Supporting Information for

Push-pull thiophene chromophores for electro-optic applications: from 1D linear to β-branched structures

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Table of Contents:

1. Synthetic Part S3
2. Thermal properties S45
3. Absorption properties S47
4. Electrochemical measurements S48
5. DFT Calculations S50
6. NLO measurements S56
7. References S57
1. Synthetic Part

1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline

\[
\text{HN} \quad \text{C}_9\text{H}_{13}\text{N} \quad \text{C}_9\text{H}_{13}\text{N} \\
\]  

To a solution of 2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (8.83 g, 46.7 mmol) in THF (dry, 60 mL) a solution of \( n \)-BuLi in hexane (2.5 M, 20.5 mL, 51.4 mmol) was added slowly at -15 °C. The solution was stirred for 30 minutes, then 1-bromohexane (8.48 g, 51.4 mmol) was added. The reaction mixture was refluxed for 16 hours. The reaction was quenched by addition of water (100 mL). The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (2x 100 mL). The combined organic extracts were dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure. Fractional distillation of the crude product under reduced pressure gave the product as a colorless liquid (3.27 g, 12 mmol, 26%).

\( ^1 \)H-NMR (250 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.03 (d, \( J = 7.6 \) Hz, 1H), 6.45 (d, \( J = 7.6 \) Hz, 1H), 6.33 (s, 1H), 3.36-3.23 (m, 1H), 3.07-2.95 (m, 1H), 2.93-2.79 (m, 1H), 2.29 (s, 3H), 1.74-1.47 (m, 4H), 1.39-1.28 (m, 12H), 1.16 (s, 3H), 0.93 (t, \( J = 6.4 \) Hz, 3H). \( ^{13} \)C-NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 145.0, 136.4, 125.9, 124.8, 115.9, 112.0, 54.3, 47.3, 45.3, 31.8, 29.9, 29.4, 27.1, 27.0, 25.0, 22.9, 21.9, 20.3, 14.2.

6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline

\[
\text{C}_9\text{H}_{13}\text{N} \quad \text{Br} \quad \text{C}_9\text{H}_{13}\text{N} \\
\]  

To a solution of 1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (1.56 g, 5.56 mmol) in DMF (dry, 10 mL) a solution of NBS (1.18 g, 6.63 mmol) in DMF (dry, 10 mL) was added drop wise. The reaction mixture was stirred at room temperature for 21 hours. The solution was rinsed with water (50 mL). The mixture was extracted with CH\(_2\)Cl\(_2\) (3x, 50 mL). The combined organic extracts were dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure. Purification via column chromatography on silica gel (eluent cyclohexane) gave the brominated product (1.61 g, 4.57 mmol, 83%) as a colorless oil.

\( ^1 \)H-NMR (250 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.20 (s, 1H), 6.35 (s, 1H), 3.34-3.19 (m, 1H), 3.04-2.89 (m, 1H), 2.89-2.76 (m, 1H), 2.31 (s, 3H), 1.75-1.64 (m, 1H), 1.64-1.42 (m, 3H), 1.38-1.25 (m, 12H), 1.14 (s, 3H), 0.91 (t, \( J = 6.5 \) Hz, 3H). \( ^{13} \)C-NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 144.3, 135.6, 129.4, 127.7, 113.6, 109.8, 54.4, 46.9, 45.3, 31.7, 29.6, 29.1, 27.1, 27.0, 25.1, 23.2, 22.8, 20.1, 14.2.
2-(thiophen-2-yl)-1,3-dioxolane

\[
\begin{align*}
\text{S} & \quad \text{O} \\
\end{align*}
\]

2-Thiophenecarboxaldehyde (15.0 g, 133.8 mmol), ethylene glycol (12.45 g, 200.6 mmol) and p-TsOH (35.5 mg, 0.20 mmol) were dissolved in toluene (60 mL) and heated to 160 °C. The solution was refluxed at this temperature for 3 hours. Water was continuously removed by a Dean-Stark apparatus. After 2 hours additional ethylene glycol (2.22 g, 35.8 mmol) was added to the mixture. The solvent was removed under reduced pressure. Subsequent fractional distillation of the crude product under reduced pressure gave the protected aldehyde (19.7 g, 126.1 mmol, 94%) as a colorless liquid.

