Effect of alkyl chain spacer on charge transport in n-type dominant polymer semiconductors with a diketopyrrolopyrrole-thiophene-bithiazole acceptor–donor–acceptor unit†

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Although the effects of alkyl chain spacers have been extensively studied for p-type conjugated polymers with a donor (D)–acceptor (A) repeating unit, few studies have examined their effects for n-type polymers with an A–D–A architecture having two different acceptors in the repeating unit. Herein, diketopyrrolopyrrole-thiophene-bithiazole A–D–A type polymer semiconductors (DPPBTz) containing branched alkyl chains of 24-alkyl with C1 spacer (P-24-DPPBTz) and 29-alkyl with C6 spacer (P-29-DPPBTz) were designed and synthesized to elucidate the effect of the alkyl chain branching position on the electron-dominant charge transport system. Due to the strong electron deficiency and trans-planar conformation of the bithiazole group, DPPBTz-based polymer semiconductors exhibit n-type dominant electrical properties with a high electron mobility of up to 1.87 cm²V⁻¹s⁻¹. Systematic studies on the photophysical properties, thin-film microstructures, and electrical properties of the DPPBTz polymers revealed that upon modification of the branching position, A–D–A n-type dominant semiconductors differently behave compared to D–A p-type dominant semiconductors. This is attributed to the relatively weaker intermolecular interactions in A–D–A type semiconductors, making the C1 spacer more efficient for electron transport. These findings reveal the molecular design rule of alkyl side-chains in A–D–A n-type-dominant conjugated polymers for the first time.

Introduction

Polymeric semiconductors for organic field-effect transistors (OFETs) have been extensively studied as structural modifications and solution processability can be easily performed and device fabrication is relatively inexpensive.1,2 Recently, great advances in polymeric semiconductors have been made through molecular design and device optimization.3–14 A number of polymers exhibit high carrier mobility, exceeding 0.1 cm²V⁻¹s⁻¹, comparable to that of amorphous silicon. Especially, donor(D)–acceptor(A)-type copolymers containing diketopyrrolopyrrole (DPP) and isoindigo-based copolymers have attracted significant interest for promising applications in OFETs.5–7,12–17 Optimization of the molecular structure is one of the most effective ways to achieve a high carrier mobility. It has been reported that charge transport in organic semiconductors not only involves intramolecular transport, but also intermolecular and interdomain transport.3 Various D–A polymers have been designed to obtain a π-planar backbone, which enables high crystallinity in thin films. In general, π-conjugated backbone structures critically affect the coplanarity, solubility, molecular weight, energy level, and molecular packing of the polymers. Long-branched alkyl side chains are highly beneficial for improving the solubility of the polymers; however, as insulators, they tend to degrade the charge transport, and their bulkiness inhibits intermolecular interactions. Recent studies, including work from our research groups, have demonstrated that control over the branching position of the linear spaced-alkyl chains can result in a dramatic increase in the charge carrier mobilities of p-type and p-type-dominant ambipolar polymers.7,12,16–21

Tuning the alkyl spacer length between the branching point and the backbone from C1 to C6 in DPP-based highly π-extended...
p-type polymers causes the maximum hole mobility to increase by as much as 17.8 cm² V⁻¹ s⁻¹.¹⁰,²² The dramatic change in the charge transport properties via side-chain engineering can be achieved because the side chains induce backbone planarity such that to reduce steric hindrance, and this increases crystallinity due to long-range ordering. The side chain also affects the chain packing density, and mobility depends on the odd–even number of linear alkyl spacers.²²,²³ Although many systematic studies for p-type and ambipolar semiconducting polymers have been carried out, studies on n-type dominant polymers are relatively rare.

