Electronic Supplementary Information

New Poly(Selenophene-Thiophene) Bearing \( \pi \)-Conjugating Spacers for

Polymer Field-Effect Transistors and Photovoltaic Cells†

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Synthesis of Se4T and 2Se4T monomers:

Scheme S1. The synthetic route on synthesizing Se4T and 2Se4T monomers.

**2-dodecylthiophene (I)**

n-Butyllithium (2.5 M in hexanes, 87.9 ml, 220 mmol) was added dropwise to a solution of thiophene (16.8 g, 200 mmol) in anhydrous THF (200 ml) at -78 °C under nitrogen and then the reaction mixture was brought to room temperature. After the mixture was stirred for 1.5 h, 1-bromododecane (64.7g, 260 mmol) was added in one portion and the solution was stirred at room temperature overnight. The solution was added into deionized water and extracted with hexanes twice. The organic extract was dried over MgSO₄ to remove water and purified by vacuum distillation to obtain 25.6g (50.7%) yellow viscous liquid; ¹H NMR (400 MHz, CDCl₃, δ): aromatic (C-H), 7.10-7.08 (d, 1H), 6.91-6.89 (t, 1H), 6.75 -6.76 (d, 1H), aliphatic (C-H) 2.83-2.78 (t,
2H), 1.68-1.64 (s, 4H), 1.39-1.18 (m, 13H), 0.87-0.85 (t, 6H).

![Fig. S1. ¹H NMR Spectrum of 2-dodecylthiophene in CDCl₃.(x: CDCl₃, y: H₂O)](image)

**2-dodecyl-5-trimethylstannylthiophene (2)**

Compound 1 (5 g, 20 mmol) was dissolved in anhydrous THF (100 ml) at -78 °C under nitrogen and then n-butyllithium (2.5 M in hexanes, 9.5 ml, 24 mmol) was added dropwise. The mixture was stirred for 4 h and trimethyltin chloride (5.5 g, 28 mmol) in 5 ml THF was added in one portion and the solution was stirred at room temperature overnight. The solution was poured into deionized water and extracted with hexanes. The organic extract was dried over MgSO₄ to remove water and evaporated to remove solvent. Yellow viscous liquid was obtained. (6.85 g, 83.3 %);

¹H NMR (400 MHz, CD₂Cl₂, δ): aromatic (C-H), 7.00-6.99 (d, 1H), 6.89 -6.88 (d, 1H), aliphatic (C-H) 2.83-2.78 (t, 2H), 1.68-1.64 (m, 4H), 1.39-1.18 (m, 13H), 0.87-
0.85 (t, 6H), 0.39-0.28 (m, 18H).

Fig. S2. $^1$H-NMR Spectrum of 2-dodecyl-5-trimethylstannylthiophene in CD$_2$Cl$_2$. (x: CD$_2$Cl$_2$, y: H$_2$O)

$5'$-dodecyl-3,2$'$-bithiophene (3)

A solution of 3-bromothiophene (0.98 g, 6.01 mmol), compound 2 (4.4 g, 10.62 mmol), and Pd(PPh$_3$)$_4$ (250 mg, 0.21 mmol) DMF (20 mL) and toluene (80 mL) was mixed in a one-neck flask. After three freeze-thaw cycles, the mixtures was heated up to 110 °C for 24 h under nitrogen purging. After cooling to room temperature, water was added and then the aqueous phase was extracted with hexane. The organic extract was dried over MgSO$_4$ to remove water, and the solvent was evaporated under vacuum. The crude product was purified by flash column using hexane as eluent to give compound 3 (804 mg, 40%) as yellow oil; $^1$H NMR (400MHz, CD$_2$Cl$_2$, δ):
aromatic (C-H), 7.36-7.34 (d, 1H), 7.31 (s, 1H), 7.02-7.01 (d, 1H), aliphatic (C-H) 2.83-2.78 (t, 2H), 1.68-1.64 (m, 4H), 1.39-1.18 (m, 13H), 0.87-0.85 (t, 6H).

