Bioderived and Eco-Friendly Solvent-Processed High-Mobility Ambipolar Plastic Transistors through Controlled Irregularity of the Polymer Backbone

So-Huei Kang, Ayoung Jeong, Hae Rang Lee, Joon Hak Oh, and Changduk Yang

INTRODUCTION

π-Conjugated polymers have attracted considerable attention for application in organic electronic devices because of their easily modifiable structures, excellent solution processability, and potential for low-cost device fabrication. Developing high-performance π-conjugated polymers for optoelectronic applications highly relies on their molecular engineering and synthetic methodologies. In fact, refining the design of the π-conjugated polymers via the toolbox of various donors–acceptor (D–A) units has resulted in charge-carrier mobility in organic field-effect transistors (OFETs) similar to or higher than that of amorphous silicon. Nevertheless, the commercial use of these high-performance OFETs is difficult given that most of them are generally fabricated by using chlorinated aromatics or alkanes such as chloroform and chlorobenzene (CB), which can cause significant environmental damage during manufacturing, use, and disposal. Besides, in many countries, more and increasingly strict policies have been established to protect the environment and human health. Therefore, nonchlorinated solvents must replace such toxic solvents to enable the industrialization of OFETs. To achieve this goal, good solubility of the polymers in nonchlorinated solvents is a basic requirement and can be achieved by manipulating flexible side chains (e.g., longer, oligoether, and ionic side chains). However, such a variation in the alkyl chains often results in reduced OFET performance, and the solubility in the non-chlorinated solvents still remain insufficient. As another pioneering attempt, reducing the regularity of the copolymers via random copolymerization improves their solubility/processability, thus leading to excellent OFET performance in some non-

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chlorinated solvents such as toluene, tetrahydrofuran, xylene, and tetralin.35–56

Inspired by the successful synthetic approaches toward semiconducting polymers that can be processed from non-chlorinated solvents, in this study we introduce random copolymerization between two dithienylvinylene (TVT) and selenophene (Se) donor units in conjugation with diketopyrrolopyrrole (DPP) as an acceptor moiety, which affords a series of copolymers with different TVT to Se composition ratios in the DPP backbone.57–59 In addition to the systematic study of the optical, physical, and structural properties of these copolymers, the morphological trends and crystalline structures were also investigated, thus shedding light on the effects of the rational compositional variations. We first used the resulting copolymers as active channel semiconductors in ambipolar OFETs, using the most widely used processing solvent CB; the best hole ($\mu_h$) and electron ($\mu_e$) mobilities, up to 6.31 and 0.78 cm$^2$ V$^{-1}$ s$^{-1}$, are achieved from the CB-processed OFET. More importantly, a switch of the processing solvent from CB to bioderived and eco-friendly 2-methyltetrahydrofuran (MeTHF) still leads to $\mu_h$ and $\mu_e$ values as high as 4.15 V$^{-1}$ s$^{-1}$ and 0.34 cm$^2$ V$^{-1}$ s$^{-1}$, which is attributed to the dramatically improved solubility induced by adjusting the irregularity of the backbone structure. These values are among the highest reported for non-chlorinated solvent-processed ambipolar OFETs. It is noteworthy that MeTHF is much less hazardous and sustainable greener than the aforementioned non-chlorinated solvents, according to the SDS Search & Product Safety (see the Chart S1, Supporting Information).37 Moreover, MeTHF is generally considered as a bioderived solvent because it is derived from renewable sources through the catalytic reduction of furfural which is itself available by dehydration of pentosan sugars present in biomass.60 Therefore, our results should help move the OFET community one step closer toward green and sustainable organic transistors.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization.** As shown in Figure 1a, DPP-based copolymers were prepared by palladium-catalyzed Stille polycondensation using DPP, TVT, and Se monomers, and they are named according to the molar percentage of total donor segments [TVT to Se] in the backbone as [10-0], [7-3], [5-5], [3-7], [2-8], [1-9], and [0-10], respectively. In order to obtain high molecular weights of each copolymer, the reaction conditions of the polymerization in CB were carefully modified by using different catalytic systems (Pd$_2$(dba)$_3$/P(o-tol)$_3$ vs Pd(PPh$_3$)$_4$). We found that for the copolymers with high Se content ([3-7], [2-8], [1-9], and [0-10]), the polymerization employing Pd$_2$(dba)$_3$/P(o-tol)$_3$ produced high-molecular-weight fractions in a good yield over 85%, whereas in the high TVT content ones ([10-0], [7-3], and [5-5]), the use of Pd(PPh$_3$)$_4$ resulted in high-molecular-weight copolymers. This observation suggests that the optimal Pd-mediated coupling reaction depends on the type of the monomers used during the polymerization.