\(^1\)H-NMR (250 MHz, CDCl\(_3\)): δ (ppm) = 7.33 (d, \(J = 5.0\) Hz, 1H), 7.18 (d, \(J = 3.5\) Hz, 1H), 7.00 (dd, \(J = 5.0\) Hz, 3.5 Hz, 1H), 6.13 (s, 1H), 4.20-3.97 (m, 4H). \(^13\)C-NMR (62.5 MHz, CDCl\(_3\)): δ (ppm) = 141.8, 126.8, 126.5, 126.4, 100.4, 65.4.

2-(5-(1,3-dioxolane-2-yl)thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane

\[
\begin{align*}
\text{S} & \quad \text{O} & \quad \text{B} & \quad \text{S} & \quad \text{O} \\
\end{align*}
\]

2-(thiophen-2-yl)-1,3-dioxolane (5.73 g, 36.7 mmol) was dissolved in THF (dry, 50 mL) and cooled to -78 °C. n-BuLi (2.5 M in hexanes, 14.7 mL, 37.5 mmol) was added slowly. The mixture was stirred for 15 minutes at -78 °C. The cooling bath was removed and the solution was stirred for 1 hour. After cooling again to -78 °C 2-isopropano-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.51 g, 40.35 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 16 hours. The reaction was quenched by addition of saturated sodium bicarbonate solution (100 mL). The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (4x 50 mL). The combined organic extracts were dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure. The product was obtained as a wax like pale yellow solid (5.82 g, 20.6 mmol, 56%). The product was used without further purification.

\(^1\)H-NMR (250 MHz, CDCl\(_3\)): δ (ppm) = 7.51 (d, \(J = 3.5\) Hz, 1H), 7.21 (d, \(J = 3.5\) Hz, 1H), 6.17 (s, 1H), 4.16-3.96 (m, 4H), 1.33 (s, 12H). \(^13\)C-NMR (62.5 MHz, CDCl\(_3\)): δ (ppm) = 149.3, 137.0, 127.3, 100.2, 84.3, 65.3, 24.9.
5-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)thiophene-2-carbaldehyde

A solution of 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (500 mg, 1.42 mmol), Aliquat 336 (1 mL), Na₂CO₃ (2 M, 3.8 mL, 3.80 mmol) and 2-(5-(1,3-dioxolan-2-yl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (400 mg, 1.42 mmol) in THF/Toluene (50:50, 30 mL) was degassed for 90 minutes. A solution of tetrakis(triphenylphosphine)palladium (67.0 mg, 58.0 µmol) in degassed THF (2 mL) was added and the reaction mixture was heated to reflux for 19 hours. The mixture was washed with brine (100 mL). The aqueous phase was extracted with CH₂Cl₂ (2x, 50 mL). The combined organic extracts were dried over Na₂SO₄. The solvent was removed under reduced pressure. Purification via column chromatography on silica gel (eluent cyclohexane/ethyl acetate 10 : 1) gave the product as an orange oil (165.0 mg, 0.39 mmol, 27%).

Deprotection of the aldehyde: A mixture of 6-(5-(1,3-dioxolan-2-yl)thiophen-2-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (106.0 mg, 0.25 mmol) and p-TsOH (40.3 mg, 0.23 mmol) in acetone/water (10 : 1, 11 mL) were heated to reflux for 2 hours. The reaction mixture was washed with NaHCO₃ (sat., 30 mL) and brine (30 mL). The aqueous phase was extracted with CH₂Cl₂ (4x, 20 mL). The combined organic extracts were dried over Na₂SO₄. Removal of the solvent under reduced pressure yielded the deprotected product as an orange oil (94 mg, 0.25, 99%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 9.85 (s, 1H), 7.70 (d, J = 4.0 Hz, 1H), 7.25 (s, 1H), 7.10 (d, J = 4.0 Hz, 1H), 6.38 (s, 1H), 3.41-3.26 (m, 1H), 3.15-3.00 (m, 1H), 2.97-2.82 (m, 1H), 2.44 (s, 3H), 1.97-1.50 (m, 4H), 1.40-1.31 (m, 12H), 1.20 (s, 3H), 0.93 (t, J = 6.6 Hz, 3H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 182.8, 156.3, 145.8, 141.2, 137.2, 134.7, 128.1, 126.0, 125.7, 119.5, 113.4, 54.7, 46.7, 45.3, 31.7, 29.8, 29.1, 27.0, 25.4, 22.8, 22.0, 20.1, 14.2.