Recently, one of our groups reported a dramatic polarity change in an n-type material by introducing a cyano group on a well-known p-type DPP-TVT polymer and as a result, DPP-CN TVT was obtained.¹⁴ Reichmanis et al. reported that poly(dithienylidketopyrrolopyrrolethiazole), which is composed of DPP containing alkyl side chains of 27 carbons with a linear spacer of 4 carbons and bithiazole, exhibits an electron mobility approaching 0.3 cm² V⁻¹ s⁻¹.²⁴ The introduction of electron-deficient bithiazole units with transplanar conformation induced n-type characteristics in a low work-function electrode and passivating dielectric system. In addition, to minimize steric effects within the DPPBTz backbone, 5-decylheptadecyl side chains were introduced. The 27-carbon alkyl with 4-carbon linear spacers not only increased solubility in an eco-friendly solvent, but also promoted π–π interchain interactions.²⁴

In this study, we designed two polymers, P-24-DPPBTz and P-29-DPPBTz, which are composed of two electron-accepting units, bithiazole and DPP, and contain 24-carbon alkyl chains with a 1-carbon linear spacer (C1) and 29-carbon alkyl chains with a 6-carbon linear spacer (C6), respectively. Although the effect of the alkyl chain on the dramatic increase in charge carrier mobility in p-type polymers has been extensively and systematically studied by adjusting the branching position, few studies have examined the development of n-type semiconductors, particularly polymers with an A–D–A architecture, which have two different acceptors in the repeating unit. Thus, to the best of our knowledge, this is the first report on the effect of the alkyl side chain on n-type-dominant semiconducting polymers.

**Results and discussion**

**Synthesis and characterization**

Synthesis of P-24-DPPBTz and P-29-DPPBTz was carried out via the Stille coupling reaction using Pd₂(db₃)₃ and P(oTol)₃, for 48 h in chlorobenzene (Fig. 1). The synthesis details are provided in the ESI† (Fig. S1). The crude polymers were purified by precipitation from methanol, followed by successive Soxhlet extractions. The polymers had good solubility in common organic solvents such as tetrahydrofuran, chloroform, and chlorobenzene. Gel-permeation chromatography (GPC) analysis revealed a number average molecular weight (\(M_n\)) of 56 kg mol⁻¹ for P-24-DPPBTz and 64 kg mol⁻¹ for P-29-DPPBTz, with polydispersities of 1.55 and 1.78, respectively.

The absorption spectra of P-24-DPPBTz and P-29-DPPBTz were obtained in chloroform solution. Both polymers showed a distinct dual band absorption (Fig. 2). P-29-DPPBTz showed a marked red-shifted absorption in solution as a planar backbone was formed such that to reduce steric hindrance by placing branching points away. This result was similar to that obtained for p-type polymers.¹⁰,²² Both the as-prepared and annealed polymer films showed slightly red-shifted and very broad absorption peaks compared with those in solution. The optical band gaps of the polymers (1.35 eV and 1.29 eV) were calculated from the absorption edge of 916 nm for P-24-DPPBTz and 954 nm for P-29-DPPBTz, respectively (Table 1). Cyclic voltammetry (CV) measurements were performed to determine the electronic energy structure of both polymers. The highest occupied molecular orbital (HOMO) levels of P-24-DPPBTz and P-29-DPPBTz were –5.31 eV and –5.35 eV, respectively, and the lowest unoccupied molecular orbital (LUMO) levels were –3.96 eV and –4.06 eV, respectively. The low-lying LUMO levels of P-24-DPPBTz and P-29-DPPBTz provided a high potential for good ambient stability in electron transport organic semiconductors (Fig. S2, ESI†).

Both P-24-DPPBTz and P-29-DPPBTz showed good thermal stability, with the decomposition temperatures above 420 °C. There was no evidence of phase transitions for either polymer in differential scanning calorimetry (DSC) measurements (Fig. S3, ESI†).

![Fig. 1 Schematic for the synthesis of P-24-DPPBTz and P-29-DPPBTz.](image-url)
Microstructural analysis of polymer films

The molecular packing and crystallinity of P-24-DPPBTz and P-29-DPPBTz films were investigated by out-of-plane X-ray diffraction (XRD) and grazing incident X-ray diffraction (GIXD). Out-of-plane XRD was performed for P-24-DPPBTz and P-29-DPPBTz films annealed at 260 °C and 300 °C (Fig. S4, ESI†). For P-29-DPPBTz, relatively sharp and strong (00) peaks were observed in the spectrum of the films annealed at 300 °C, whereas the crystalline peaks of P-24-DPPBTz films showed almost identical peak intensities at both temperatures. However, sharper peaks with slightly shorter d-spacing values were found for the P-24-DPPBTz films annealed at 260 °C.

