transport in OFET devices.\[5\] By varying the flanking moieties on
both sides of the DPP core and copolymerizing with different comonomers (electron donor or
electron acceptor), the resulting polymers can behave as $p$-type, $n$-type or ambipolar
semiconductors according to the dominant charge carriers flowing along the conducting
channel of OFETs.\[6\] Thiophen-flanked DPP (TDPP) has been widely studied, and a series of
TDPP-based organic semiconductors have demonstrated record mobility values at different
stages of scientific development.\[6a\] However, other aromatic ring-flanked DPPs were
relatively unexplored, for example, the furan,\[6b\] selenophene (Se),\[6c\] pyridine (Py),\[6d\]
phenyl,\[6e\] naphthalene,\[3d\] thieno[3,2-$b$]thiophene,\[6f\] and benzothiophene\[6g\] substitutions.
Substitution of either electron donating or electron accepting flanking groups on both sides of
the DPP core can significantly modify the charge carrier transport and semiconducting
properties of the products.

Chalcogen-based five-membered heterocycles, furan and selenophene, and a six-
membered pyridine as the DPP substituents, have the potential of modulation and improvement
of optoelectronic properties.\[7\] Importantly, the furan ring can be thought as a renewable and
sustainable resource because of possibility of synthesis from a variety of natural products.\[7a, 7d, 7e\]
The high polarizability of Se makes the selenophene-flanked DPP (DPSe) easily form an
intramolecular Se-O interaction (a distance of 2.94 Å was estimated from theoretical
calculations), which favours a planar backbone.\[7c\] Most significantly, the high polarizability
of Se induces attractive intermolecular Se-Se or Se-aromatic interactions between Se-
containing molecules, which greatly benefits the charge carrier transport.\[7g\] The last class of
DPPs is the pyridine-flanked DPP (DPPy). The pyridine ring lacks the hydrogen atom at the 2-position, leading to a decreased steric hindrance between the pyridine and DPP units or between the pyridine and N-CH₂ of the alkyl chains. This would help to improve the co-planarity of the resulting DPPy-based semiconductors. In addition, DPPy becomes a stronger electron-accepting group than other DPP derivatives due to the pyridine rings, leading to deep lowest unoccupied molecular orbital (LUMO) energy level and thus efficient electron injection and transport. For the comonomer selection, difluoro bithiophene (DTF2) has several interesting and promising properties for constructing high-performance OFET semiconductors. DTF2 has a planar conformation due to the intramolecular F···S noncovalent interaction. In addition, the F atom substitution decreases both the HOMO and LUMO energy levels. The HOMO decrease enhances the oxidative stability, and the LUMO decrease facilitates electron injection from the metal electrodes.

In the current work, we are reporting three new semiconducting polymers, namely, pDPF-DTF2, pDPSe-DTF2, and pDPPy-DTF2, respectively, using DPF, DPSe, and DPPy monomers with difluoro bithiophene (DTF2) via Stille coupling polymerization. The effect of the different flanking groups on the thermal, optical, electronic, and charge transport properties of these polymers was comprehensively studied. OFETs based on the three polymers exhibited p-type behaviour in air with the highest $\mu_h$ of up to 1.51 (1.22 for average) cm² V⁻¹ s⁻¹ achieved with pDPSe-DTF2. However, charge-carrier-polarity change occurred under vacuum, producing balanced ambipolar performance for pDPF-DTF2 ($\mu_h/\mu_e = 1.9$), p-type dominant behaviour for pDPSe-DTF2 ($\mu_h/\mu_e = 26.7$), and n-type unipolar performance for pDPPy-DTF2 ($\mu_e = 0.20$ cm² V⁻¹ s⁻¹). Overall, we have successfully demonstrated a simple yet effective method to reverse the polarity and charge transport behaviour of DPP-based copolymers by variation of the electron affinity of flanking groups of DPP core and measurement environments.
Results and Discussion

