Supplementary Information

Divergent Synthesis of 3-Substituted Thieno[3,4-b]thiophene Derivatives via Hydroxy-based Transformations

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1. Materials and instrumentation methods

All reactions were carried out in a dry reaction vessel under a positive pressure of nitrogen, unless otherwise stated. Dry solvents (<50 ppm H$_2$O) were purchased from Acros Organics, Sigma-Aldrich or Carl Roth and stored over molecular sieves under argon atmosphere and were transferred under argon. Starting materials were obtained from Acros Organics, Aldrich Chemical Co., J&K and Energy Chemical and were used without further purification. Anhydrous THF and toluene were distilled over Na/benzophenone prior to use. Anhydrous DMF was distilled over CaH$_2$ prior to use. These dry solvents stored over molecular sieves under argon atmosphere and were transferred under argon.

UV-vis was recorded with SPECORD® 210 PLUS spectrometers. Fluorescence spectrometry was recorded with Spectrofluorometer FS5. Cyclicvoltammetry (CV) was performed with a CHI660E potentiostat. All measurements were carried out in a one-compartment cell under a nitrogen atmosphere, equipped with a glassy-carbon electrode, a platinum-counter-electrode, and an Ag/Ag$^+$ reference electrode with a scan rate of 100 mV s$^{-1}$. The supporting electrolyte was a 0.1 mol/L acetonitrile solution of tetrabutylammoniumhexafluorophosphate. All potentials were corrected against Fe/Fe$^+$. 

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV 300, Bruker AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicated. Chemical shifts (δ) for $^1$H and $^{13}$C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra and the chemical shifts converted to the TMS scale (CDCl$_3$: δ$_H$ = 7.26 ppm, δ$_C$ = 77.16 ppm; (CD$_3$)$_2$SO: δ$_H$ = 2.50 ppm, δ$_C$ = 39.52 ppm). Elemental analyses were performed with vario EL CUBE from elementar.. HRMS spectra were recorded on Varian 7.0T FTMS. GPC spectra were performed with Waters 1525.

2. Detailed experimental procedures

Compound 1a was synthesized according to the procedure in the literature.$^1$ 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, J = 3.6 Hz, 1H), 7.31 (d, J = 3.6 Hz, 1H), 
4.30 (t, J = 6.6 Hz, 2H), 1.74 (dt, J = 14.6, 6.7 Hz, 2H), 1.47 (dt, J = 14.6, 7.4 Hz, 2H),
0.97 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.37, 134.06, 131.48, 125.20, 110.76, 64.82, 30.62, 19.21, 13.66. HRMS (ESI): calcd. for C$_9$H$_{11}$BrO$_2$S $[M+Na]^{+}$: 284.9561, found: 284.9558. Anal. Calca. for C$_9$H$_{11}$BrO$_2$S: C: 41.08; H: 4.21; Found: C: 41.09; H: 4.57.

**Butyl 4-((2-ethoxy-2-oxoethyl)thio)thiophene-3-carboxylate (3a)**

In a Schlenk flask equipped with a magnetic stirrer were placed butyl 4-bromothiophene-3-carboxylate (1a, 1.31 g, 5 mmol, 1.0 eq), Pd$_2$dba$_3$ (0.46 g, 10 mol%), XantPhos (0.58 g, 20 mol%), DIPEA (1.2 mL, 1.5 eq) and anhydrous toluene (28 mL). After stirring for a few minutes, ethyl 2-mercaptoacetate (1.1 mL, 2.0 eq) was added drop by drop, then the reaction mixture was refluxed at 120 °C and stirred for 24 h. Then, it was cooled at room temperature and the precipitate was collected by filtration, washed with saturated NaHCO$_3$, extracted with CH$_2$Cl$_2$. After drying over MgSO$_4$, the residue was purified by column chromatography (PE:EA= 10:1) as eluent to obtain 3a (1.45 g, 96%) as yellow oily liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, J = 3.4 Hz, 1H), 7.04 (d, J = 3.4 Hz, 1H), 4.27 (t, J = 6.6 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.67 (s, 2H), 1.75 – 1.67 (m, 2H), 1.46 (dt, J = 14.9, 7.4 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.52 (s), 162.13 (s), 134.57 (s), 133.86 (s), 131.25 (s), 119.50 (s), 64.75 (s), 61.60 (s), 35.82 (s), 30.65 (s), 19.20 (s), 14.04 (s), 13.68 (s). HRMS (ESI): calcd. for C$_{13}$H$_{18}$O$_4$S$_2$ $[M+Na]^{+}$: 325.0544, found: 325.0543.

**Ethyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (4)**

In a Schlenk flask equipped with a magnetic stirrer, to a solution of tBuOK (1.55 g, 2.1 eq), in THF (18 mL), after stirring for a few minutes, butyl 4-((2-ethoxy-2-oxoethyl)thio)thiophene-3-carboxylate (3a, 2 g, 6.6 mmol, 1.0 eq) of THF solution was added dropwise at 0 °C and stirred for 1 h. The reaction mixture was quenched with sat. NH$_4$Cl, and washed with H$_2$O, extracted with CH$_2$Cl$_2$. After drying over MgSO$_4$, the solvent was removed by rotary evaporation. The crude product was
purified by column chromatography (PE:acetone= 5:1) as eluent to obtain 4 (1.21 g, 80.1%) as green oily liquid. 1H NMR (400 MHz, CDCl3) δ 10.29 (s, 1H), 7.73 (d, J = 2.6 Hz, 1H), 7.20 (d, J = 2.6 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 167.84 (s), 154.81 (s), 138.66 (s), 135.22 (s), 117.24 (s), 112.26 (s), 105.79 (s), 61.38 (s), 14.28 (s). HRMS (ESI): calcd.for C10H8Br2O3S2[M+Na]+: 250.9813, found: 250.9843.

Ethyl 3-methoxythieno[3,4-b]thiophene-2-carboxylate (5)
In a Schlenk flask equipped with a magnetic stirrer, were placed ethyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (4, 2.28 g, 10.0 mmol, 1.0 eq), DMF (50 mL), and DBU (1.64 mL, 1.1eq), after stirring for ten minutes, CH3I (3.1 mL, 5eq) was added at r.t. and stirred for 12 h. The reaction mixture was quenched with H2O, extracted with EA, dried over Na2SO4, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE:EA= 20:1) as eluent to obtain 5 (507 mg, 20.9%) as yellow solid. 1H NMR (400 MHz, CDCl3) δ 7.68 (d, J = 2.7 Hz, 1H), 7.21 (d, J = 2.7 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 4.26 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 162.41 (s), 151.58 (s), 139.93 (s), 135.61 (s), 116.64 (s), 111.88 (s), 60.99 (s), 60.75 (s), 14.30 (s). HRMS (ESI): calcd.for C10H10O3S2[M+Na]+: 264.9969, found: 264.9967. Anal. Calca. for C10H10O3S2: C: 49.57; H: 4.16; Found: C: 49.47; H: 4.59.

Ethyl 4,6-dibromo-3-methoxythieno[3,4-b]thiophene-2-carboxylate (6)
In a Schlenk flask equipped with a magnetic stirrer, were placed ethyl 3-methoxythieno[3,4-b]thiophene-2-carboxylate (5, 48 mg, 0.2 mmol, 1.0 eq), and DMF (1 mL), then NBS (88 mg, 0.5 mmol, 2.5 eq) in DMF (1 mL) was added at r.t. and stirred for 24 h and the reaction was protected from light. The reaction mixture was quenched with H2O, extracted with CH2Cl2, dried over Na2SO4, filtered and the
solvent was evaporated. The crude product was purified by column chromatography (PE:EA=50:1) as eluent to obtain 6 (47.8 mg, 60.3%) as light yellow solid. \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta 4.36 (q, J = 7.1 \text{ Hz, } 2\text{H}), 4.06 (s, 3\text{H}), 1.39 (t, J = 7.1 \text{ Hz, } 3\text{H}).\)
\(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta 161.46 (s), 151.80 (s), 139.01 – 138.81 (m), 136.43 (s), 101.86 (s), 98.01 (s), 63.03 (s), 61.56 (s), 14.13 (s).\) HRMS (ESI): calcd.for \(\text{C}_{10}\text{H}_8\text{Br}_2\text{O}_3\text{S}_2\[\text{M+Na}]^+: 420.8179, \text{found: 420.8178.}\)