For in-depth analysis of the crystalline properties of P-24-DPPBTz and P-29-DPPBTz films, GIXD analysis was performed for P-24-DPPBTz and P-29-DPPBTz films annealed at 260 °C and 300 °C, respectively. In both films, well-defined strong (00) reflection peaks were observed with higher-order diffraction peaks up to the fifth and sixth order, respectively, as shown in Fig. 3. The qy(100) peaks of P-24-DPPBTz films, with shorter alkyl spacers, were sharper and with a much shorter d⊥-spacing value (24.39 Å) than those of the P-29-DPPBTz polymer (30.02 Å). Side-chain relaxation in the P-29-DPPBTz polymer via the long spacer group (C6) may result in less dense side-chain packing in the out-of-plane direction. The corresponding data are summarized in Table 2. These results are in agreement with our previous report on P-29-DPPDTSE and P-29-DPPDTSe polymers, suggesting that molecular packing density is affected by the type of alkyl chain spacers.10

P-24-DPPBTz thin films exhibited a higher degree of molecular order, as evidenced by a larger (100) coherence length of 307.70 Å compared with that of 242.72 Å in P-29-DPPBTz thin films. This indicates that a higher degree of π-stacked polymer domains exist in the P-24-DPPBTz lamellar structure (the average number of n00 planes is 12.6 for P-24-DPPBTz and 8.1 for P-29-DPPBTz).

With respect to the in-plane direction, interestingly, only the P-24-DPPBTz thin film showed a qy(010) peak, indicating a dxy(100) value of 24.39 Å. This suggests that the texture of the P-24-DPPBTz thin films consists of both in-plane and out-of-plane lamellar structures.25 This high degree of molecular packing would favour a more efficient formation of charge transport pathways.20,26,27 These results suggest that a much shorter d⊥-spacing value and a larger degree of molecular ordering in the P-24-DPPBTz polymer films can enhance the charge transport capability.

The π–π stacking distance, based on the qy(010) peak, decreased from 3.631 Å for a P-24-DPPBTz chain to 3.563 Å for a P-29-DPPBTz chain. This may result from the stronger intermolecular π–π interactions induced by the longer alkyl spacer of the P-29-DPPBTz chain, alleviating the steric effect of branched alkyl chains to the conjugated backbone. However, unlike other p-type dominant D–A type copolymers with long alkyl spacers,18,22,26 the GIXD spectrum of the A–D–A-type copolymers designed herein for n-type-dominant semiconductors did not show a qy(010) peak, which is a critical factor for forming three-dimensional (3D) charge transport pathways. We concluded that these results are due to the relatively weaker intermolecular interactions in A–D–A-type copolymers compared with those in D–A-type copolymers.

Table 1 UV-vis absorption and electrochemical properties of the P-24-DPPBTz and P-29-DPPBTz polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(\lambda_{\text{max}}) sol(^a) [nm]</th>
<th>(\lambda_{\text{max}}) film(^b) [nm]</th>
<th>(\lambda_{\text{max}}) annealed film(^c) [nm]</th>
<th>Band edge (\text{[optical]}) [eV]</th>
<th>Band gap (\text{[electrochemical]}) [eV]</th>
<th>LUMO (\text{[electrochemical]}) [eV]</th>
<th>LUMO (\text{[optical]}) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-24-DPPBTz</td>
<td>443, 688, 743</td>
<td>443, 693, 763</td>
<td>446, 693, 764</td>
<td>916</td>
<td>1.35</td>
<td>−3.31</td>
<td>−3.91</td>
</tr>
<tr>
<td>P-29-DPPBTz</td>
<td>447, 701, 764</td>
<td>447, 698, 765</td>
<td>448, 698, 767</td>
<td>954</td>
<td>1.29</td>
<td>−3.35</td>
<td>−3.98</td>
</tr>
</tbody>
</table>