1T-DCV:

2-((5-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-thiophene-2-y1)methylene)malononitrile
5-(1-Hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)thiophene-2-carbaldehyde (93.0 mg, 0.24 mmol), CH$_2$(CN)$_2$ (19.4 mg, 0.29 mmol) and four drops of NaOH (0.1 M in water) were dissolved in EtOH (5 mL) and heated to reflux for 2.5 hours. The reaction mixture was washed with brine (20 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (5x, 20 mL). The combined organic extracts were dried over Na$_2$SO$_4$, the solvent was removed under reduced pressure. Purification via column chromatography on silica gel (eluent cyclohexane/ethyl acetate 10 : 1) gave the product as a dark violet solid (79 mg, 0.18 mmol, 76%).

$^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ (ppm) = 7.72 (s, 1H), 7.69 (d, $J$ = 4.2 Hz, 1H), 7.29 (s, 1H). 7.18 (d, $J$ = 4.2 Hz, 1H), 6.39 (s, 1H), 3.43-3.29 (m, 1H), 3.18-3.04 (m, 1H), 2.97-2.82 (m, 1H), 2.48 (s, 3H), 1.80-1.55 (m, 4H), 1.38-1.33 (m, 12H), 1.21 (s, 3H), 0.94 (t, $J$ = 6.5 Hz, 3H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): $\delta$ (ppm) = 159.3, 150.4, 146.5, 139.6, 135.2, 132.9, 128.2, 126.3, 126.0, 118.7, 115.2, 114.2, 113.8, 73.7, 54.9, 46.6, 45.3, 31.7, 29.7, 29.0, 27.0, 26.9, 25.5, 22.8, 22.4, 20.1, 14.2. MS (ESI-TOF): Calculated for C$_{27}$H$_{33}$N$_3$S [M+H]$^+$: 432.2468, found: 432.2453.

**Figure S 1.** $^1$H-NMR spectrum (250 MHz) in CDCl$_3$ of 1T-DCV. [1]
Figure S 2. Mass spectrum of 1T-DCV.\textsuperscript{[1]}

2-([2,2’-bithiophene]-5-yl)-1,3-dioxolane

![Reaction Scheme]

A solution of 2-bromothiophene (867 mg, 5.32 mmol), Aliquat 336 (1.10 mL), Na$_2$CO$_3$ (2 M, 14.1 mL, 28.2 mmol) and 2-(5-(1,3-dioxolane-2-yl)thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.50 g, 5.32 mmol) in THF/toluene (50:50, 60 mL) was degassed for 60 minutes. A solution of tetrakis(triphenylphosphine)palladium (370 mg, 0.32 mmol) in degassed THF (20 mL) was added and the reaction mixture was heated to reflux for 24 hours. The mixture was washed with brine (100 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (100 mL). The combined organic extracts were dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure. Purification via column chromatography on silica gel (eluent cyclohexane/ethyl acetate 10 : 1) gave the product as a yellowish liquid (582 mg, 2.44 mmol, 46%).

$^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ (ppm) = 7.22 (dd, $J = 1.2$ Hz, 5.1 Hz, 1H), 7.16 (dd, $J = 1.2$ Hz, 3.6 Hz, 1H), 7.07 (d, $J = 3.7$ Hz, 1H), 7.05 (d, $J = 3.7$ Hz, 1H), 7.01 (dd, $J = 3.6$ Hz, 5.1 Hz, 1H), 6.08 (s, 1H), 4.18-4.09 (m, 2H), 4.09-4.00 (m, 2H).
2-(5'(1,3-dioxolane-2-yl)-[2,2'-bithiophene]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