Ethyl 3-(((trifluoromethyl)sulfonyl)oxy)thieno[3,4-b]thiophene-2-carboxylate (7)

In a Schlenk flask equipped with a magnetic stirrer, were added ethyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (4, 1.6 g, 7.0 mmol, 1.0 eq), dry \(\text{CH}_2\text{Cl}_2\) (35 mL) and pyridine (2.37 mL, 2.0 eq), then Tf\(_2\text{O}\) (1.1 mL, 2.0 eq) at 0 °C was added dropwise. The reaction mixture was stirred for 5 h at room temperature, quenched with saturated \(\text{NaHCO}_3\), extracted with \(\text{CH}_2\text{Cl}_2\), dried over MgSO\(_4\), filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: \(\text{CH}_2\text{Cl}_2\)= 5:1) as eluent to obtain 7 (1.75 g, 70%) as yellow solid. \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta 7.64 (d, J = 2.5 \text{ Hz, } 1\text{H}), 7.38 (d, J = 2.7 \text{ Hz, } 1\text{H}), 4.44 (q, J = 7.1 \text{ Hz, } 2\text{H}), 1.41 (t, J = 7.1 \text{ Hz, } 3\text{H}).\) \(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta 160.70 (s), 137.63 (s), 134.72 (s), 133.80 (s), 128.71 (s), 123.32 (s), 120.13 (s), 116.94 (s), 116.34 (s), 113.61 (s), 62.52 (s), 14.06 (s).\) HRMS (ESI): calcd.for \(\text{C}_{10}\text{H}_7\text{F}_3\text{O}_5\text{S}_3\[\text{M+Na}]^+: 382.9305, \text{found: 382.9305.}\)

Ethyl 3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (8)

In a Schlenk flask equipped with a magnetic stirrer, were added ethyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (7, 36 mg, 0.1 mmol, 1.0 eq), Pd\(_2\)(dba)\(_3\) (0.5 mg, 0.006mmol, 6mol%), XantPhos (7 mg, 0.012mmol, 12mol%), toluene (2 mL), DIPEA (31 mg, 1.2 eq) and NaSMe (aq., 20%) (55 mg, 0.15 mmol, 1.5 eq). The reaction mixture was stirred for 24 h at 100 °C. Then quenched with saturated
NaHCO$_3$, extracted with CH$_2$Cl$_2$, dried over MgSO$_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: EA= 20:1) as eluent to obtain 8 (23.5mg, 91%) as oily liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, J = 2.7 Hz, 1H), 7.28 (d, J = 2.7 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 2.73 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.51 (s), 147.42 (s), 137.04 (s), 132.25 (d, J = 19.9 Hz), 117.29 (s), 111.55 (s), 61.51 (s), 17.57 (s), 14.28 (s). HRMS (ESI): calcd.for C$_{10}$H$_{10}$O$_2$S$_3$ [M+Na]$^+$: 280.9741, found: 280.9740.

