High-Performance Furan-Containing Conjugated Polymer for Environmentally Benign Solution Processing

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ABSTRACT: Developing semiconducting polymers that exhibit both strong charge transport capability via highly ordered structures and good processability in environmentally benign solvents remains a challenge. Given that furan-based materials have better solubility in various solvents than analogous thiophene-based materials, we have synthesized and characterized furanyl-diketopyrrolopyrrole polymer (PFDPPTT-Si) together with its thienyl-diketopyrrolopyrrole-based analogue (PTDPPTT-Si) to understand subtle changes induced by the use of furan instead of thiophene units. PTDPPTT-Si films processed in common chlorinated solvent exhibit a higher hole mobility (3.57 cm² V⁻¹ s⁻¹) than PFDPPTT-Si films (2.40 cm² V⁻¹ s⁻¹) under the same conditions; this greater hole mobility is a result of tightly aggregated π-stacking structures in PTDPPTT-Si. By contrast, because of its enhanced solubility, PFDPPTT-Si using chlorine-free solution processing results in a device with higher mobility (as high as 1.87 cm² V⁻¹ s⁻¹) compared to that of the corresponding device fabricated using PTDPPTT-Si. This mobility of 1.87 cm² V⁻¹ s⁻¹ represents the highest performances among furan-containing polymers reported to the best of our knowledge for nonchlorinated solvents. Our study demonstrates an important step toward environmentally compatible electronics, and we expect the results of our study to reinvigorate the furan-containing semiconductors field.

KEYWORDS: diketopyrrolopyrrole, furan-containing conjugated polymers, siloxane-hybrid chains, organic field-effect transistors, nonchlorinated solvents

1. INTRODUCTION

A central approach in the synthesis of materials for organic field-effect transistors (OFETs) is to manipulate electron donor (D) and acceptor (A) blocks in π-conjugated semiconducting polymers to achieve controllable energy band gaps and tunable charge transport properties in the conjugation systems.1–5 Among such alternating D–A polymers, diketopyrrolopyrrole (DPP)-containing polymers exhibit dense π–π stacking and long-range order because of the coplanar nature of a DPP moiety with less conformational disorder and a high charge transport capability; DPP-based polymers have thus led to rapid progress in the development of high-performance OFETs.6–10

Despite DPP-containing polymers’ beneficial characteristics for use in electronics, their rigid DPP skeleton leads to poor solubility in various commercial solvents, except chlorine-containing solvents. Thus, the use of such chlorinated solvents is a prerequisite to realizing high-performance OFETs based on DPP polymers.11–15 However, chlorinated solvents are well-known for energy-intensive chemicals that harm the environment,16–18 which pose a substantial obstacle to the manufacture of electronic devices beyond the laboratory scale.19–22 Driven by the urgent demand for high performing DPP-based materials with good solubility for solving aggregating properties to some extent, considerable attention has been devoted to introducing long or bulky solubilizing chains into the main backbones;13,23–26 however, the resultant polymers form less-crystalline structures in the films and these structures adversely affect charge mobility in OFETs.

In addition to the side chain engineering, irregular synthetic approaches (e.g., random polymerization27,28 and structural asymmetry29,30) in DPP-based polymers have beneficial microstructures with good solubility/processability, enabling

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excellent performance of OFETs fabricated using DPP-containing polymers in nonchlorinated solvents. Nonetheless, variations in the composition of random DPP polymers with a lower molecular precision can result in batch-to-batch errors for the processing properties and performance.\textsuperscript{31–33} In addition, incorporating two different aromatic substituents for the asymmetric DPP polymers is complex.