2-((2,2'-Bithiophene)-5-yl)-1,3-dioxolane (170 mg, 0.71 mmol) was dissolved in THF (dry, 10 mL) and cooled to -78 °C. n-BuLi (2.5 M in hexane, 0.30 mL, 0.74 mmol) was added slowly. The mixture was stirred for 15 minutes at -78 °C. The cooling bath was removed and the solution was stirred for 75 minutes. After cooling to -78 °C 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (145 mg, 0.91 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 62 hours. The reaction was quenched by addition of a saturated solution of NaHCO₃ (100 mL). The aqueous phase was extracted with CH₂Cl₂ (3x 50 mL). The combined organic extracts were dried over Na₂SO₄. The solvent was removed under reduced pressure. The product was obtained as a dark green solid (257 mg, 0.70 mmol, 99%). The product was used without further purification.

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.51 (d, J = 3.6 Hz, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.11 (d, J = 3.7 Hz, 1H), 7.06 (d, J = 3.7 Hz, 1H), 6.08 (s, 1H), 4.18-4.09 (m, 2H), 4.09-4.00 (m, 2H), 1.35 (s, 12H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 144.0, 141.3, 138.4, 138.1, 127.2, 125.3, 124.0, 100.3, 84.4, 65.4, 24.9.

5'(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-[2,2'-bithiophene]-5-carbaldehyde

A solution of 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (242 mg, 0.69 mmol), Aliquat 336 (0.70 mL), Na₂CO₃ (2 M, 1.8 mL, 3.6 mmol) and 2-(5'(1,3-dioxolane-2-yl)-[2,2'-bithiophene]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (250 mg, 0.69 mmol) in THF/toluene (50:50, 20 mL) was degassed for 60 minutes. A solution of tetakis(triphenylphosphine)palladium (33.0 mg, 28.6 µmol) in degassed THF (10 mL) was added and the reaction mixture was heated to reflux for 16 hours. The mixture was washed with brine (150 mL). The aqueous phase was extracted with CH₂Cl₂ (3x, 50 mL). The combined organic extracts were dried over Na₂SO₄. The solvent was removed under reduced pressure. Purification via column chromatography on silica gel (eluent cyclohexane/ethyl acetate 10 : 1) gave the product as a yellow solid (38.0 mg, 74.5 µmol, 11%).
Deprotection of the aldehyde: A mixture of 6-(5′-(1,3-dioxolane-2-yl)-[2,2′-bithiophene]-5-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (70 mg, 0.14 mmol) and p-TsOH (24 mg, 0.14 mmol) in acetone/water (6 mL/0.5 mL) was heated to reflux for 2 hours. The reaction mixture was washed with Na₂CO₃ (sat., 50 mL) and brine (50 mL). The aqueous phase was extracted with CH₂Cl₂ (2x, 30 mL). Removal of the solvent under reduced pressure gave the product as an orange solid (63.0 mg, 0.14 mmol, 99%).

1H-NMR (250 MHz, CDCl₃): δ (ppm) = 9.85 (s, 1H), 7.66 (d, J = 4.0 Hz, 1H), 7.32 (d, J = 3.8 Hz, 1H), 7.23 (d, J = 4.0 Hz, 1H), 7.20 (s, 1H), 6.93 (d, J = 3.8 Hz, 1H), 6.39 (s, 1H), 3.40-3.27 (m, 1H), 3.13-3.01 (m, 1H), 2.95-2.82 (m, 1H), 2.43 (s, 3H), 1.78-1.51 (m, 4H), 1.39-1.31 (m, 12H), 1.19 (s, 3H). 13C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 182.6, 148.2, 147.5, 145.2, 141.0, 137.7, 134.5, 133.8, 128.0, 126.6, 126.4, 125.5, 123.5, 119.8, 113.3, 54.6, 46.9, 45.3, 31.7, 29.8, 29.2, 27.0, 26.9, 25.3, 22.9, 21.8, 20.2, 14.2.