Synthesis and Characterization

The chemical structures and synthetic routes to the DPP monomers and target polymers are shown in Scheme 1 and the detailed procedures are described in the electronic supplementary information (ESI). The polymers synthesis started using reported furan, selenophene, and pyridine flanked dibromo DPP monomers with same long branched side alkyl chains to induce solution processability for the targeted polymers. These dibrominated DPP derivatives were copolymerized with bis-stannylated fluorinated bithiophene (Sn-DTF2) by palladium-catalyzed Stille coupling polymerization route using anhydrous toluene to afford pDPF-DTF2, pDPSe-DTF2, and pDPPy-DTF2 new copolymers. Purification of the crude polymers was carried out by Soxhlet extraction method using various polar and nonpolar solvents, such as
methanol, acetone, and hexane, to remove ionic and oligomeric impurities. The residue was finally extracted with either chloroform or chlorobenzene. The extracted polymer solution in chloroform and chlorobenzene was then precipitated into methanol to yield the title purified polymers. One of the polymers, pDPF-DTF2, exhibited an excellent solubility in common organic solvents, such as chloroform, toluene, chlorobenzene, and 1,2-dichlorobenzene. However, the solubility of pDPSe-DTF2 and pDPPy-DTF2 was lower at room temperature, and they could be dissolved in hot chloroform and chlorobenzene by simply stirring at 60°C (chloroform) or 100°C (chlorobenzene) (for the detailed conditions, see ESI). It has been well documented that the furan-based DPP has a higher solubility in most of the common organic solvents than their thiophene and pyridine counterparts.[9] The molecular weights of all three polymers was characterized by gel permeation chromatography (GPC) using polystyrene (PS) as the internal standard and 1,2-dichlorobenzene as the eluent at 40°C. The respective molecular weight chart and data are shown in Figure S1. GPC studies suggested that the copolymers have the following number-average molecular weight ($M_n$) and polydispersity (PDI, $M_w/M_n$): pDPF-DTF2 ($M_n = 95.9$ kg mol$^{-1}$, PDI = 3.4), pDPSe-DTF2 ($M_n = 10.8$ kg mol$^{-1}$, PDI = 3.3), and pDPPy-DTF2 ($M_n = 43.6$ kg mol$^{-1}$, PDI = 4.5).

Thermal properties of pDPF-DTF2, pDPSe-DTF2, and pDPPy-DTF2 polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere at the heating rate of 10°C min$^{-1}$ and cooling rate of 5°C min$^{-1}$. From TGA thermograms (Figure S2a), all the polymers exhibited good thermal stability with the decomposition temperatures ($T_d$, 5% weight loss) of 370-400°C. The high thermal stability of these polymers provides not only an adequate guarantee for practical applications in organic electronics but also a wide thermal annealing temperature range for optimizing the device performances. From the DSC measurements (Figure S2b), no well-defined transitions were observed during heating (up to 300°C) and cooling processes for all three polymers. It has been
reported that the thermal transitions of semiconducting polymers with highly rigid backbones are not possible and such polymers usually start to decompose before any thermal transitions.\cite{10}

**Optical Properties and Energy Levels of the Polymers**

![Figure 1.](image)

**Figure 1.** UV-Vis absorption spectra (a) in solutions (chloroform) and (b) as thin films; (c) Photoelectron spectroscopy in air (PESA) measurements and (d) HOMO-LUMO energy levels diagram.