Fig. S3. $^1$H-NMR Spectrum of 5'-dodecyl-3,2'-bithiophene in CD$_2$Cl$_2$. (x: CD$_2$Cl$_2$, y: H$_2$O)

2-bromo-5'-dodecyl-3,2'-bithiophene (4)

A solution of compound 3 (804 mg, 2.4 mmol) in chloroform (25 mL) and glacial acetic acid (25 mL) was charged in a three-neck flash under nitrogen-filled dark environment. After the mixture was cooled to 0 °C, n-bromosuccinimide (470.5 mg, 2.64 mmol) was added in one portion. Then the mixture was warmed to room temperature and stirred for 12 h. Water was added and then the aqueous phase was extracted with diethyl ether. The organic extracts were dried over MgSO$_4$ and concentrated. The crude product was purified by flash column using hexane/dichloromethane (20/1) as eluent to give compound 4 (893 mg, 90 %) as
yellow oil; $^1$H NMR (400MHz, CD$_2$Cl$_2$, δ): aromatic (C-H), 7.30-7.28 (d, 1H), 7.28-7.26 (d, 1H), 7.18-7.10 (d, 1H), 6.81-6.70 (d, 1H), aliphatic (C-H) 2.83-2.78 (t, 2H), 1.68-1.64 (m, 4H), 1.39-1.18 (m, 13H), 0.87-0.85 (t, 6H).

Fig. S4. $^1$H-NMR Spectrum of 2-bromo-5'-dodecyl-3,2'-bithiophene in CD$_2$Cl$_2$. (x: CD$_2$Cl$_2$, y: H$_2$O)

2,5-bis(5-dodecyl-[2,3'-bithiophen]-2'-yl)selenophene (5)

A solution of compound 4 (893 mg, 2.2 mmol), 2,5-bis(trimethylstannyl)selenophene (Se) (448 mg, 1 mmol), and Pd(PPh$_3$)$_4$ (34 mg, 29.4 mmol) DMF (20 mL) and toluene (80 mL) was mixed in a one-neck flask. After three freeze-thaw cycles, the mixtures was heated up to 110 °C for 24 h under nitrogen purging. After cooling to room temperature, water was added and then the aqueous phase was extracted with ethyl acetate. The organic extract was dried over MgSO$_4$ to remove water, and the solvent was evaporated under vacuum. The crude product was purified by flash
column using hexane/chloroform (20/1) as eluent to give compound 5 (351 mg, 45 %) as yellow oil; \(^1\)H NMR (400MHz, CD\(_2\)Cl\(_2\), \(\delta\)): aromatic (C-H), 7.22-7.21 (d, 2H), 7.21-7.20 (d, 2H), 7.06-7.04 (d, 2H), 6.87-6.86 (d, 2H), 6.67-6.66(d, 2H), aliphatic (C-H) 2.83-2.78 (t, 2H), 1.68-1.64 (m, 4H), 1.39-1.18 (m, 13H), 0.87-0.85 (t, 6H).

**Fig. S5.** \(^1\)H-NMR Spectrum of 2,5-bis(5-dodecyl-[2,3'-bithiophen]-2'-yl)selenophene in CD\(_2\)Cl\(_2\). (x: CD\(_2\)Cl\(_2\), y: H\(_2\)O)