\(^a\) UV-absorption in solution was measured in chloroform at the concentration of 10⁻⁴ M. \(^b\) UV-absorption of the as-cast film was measured from a spin-coated film with a 0.2 wt% solution. \(^c\) UV-absorption of the annealed film was measured from a film annealed at 200 °C. \(^d\) CV was measured in a solution containing Bu₄NClO₄ (0.1 M) in acetonitrile. \(^e\) The LUMO levels were determined from the HOMO levels and optical band gap.
Table 2  Crystallographic parameters calculated from the GIXD diffractogram profiles of the optimized P-24-DPPBTz and P-29-DPPBTz thin films

<table>
<thead>
<tr>
<th>Crystallographic parameters&lt;sup&gt;a&lt;/sup&gt;</th>
<th>24-DPPBTz</th>
<th>29-DPPBTz</th>
</tr>
</thead>
<tbody>
<tr>
<td>From q&lt;sub&gt;x&lt;/sub&gt; profile (100) lamellar spacing</td>
<td>q (Å&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.2576</td>
</tr>
<tr>
<td></td>
<td>d-Spacing (Å)</td>
<td>24.39</td>
</tr>
<tr>
<td></td>
<td>Coherence length (Å)</td>
<td>307.70</td>
</tr>
<tr>
<td></td>
<td>Avg. # of h00 plane</td>
<td>12.6</td>
</tr>
<tr>
<td>From q&lt;sub&gt;y&lt;/sub&gt; profile (100) lamellar spacing</td>
<td>q (Å&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.2614</td>
</tr>
<tr>
<td></td>
<td>d-Spacing (Å)</td>
<td>24.04</td>
</tr>
<tr>
<td></td>
<td>(010) π–π stack</td>
<td>1.7304</td>
</tr>
<tr>
<td></td>
<td>d-Spacing (Å)</td>
<td>3.63</td>
</tr>
</tbody>
</table>

<sup>a</sup> Polymer films were prepared by drop-casting and thermal treatment at the optimized temperature (260 °C and 300 °C for P-24-DPPBTz and P-29-DPPBTz, respectively), and their parameters were calculated from the GIXD profiles. <sup>b</sup> For 29-DPPBTz films, the (100) lamellar peak was not observed in the in-plane GIXD patterns.

To elucidate the molecular packing characteristics in terms of morphological aspects, we investigated the morphologies of the P-24-DPPBTz and P-29-DPPBTz polymer films (annealed at their respective optimized temperatures) by tapping-mode atomic force microscopy (AFM). Fig. 4 shows the AFM height images (3 × 3 µm scan) of the P-24-DPPBTz and P-29-DPPBTz polymer films. The corresponding phase images are presented in Fig. S2 (ESI†). The P-29-DPPBTz polymer films were composed of nanoscale fibrillar domains with a good intergrain connectivity. Remarkably, however, the P-24-DPPBTz films exhibited large aggregates of fibrils with the formation of voids in a multilayer structure, which indicates a rough surface coverage.28

**Fabrication of solution-processed FETs and I–V characterizations**

To investigate the charge transport properties of P-24-DPPBTz and P-29-DPPBTz polymer films, bottom-gate top-contact FETs were fabricated. The polymer solutions were prepared in chlorobenzene at the concentration of 2 mg mL<sup>-1</sup>. The films were deposited on a n-octadecyltrimethoxysilane (OTS)-modified SiO<sub>2</sub>/Si substrate by spin-coating and drop-casting methods. The experimental details are included in the Experimental section. The P-24-DPPBTz and P-29-DPPBTz FETs exhibited electron-dominant ambipolar transport, most likely due to the energetically low-lying LUMO levels promoted by the bithiazole group and the lower injection barriers for electrons with regard to gold electrodes (work function: ~ 5.1 eV). The electrical performances of the FETs based on P-24-DPPBTz and P-29-DPPBTz polymer films are listed in Table 3. The bithiazole group in the polymer backbone strengthen the electron charge-carrier transport in the FETs and is expected to afford n-channel dominant ambipolar OFETs, in line with our aforementioned hypothesis. To explore the optimized heat treatment conditions with high thermal stability considerations, 23 spin-coated and drop-cast polymer thin films were annealed at 220 °C, 260 °C, and 300 °C for 30 min.