Ethyl 3-aminothieno[3,4-b]thiophene-2-carboxylate (9)

In a Schlenk flask equipped with a magnetic stirrer, were added (7, 180 mg, 0.5 mmol, 1.0 eq), Pd$_2$(dba)$_3$ (46 mg, 0.05 mmol, 10 mol%), XantPhos (29 mg, 0.05 mmol, 10 mol%), K$_3$PO$_4$ (212.2 mg, 1.0 mmol, 2.0 eq), toluene (10 mL) and diphenylmethanimine (0.125 mL, 0.76 mmol, 1.52 eq). The reaction mixture was stirred for 24 h at 90 °C. Then, it was cooled at room temperature, quenched with H$_2$O, extracted with EA, dried over Na$_2$SO$_4$, filtered and the solvent was evaporated. The crude product was dissolved in methanol stirring for 1 h and was added ice water, extracted with EA, dried over Na$_2$SO$_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: EA= 5:1) as eluent to obtain 10 (98 mg, 86%) as light yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (s, 1H), 7.16 (s, 1H), 5.83 (s, 2H), 4.32 (dd, J = 13.9, 6.9 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.89 (s), 143.22 (s), 140.95 (s), 136.40 (s), 115.04 (s), 111.88 (s), 102.42 (s), 60.35 (s), 14.46 (s). HRMS (ESI): calcd.for C$_9$H$_9$NO$_2$S$_2$ [M+Na]$^+$: 249.9972, found: 249.9972. Anal. Calca. for C$_9$H$_9$NO$_2$S$_2$: C: 47.56; H: 3.99; N: 6.16; Found: C: 47.89; H: 4.59; N: 6.17.

Ethyl 3-phenylothieno[3,4-b]thiophene-2-carboxylate (10)

In a Schlenk flask equipped with a magnetic stirrer, were added (7, 72 mg, 0.2 mmol,
1.0 eq), phenylboronic acid (32 mg, 0.26 mmol, 1.3 eq), Pd(PPh₃)₄ (7.0 mg, 0.006 mmol, 3 mol%), K₃PO₄ (68 mg, 0.32 mmol, 1.6 eq) and 1,4-dioxane (2 mL). The reaction mixture was stirred for 24 h at 110 °C. Then, it was cooled at room temperature, quenched with sat. NH₄Cl, and washed with H₂O, extracted with CH₂Cl₂, dried over MgSO₄, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: CH₂Cl₂= 5:1) as eluent to obtain 10 (56 mg, 97%) as light yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.48 (dtd, J = 10.8, 3.8, 1.9 Hz, 5H), 7.39 (d, J = 2.7 Hz, 1H), 7.31 (d, J = 2.7 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.90 (s), 149.02 (s), 137.55 (s), 136.98 (s), 134.64 (s), 132.97 (s), 129.14 (s), 128.22 (s), 127.98 (s), 117.19 (s), 111.39 (s), 61.27 (s), 13.92 (s). HRMS (ESI): calcd.for C₁₅H₁₂O₂S₂ [M+Na]⁺: 311.0176, found: 311.0175.

**Ethyl 3-(phenylethynyl)thieno[3,4-b]thiophene-2-carboxylate (11)**

In a Schlenk flask equipped with a magnetic stirrer, were added (7, 72 mg, 0.2 mmol, 1.0 eq), phenylacetylene (31 mg, 0.3 mmol, 1.5 eq), PdCl₂(PPh₃)₂ (4.2 mg, 0.006 mmol, 3 mol%), 0.12 mL Et₃N, 2 mL DMF, the reaction mixture was stirred for 24 h at 90 °C. Then, it was cooled at room temperature, quenched with H₂O, extracted with CH₂Cl₂, dried over MgSO₄, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: CH₂Cl₂= 3:1) as eluent to obtain 11 (57 mg, 91%) as yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.77 (d, J = 2.7 Hz, 1H), 7.63 (dd, J = 6.5, 2.9 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.32 (d, J = 2.7 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.42 (s), 147.33 (s), 139.70 (s), 136.48 (s), 131.92 (s), 129.00 (s), 128.45 (s), 122.75 (s), 117.08 (s), 116.88 (s), 112.22 (s), 98.11 (s), 82.92 (s), 61.70 (s), 14.34 (s). HRMS (ESI): calcd.for C₁₇H₁₂O₂S₂ [M+Na]⁺: 335.0176, found: 335.0275.