As summarized in Table 1, the number- and weight-average molecular weights ($M_n$ and $M_w$, respectively) and the polydispersity index (PDI) of the copolymers were measured by high-temperature gel permeation chromatography at 100 °C with 1,2,4-trichlorobenzene as an eluent. The high Se-containing copolymers ([5-5], [3-7], [2-8], [1-9], and [0-10]) are readily dissolved in organic solvents, leading to high $M_n$ values exceeding 30 kDa, which is attributed to the random arrangement of the subunits along the main backbone. On the other hand, the TVT dominant copolymers ([10-0] and [7-3]) have relatively low $M_w$ (22–25 kDa) and somewhat limited solubility that is due to the higher concentration of the rigid and flat $\pi$-conjugated TVT units in the backbone. Note that the solubility issue will be discussed later in detail. Although the structural identity of the subunits of the resulting copolymers was clearly probed using $^1$H NMR spectroscopy, quantifying the TVT to Se molar fraction through the integral ratios of the proton signals is rather difficult (even at 80 °C because of signal broadening and overlapping (Figure S1). However, the CHS elemental analysis data of the copolymers match well with the theoretical values within a discrepancy of 0.3%. Detailed synthetic procedures and structural characterization are described in the Experimental section of the Supporting Information.

**Photophysical and Electrochemical Properties and Simulation.** The absorption spectra of seven copolymers in CB solution and thin film (Figure 1a,b, respectively) and the relevant data are summarized in Table 1. All the copolymers show very broad absorption bands ranging from 350 to 1000 nm, in which they contain a high-energy transition peak at 350–500 nm and a broad, low-energy band attributed to the intramolecular charge transfer (ICT) between the DPP acceptor and the TVT and Se donor moieties. The low-energy transition band exhibits a gradual red shift with an increasing
Table 1. Photophysical and Electrochemical Properties of the Copolymers

<table>
<thead>
<tr>
<th>copolymer</th>
<th>( \lambda_{\text{onset}} ) [nm]</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
<th>( \lambda_{\text{abs}} ) [nm]</th>
<th>( E_{\text{opt}} ) [eV]</th>
<th>( E_{\text{HOMO}} ) [eV]</th>
<th>( E_{\text{LUMO}} ) [eV]</th>
<th>( M_r ) [kDa]</th>
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<tr>
<td>[0-10]</td>
<td>3839</td>
<td>780</td>
<td>978</td>
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<td>-5.18</td>
<td>-3.40</td>
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<td>22.7</td>
<td>2.99</td>
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</tbody>
</table>

*Calculated from the absorption band edge of the copolymer film, \( E_{\text{opt}} = \frac{1240}{\lambda_{\text{onset}}} \). Thin films in n-Bu4NPF6/CH3CN, vs ferrocene/ferrocenium at 100 mV s\(^{-1}\). HOMO and LUMO estimated from the onset oxidation and reduction potentials, respectively, assuming the absolute energy level of ferrocene/ferrocenium to be 4.8 eV below vacuum.