**2T-DCV:**

5-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)thiophene-2-carbaldehyde (199.5 mg, 42.8 mmol), CH₂(CN)₂ (81.0 mg, 1.23 mmol) and β-alanine (5 mg, 0.06 mmol) were dissolved in a mixture of CH₂Cl₂/EtOH (20/20 mL) and stirred at 50 °C for 19 hours. The reaction mixture was washed with brine (50 mL). The aqueous phase was extracted with Et₂O (3x, 30 mL). The combined organic extracts were dried over MgSO₄, the solvent was removed under reduced pressure. Purification via column chromatography on silica gel (eluent petrol ether/ethyl acetate 10 : 1) gave the product as a dark violet solid (81 mg, 0.16 mmol, 37%)

1H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.73 (s, 1H), 7.61 (d, J = 4.2 Hz, 1H), 7.40 (d, J = 3.9 Hz, 1H), 7.23 (d, J = 4.2 Hz, 1H), 7.22 (s, 1H), 6.99 (d, J = 3.90 Hz, 1H), 6.39 (s, 1H), 3.40-3.28 (m, 1H), 3.15-3.00 (m, 1H), 2.97-2.82 (m, 1H), 2.45 (s, 3H), 1.79-1.50 (m, 4H), 1.42-1.31 (m, 12H), 1.20 (s, 3H), 0.93 (t, J = 6.7 Hz, 3H). 13C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 150.7, 150.2, 149.4, 145.4, 140.6, 134.5, 132.83, 132.81, 127.97, 127.93, 126.6, 125.6, 123.8, 119.5, 114.8, 113.9, 113.4, 74.9, 54.7, 46.8, 45.3, 31.7, 29.8, 29.2, 26.99, 26.95, 25.3, 22.8, 22.0, 20.2, 14.2. MS(ESI-TOF): Calculated for C₃₁H₃₅N₃S₂ [M+H]⁺: 514.2345, found: 514.2334.
Figure S 3. $^1$H-NMR spectrum (250 MHz) in CDCl$_3$ of 2T-DCV.$^{[1]}$

Figure S 4. Mass spectrum of 2T-DCV.$^{[1]}$
2-(3-bromothiophene-2-yl)-1,3-dioxolane

\[
\begin{array}{c}
\text{S} \\
\text{Br} \\
\text{O}
\end{array}
\rightarrow
\begin{array}{c}
\text{S} \\
\text{Br} \\
\text{O}
\end{array}
\]

To a solution of LDA (2 M in THF, 12.3 mL, 24.5 mmol) in THF (dry, 40 mL) 3-bromothiophene (4.00 g, 2.30 mL, 24.5 mmol) was added slowly at 0 °C. The reaction mixture was stirred at 0 °C for one hour. After adding DMF (1.79 g, 1.9 mL, 24.5 mmol) the ice bath was removed and the solution was stirred for 3.5 hours. The reaction was terminated by pouring into water (25 mL). The aqueous phase was extracted with CH₂Cl₂ (50 mL). The organic phase was dried over Na₂SO₄ and the solvent removed under reduced pressure. The resulting crude product (4.7 g, 24.5 mmol, 100%) was used for the following protection.

3-Bromothiophene-2-carbaldehyde (4.44 g, 23.24 mmol), ethylene glycol (2.22 g, 2.00 mL, 35.77 mmol) and p-TsOH (16 mg, 93 µmol) were dissolved in toluene (50 mL) and heated to 160 °C. The solution was refluxed at this temperature for three hours under continuous removal of water. After 50 and the following 40 minutes, additional ethylene glycol was added (1.11 g, 1 mL, 17.90 mmol). The reaction mixture was washed with a saturated solution of NaHCO₃ (40 mL) and water (40 mL). The organic phase was dried over Na₂SO₄ and the solvent removed under reduced pressure. Non-converted educt was separated by vacuum distillation (p = 0.14 mbar, T = 90 °C). The product was isolated as brown liquid (2.01 g, 8.55 mmol, 35%).

\(^1\)H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.31 (d, J = 5.4 Hz, 1H), 6.97 (d, J = 5.4 Hz, 1H), 6.14 (s, 1H), 4.22-3.98 (m, 4H).

\(^13\)C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 136.1, 130.5, 126.6, 110.4, 99.7, 65.6.