**5,5'-bis(5-dodecyl-[2,3'-bithiophen]-2'-yl)-2,2'-biselenophene (6)**

A solution of compound 4 (880 mg, 2.13 mmol), 5,5'-Bis(trimethylstanny)-2,2'-biselenophene (2Se) (567 mg, 0.97 mmol), and Pd(PPh\(_3\))\(_4\) (33 mg, 29.1 mmol) DMF (20 mL) and toluene (80 mL) was mixed in a one-neck flask. After three freeze-thaw cycles, the mixtures was heated up to 110 °C for 24 h under nitrogen purging. After cooling to room temperature, water was added and then the aqueous phase was
extracted with ethyl acetate. The organic extract was dried over MgSO₄ to remove water, and the solvent was evaporated under vacuum. The crude product was purified by flash column using hexane/chloroform (20/1) as eluent to give compound 6 (461 mg, 50 %) as yellow oil; ¹H NMR (400 MHz, CD₂Cl₂, δ): aromatic (C-H), 7.25-7.23 (d, 2H), 7.22-7.20 (d, 2H), 7.07-7.06 (d, 2H), 7.06-7.05 (d, 2H), 6.92-6.91 (d, 2H), 6.74-6.73 (d, 2H), aliphatic (C-H), 2.83-2.78 (t, 2H), 1.68-1.64 (m, 4H), 1.39-1.18 (m, 13H), 0.87-0.85 (t, 6H).

Fig. S6. ¹H-NMR Spectrum of 5,5'-bis(5-dodecyl-[2,3'-bithiophen]-2'-yl)-2,2'-biselenophene in CD₂Cl₂. (x: CD₂Cl₂, y: H₂O)

2,5-bis(5'-bromo-5-dodecyl-[2,3'-bithiophen]-2'-yl)selenophene (Se₄T)

A solution of compound 5 (351 mg, 0.4 mmol) in DMF (40 mL) and toluene (10 mL) was charged in a three-neck flash under nitrogen-filled dark environment. After the mixture was cooled to 0 ºC, n-bromosuccinimide (172.3 mg, 0.96 mmol) was
added in one portion. Then the mixture was warmed to room temperature and stirred for 12 h. Water was added and then the aqueous phase was extracted with diethyl ether. The organic extracts were dried over MgSO$_4$ and concentrated. The crude product was purified by flash column using hexane as eluent to give Se4T (411.4 mg, 98%) as orange oil; $^1$H NMR (400 MHz, CD$_2$Cl$_2$, δ): aromatic (C-H), 7.24-7.23 (d, 2H), 7.22-7.21 (d, 2H), 7.07-7.06 (d, 2H), 6.67-6.66 (d, 2H), aliphatic (C-H), 2.83-2.78 (t, 4H), 1.68-1.64 (m, 8H), 1.39-1.18 (m, 26H), 0.87-0.85 (t, 12H).

5,5'-bis(5'-bromo-5-dodecyl-[2,3'-bithiophen]-2'-yl)-2,2'-biselenophene (2Se4T)

A solution of compound 6 (351 mg, 0.4 mmol) in DMF (40 mL) and toluene (10 mL) was charged in a three-neck flash under nitrogen-filled dark environment. After the mixture was cooled to 0 °C, n-bromosuccinimide (189.5 mg, 1.1 mmol) was added in one portion. Then the mixture was warmed to room temperature and stirred for 12 h.
Water was added and then the aqueous phase was extracted with diethyl ether. The organic extracts were dried over MgSO$_4$ and concentrated. The crude product was purified by flash column using hexane as eluent to give 2Se4T (513.7 mg, 98%) as an orange oil; $^1$H NMR (400 MHz, CD$_2$Cl$_2$, δ): aromatic (C-H), 7.22-7.20 (s, 2H), 7.07-7.06 (d, 2H), 7.06-7.05 (d, 2H), 6.92-6.91 (d, 2H), 6.74-6.73 (d, 2H), aliphatic (C-H), 2.83-2.78 (t, 4H), 1.68-1.64 (m, 8H), 1.39-1.18 (m, 26H), 0.87-0.85 (t, 12H).