Furan-containing polymers have been found to not only exhibit greater solubility in common solvents than the thiophene analogues but also comparable performance in electronic applications.\textsuperscript{34–38} This interest in furan-based materials potentially useful for green electronics has recently expedited the development of OFETs of furanyl-DPP (FDPP)-based polymers\textsuperscript{39–45} using nonchlorinated solution processing;\textsuperscript{46} however, the mobilities of the FDPP-based polymers remains no greater than 0.26 cm\(^2\) V\(^{-1}\) s\(^{-1}\), which is substantially lower than the analogous thienyl-DPP (TDPP)-based materials.

In the work described herein, our growing interest in the development of high-performing OFETs fabricated using an environmentally friendly process prompted us to explore the OFET properties of a new FDPP-based polymer, where the FDPP with siloxane-side chains was polymerized with a thieno[3,2-b:5,6-b]thiophene (TT) to generate PFDPPTT-Si. To systematically investigate the heterocyclic change, we also synthesized and characterized the corresponding thiophene analogue PTDPPTT-Si.

The high hole mobilities of PTDPPTT-Si and PFDPPTT-Si cast from CF were 3.57 and 2.40 cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively. Importantly, PFDPPTT-Si exhibits better solubility in various nonchlorinated solvents, which can minimize detrimental changes in morphology in nonchlorinated processing solvents, thereby providing a higher mobility of 1.33–1.87 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in the films processed from environmentally benign solvents compared with the mobilities in the PTDPPTT-Si devices. Our measured values of PFDPPTT-Si, in the case of samples cast using chlorine-free solvents, is the highest mobilities reported to date for benign furan-containing-polymer-based OFETs, indicating that PFDPPTT-Si as a promising candidate for environmentally compatible OFETs.

### 2. RESULTS AND DISCUSSION

#### 2.1. Synthesis and Characterization

The synthesis procedures for the two polymers, PTDPPTT-Si and PFDPPTT-Si, are shown in Scheme 1. We previously demonstrated that the use of siloxane-terminated pentyl chains in DPP-based polymers can impart sufficient solubility and excellent charge-carrier mobility.\textsuperscript{15,23,47} Therefore, we chose siloxane-terminated pentyl chains as solubilizing groups in this study. First, 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2\textsuperscript{H},5\textsuperscript{H})-dione and 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2\textsuperscript{H},5\textsuperscript{H})-dione were synthesized according to the reported procedures.\textsuperscript{40,48} Each of the dibrominated TDPP and FDPP monomers was achieved via successive three-step reactions (i.e., alkylation, hydrosilylation, and bromination). The detailed synthetic procedures with the characterization data are described in the Supporting Information. Finally, PTDPPTT-Si and PFDPPTT-Si were prepared via Stille coupling polymerization of their dibrominated monomers with the bis-stannylated TT comonomer. Soxhlet extraction with methanol, acetone, and hexane sequentially was carried out to remove the catalytic residues and oligomer mixtures in both polymers. The gel permeation chromatography (GPC) at room temperature in tetrahydrofuran shows similarly high number-average molecular weights (M\(_n\)) of PTDPPTT-Si (55.4 kDa) and PFDPPTT-Si (47.2 kDa) with a relatively broad range of polydispersity.
indices (PDIs). This step can minimize possible interference from $M_n$ variations.

2.2. Optical and Electrochemical Properties and Theoretical Calculations. The optical properties with UV−vis absorption spectra of solutions in chloroform and thin films of both polymers are displayed in Figure 1; the relevant data are summarized in Table 1. Both polymers showed similarly broad absorptions from 350 to 950 nm. The $\pi-\pi^*$ transition band and intramolecular charge transfer (ICT) between the A and D moieties are exhibited as shorter- and longer-wavelength peaks, respectively. The absorptions of PTDPPTT-Si both in solution and as films are much broader than those of PFDPPTT-Si, confirming the stronger interchain aggregation of PTDPPTT-Si. Notably, a blue shift of the absorption features from PTDPPTT-Si to PFDPPTT-Si in both solution and films was observed, indicating that the PFDPPTT-Si polymer chains were less aggregated because of the smaller heteroatoms of the furan unit. Consequently, the optical band gap ($E_g$) as estimated from the absorption onset (1.31 eV) of the PTDPPTT-Si film was smaller than that of PFDPPTT-Si (1.39 eV).