Compounds of 12, 13, 15 and 16 were synthesized with corresponding starting materials by similar procedure for preparation of 4, 5, 6, 7, and 8.
2-Ethylhexyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (12)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.26 (s, 1H), 7.73 (d, $J = 2.6$ Hz, 1H), 7.19 (d, $J = 2.6$ Hz, 1H), 4.24 (d, $J = 5.3$ Hz, 2H), 1.69 (dd, $J = 11.8$, 5.9 Hz, 1H), 1.44 – 1.30 (m, 8H), 0.94 (dd, $J = 13.2$, 5.7 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.92 (s), 154.66 (s), 138.69 (s), 135.29 (s), 117.21 (s), 112.20 (s), 105.97 (s), 67.64 (s), 38.77 (s), 30.39 (s), 28.89 (s), 23.84 (s), 22.92 (s), 14.01 (s), 11.04 (s). HRMS (ESI): calcd for C$_{15}$H$_{20}$O$_3$S$_2$ [M+Na$^+$]: 335.0752, found: 335.0750.

2-Ethylhexyl 3-methoxythieno[3,4-b]thiophene-2-carboxylate (13)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J = 2.6$ Hz, 1H), 7.22 (d, $J = 2.6$ Hz, 1H), 4.26 (s, 3H), 4.20 (dd, $J = 5.5$, 2.9 Hz, 2H), 1.73 – 1.61 (m, 1H), 1.43 – 1.28 (m, 8H), 0.93 (dd, $J = 13.6$, 6.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.59 (s), 151.50 (s), 139.83 (s), 135.70 (s), 116.66 (s), 116.24 (s), 111.86 (s), 67.21 (s), 60.67 (s), 38.85 (s), 30.49 (s), 28.92 (s), 23.91 (s), 22.97 (s), 14.05 (s), 11.09 (s). HRMS (ESI): calcd for C$_{16}$H$_{22}$O$_3$S$_2$ [M+Na$^+$]: 349.0908, found:349.0906.

2-Ethylhexyl 4,6-dibromo-3-methoxythieno[3,4-b]thiophene-2-carboxylate (14)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.22 (s, 2H), 4.07 (s, 3H), 1.73 – 1.64 (m, 1H), 1.47 – 1.31 (m, 8H), 0.97 – 0.88 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.57 (s), 151.75 (s), 138.94 (s), 136.50 (s), 122.62 (s), 101.80 (s), 98.00 (s), 67.77 (s), 63.11 (s), 38.85
(s), 30.42 (s), 28.93 (s), 23.85 (s), 22.94 (s), 14.02 (s), 11.03 (s). HRMS (ESI): calcd. for \( \text{C}_{16}\text{H}_{20}\text{Br}_{2}\text{O}_{3}\text{S}_{2} \cdot \text{Na}^{+} \): 504.9118, found: 504.9118.

\[
\begin{align*}
\text{C}_4\text{H}_{9} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{C}_4\text{H}_{9} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{C}_4\text{H}_{9} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{C}_4\text{H}_{9} & \quad \text{O} \\
\end{align*}
\]