2-octylthiophene

\[
\begin{array}{c}
\text{S} \\
\rightarrow
\begin{array}{c}
\text{S} \\
\text{C}_8\text{H}_{17}
\end{array}
\]

To a solution of thiophene (6.00 g, 5.70 mL, 71.32 mmol) in THF (dry, 60 mL), n-BuLi (1.6 M in hexane, 34.30 mL, 54.86 mmol) was added slowly at -78 °C. The cooling bath was removed and the solution stirred for one hour. 1-Bromoctane (10.59 g, 9.50 mL, 54.86 mmol) was added at room temperature and the reaction mixture refluxed for 90 hours. The reaction mixture was washed with brine (60 mL) and the aqueous phase was extracted with Et₂O (2x 50 mL). The combined organic phases were dried over MgSO₄ and the solvent removed under reduced pressure. The product was obtained via fractional vacuum distillation (p = 0.14 mbar) as colorless liquid (8.15 g, 41.5 mmol, 76%).

\(^1\)H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.12 (dd, J = 5.1 Hz, 1.2 Hz, 1H), 6.93 (dd, J = 5.1 Hz, 3.4 Hz, 1H), 6.80 (ddd, J = 5.1 Hz, 3.4 Hz, 1.2 Hz, 1H), 2.84 (t, J = 7.7 Hz, 2H), 1.78-1.64 (m, 2H), 1.43-1.26 (m, 10H), 0.91 (t, J = 6.6 Hz, 3H). \(^13\)C-NMR (62.5 MHz,
CDCl3): δ (ppm) = 146.0, 126.7, 124.0, 122.8, 32.01, 31.97, 30.1, 29.5, 29.4, 29.3, 22.8, 14.3.

4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane

To a solution of 2-octylthiophene (4.00 g, 20.37 mmol) in THF (dry, 40 mL), n-BuLi (2.5 M in hexane, 8.6 mL, 21.39 mmol) was added slowly at -78 °C. The solution was stirred at -78 °C for 25 minutes and slowly heated to room temperature. After cooling the solution to -78 °C 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.17 g, 4.6 mL, 22.41 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 62 hours. The solution was diluted with Et2O (100 mL) and washed with a saturated solution of Na2CO3 (2x 50 mL). The organic phase was dried over Na2SO4 and the solvent removed under reduced pressure. The product was isolated as brown liquid (6.51 g, 20.20 mmol, 99%) and used without further purification.

1H-NMR (250 MHz, CDCl3): δ (ppm) = 7.46 (d, J = 3.4 Hz, 1H), 6.85 (d, J = 3.4 Hz, 1H), 2.85 (t, J = 7.5 Hz, 2H), 1.74-1.61 (m, 2H), 1.36-1.24 (m, 10H), 1.33 (s, 12H), 0.87 (t, J = 6.5 Hz, 3H). 13C-NMR (62.5 MHz, CDCl3): δ (ppm) = 153.8, 137.4, 125.8, 83.9, 31.9, 31.7, 30.2, 29.3, 29.2, 29.1, 24.8, 22.7, 14.1.

2-(5-octyl-[2,3'-bithiophene]-2'-yl)-1,3-dioxolane

A solution of 2-(3-bromothiophene-2-yl)-1,3-dioxolane (1.00 g, 4.25 mmol), Aliquat 336 (0.8 mL), Na2CO3 (1 M, 11.0 mL, 11.0 mmol) and 4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane (1.37 g, 4.25 mmol) in THF/toluene (50:50, 60 mL) was degassed for 60 minutes. A solution of tetrakis(triphenylphosphine)palladium (392.0 mg, 340 µmol) in degassed THF (15 mL) was added and the reaction mixture refluxed for 23 hours. The mixture was washed with brine (50 mL). The organic phase was dried over Na2SO4 and the solvent removed under reduced pressure. Purification via column chromatography (eluent PE/EE 10 : 1) gave the product as yellow oil (837 mg, 2.39 mmol, 56%).

1H-NMR (250 MHz, CDCl3): δ (ppm) = 7.29 (d, J = 5.2 Hz, 1H), 7.12 (d, J = 5.2 Hz, 1H), 7.07 (d, J = 3.5 Hz, 1H), 6.74 (d, J = 3.5 Hz, 1H), 6.18 (s, 1H), 4.27-3.98 (m, 4H), 2.80 (t, 7.6 Hz, 2H), 1.75-1.63 (m, 2H), 1.42-1.22 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H). 13C-
NMR (62.5 MHz, CDCl₃): δ (ppm) = 146.4, 135.1, 134.59, 134.56, 129.0, 126.3, 125.4, 124.7, 99.5, 65.6, 32.0, 30.3, 29.5, 29.4, 29.3, 22.8, 14.3.