![Figure S8. $^1$H-NMR Spectrum of 2Se4T in CD$_2$Cl$_2$. (x: CD$_2$Cl$_2$, y: H$_2$O)](image)

**Table S1.** Solubility behavior of the synthesized conjugated polymers
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chloroform$^a$</th>
<th>$o$-Dichlorobenzene$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSe4TV</td>
<td>5.4 mg ml$^{-1}$</td>
<td>9.6 mg ml$^{-1}$</td>
</tr>
<tr>
<td>PSe4TT</td>
<td>4.9 mg ml$^{-1}$</td>
<td>9.1 mg ml$^{-1}$</td>
</tr>
<tr>
<td>PSe4T2T</td>
<td>6.3 mg ml$^{-1}$</td>
<td>9.7 mg ml$^{-1}$</td>
</tr>
<tr>
<td>PSe4TTT</td>
<td>&gt; 10 mg ml$^{-1}$</td>
<td>&gt; 10 mg ml$^{-1}$</td>
</tr>
<tr>
<td>P2Se4TTT</td>
<td>&gt; 10 mg ml$^{-1}$</td>
<td>&gt; 10 mg ml$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$The polymer solutions were prepared as 10 mg ml$^{-1}$ initially.

### Table S2. Photovoltaic characteristics of Se4T- and 2Se4T-based polymer/PC$_{61}$BM blends$^a$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer:PC$_{61}$BM</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (-)</th>
<th>PCE$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSe4TV</td>
<td>1:2</td>
<td>0.63</td>
<td>2.17</td>
<td>0.316</td>
<td>0.43</td>
</tr>
<tr>
<td>PSe4T2T</td>
<td>1:2</td>
<td>0.45</td>
<td>3.21</td>
<td>0.295</td>
<td>0.42</td>
</tr>
<tr>
<td>PSe4TTT</td>
<td>1:2</td>
<td>0.61</td>
<td>3.21</td>
<td>0.308</td>
<td>0.61</td>
</tr>
<tr>
<td>P2Se4TTT</td>
<td>1:2</td>
<td>0.76</td>
<td>4.19</td>
<td>0.371</td>
<td>1.18</td>
</tr>
</tbody>
</table>

$^a$o-$Dichlorobenzene as the processing solvent. $^b$The average value of PCE is calculated from at least 5 devices.
Fig. S9. $^1$H-NMR Spectra of (a) PSe4TV, (b) PSe4TT, (c) PSe4T2T, and (d) PSe4TTT in CDCl$_3$. (x: CDCl$_3$, y: H$_2$O)
Fig. S10. DSC traces of the studied polymers with a scanning rate of 10 °C min⁻¹ under nitrogen atmosphere.

Fig. S11. UV-Vis spectra of the studied polymers in o-dichlorobenzene solution.
Fig. S12. Topographical AFM images of the (a) PSe4TV, (b) PSe4TT, (c) PSe4T2T, (d) PSe4TTT, and (e) P2Se4TTT spin-coated thin film.
Fig. S13. TEM and AFM phase images of PSe4TT thin film surfaces. Large aggregates (> 100 nm) could be found on PSe4TT surface (red dash line).

Fig. S14. Representative 2D GIXD pattern of (a) PSe4TV and (b) PSe4TT thin films annealed at 140 °C for 1 h under vacuum.
Fig. S15. Output characteristics of the (a) PSe4TV, (b) PSe4TT, (c) PSe4T2T, and (d) PSe4TTT.

Fig. S16. PV characteristics of Se4T- or 2Se4T-based polymer/PC61BM blends under the illumination with AM 1.5G solar simulated light (100 mW cm⁻²).
Fig. S17. TEM images of P2Se4TTT/PC\textsubscript{71}BM (1:2, w/w) blending thin film using (a) pure o-DCB and (b) o-DCB/DIO (98/2 v/v) as processing solvent. Large aggregates (> 100 nm) are observed in the films prepared using pure o-DCB. After adding DIO into P2Se4TTT/PC\textsubscript{71}BM blends, the size of aggregates are significantly reduced, exhibiting the thin film with better uniformity.