Se content can that likely be attributed to the increased quinoidal characteristic of the copolymer backbone because of the inclusion of Se units despite the extended \( \pi \)-conjugation length of TVT over the Se unit. Similar spectral characteristics were also observed in other conjugated copolymers based on bicyclic lactam dyes reported by our group.\(^{61}\) The low-energy bands of all the copolymer films are much broader than those of the copolymer solutions. However, no meaningful chromic shift is observed when comparing the solution and film copolymers, except for the [0-10] sample whose film has a strong red-shifting tendency and a notable shoulder, as a consequence of the tendency to the aggregates or crystallites of the copolymer chains. These results imply that the tendency to the aggregates or crystallites of the copolymer chains and intermolecular distances in the solid state. The [0-10] film, in particular, has a higher degree of such aggregation. The optical bandgaps (\( E_{\text{opt}} \)) of the copolymers are estimated to be in the range of 1.22–1.28 eV based on the onset of the film absorption.

To evaluate the electrochemical properties of the copolymer films, cyclic voltammetry measurements were also carried out in n-Bu4NPF6/CH3CN solution. All the copolymer films display reversible oxidation and reduction behavior where the oxidative peaks are stronger than reductive ones (Figure S2), indicating that they are more easily oxidized than reduced. As the Se content increases, the highest unoccupied molecular orbital (HOMO) levels show a slight but gradual down-shifting, whereas the lowest unoccupied molecular orbital (LUMO) levels are relatively constant with a rather nonlinear trend (≈3.38 to ≈3.43 eV). The detailed data are listed in Table 1. Previously, we also observed such selective fine-tuning of the HOMO or LUMO by replacing thiophene with a Se unit in another copolymer backbone.\(^{62}\)

Molecular simulation on the dimeric models was performed using density functional theory (DFT) calculations at B3LYP/6-31G*, where DPP-alt-TVt (DPP-TVt–DPP-TVt), DPP-ran-Se/TVt (DPP–Se–DPP–TVt), and DPP-alt-Se (DPP–Se–DPP–Se) models were chosen to explore the molecular geometries and the electron density distributions as a function of different sequences of TVt and Se units in the backbone. In addition to their high degree of structural coplanarity with negligibly low torsional angles (\( \phi < 5^\circ \)) between the building blocks, both HOMO and LUMO charge densities for all the copolymers were well delocalized along the main backbone (Figure 2 and Table S1). We also calculated the dipole moment of each model. The net dipole moments of DPP-alt-TVt, DPP-ran-Se/TVt, and DPP-alt-Se are 1.87, 2.17, and 1.21 D with similar directions, respectively, indicating that the hybrid backbone pattern renders a higher dipole moment than the parent alternating ones because of its irregular structure, which will contribute to the charge-transport properties (vide infra).

**Thin-Film Microstructural Analyses.** Morphology and microstructure (e.g., topography, crystallinity, and molecular organization) of the copolymers were analyzed by tapping-mode atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXD). The copolymer films were fabricated by drop-casting on n-octadecyltrimethoxysilane (OTS)-treated SiO2/Si substrates and then thermally annealing at 220 °C for 30 min in a N2 atmosphere. The AFM images of the annealed films exhibited larger microstructural domains with slightly higher root-mean-square (rms) roughness compared to the corresponding as-cast films (Figures 3 and S3) because of the aggregation of copolymer chains by thermal annealing. All the films showed highly interconnected nanofibrillar networks, except for [10-0] exhibiting agglomerated grains that yield the poor film formation. This is most likely because of the reduced solubility of [10-0] relative to others.