The absorption profile of all three polymers in both chloroform solutions and as thin films displayed a similar feature with a dominant absorption band between 550-850 nm for pDPF-DTF2, 550-950 nm for pDPSe-DTF2, and 550-750 nm for pDPPy-DTF2. The above data clearly indicates that the pDPSe-DTF2 polymer has the lowest band gap among all polymers based on the higher absorption cut off value compared to the other two. This is confirmed by ab initio calculations which resulted in absorption peak maxima of 760, 780, and 670 nm,
respectively for pDPF-DTF2, pDPSe-DTF2, and pDPPy-DTF2 (Figure S3). Calculations also confirm a significant blueshift with Py vs. both furan and selenophene based molecules and an only mild redshift of selenophene vs. furan-based molecule observed experimentally. The longer wavelength bands are attributed to the intramolecular charge transfer (ICT) from the bithiophene to the electron-withdrawing DPP moiety (Figure 1a-b).[11] The shoulder peaks at 706 nm for pDPF-DTF2 and 626 nm for pDPPy-DTF2 indicate the J-aggregate formation in both solutions and as thin films due to the higher backbone planarity as compared to pDPSe-DTF2, which was evidenced from the dihedral angles and optimized side view geometry structures of the dimer models (Figures 2 & S3 and Table S1). This is consistent with absence of such features in computed spectra which do not include aggregation effects (Figure S3). The solution spectrum of pDPSe-DTF2 possessed a featureless broad low-energy band, but its film displayed a peak splitting and the longest absorption wavelength was significantly red-shifted by 46 nm, indicating that the polymer backbones self-assembled to form more ordered structures due to the strong donor-acceptor dipolar and π-π interactions partially assisted by the introduction of a large heteroatom, selenium.[12]

Table 1. Summary of optical properties and energy levels.

| Materials    | \( \lambda_{\text{max}}^{\text{sol}} \)/nm | \( \lambda_{\text{max}}^{\text{film}} \)/nm | \( \lambda_{\text{onset}}^{\text{film}} \)/nm | \( E_g^{\text{opt}} \)/eV | HOMO/eV | LUMO/eV |
|--------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|--------------------------|---------|---------|
| pDPF-DTF2    | 769, 706                                  | 765, 700                                  | 848                                       | 1.46 a)                  | -5.39 b), -5.04 d)     | -3.93 c), -3.12 d)     |
| pDPSe-DTF2   | 790, ---                                  | 836, 776                                  | 934                                       | 1.33 a)                  | -5.30 b), -5.16 d)     | -3.97 c), -3.28 d)     |
| pDPPy-DTF2   | 675, 626                                  | 684, 630                                  | 720                                       | 1.72 a)                  | -5.78 b), -5.47 d)     | -4.06 c), -3.33 d)     |

\( a) E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}^{\text{film}} \); \( b) \) PESA results; \( c) \) LUMO = HOMO + \( E_g^{\text{opt}} \); \( d) \) DFT results.

The bandgaps (\( E_g \)) of the polymers, calculated from the onset of thin film absorption spectra, were in the order of pDPSe-DTF2 (1.33 eV) < pDPF-DTF2 (1.46 eV) < pDPPy-DTF2 (1.72 eV). pDPSe-DTF2 had a lower bandgap than pDPF-DTF2, which was attributed to the
replacement of oxygen with the electron-rich selenium atom.\textsuperscript{[12]} The electron-deficient character of the pyridine ring as well as its six membered ring nature of flanking group in pDPPy-DTF2 polymer structure resulted in the largest bandgap among the three polymers.\textsuperscript{[6d, 7b, 7f]} The corresponding data extracted from the absorption spectra are summarized in Table 1.

![Chemical structures and orbital distributions](image)

**Figure 2.** Chemical structures of the model dimers used for DFT calculations; DFT calculated optimized side view geometry structures and molecular frontier orbital distributions.