Fig. S3 (ESI†) shows the average field-effect mobility variations of P-24-DPPBTz and P-29-DPPBTz FETs with standard deviation values at various annealing temperatures. The optimal films were obtained by the drop-casting method. The best performances were achieved by applying a heat treatment of up to 260 °C and 300 °C for P-24-DPPBTz and P-29-DPPBTz, respectively. The typical transfer and output curves of optimized FETs based on the P-24-DPPBTz and P-29-DPPBTz films are shown in Fig. 5. In both FETs based on P-24-DPPBTz and P-29-DPPBTz, n-channel dominant ambipolar characteristics were observed. According to the FET mobility results, FETs based on P-24-DPPBTz mostly exhibited a higher performance in both electron and hole transport than FETs based on P-29-DPPBTz, exhibiting remarkably high maximum (average) μ<sub>e</sub> and μ<sub>h</sub> values of 1.87 and 0.30 (1.49 and 0.15, respectively) cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 260 °C, respectively (Table 3). Maximum and average electron mobilities of 0.89 and 0.77 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, were obtained from the optimized P-29-DPPBTz films (annealed at 300 °C), whereas the hole mobilities were approximately 0.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> under several annealing conditions. These findings indicate that charge transport in these polymers containing a bithiazole group is more significantly affected by the molecular packing orientation and density than the morphological features.

More importantly, note that in our bithiazole-based polymer backbone system, a shorter alkyl spacer (C1) was more efficient (C6). This result is contrary to that obtained in our previous report on DPP-SVS and DPP-TVT polymer series that contain selenophene–vinylene–selenophene and thiophene–vinylene–thiophene units, respectively; herein, the optimized alkyl chain spacer unit was C6.7,22,23 Other than this exception, the longer
Table 3 OFET performance of P-24-DPPBTz and P-29-DPPBTz films

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Films</th>
<th>Thermal annealing (°C)</th>
<th>$\mu_{h,max}^{{\text{p-channel}}} [\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$</th>
<th>$\mu_{h,avg}^{{\text{p-channel}}} [\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$</th>
<th>$I_{on}/I_{off}$</th>
<th>$\mu_{e,max}^{{\text{n-channel}}} [\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$</th>
<th>$\mu_{e,avg}^{{\text{n-channel}}} [\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$</th>
<th>$I_{on}/I_{off}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-24-DPPBTz</td>
<td>Spin-coated</td>
<td>As-cast</td>
<td>0.054</td>
<td>0.039 (±0.009)</td>
<td>$&gt;10^3$</td>
<td>0.59</td>
<td>0.45 (±0.12)</td>
<td>$&gt;10^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>0.12</td>
<td>0.089 (±0.024)</td>
<td>$&gt;10^4$</td>
<td>0.99</td>
<td>0.65 (±0.28)</td>
<td>$&gt;10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>0.17</td>
<td>0.10 (±0.040)</td>
<td>$&gt;10^3$</td>
<td>1.53</td>
<td>0.96 (±0.46)</td>
<td>$&gt;10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>0.072</td>
<td>0.051 (±0.012)</td>
<td>$&gt;10^3$</td>
<td>1.08</td>
<td>0.71 (±0.28)</td>
<td>$&gt;10^3$</td>
</tr>
<tr>
<td></td>
<td>Drop-cast</td>
<td>As-cast</td>
<td>0.081</td>
<td>0.052 (±0.019)</td>
<td>$&gt;10^4$</td>
<td>0.59</td>
<td>0.32 (±0.12)</td>
<td>$&gt;10^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>0.15</td>
<td>0.13 (±0.018)</td>
<td>$&gt;10^4$</td>
<td>1.05</td>
<td>0.72 (±0.23)</td>
<td>$&gt;10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>0.3</td>
<td>0.15 (±0.071)</td>
<td>$&gt;10^4$</td>
<td>1.87</td>
<td>1.49 (±0.32)</td>
<td>$&gt;10^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>0.14</td>
<td>0.086 (±0.036)</td>
<td>$&gt;10^4$</td>
<td>1.23</td>
<td>0.87 (±0.27)</td>
<td>$&gt;10^4$</td>
</tr>
<tr>
<td>P-29-DPPBTz</td>
<td>Spin-coated</td>
<td>As-cast</td>
<td>0.065</td>
<td>0.048 (±0.015)</td>
<td>$&gt;10^4$</td>
<td>0.26</td>
<td>0.23 (±0.020)</td>
<td>$&gt;10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>0.063</td>
<td>0.051 (±0.013)</td>
<td>$&gt;10^5$</td>
<td>0.34</td>
<td>0.26 (±0.053)</td>
<td>$&gt;10^4$</td>
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<tr>
<td></td>
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<td>260</td>
<td>0.11</td>
<td>0.078 (±0.023)</td>
<td>$&gt;10^5$</td>
<td>0.33</td>
<td>0.20 (±0.11)</td>
<td>$&gt;10^3$</td>
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<td></td>
<td></td>
<td>300</td>
<td>0.16</td>
<td>0.076 (±0.035)</td>
<td>$&gt;10^5$</td>
<td>0.38</td>
<td>0.34 (±0.025)</td>
<td>$&gt;10^6$</td>
</tr>
<tr>
<td></td>
<td>Drop-cast</td>
<td>As-cast</td>
<td>0.057</td>
<td>0.045 (±0.012)</td>
<td>$&gt;10^4$</td>
<td>0.33</td>
<td>0.30 (±0.016)</td>
<td>$&gt;10^3$</td>
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<td>220</td>
<td>0.088</td>
<td>0.053 (±0.021)</td>
<td>$&gt;10^4$</td>
<td>0.39</td>
<td>0.30 (±0.061)</td>
<td>$&gt;10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>0.13</td>
<td>0.077 (±0.022)</td>
<td>$&gt;10^5$</td>
<td>0.58</td>
<td>0.45 (±0.053)</td>
<td>$&gt;10^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>0.09</td>
<td>0.066 (±0.023)</td>
<td>$&gt;10^4$</td>
<td>0.89</td>
<td>0.77 (±0.10)</td>
<td>$&gt;10^2$</td>
</tr>
</tbody>
</table>