As shown in Figures 4 and S4, no obvious change is observed in the diffraction patterns of the copolymer films as a function of the annealing treatment. All the films exhibited highly ordered multiple-lamellar peaks (h00) in the out-of-plane direction (\( d_{h00} \)) with a \( \pi-\pi \) stacking peak (010) in the in-plane direction (\( d_{010} \)), indicating the preferential edge-on orientation with respect to the substrate. The calculated crystallographic parameters are listed in Table S3, where the overall trends (the peak positions of the diffraction patterns and intermolecular distances) of the annealed films with different TVt/Se ratios are found to be similar to what was seen in the as-cast films. Therefore, in the rest of the paper, we discuss only the annealed films. Among the annealed films, [10-0] showed the shortest lamellar \( d \)-spacing (\( d_{100} \)) of ~23.9 Å,
implying that a denser lamellar ordering exists, which can be attributed to the rigid π-extended TVT units.

Figure 4c visualizes the TVT/Se ratio-dependent distance trends of the annealed films. We calculated the crystalline correlation length (CCL100) value, which is a parameter used to determine the grain size of a single crystalline domain, by using the Scherrer equation. The value increases from 182.9 Å for [10-0] to 258.8 Å for [7-3], 319.0 Å for [5-5], and 393.3 Å for [3-7]. However, it begins to gradually decrease when the Se content becomes higher than that in [3-7] (Figure 4c). The same trend is also observed for the dz values. Consequently, [3-7] has both the largest CCL100 and the highest CCL100/dz (defined as the number of layers forming a single crystalline grain), which is beneficial for OFET mobility via the formation of a favorable intermolecular charge transporting pathway.

**Performance of the OFETs.** The electrical characteristics of the copolymer films were analyzed by preparing OFETs in a bottom-gate top-contact configuration. The copolymer thin films drop-cast using the CB-based solution were initially investigated as the control experiment with regard to the bioderived eco-friendly processing solvent (MeTHF) system, given that CB is frequently used as a conventional processing solvent for polymer semiconductors. The as-cast copolymer films were thermally annealed at the optimal annealing temperature of 220 °C, as proven for other DPP-based copolymers previously. As expected, the annealed films had significantly better OFET performance in comparison with the as-prepared films. All the annealed copolymers films exhibited hole-dominant ambipolar charge-transport characteristics with V-shaped transfer curves as shown in Figure S5. Table S4 summarizes the annealed copolymer film OFET transport results (see Figure S7 and Table S5 for the results of the as-cast film based OFETs). Such hole-dominant ambipolar OFETs were predictable from the well-positioned HOMO/LUMO energy levels that facilitate both hole and electron injections with respect to the work function of the Au electrodes ($W_f \approx 5.1$ eV) because of HOMO energy levels being lower than the work function of Au.

For p-channel operation, the on- and off-current ratio ($I_{on}$/$I_{off}$) is estimated to be in the range of $10^5$ to $10^7$, and the threshold voltage ($V_T$) is nearly 0 V in all the OFETs. The $\mu_h$ of 1.93 cm$^2$ V$^{-1}$ s$^{-1}$ is obtained from [10-0]. The $\mu_h$ of the copolymers increases with the increasing Se content up to 70%, reaching the highest hole mobility of 6.31 cm$^2$ V$^{-1}$ s$^{-1}$ for...
With higher Se content than that in [3-7], the $\mu_h$ decreases, being 3.95 cm$^2$ V$^{-1}$ s$^{-1}$ for [2-8] despite its molecular weight being higher than the other copolymers. The $\mu_h$ increases again with higher Se content up to [0-10], leading to a $\mu_h$ of 5.74 cm$^2$ V$^{-1}$ s$^{-1}$ for [0-10], which is about twenty times larger than that of [10-0] ($\mu_e \approx 0.07$ cm$^2$ V$^{-1}$ s$^{-1}$). This result can be explained by considering the electrochemical and morphological features of the copolymers. With the increase of the Se content, the LUMO levels slightly upshifted because of the increase in the disorder in the copolymer backbone, but this was only true up to the amount of Se in [5-5]. Beyond that, that is, with more Se content, the LUMO levels downshifted. A low-lying LUMO energy level can help the reduction on the injection barriers, thus the downshifting trend of the LUMO energy level might result in enhanced n-channel performance for copolymers with higher Se content. On the other hand, despite the slightly higher lying LUMO energy level, [7-3] to [3-7] showed better electron mobilities because of their superior morphological properties in comparison to that of [10-0]. The charge mobility balance of the p- and n-channels for each copolymer film is presented as a percentage bar graph (Figure 5c). The OFETs with higher Se content exhibit more balanced ambipolar characteristics.