**2-Ethylhexyl-3-(((trifluoromethyl)sulfonyl)oxy)thieno[3,4-b]thiophene-2-carboxylate (15)**

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.65 (d, \( J = 2.6 \) Hz, 1H), 7.38 (d, \( J = 2.7 \) Hz, 1H), 4.28 (dd, \( J = 6.0, 1.1 \) Hz, 2H), 1.74 (dt, \( J = 12.3, 6.1 \) Hz, 1H), 1.45 – 1.30 (m, 8H), 0.92 (dt, \( J = 10.4, 7.2 \) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 160.60 (s), 137.54 (s), 135.04 (s), 133.84 (s), 128.19 (s), 123.31 (s), 120.12 (s), 116.93 (s), 116.30 (s), 113.54 (s), 68.72 (s), 38.57 (s), 30.20 (s), 28.76 (s), 23.65 (s), 22.90 (s), 13.95 (s), 10.85 (s). HRMS (ESI): calcd. for \( \text{C}_{16}\text{H}_{19}\text{F}_{3}\text{O}_{5}\text{S}_{3} \cdot \text{Na}^{+} \): 467.0244, found: 467.0242. Anal. Calcd. for \( \text{C}_{16}\text{H}_{19}\text{F}_{3}\text{O}_{5}\text{S}_{3} \): C: 43.23; H: 4.31; Found: C: 43.21; H: 4.23.

\[
\begin{align*}
\text{C}_4\text{H}_{9} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{C}_4\text{H}_{9} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{C}_4\text{H}_{9} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{C}_4\text{H}_{9} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\end{align*}
\]

**2-Ethylhexyl 3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (16)**

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.75 (s, 1H), 7.28 (s, 1H), 4.27 – 4.21 (m, 2H), 2.73 (s, 3H), 1.74 – 1.67 (m, 1H), 1.45 – 1.28 (m, 8H), 0.93 (dd, \( J = 14.5, 6.8 \) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 162.64 (s), 147.40 (s), 137.09 (s), 132.26 (d, \( J = 13.8 \) Hz), 117.26 (s), 111.50 (s), 67.73 (s), 38.82 (s), 30.47 (s), 28.90 (s), 23.91 (s), 22.95 (s), 17.53 (s), 14.03 (s), 11.08 (s). HRMS (ESI): calcd. for \( \text{C}_{16}\text{H}_{22}\text{O}_{3}\text{S}_{3} \cdot \text{Na}^{+} \): 365.0680, found: 365.0678.
2-Ethylhexyl 4,6-dibromo-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (17)

In a Schlenk flask equipped with a magnetic stirrer, were added (16, 1.24 g, 3.6 mmol, 1.0 eq), DMF (15 mL), then a solution of NBS (1.92 g, 10.8 mmol, 3.0 eq) in DMF (10 mL) was added at r.t. and stirred for 24 h and the reaction was protected from light. The reaction mixture was quenched with H₂O, extracted with saturated salt water and CH₂Cl₂, dried over Na₂SO₄, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: CH₂Cl₂ = 5:1) as eluent to obtain 17 (894 mg, 49%) as light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 4.27 (d, J = 4.2 Hz, 2H), 2.52 (s, 3H), 1.75 – 1.65 (m, 1H), 1.40 (dd, J = 26.2, 14.5 Hz, 8H), 0.94 (dd, J = 14.6, 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 161.49 (s), 143.10 (s), 139.42 (s), 138.43 (s), 131.64 (s), 103.13 (s), 97.42 (s), 72.07 – 71.87 (m), 68.16 (s), 38.82 (s), 30.44 (s), 29.63 – 29.43 (m), 28.92 (s), 23.88 (s), 22.94 (s), 21.60 – 21.40 (m), 20.39 (s), 14.40 – 14.20 (m), 14.03 (s), 11.06 (s). HRMS (ESI): calcd.for C₁₆H₂₀Br₂O₂S₃ [M+Na]+: 520.8890, found: 520.8888.

2-Ethylhexyl-4-bromo-6-formyl-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate(18)