UV photoelectron spectroscopy (UPS) was carried out for the highest occupied molecular orbital (HOMO) energy levels of the two polymers and the lowest unoccupied molecular orbital (LUMO) energy levels were found on the basis of the $E_g$ in the absorption spectra and the HOMO energy levels. The HOMO values of PTDPPTT-Si and PFDPPTT-Si as-spun films were −4.67 and −4.71 eV, as shown in Figure 1d. These values are slightly higher than those measured by cyclic voltammetry (Figure S1 and Table S1), although the same variation trends are observed. The calculated LUMO values are −3.36 and −3.32 eV for PTDPPTT-Si and PFDPPTT-Si, respectively. Notably, the HOMO level of PFDPPTT-Si is slightly deeper than that of PTDPPTT-Si because of the relatively high ionization potential of furan.

Furthermore, the density functional theory (DFT) method at the B3LYP/6-31G* level calculated the electron distributions of HOMO and LUMO in the single repeating units for the two polymers (Figure S2). Both models showed well-delocalized electron densities over the conjugated backbones for both the HOMO and the LUMO.

2.3. Thin-Film Microstructure Analysis. The film morphological features of PTDPPTT-Si and PFDPPTT-Si were investigated using tapping-mode atomic force microscopy (AFM). As shown in Figure 2, both as-cast and annealed polymer films exhibited densely packed nanofibrillar networks, indicating the existence of strong intermolecular interactions and the formation of highly interconnected charge transport pathways. Moreover, the thermal annealing at 260 °C caused the nanofibrous features to become more evident, with a slight increase of the root-mean-square (RMS) roughness from 1.99 to 2.65 nm for PTDPPTT-Si and from 0.96 to 1.46 nm for PFDPPTT-Si; this increased roughness suggests that the crystalline nanostructures were improved after thermal annealing. We note that the annealed PTDPPTT-Si film

Table 1. Optical and Electronic Properties of the PDPPTT-Si Polymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\lambda_{\text{sol}}$ (nm)a</th>
<th>$\lambda_{\text{film}}$ (nm)</th>
<th>$E_g$ (eV)b</th>
<th>$E_{\text{HOMO}}$ (eV)c</th>
<th>$E_{\text{LUMO}}$ (eV)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTDPPTT-Si</td>
<td>745, 807</td>
<td>739, 810</td>
<td>1.31</td>
<td>−4.67</td>
<td>−3.36</td>
</tr>
<tr>
<td>PFDPPTT-Si</td>
<td>797</td>
<td>724, 800</td>
<td>1.39</td>
<td>−4.71</td>
<td>−3.32</td>
</tr>
</tbody>
</table>

aPolymer solutions in chloroform and films on glass substrates. bDetermined from the onset of the UV−vis absorption plots in the polymer films. cMeasured by UPS measurements, incident photon energy ($h\nu = 21.2$ eV) for He I ($E_{\text{HOMO}}$ UPS = $h\nu - (E_{\text{cutoff}} - E_{\text{HOMO}})$). d$E_{\text{LUMO}} = E_{\text{HOMO}} - E_g$.}

Figure 1. Normalized UV−vis absorption profiles in chloroform solution (a) and as thin films (b), UV photoelectron spectroscopy (UPS) spectra (c), and energy level diagram (d) of PTDPPTT-Si and PFDPPTT-Si.
exhibited larger fibrous crystalline domains with an average diameter of \( \sim 56 \) nm which indicates much less grain-boundary formation compared to those observed in PFDPPTT-Si films (\( \sim 27 \) nm of average diameter). On the basis of the aforementioned UV–vis absorption spectra and AFM result, we could easily conclude that the molecular structure of PTDPPTT-Si is beneficial to form stronger aggregation.