2-(2'(1,3-dioxolane-2-yl)-5-octyl-[2,3'-bithiophene]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

To a solution of 2-(5-octyl-[2,3'-bithiophene]-2'-yl)-1,3-dioxolane (820 mg, 2.34 mmol) in THF (dry, 20 mL) n-BuLi (2.5 M in hexane, 0.98 mL, 2.46 mmol) was added slowly at -78 °C. The solution was stirred for 15 minutes at -78 °C and subsequently heated to room temperature over a period of 30 minutes. After cooling the solution to -78 °C 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (479 mg, 0.53 mL, 0.91 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 63 hours. The solution was washed with a saturated solution of Na₂CO₃ (40 mL). The organic phase was dried over Na₂SO₄ and the solvent removed under reduced pressure. The product was isolated as brown oil (1.08 g, 2.27 mmol, 97%) and used without further purification.

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.64 (s, 1H), 7.08 (d, J = 3.6 Hz, 1H), 6.72 (d, J = 3.6 Hz, 1H), 6.23 (s, 1H), 4.24-3.98 (m, 4H), 2.80 (t, J = 7.6 Hz, 2H), 1.74-1.62 (m, 2H), 1.38-1.23 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 146.4, 142.5, 138.7, 135.5, 134.5, 126.3, 124.7, 99.5, 84.4, 68.1, 65.6, 32.0, 31.8, 30.2, 29.49, 29.38, 29.28, 25.8, 25.0, 24.9, 22.9, 14.3.

(2'(1,3-dioxolane-2-yl)-5-octyl-[2,3'-bithiophene]-5'-yl)-tributylstannane

To a solution of 2-(5-octyl-[2,3'-bithiophene]-2'-yl)-1,3-dioxolane (830 mg, 2.37 mmol) in THF (dry, 25 mL) n-BuLi (1.6 M in hexane, 1.55 mL, 2.48 mmol) was added slowly at -78 °C. The solution was stirred for 15 minutes at -78 °C and heated to room temperature over a period of one hour. After cooling the solution to -78 °C tributyltin chloride (848 mg, 0.71 mL, 2.61 mmol) was added slowly. The cooling bath was removed and the reaction mixture was washed with a saturated solution of Na₂CO₃ (40 mL). The organic phase was dried over Na₂SO₄ and the solvent removed under
reduced pressure. The product was isolated as brown oil (1.64 g, 2.27 mmol, 97%) and was used without further purification.

$^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ (ppm) = 7.11 (s, 1H), 7.05 (d, $J = 3.6$ Hz, 1H), 6.73 (d, $J = 3.6$ Hz, 1H), 6.16 (s, 1H), 4.25-4.01 (m, 4H), 2.81 (t, $J = 7.6$ Hz, 2H), 1.74-1.52 (m, 8H), 1.40-1.25 (m, 16H), 1.13-1.07 (m, 6H), 0.94-0.87 (m, 12H).

$5'$-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-5-octyl-[2,3'-bithiophene]-2'-carbaldehyde

Pd(PPh$_3$)$_4$ (80 mg, 69 $\mu$mol) was added to a solution of (2'-((1,3-dioxolane-2-yl)-5-octyl-[2,3'-bithiophene]-5'-yl)tributylstannane (800 mg, 1.25 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (292 mg, 0.83 mmol) in degassed toluene (40 mL). The solution was refluxed for 16 hours. After cooling down the reaction mixture was washed with brine (80 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (1x 40 mL). The combined organic phases were dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. Purification via column chromatography (eluent cyclohexane/EE 20 : 1) gave a product mixture as yellow liquid (470 mg). The mixture contained the protected coupling product as well as 2-(5-octyl-[2,3'-bithiophene]-2'-yl)-1,3-dioxolane in a ratio of 50 : 50. The product mixture was used without further purification.