* The p-channel characteristics of P-24-DPPBTz measured at $V_{DS} = -100 \text{ V}$; *n* n-channel characteristics of P-29-DPPBTz-FETs measured at $V_{DS} = 100 \text{ V}$. * Maximum mobility over 10 FET devices with a channel length ($L$) of $\sim 50 \mu\text{m}$ and a channel width ($W$) of $\sim 1000 \mu\text{m}$. * Average mobility over 10 FET devices with a channel length ($L$) of $\sim 50 \mu\text{m}$ and a channel width ($W$) of $\sim 1000 \mu\text{m}$. * Standard deviation.

$d$-spacings in P-29-DPP-SVS showed two- to three-fold higher hole mobility than those in P-24-DPP-SVS, due to its edge-on dominant molecular orientation.\(^7\)

Intriguingly, DPPBTz polymers with a smaller alkyl spacer showed better electrical performance both in p-channel and n-channel operations. In DPPBTz polymers, which have an A–D–A architecture, P-24-DPPBTz showed higher hole and electron mobility. As described above, the XRD spectrum of the A–D–A-type copolymers designed for n-type-dominant semiconductors did not show a $q_z(010)$ peak, which is a critical factor for forming 3D charge transport pathways. This could presumably be due to the relatively weaker intermolecular interactions in A–D–A-type copolymers compared with those in D–A-type copolymers. In A–D–A architecture, the intermolecular interactions may become weaker due to the relatively poor donor moiety, which can disturb the formation of a bimodal molecular packing, unlike in p-type-dominant D–A systems.
Furthermore, P-24-DPPBTz exhibited a much shorter $d_{(100)}$-spacing (≈ 5.63 Å closer in P-24-DPPBTz than in P-29-DPPBTz). The efficient intermolecular interaction of bithiazole groups in the P-24-DPPBTz backbone shortened the distance between the adjacent polymer chains (i.e., a high degree of molecular order in P-24-DPPBTz, as evidenced by a larger coherence length). On these grounds, P-24-DPPBTz is expected to provide superior electrical performance in both p- and n-type operations.