Grazing-incidence X-ray diffraction (GIXD) analyses were conducted to clarify the crystallinities and molecular-packing orientations of the PDPPTT-Si polymers. Two-dimensional (2D) detector images are provided with their horizontal and vertical line cuts of annealed polymer films in Figure 3 (see Figure S3 for those of the as-cast films). The corresponding crystallographic parameters are shown in Table S2. Both of the as-cast films exhibited highly ordered structures with out-of-plane (100) layer distances of 21.91 and 20.90 Å for the PTDPPTT-Si and PFDPPTT-Si films, respectively; these distances are corresponding to the lamellar distances between two backbones which is determined by the length of the lateral side chains. After the films were annealed at 260 °C, the...
Diffraction images exhibited slightly intensified peaks and decreased (100) d-spacing values of 21.61 and 20.88 Å for PTDPPTT-Si and PFDPPTT-Si films, respectively, which implies that thermal annealing induced side chains of adjacent backbones to closely interdigitate.55 However, in the case of both polymers, the observation of (010) π−π stacking peaks along both qxy and qz directions indicates bimodal packing with coexisting edge-on and face-on orientations. PTDPPTT-Si films exhibited stronger (010) diffraction peaks with denser (spacing of ∼3.65 Å) π−π stacking than those of PFDPPTT-Si films (∼3.74 Å), indicating that the thiophene spacer facilitates microstructures that favor charge transport with stronger intermolecular interactions in PTDPPTT-Si. In principle, these stronger π−π interactions are due to the nature of sulfur in thiophene with greater overlap integrals and polarizabilities with enhanced aromaticity compared to that of oxygen in furan units.56,57 Yet, simultaneously, this observation leads us to expect an adverse effect on the solubility of PTDPPTT-Si in various common solvents. Overall, the aforementioned AFM and GIXD data establish an important trend in the film morphology with respect to thiophene versus furan.

2.4. Electrical Characterization and the Performance of OFETs. To investigate the electrical properties of PTDPPTT-Si and PFDPPTT-Si, we first fabricated bottom-gate top-contact CF-cast OFET devices, as depicted in Figure 4a, and measured their charge transport characteristics under a nitrogen atmosphere. The detailed OFET fabrication and characterization steps are provided in the Supporting Information. Both polymers exhibited unipolar p-type field-effect behaviors because of the lower energetic barriers with regard to the gold electrode contacts. The solution-sheared films were thermally annealed at various temperatures (220, 260, and 300 °C) to investigate the optimal post-treatment conditions (Figure 4b, Figure S4, and Table 2). The as-cast polymer films exhibited hole mobilities of 1.20 and 0.43 cm² V⁻¹ s⁻¹ for PTDPPTT-Si and PFDPPTT-Si, respectively. Thermal annealing was found to further enhance the electrical properties, and the optimal annealing temperature was 260 °C.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Schematic illustration of CF-processed PDPPTT-Si OFETs and their optimal electrical characteristics after thermal annealing treatment. (a) Device structure of the fabricated OFET structure with Au electrodes of L = 50 μm and W = 1000 μm. (b) Comparison of the average hole mobilities of PDPPTT-Si films with various annealing temperature from up to 300 °C. Transfer and output curves of the optimized devices of (c) PTDPPTT-Si and (d) PFDPPTT-Si after annealing at 260 °C.