To determine the absolute energy levels of all three polymers, we performed the photoelectron spectroscopy in air (PESA) measurements on the polymer thin films deposited on the glass substrates. The highest occupied molecular orbital (HOMO) energy levels were extracted from the PESA spectra (Figure 1c), and the corresponding lowest unoccupied molecular orbital (LUMO) levels were estimated from $\text{LUMO} = \text{HOMO} + E_{g}^{opt}$. As shown in Table 1, pDPSe-DTF2 showed the relatively shallower HOMO of -5.30 eV, while pDPF-DTF2 and pDPPy-DTF2 exhibited deeper HOMO of -5.39 and -5.78 eV, respectively. The deeper HOMO of pDPPy-DTF2 clearly indicates the effect of electron withdrawing pyridine-flanking group
compared to electron donating selenophene and furan groups present in pDPSe-DTF2 and pDPF-DTF2 polymers. It should be noted that the energy offset between the HOMO of pDPSe-DTF2 and the work function of commonly used gold electrode (~5.0 eV) is merely 0.3 eV, which will allow for efficient hole injection from the gold to this polymer. As a result, a higher hole transfer rate is expected for pDPSe-DTF2. The LUMO energy levels of pDPF-DTF2, pDPSe-DTF2, and pDPPy-DTF2 were -3.93, -3.97, and -4.06 eV, respectively. pDPPy-DTF2 demonstrated the lowest LUMO among the three polymers, which will increase the electron mobility and device stability of the resulting OFETs.[13]

In order to get an insight into the structural and electronic properties of these polymers, we also performed the theoretical investigation and calculated the optimized molecular structures with minimum internal energy by using density functional theory (DFT) method at the B3LYP/6-31+G(d,p) level. We used the dimer as the corresponding representative of polymer backbone using full alkyl side chains and estimated the dihedral angles between two monomer units. The optimized side view geometry structures, the HOMO and LUMO energy levels and their distribution are shown in Figure 2, and the detailed dihedral angles and front view geometry structures are available in Figure S3 and Table S1. We found that both HOMOs and LUMOs are distributed over the entire conjugated backbones, which are beneficial for the charge carrier (holes and electrons) transport. The order of the experimentally measured band gaps is confirmed by DFT simulations on dimers (results also given in Table 1), as is the order of LUMO levels. The absolute values of LUMO energies are higher with DFT than in an experiment, as expected, given that the experimental values are obtained from the absorption onset and thus include broadening. DFT calculations also confirm a much lower HOMO with Py. The HOMO of Se and furan-based molecules are within 0.1 eV of each other, and a different order might be caused by solid state packing effects (not included in the calculation) and uncertainties of pinpointing HOMO with PESA (Figure 1c). The optimized side view
geometry structures and dihedral angles revealed that pDPF-DTF2 and pDPPy-DTF2 have relatively planar polymer backbone structures as compared with pDPSe-DTF2 (Figures 2 and S3 and Table S1). This was most likely due to the lower steric hindrance between the DPP and furan/pyridine rings. Overall, although there is a slight difference in the dihedral angles, all three polymers possess relatively planar polymer backbones.