A solution of 16 in 1,2-dichloroethane (DCE, 100 mL) was degassed with argon for 15 min and then the Vilsmerier reagent (was prepared according to the literature)² was added into the reaction slowly and stirred at room temperature for 1 h. The reaction solution was stirred at 100 °C for another 24 h. Then saturated sodiumacetate solution was added slowly to quench the reaction. The reaction solution was washed with water for three times and extracted with CH₂Cl₂, dried over anhydrous Na₂SO₄,
filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: EA=10:1) as eluent to obtain 2-ethylhexyl 6-formyl-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (5.3 g, 91%) as yellow solid. **1H NMR (400 MHz, CDCl₃)** δ 9.89 (s, 1H), 8.19 (s, 1H), 4.23 (dd, J = 10.4, 5.0 Hz, 2H), 2.71 (s, 3H), 1.68 (dt, J = 12.1, 6.0 Hz, 1H), 1.44 – 1.28 (m, 8H), 0.94 – 0.88 (m, 6H). **13C NMR (101 MHz, CDCl₃)** δ 179.63 (s), 162.07 (s), 148.11 (s), 143.12 (s), 133.55 (s), 132.25 (s), 127.58 (s), 127.02 (s), 68.05 (s), 53.41 (s), 38.81 (s), 30.41 (s), 28.93 (s), 23.85 (s), 22.94 (s), 17.96 (s), 14.05 (s), 11.05 (s). HRMS (ESI): calcd.for C₁₇H₂₂O₃S₃[M+Na]⁺: 393.0629, found: 393.0624.

In a Schlenk flask equipped with a magnetic stirrer, were added 2-ethylhexyl 6-formyl-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (5.0 g, 14 mmol, 1.0 eq), DMF (50 mL), then NBS (3.7 g, 21 mmol, 1.5 eq) was added one-pot at 0 °C and then stirred for 24 h and the reaction was protected from light. The reaction solution was washed with water for three times and extracted with CH₂Cl₂, dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: EA=10:1) as eluent to obtain 18 (2.89 g, 91%) as yellow-brown viscous liquid. **1H NMR (400 MHz, CDCl₃)** δ 9.81 (s, 1H), 4.28 (t, J = 4.5 Hz, 2H), 2.55 (s, 3H), 1.74 – 1.68 (m, 1H), 1.47 – 1.31 (m, 8H), 0.94 (dd, J = 15.1, 7.5 Hz, 6H). **13C NMR (101 MHz, CDCl₃)** δ 178.31 (s), 161.30 (s), 144.44 (s), 143.04 (s), 139.71 (s), 131.04 (s), 126.72 (s), 117.14 (s), 68.34 (s), 38.85 (s), 30.43 (s), 28.93 (s), 23.87 (s), 22.93 (s), 17.96 (s), 14.02 (s), 11.04 (s). HRMS (ESI): calcd.for C₁₇H₂₁BrO₃S₃[M+Na]⁺: 470.9734, found: 470.9730.

The procedure for preparation and purification of Polymer P1

In a 100 mL Schlenk flask, 2-ethylhexyl 4,6-dibromo-3-methoxythieno[3,4-b]thiophene-2-carboxylate 14 (202 mg, 0.417 mmol) and (4,8-bis(2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (322 mg, 0.417 mmol) were dissolved in anhydrous toluene (10 mL) and DMF (2.5 mL).
After being purged with nitrogen for 20 min, 21 mg (4.0 mol%) of Pd(PPh₃)₄ was added into the flask as the catalyst, and then the reaction mixture was purged with nitrogen for another 30 min. The reaction mixture was stirred and heated to reflux (120 °C) for 48 h under an nitrogen atmosphere (according to the procedure in the literature). After the reaction mixture was cooled down to room temperature, 41 mg of tributyl(thiophen-2-yl)stannane was added under nitrogen atmosphere and the reaction was refluxed for another 10 h. The reaction mixture was cooled to room temperature and added dropwise to 100 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum to get polymer P1 (276 mg, yield 87%). GPC: Mw = 30.1 KD, PDI= 2.1.