<table>
<thead>
<tr>
<th>polymer</th>
<th>T_a [°C]</th>
<th>μ_h,max b [cm² V⁻¹ s⁻¹]</th>
<th>μ_h,avg c [cm² V⁻¹ s⁻¹]</th>
<th>I_on/I_off V_T [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTDPPTT-Si</td>
<td>220</td>
<td>1.93</td>
<td>1.41 (±0.26)</td>
<td>&gt;10⁴</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>3.57</td>
<td>2.75 (±0.36)</td>
<td>&gt;10⁵</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2.56</td>
<td>2.20 (±0.22)</td>
<td>&gt;10⁵</td>
</tr>
<tr>
<td>PFDPPTT-Si</td>
<td>220</td>
<td>1.35</td>
<td>0.94 (±0.20)</td>
<td>&gt;10⁴</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>2.40</td>
<td>1.87 (±0.24)</td>
<td>&gt;10⁴</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.44</td>
<td>1.15 (±0.12)</td>
<td>&gt;10⁴</td>
</tr>
</tbody>
</table>

*The OFET performance of more than 20 devices with various thermal annealing conditions was tested. The maximum mobility of the OFET devices (L = 50 μm and W = 1000 μm). The average mobility of the OFET devices (L = 50 μm and W = 1000 μm). Thermal annealing was not applied. The standard deviation.
In addition, we compared the charge transport characteristics of drop-cast and solution-sheared films annealed at 260 °C. As shown in Figure 4c,d, solution-sheared PTDPPTT-Si and PFDPPTT-Si films showed hole mobilities as high as 3.57 and 2.40 cm² V⁻¹ s⁻¹, respectively, whereas drop-cast films exhibited relatively lower electrical performances (hole mobilities of 2.70 and 2.01 cm² V⁻¹ s⁻¹ for PTDPPTT-Si and PFDPPTT-Si, respectively) (Figure S5 and Table S3). This result is closely related to the positive effects of solution-shearing, such as an elongated crystallite texture along the conducting channel and a well-organized polymer chain packing with a reduced π-planar distance.58,59 The OFETs with thiophene spacers exhibited...
better performance than the OFETs fabricated using furan spacers owing to the optimized microstructures with stronger intermolecular interactions. It is because of the enhanced aromaticity of the thiophene unit in PTDPPTT-Si efficiently facilitated denser π-stacking, as observed by AFM and GIXD and various analyses, revealing that morphological factors more critically affect charge transport compared to energetic factors in these polymer films.

2.5. Solubility Characteristics. Before starting our work on chlorine-free OFETs as a main topic in this study, we carried out solubility tests of the two polymers in common nonchlorinated solvents, toluene (Tol), tetrahydrofuran (THF), o-xylene (Xyl), and 1,4-dioxane (Diox), to measure the quantitative solubilities by UV–vis absorption (Figure S6 and Table S4) and confirm their solution processability (Figure 5a). PFDPPTT-Si exhibited better solubility at room temperature in the tested solvents because of the large dipole moment of PFDPPTT-Si; by contrast, PTDPPTT-Si exhibited sufficient solubility in THF and Tol only when heated at ~60 °C. To estimate accurate solubility boundaries for both polymers, we adopted Hansen solubility theory, which considers the energy from dispersion ($\delta_d^2$), the dipolar intermolecular ($\delta_p$), and the hydrogen bonding ($\delta_h$) forces between molecules as constitutive interaction parameters.60 Figure 5b is a plot of the comprehensive solubility parameters of the tested solvents calculated from the equation ($\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$. In addition, the detailed constitutive parameters and two-dimensional (2D) representation of $\delta_d$ and $\delta_p$ are depicted in Figure S5c,d, where we excluded the effect of $\delta_h$ because both polymers are lack of probability to form hydrogen bonding with used solvents. PFDPPTT-Si exhibited an enhanced solubility range with a larger radius of sphere in 2D Hansen space compared to PTDPPTT-Si.