As the target set of experiments, we carried out solubility tests of the copolymers at room temperature in detail, where CB and MeTHF were chosen as solvents because the former is the conventional but toxic-processing solvent used for polymer semiconductors, and the latter is a bioderived, eco-friendly processing solvent being studied here. Note that their absorption spectra with the MeTHF solvent are provided in Figure S9, showing almost identical features when compared with those obtained from CB. We quantified the solubility by creating a standard copolymer solution for each copolymer in the chosen solvent at known concentrations, then, diluting the solution to achieve an optical density suitable for absorption measurement, measuring the $\lambda_{\text{max}}$ of the diluted solution, and finally, comparing the $\lambda_{\text{max}}$ of a diluted solution of a saturated solution with the calibrated linear fit curves (see Supporting Information for the detailed measurements). The absorption spectra and calibration plots are shown in Figures S10–S13 (Supporting Information), and the solubility results are reported in Figure S14 and Table 2. All copolymers showed a better solubility in CB than in MeTHF. The Se-containing copolymers have enhanced solubility in the solvents compared to those only containing TVT ([10-0]). In particular, [3-7] displays the best solubility in both CB (6.32 mg mL$^{-1}$) and MeTHF (1.50 mg mL$^{-1}$). Furthermore, when the contact,

<table>
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<th>Copolymer</th>
<th>CB (mg/mL)</th>
<th>MeTHF (mg/mL)</th>
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<tr>
<td>[10-0]</td>
<td>1.33</td>
<td>0.04</td>
</tr>
<tr>
<td>[7-3]</td>
<td>2.80</td>
<td>0.05</td>
</tr>
<tr>
<td>[5-5]</td>
<td>4.34</td>
<td>0.21</td>
</tr>
<tr>
<td>[3-7]</td>
<td>6.32</td>
<td>1.50</td>
</tr>
<tr>
<td>[2-8]</td>
<td>6.16</td>
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</tr>
<tr>
<td>[1-9]</td>
<td>5.53</td>
<td>0.14</td>
</tr>
<tr>
<td>[0-10]</td>
<td>5.42</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Figure 5. (a) Transfer curves of OFETs based on annealed [3-7] films at p-channel and n-channel operation with $V_{DS} = -100$ and +100 V, respectively. (b) Hole/electron mobilities. (c) Percentage graph of hole/electron mobilities for each annealed copolymer film obtained from CB- (left) and MeTHF-processed (right) OFETs.
gate voltage mobility,
\[ V_r \] slope changes greatly was not clearly observed. However, a reason, we implemented the complemented reliability factor channel characteristics of the ambipolar materials. For this derived in the saturation regime using Shockley equation.

nonlinear. To complement the inaccuracy of the extracted the Shockley equation for low gate voltage with a high slope, in di

μ changes, and another (e

voltage region with a low slope after the point where the slope multiplying the reliability factor (Figures S15 and S16), the two solution types showed which exhibits a clear ambipolar charge transport with the MeTHF, respectively. For the n-channel mobility, only the ability (Figures 5 and S18 and Table 3). Considering the MeTHF solubility results, we also prepared the on- and o-off-current ratio. 3 Threshold voltage. The subscripts, h and e, denote for hole and electron, respectively. About 20 devices were tested for each copolymer type.

angle of each CB and MeTHF solution was measured on the OTS-treated SiO2/Si substrate to estimate solution processability (Figures S15 and S16), the two solution types showed the same trend. In general, the contact angle increased with increasing Se content, indicating that a higher Se ratio would be unfavorable for easier film processing.