**Fabrication and Measurements of Polymer Thin Film Transistors**

**Figure 3.** Current-voltage (I-V) transfer characteristics of OFETs based on the polymer (a) pDPF-DTF2; (b) pDPSe-DTF2; (c) pDPPy-DTF2 after thermal annealing at the optimized temperature. Further device optimization via incorporating an ionic additive (the best molar ratio of NMe4I/polymer repeat unit is 30) based on the polymer (d) pDPF-DTF2; (e) pDPSe-DTF2; (f) pDPPy-DTF2 (L = 100 μm and W = 1 mm, all the OFETs were measured under laboratory ambient conditions).
In order to elucidate the effects of the different flanking substituents of the DPP unit on the charge-transport properties, polymer thin film transistors were fabricated. Bottom-gate/top-contact devices were fabricated by spin-coating the polymer solutions onto an octadecyltrimethylsilane (OTMS)-treated SiO$_2$ (300 nm)/n$^{++}$-Si substrate. After thermal annealing at a selected temperature (150, 200, and 250°C), ~50 nm thick gold was deposited as the source and drain contacts using a shadow mask. The detailed fabrication procedure is described in the ESI. All the three polymers exhibited typical $p$-type OFET transfer characteristics when measured in air (Figures 3a-c, S4, and Tables 2 and S2). The pDPF-DTF2-based OFETs exhibited the maximum and average $\mu_h$ of 0.61 and 0.56 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, after thermal annealing optimization at 200°C for 10 min (Figure 3a). More promisingly, the selenium substituted polymer pDPSe-DTF2 showed its highest and average $\mu_h$ value of 0.95 and 0.72 cm$^2$ V$^{-1}$ s$^{-1}$, respectively (Figure 3b). The higher observed mobility was due to the shallower HOMO of -5.30 eV allowing for more efficient hole injection from the electrode and stronger intermolecular interactions originating from the Se-Se or Se-aromatic attractive forces.$^{[12a]}$ On the other hand, pDPPy-DTF2-based devices showed a lower measured mobility of 0.21 (0.19 for average) cm$^2$ V$^{-1}$ s$^{-1}$ (Figure 3c), which was ascribed to its deep HOMO of -5.78 eV. Taking into account the work function of Au (-5.0 eV), the HOMO level of pDPPy-DTF2 was not suitable for the efficient hole injection from the Au electrode. In order to further improve the OFET performances, we incorporated an ionic additive (tetramethylammonium iodide, NMe$_4$I) to the active layer according to a recent report$^{[14]}$ where the authors have revealed the effect of NMe$_4$I on the thin films of DPP-based semiconducting polymers in detail by using a series of characterization methods. When the molar ratio of NMe$_4$I with respect to the repeat unit of the polymers was optimized, higher hole mobilities were achieved (Figures 3d-f, S5, and Tables 2 and S3). For instance, pDPSe-DTF2 demonstrated the increased $\mu_h$ of 1.51 (1.22 for average) cm$^2$ V$^{-1}$ s$^{-1}$ with the NMe$_4$I/polymer repeat unit ratio of 30. As reported
for the GIWAXS, AFM and theoretical calculations of similar DPP-based polymers\cite{14}, this significant increase in the charge mobility upon addition of NMe$_4$I was due to the inhibited torsion of the alkyl chains, thus leading to more ordered packing structures and stronger interchain interactions.

**Table 2.** Summary of OFET performances measured in air.

| Polymers | $\mu_h$ max. ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) | $\mu_h$ avg. ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) | $V_{th}$ (V) | $I_{on}/I_{off}$ |
|----------|---------------------------------|---------------------------------|--------------|---------------|
| pDPF-DTF2 | 0.61 / 0.87\textsuperscript{b)} | 0.56 / 0.75\textsuperscript{b)} | 5            | $10^6$-$10^7$ |
| pDPSe-DTF2 | 0.95 / 1.51\textsuperscript{b)} | 0.72 / 1.22\textsuperscript{b)} | -5           | $10^5$-$10^6$ |
| pDPPy-DTF2 | 0.21 / 0.36\textsuperscript{b)} | 0.19 / 0.23\textsuperscript{b)} | 12           | $10^5$-$10^6$ |

\textsuperscript{a)} The maximum mobility values under optimized annealing conditions. \textsuperscript{b)} The mobility values optimized upon incorporating an ionic additive. \textsuperscript{c)} The average values are calculated from at least 3 devices.

Interestingly, we observed an enhancement in the electron transport properties when the devices were measured under vacuum. As a result, the furan substituted polymer pDPF-DTF2 demonstrated balanced hole and electron charge transport properties. The device based on pDPF-DTF2 displayed $\mu_h$ and $\mu_e$ of 0.065 and 0.035 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, which amounted to $\mu_h/\mu_e = 1.9$ (Figure 4a-b and Table 3). However, the selenophene-substituted polymer pDPSe-DTF2 still exhibited hole dominated transport properties with the $\mu_h$ of 0.16 cm$^2$ V$^{-1}$ s$^{-1}$ and a marginal $\mu_e$ of 0.006 cm$^2$ V$^{-1}$ s$^{-1}$, which amounted to $\mu_h/\mu_e = 26.7$ (Figure 4c-d and Table 3). This might be due to the very strong electron-donating properties of the selenophene moieties, which were not favorable for the electron transport through the polymer backbone. Most intriguingly, pDPPy-DTF2 with the electron-accepting pyridine substituents showed a
dramatic inversion of the charge polarity when measured under vacuum. Unipolar \( n \)-type charge transport properties with the highest \( \mu_e \) of 0.20 cm\(^2\) V\(^{-1}\) s\(^{-1}\) were achieved (Figure 4e-f and Table 3). The significantly enhanced \( \mu_e \) was fundamentally attributed to its very deep LUMO of -4.06 eV, allowing for the efficient electron injection and transport. This intrinsic \( n \)-type characteristic of pDPPy-DTF2 became evident by removing oxygen.