Table 3. OFET Performance of PDPPTT-Si Films Processed with Environmentally Benign Solvents

<table>
<thead>
<tr>
<th>polymer</th>
<th>solvent</th>
<th>$\mu_{\text{h,avg}}$ [cm$^2$ V$^{-1}$ s$^{-1}$]</th>
<th>$\mu_{\text{h,max}}$ [cm$^2$ V$^{-1}$ s$^{-1}$]</th>
<th>$I_{\text{on}}/I_{\text{off}}$</th>
<th>$V_T$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTDPPTT-Si</td>
<td>toluene</td>
<td>1.82</td>
<td>1.54 (±0.15)</td>
<td>&gt;10$^7$</td>
<td>-28.2</td>
</tr>
<tr>
<td></td>
<td>tetrahydrofuran</td>
<td>0.97</td>
<td>0.55 (±0.14)</td>
<td>&lt;10$^3$</td>
<td>-26.5</td>
</tr>
<tr>
<td>PFDPPTT-Si</td>
<td>toluene</td>
<td>1.87</td>
<td>1.55 (±0.18)</td>
<td>&gt;10$^7$</td>
<td>-28.6</td>
</tr>
<tr>
<td></td>
<td>tetrahydrofuran</td>
<td>1.33</td>
<td>0.80 (±0.22)</td>
<td>&gt;10$^7$</td>
<td>-22.6</td>
</tr>
</tbody>
</table>

3. CONCLUSION

Following recent broad interest in environmentally compatible electronic devices, we carried out a comprehensive investigation of two DPP-based polymers (PTDPPTT-Si and PFDPPTT-Si). The inherent differences between flanking thiophene and furan units in the backbones influenced the optoelectronic properties of the resulting polymers. For example, as a result of the smaller atomic radius and larger dipole moment of oxygen in the furan units, PFDPPT-Si not only has a deeper-lying HOMO level with a slightly larger optical band gap but also greater solubility in nonchlorinated solvents compared to PTDPPTT-Si. The CF-cast OFETs of PTDPPTT-Si exhibited a greater mobility (3.57 cm$^2$ V$^{-1}$ s$^{-1}$) as compared with that of PFDPPTT-Si (2.40 cm$^2$ V$^{-1}$ s$^{-1}$) because of the stronger aggregation behavior in PTDPPTT-Si; conversely, the OFETs fabricated using PFDPPTT-Si processed in nonchlorinated solvents delivered better mobility, 1.87 cm$^2$ V$^{-1}$ s$^{-1}$. This mobility value is the highest reported thus far for “green” OFETs fabricated using furan-based polymers, demonstrating the strong potential for developing high-performance environmentally friendly organic semiconductors via incorporation of furan into polymer backbones.

4. EXPERIMENTAL SECTION

4.1. Instruments for Characterizations. A Cary 5000 spectrophotometer, VersaSTAT3 Princeton Applied Research Potentiostat,21 and MultiMode 8 scanning probe microscope were used to obtain the UV–vis-NIR spectra, CV plots, and tapping-mode AFM images according to the reported methods. GPC was carried out through Agilent 1200 HPLC and miniDawn TREOS,62 and DFT calculations were obtained with Gaussian 09 package.63 GIXD measurements were performed at PLS-II 9A U-SAXS beamline of Pohang Accelerator Laboratory in Korea, with the experimental details shown in our previous papers.15,16,64 Performances of fabricated OFETs were tested using a Keithley 4200 semiconductor parameter analyzer as reported previously.3,65 The specific conditions for GIXD measurements and OFETs fabrication were provided in the Supporting Information.

4.2. Solubility Measurement. The solubilities of PTDPPTT-Si and PFDPPTT-Si were determined in the test solvents. For calibration, absorption spectra of both polymers were obtained with different concentrations in chloroform, in which the absorbance values at 807 nm for PTDPPTT-Si and at 797 nm for PFDPPTT-Si were varied linearly on the concentrations. Then, the saturated solutions of two polymers filtered for removal of an excess of solids in each test solvent, were diluted with additional solvent to lower the absorbance, followed by measuring UV absorptions. On the basis of Beer–Lambert’s law, the quantitative data were collected from a linear relationship of concentration with absorbance. In the case of 1,4-dioxane as a solvent, the solubilities for both polymers were too low to take the reliable spectra in UV–vis absorption.
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Research Article


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