To exploit their ambipolar charge transport properties, P-24-DPPBTz and P-29-DPPBTz polymers were integrated into a complementary metal-oxide–semiconductor (CMOS)-like inverter. The inverter devices based on the P-24-DPPBTz and P-29-DPPBTz polymer FETs exhibited similar gain values of 29.3 and 26.3, respectively, at the constant supply voltage ($V_{DD}$) of +100 V (Fig. 6).

### Conclusion

Bithiazole-based polymers, P-24-DPPBTz and P-29-DPPBTz, containing C1 and C6 linear alkyl spacers showed electron-dominant ambipolar behaviors in the presence of electron-agitative nitrogen atoms in the bithiazole group. P-29-DPPBTz exhibited a red-shifted absorption compared with P-24-DPPBTz, due to the planar backbone formed as a result of placing branching points away to reduce steric hindrance. However, in contrast with the 24- and 29-based p-type polymers, higher charge carrier mobilities were observed from P-24-DPPBTz, indicating that the shorter alkyl spacer (C1) could facilitate effective charge transport. Unlike other p-type-dominant D-A-type copolymers with long alkyl spacers, the XRD spectrum of A–D–A-type copolymers with a long alkyl spacer for n-type-dominant semiconductors did not display a $g_0(010)$ peak, which is a critical factor for forming 3D charge transport pathways. This can be attributed to the relatively weaker intermolecular interactions in A–D–A-type copolymers compared with those in D–A-type copolymers.

In P-24-DPPBTz, a strong interchain interaction was achieved by the shorter alkyl spacer system over larger crystalline domains. The maximum electron mobilities of P-24-DPPBTz and P-29-DPPBTz were 1.87 and 0.89 cm² V⁻¹ s⁻¹, respectively, at the optimized annealing temperatures of 260 °C and 300 °C, respectively. Our findings demonstrate conflicting results with the research in p-type-dominant D–A DPP-based polymers and suggest for the first time that the alkyl side-chain has an effect on the carrier mobility of A–D–A n-type-dominant conjugated polymers.

### Experimental

#### AFM characterization

An Agilent 5500 (Agilent, USA) scanning probe microscope (SPM) running with a Nanoscope V controller was used to obtain AFM images of the P-24-DPPBTz and P-29-DPPBTz thin films. AFM images were obtained in the high-resolution tapping mode under ambient conditions.

#### FET fabrication and testing

FET devices with bottom-gate top-contact configuration were prepared to characterize the electrical performance of the P-24-DPPBTz and P-29-DPPBTz thin films. A highly n-doped (100) Si wafer (<0.004 Ω cm) with a thermally grown SiO₂ (300 nm, $G_i = 10 \text{ nF cm}^{-2}$) was utilized as the substrate and dielectric layer. The surface of SiO₂ was modified with a n-octadecyltrimethoxysilane (OTS) self-assembled monolayer (SAM). A 3 mM OTS solution in trichloroethylene was spun-coated onto the piranha-cleaned wafer at 3000 rpm for 30 s. Then, the wafer was exposed to ammonia vapors for ~12 h to facilitate the formation of the OTS SAM, followed by cleaning under sonication, sequential washing, and drying. The contact angle on the hydrophobic OTS-modified wafer, as measured with a D.I. water droplet, was >106°. The P-24-DPPBTz and P-29-DPPBTz polymers were dissolved in chlorobenzene to the concentration of 2 mg mL⁻¹, and the film was prepared on the substrate by spin-coating and drop-casting. Then, the polymer thin-film was annealed on a hot plate at 220, 260, and 300 °C for 30 min under a N₂ atmosphere. Gold contacts (40 nm) were thermally evaporated onto the polymer film to form the source and drain electrodes with a channel length ($L$) of ~50 μm and a channel width ($W$) of ~1000 μm using a shadow mask. The electrical performance of FETs was measured in a N₂-filled glove box using a Keithley 4200 semiconductor parametric analyzer. The field-effect mobility was calculated in the saturation regime using the following equation:

$$I_D = \frac{W}{2L} \mu C_0 (V_{GS} - V_T)^2$$

where $I_D$ is the drain-to-source current, $W$ and $L$ are the semiconductor channel width and length, respectively, $\mu$ is the mobility, and $V_{GS}$ and $V_T$ are the gate voltage and threshold voltage, respectively.

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