Figure 4. Current-voltage (I-V) transfer characteristics of the best-performed OFETs based on the polymer (a, b) pDPF-DTF2; (c, d) pDPSe-DTF2; (e, f) pDPPy-DTF2 measured under vacuum (L = 100 \( \mu \)m and W = 1 mm, all the OFETs were measured at \( \sim \)10\(^{-4}\) mbar).

Table 3. Summary of OFET performances measured under vacuum.

| Polymers     | \( \mu_h \) (cm\(^2\) V\(^{-1}\) s\(^{-1}\) \(^{a)} \) | \( \mu_e \) (cm\(^2\) V\(^{-1}\) s\(^{-1}\) \(^{a)} \) | \( V_{th} \) (V) | \( I_{on}/I_{off} \) |
|--------------|---------------------------------------------------|---------------------------------------------------|-----------------|---------------------|
| pDPF-DTF2    | 0.065 (0.051) \(^{b)} \)                         | 0.035 (0.023) \(^{b)} \)                         | \( p: 5; n: 71 \) | \( p: \sim 10^3; n: \sim 10^2 \) |
Characterization of Molecular Organization and Film Morphologies

Besides the HOMO/LUMO energy levels, the molecular packing structure of semiconducting polymers also plays an influential role in dictating the charge carrier mobilities.\textsuperscript{[15]} Therefore, thin film microstructures were examined by wide angle scattering in the grazing incidence mode. Similar to the fabrication of the OFETs, the polymer thin films were spin-cast on an OTMS-treated SiO$_2$/Si substrate. The thin films of all three polymers demonstrated well-defined grazing incident wide angle X-ray scattering (GIWAXS) patterns (Figure 5a-c). The pDPF-DTF2 film displayed a very strong (010) $\pi$-$\pi$ stacking peak only in the out-of-plane (OOP) direction (Figure 5a, d, and g), suggesting that the polymer backbones tended to form a face-on packing texture with respect to the substrate.\textsuperscript{[15]} On the other hand, the pDPSe-DTF2 film was highly ordered with the OOP reflections up to third order (Figure 5b and e). The (010) $\pi$-$\pi$ stacking peaks were both observed in the OOP and in-plane (IP) directions (Figure 5e and h), indicating the co-existence of both edge-on and face-on textures.\textsuperscript{[15]} The $\pi$-$\pi$ stacking distance in the IP direction was 3.41 Å (Table S4). The thin film of pDPPy-DTF2 was also highly crystalline with the OOP reflections up to third order (Figure 5c and f). However, the $\pi$-$\pi$ stacking (010) diffraction with the distance of 3.32 Å was observed only in the IP direction (Figure 5i), implying that the polymer backbones tended to form a uniform edge-on packing texture perpendicular to the substrate. Collectively, the face-on orientation of pDPF-DTF2 is not favorable for the efficient charge transport in the OFETs, thus leading to its lower hole mobility. In contrast, pDPSe-DTF2 had a bimodal packing texture. This texture has recently
been proved as a promising polymer microstructure due to its utilization of 3-D conduction channels to achieve high charge transport properties.\cite{15c, 16} Therefore, pDPSe-DTF2 showed better OFET performances than pDPF-DTF2. The edge-on orientation of pDPPy-DTF2 is intrinsically regarded as a packing texture suitable for OFETs. Because of the synergic effect of the deep LUMO level and the favorable edge-on orientation, pDPPy-DTF2 displayed the highest electron mobility among the three polymers when measured under vacuum. Furthermore, in order to obtain information about the crystallite size and long-range order, the numbers of lamellar packing layers and $\pi$-$\pi$ stacking layers were estimated from the crystalline coherence length ($L_c(100)/\text{lamellar distances (d(100))}$ and the crystalline coherence length ($L_c(010)/\pi$-$\pi$ stacking distances (d(010)), respectively (Table S4).\cite{17} The $L_c(100)/d(100)$ values of pDPF-DTF2, pDPSe-DTF2, and pDPPy-DTF2 were 8.05, 6.54, and 6.53 lamellar layers, respectively. The $L_c(010)/d(010)$ values of pDPSe-DTF2 and pDPPy-DTF2 were 17.0 and 22.8 $\pi$-$\pi$ stacking layers, respectively. Overall, these data were consistent with the previous discussion. pDPF-DTF2 forms a face-on packing texture, while pDPSe-DTF2 and pDPPy-DTF2 possess the promising long-range order in the IP direction.
Figure 5. 2D-GIWAXS patterns of the thin films of (a) pDPF-DTF2; (b) pDPSe-DTF2; and (c) pDPPy-DTF2 and their corresponding 1-D profiles of (d, g) pDPF-DTF2; (e, h) pDPSe-DTF2; (f, i) pDPPy-DTF2 after the treatment under optimized annealing conditions.