Considering the MeTHF solubility results, we also prepared a series of MeTHF-processed OFETs based on the copolymers under the same conditions as the CB-processed ones. The MeTHF-processed OFETs show good performance comparable to the CB-based OFETs (Figures 5 and S18 and Table 3). The highest \( \mu_h \) (4.15 cm² V⁻¹ s⁻¹) is obtained from [3-7] which exhibits a clear ambipolar charge transport with the \( \mu_e \) being 0.34 cm² V⁻¹ s⁻¹. The other copolymers also had ambipolar charge-transport characteristics, and the highest \( \mu_e \) (0.64 cm² V⁻¹ s⁻¹) was obtained from [0-10] due to the linear, direct trend with increasing Se content. The maximum hole and electron mobilities (\( \mu_{max} \)) of the OFETs were calculated by the Shockley equation for low gate voltage with a high slope, though the mobilities derived in that method may be fairly inaccurate parameters if the FET transport characteristics are nonlinear. To complement the inaccuracy of the extracted mobility, we further obtained two different mobilities derived in different ways (Tables 3, S4, and Figure S20); one (high gate voltage mobility, \( \mu_{high} \)) was derived from the high gate voltage region with a low slope after the point where the slope changes, and another (effective mobility, \( \mu_{eff} \)) was calculated by multiplying the reliability factor \( r \) by the \( \mu_{max} \) (\( \mu_{eff} = r \times \mu_{max} \)). For p-channel mobility, the obtained \( \mu_{h,high} \) was 0.19–0.23 times the \( \mu_{h, max} \) in both CB and MeTHF. The \( \mu_{e,eff} \) was calculated for \( r \) of 22.1–25.2 and 20.2–24.9% in CB and MeTHF, respectively. For the n-channel mobility, only the effective mobility was determined because the point where the slope changes greatly was not clearly observed. However, a relatively small \( r \) of 4.2–9.5% was obtained because of the highly positively shifted threshold voltage \( (V_T) \) for the n-channel characteristics of the ambipolar materials. For this reason, we implemented the complemented reliability factor \( (r') \), which was defined in the Experimental Section (see Supporting Information). The \( \mu_{e,eff} \) was calculated with \( r' \) of 32.4–51.3 and 31.4–48.4% in CB and MeTHF, respectively.

to observe an enhanced electron mobility because of the well-aligned work function of Al (\( W_f \approx 4.06 \) eV) with regard to the LUMO levels (Figure S22, Table S7). As shown in the results, threshold voltage during n-channel operation was less shifted as compared to the Au electrodes. However, the performance of OFETs with Al electrodes was generally degraded because of the oxidation of Al electrodes and lower penetration of evaporated Al into the copolymer films.

Because ambipolar semiconducting materials are useful in complementary metal-oxide semiconductor (CMOS) inverters, the inverter characteristics of the copolymer films were also investigated (Figure S21). The inverters exhibit quite a high gain, up to 65.6, but the change in the output voltage \( (V_{OUT}) \) occurred at high input voltage \( (V_{IN}) \), which can be explained by the imbalance in the p- and n-channel performance.

In fact, preparing high-quality copolymers using less toxic solvents is also a necessary step toward the eventual development of environmentally friendly OFETs. Therefore,