The procedure for preparation and purification of Polymer P2

In a 25 mL pressure tube, 2-ethylhexyl 4,6-dibromo-3-methoxythieno[3,4-b]thiophene-2-carboxylate 14 (97 mg, 0.2 mmol) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl)bis(trimethylstannane) (181 mg, 0.2 mmol) were dissolved in anhydrous toluene (4 mL) and DMF (1.0 mL). After being purged with nitrogen for 20 min, 10 mg (4.0 mol%) of Pd(PPh₃)₄ was added into the flask as the catalyst, and then the reaction mixture was purged with nitrogen for another 30 min. The reaction mixture was stirred and heated to reflux (120 °C) for 48 h under an nitrogen atmosphere. After the reaction mixture was cooled down to room temperature, 20 mg of tributyl(thiophen-2-yl)stannane was added under nitrogen atmosphere and the reaction was refluxed for another 10 h. The reaction mixture was cooled to room temperature and added dropwise to 100 mL methanol. The precipitate was collected and further purified by
Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum to get polymer P2 (148 mg, yield 84%). GPC: Mw = 20.4 KD, PDI = 1.9.

In a 100 mL Schlenk flask, 2-ethylhexyl 4,6-dibromo-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate 17 (200 mg, 0.4 mmol) and (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (309 mg, 0.4 mmol) were dissolved in anhydrous toluene (8 mL) and DMF (2 mL). After being purged with nitrogen for 20 min, 18.5 mg (4.0 mol%) of Pd(PPh₃)₄ was added into the flask as the catalyst, and then the reaction mixture was purged with nitrogen for another 30 min. The reaction mixture was stirred and heated to reflux (120 °C) for 48 h under an nitrogen atmosphere. After the reaction mixture was cooled down to room temperature, 40 mg of tributyl(thiophen-2-yl)stannane was added under nitrogen atmosphere and the reaction was refluxed for another 10 h. The reaction mixture was cooled to room temperature and added dropwise to 100 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum to get polymer P3 (152 mg, yield 48%). GPC: Mw = 39.8 KD, PDI = 1.9.
In a 25 mL pressure tube, 2-ethylhexyl 4,6-dibromo-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate 17 (150 mg, 0.3 mmol) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diy)bis(trimethylstannane) (272 mg, 0.3 mmol) were dissolved in anhydrous toluene (6 mL) and DMF (1.5 mL). After being purged with nitrogen for 20 min, 15 mg (4.0 mol%) of Pd(PPh$_3$)$_4$ was added into the flask as the catalyst, and then the reaction mixture was purged with nitrogen for another 30 min. The reaction mixture was stirred and heated to reflux (120 °C) for 48 h under an nitrogen atmosphere. After the reaction mixture was cooled down to room temperature, 31 mg of tributyl(thiophen-2-yl)stannane was added under nitrogen atmosphere and the reaction was refluxed for another 10 h. The reaction mixture was cooled to room temperature and added dropwise to 100 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum to get polymer P4 (242 mg, yield 89%). GPC: Mw = 25.8 KD, PDI= 2.1.

3. Optoelectronic properties

![Figure S1](image-url). Normalized UV/Vis absorption spectra of 5, 8, 9, 10, 11 and TT as a film
Figure S2. Reductive CV curves of P1, P2, P3 and P4 film in diluted CH$_3$CN solution with a scan rate of 100 mV s$^{-1}$.

Figure S3. Oxidative CV curves of P1, P2, P3 and P4 in film in diluted CH$_3$CN solution with a scan rate of 100 mV s$^{-1}$.

4. References

5. GPC and NMR spectra

Cirrus GPC Sample Injection Report
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Detector: RI
Flow Rate: 1.00 ml/min
Temperature: 150
Injection Volume: 200.0 ul

Analysis Using Method: 20171022
Comments:

Calibration Used: 10/26/2017 2:28:28 PM
High Limit MW RT: 16.35 mins
High Limit MW: 5198272
K: 17.5000

Low Limit MW RT: 25.32 mins
Low Limit MW: 529
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Distribution Plots

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Citrus GPC Version 3.4
Page 1
11/3/2017 9:48 AM

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Detector: RI
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Temperature: 150
Injection Volume: 200.0 ul

Analysis Using Method: 20171022
Comments:

Calibration Used: 10/26/2017 2:28:28 PM
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Analysis Using Method: 20171022

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Distribution Plots

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Analysis Using Method: 20171022
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