Furthermore, the surface morphology of the polymer thin films was investigated by using tapping-mode atomic force microscopy (AFM). The AFM height images, and their corresponding 3D profiles are shown in Figures S6 to S8. The root-mean-square (RMS) roughness increased as the thermal annealing temperature was elevated. For instance, the RMS value of the as-cast film of pDPF-DTF2 was 0.53 nm (Figure S6a). When the pDPF-DTF2 film was annealed at 150°C for 10 min, it formed larger domains and the RMS value increased to 0.63 nm (Figure S6b). Further increasing the temperature to 200°C led to an even larger RMS value of 1.04 nm with higher crystalline domains (Figure S6c). This result was consistent with the observed increase in the OFET mobilities upon thermal annealing (Table S2). Similar to pDPF-DTF2, thermal annealing of the pDPSe-DTF2 and pDPPy-DTF2 films could also
produce larger crystalline domains, as represented by the increase in the RMS roughness (Figures S7 and S8). Overall, the AFM morphology was in good agreement with the mobility change in the OFETs.

**Conclusion**

In summary, three new semiconducting polymers, pDPF-DTF2, pDPSe-DTF2, and pDPPy-DTF2, were designed and synthesized by using furan, selenophene, and pyridine-flanking group-based DPP monomers. The optoelectronic properties of all three polymers were investigated using various characterization techniques. Upon using these polymers as active channel semiconductors in organic transistor devices, all of them exhibited \( p \)-type OFET performances. As anticipated from the electronic characteristics of the DPP substituents, pDPSe-DTF2 with the selenophene units demonstrated the highest hole mobility of 1.51 (1.22 for average) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in air among the three polymers. However, intriguingly, we observed a charge-carrier-polarity change when the devices were measured under vacuum. While pDPF-DTF2 exhibited the balanced ambipolar performance with the \( \mu_h/\mu_e \) value of 1.9, pDPSe-DTF2 showed hole-dominant ambipolar charge transport properties with the \( \mu_h/\mu_e \) value of 26.7. In addition, the polarity of pDPPy-DTF2 was completely reverted due to the electron-accepting character of the pyridine ring. In other words, pDPPy-DTF2 showed unipolar \( n \)-type charge transport properties with the electron mobility as high as 0.20 cm\(^2\) V\(^{-1}\) s\(^{-1}\). Overall, this comprehensive study demonstrated a simple yet effective approach to switch the charge carrier polarity in OFETs.

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