<table>
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<th>copolymer</th>
<th>( \mu_{e,avg} ) [cm² V⁻¹ s⁻¹]</th>
<th>( \mu_{h,avg} ) [cm² V⁻¹ s⁻¹]</th>
<th>( \mu_{eff} ) [cm² V⁻¹ s⁻¹]</th>
<th>( r' ) [%]</th>
<th>R [%]</th>
<th>( V_{h,low} ) [V]</th>
<th>( V_{h,high} ) [V]</th>
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<tr>
<td>[10-0]</td>
<td>1.51 (±2.73 × 10⁻⁴)</td>
<td>0.33 (±0.22)</td>
<td>0.34</td>
<td>24.9</td>
<td>10⁷</td>
<td>10⁷ to 10⁸</td>
<td>11.1</td>
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<tr>
<td>[7-3]</td>
<td>2.33 (±2.60 × 10⁻⁴)</td>
<td>0.47 (±0.20)</td>
<td>0.49</td>
<td>22.4</td>
<td>10⁷</td>
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<tr>
<td>[5-5]</td>
<td>3.12 (±1.62 × 10⁻⁴)</td>
<td>0.62 (±0.20)</td>
<td>0.65</td>
<td>21.4</td>
<td>10⁷</td>
<td>10⁷ to 10⁸</td>
<td>−13.9</td>
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<tr>
<td>[3-7]</td>
<td>4.15 (±2.49 × 10⁻⁴)</td>
<td>0.95 (±0.23)</td>
<td>1.00</td>
<td>24.7</td>
<td>10⁷</td>
<td>10⁷ to 10⁸</td>
<td>−15.0</td>
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<tr>
<td>[2-8]</td>
<td>2.95 (±5.64 × 10⁻⁴)</td>
<td>0.56 (±0.19)</td>
<td>0.57</td>
<td>20.8</td>
<td>10⁷</td>
<td>10⁷ to 10⁸</td>
<td>−8.8</td>
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<tr>
<td>[1-9]</td>
<td>3.01 (±6.06 × 10⁻⁴)</td>
<td>0.57 (±0.19)</td>
<td>0.59</td>
<td>20.2</td>
<td>10⁷</td>
<td>10⁷ to 10⁸</td>
<td>−12.2</td>
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<tr>
<td>[0-10]</td>
<td>3.51 (±2.85 × 10⁻⁴)</td>
<td>0.77 (±0.22)</td>
<td>0.80</td>
<td>23.2</td>
<td>10⁷</td>
<td>10⁷ to 10⁸</td>
<td>−14.7</td>
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The OFETs were fabricated by solution process based on MeTHF. The OFET performance was measured in N₂ atmosphere. Charge mobilities derived in the saturation regime using Shockley equation. Maximum mobility at low gate voltage with high slope. Average mobility at high gate voltage with low slope. The ratio of the mobility at high gate voltage to maximum mobility. Reliability factor calculated by the equation from reference paper. Effective mobility calculated by \( \mu_{eff} = r \times \mu_{max} \). Complemented reliability factor. Effective mobility calculated by \( \mu_{eff} = r' \times \mu_{max} \). CCL (C = 11.5 m² cm⁻², L = 50 μm and W = 1000 μm). The range of on- and o-off-current ratio. Threshold voltage. The subscripts, h and e, denote for hole and electron, respectively. About 20 devices were tested for each copolymer type.
herein, the polymerization of [3-7] showing the best solubility and charge-transport property was also carried out using MeTHF solvent with an optimal solution concentration, resulting in $M_n$ of 33.7 kDa and PDI of 3.42 values similar to those obtained from the same reaction in CB (see the detailed procedure in Experimental Section of the Supporting Information).

**CONCLUSIONS**

We have demonstrated that tuning the TVT/Se donor ratio in a new series of DPP-based copolymers ([10-0], [7-3], [5-5], [3-7], [2-8], [1-9], and [0-10]) enables gradual changes in optical, electrochemical, morphological, and charge-transport properties. The resulting copolymers with more Se content display red-shifted absorption properties. The resulting copolymers with more Se content showed improved solubility and processability of [3-7] also resulted in excellent optical, electrochemical, morphological, and charge-transport properties. The measured mobilities are among the highest reported to date for a bioderived and eco-friendly processing solvent; the measured mobility exceeding 10 cm$^2$/V·s) in Donor-Acceptor Polymer Transistors with Band-like Charge Transport. *Chem. Mater.* 2016, 28, 420–424.

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