To deprotect the aldehyde the isolated product mixture (470 mg) was dissolved in $p$-TsOH (130 mg, 760 $\mu$mol) and water (1 mL) in acetone (20 mL) and refluxed for 100 minutes. The mixture was washed with a saturated NaHCO$_3$ solution (20 mL) and brine (20 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ until no color was left. The combined organic phases were dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. Multiple purification steps via column chromatography (eluent cyclohexane/EE 20 : 1) and reverse phase silica gel (C18, eluent THF/water 3 : 1) gave the product as yellow solid (92 mg, 159 $\mu$mol, 21%).

$^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ (ppm) = 10.09 (s, 1H), 7.27 (s, 1H), 7.12 (d, $J = 3.5$ Hz, 1H), 7.11 (s, 1H), 6.81 (d, $J = 3.5$ Hz, 1H), 6.38 (s, 1H), 3.42-3.26 (m, 1H), 3.16-3.00 (m, 1H), 2.96-2.83 (m, 1H), 2.85 (t, $J = 7.7$ Hz, 2H), 2.47 (s, 3H), 1.79-1.52 (m, 6H), 1.39-1.26 (m, 22H), 1.20 (s, 3H), 0.95-0.86 (m, 6H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): $\delta$ (ppm) = 183.5, 154.7, 148.8, 145.9, 143.8, 135.0, 134.8, 133.4, 128.4, 127.7, 125.7, 125.1, 119.2, 113.5, 54.7, 46.7, 45.3, 32.0, 31.8, 31.7, 30.4, 29.8, 29.5, 29.4, 29.3, 29.1, 26.99, 26.94, 25.4, 22.84, 22.81, 22.1, 20.1, 14.3, 14.2.
1Tβ-DCV:

2-((5’-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-5-octyl-[2,3’-bithiophene]-2’-yl)methylene)malononitrile

5’-(1-Hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-5-octyl-[2,3’-bithiophene]-2’-carbaldehyde (150 mg, 260 µmol), CH₂(CN)₂ (21 mg, 324 µmol) and six droplets of a solution of NaOH (0.1 M in water) were dissolved in EtOH (dry, 30 mL) and refluxed for 2.5 hours. The reaction mixture was washed with brine (40 mL) and the aqueous phase was extracted with CH₂Cl₂ (30 mL). The organic phase was dried over Na₂SO₄ and the solvent removed under reduced pressure. Multiple purification steps via column chromatography (eluent cyclohexane/EE 30 : 1), reverse phase silica gel (C₁₈, eluent THF/water 3 : 1) and size exclusion chromatography gave the product as violet solid (16 mg, 25.6 µmol, 10%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.99 (s, 1H), 7.30 (s, 1H), 7.16 (s, 1H), 6.97 (d, J = 3.6 Hz, 1H), 6.86 (d, J = 3.6 Hz, 1H), 6.38 (s, 1H), 3.42-3.28 (m, 1H), 3.18-3.03 (m, 1H), 2.96-2.84 (m, 1H), 2.86 (t, J = 7.7 Hz, 2H), 2.50 (s, 3H), 1.80-1.52 (m, 6H), 1.41-1.26 (m, 22H), 1.20 (s, 3H), 0.97-0.86 (m, 6H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 156.9, 150.1, 149.7, 147.1, 146.6, 135.3, 133.0, 129.4, 128.2, 127.6, 127.2, 126.0, 125.6, 118.5, 115.8, 114.4, 113.8, 73.1, 55.0, 46.6, 45.3, 32.0, 31.8, 31.7, 30.4, 29.7, 29.44, 29.36, 29.31, 29.1, 26.98, 26.89, 25.5, 22.84, 22.81, 22.5, 10.2, 14.3, 14.2. MS(ESI-TOF): Calculated for C₃₉H₅₁N₃S₂ [M+Na]⁺: 648.3417, found: 648.3397.
Figure S 5. $^1$H-NMR spectrum (250 MHz) in CDCl$_3$ of 1Tβ-DCV. [1]

Figure S 6. Mass spectrum of 1Tβ-DCV. [1]
2-(3'-bromo-[2,2'-bithiophene]-5-y1)-1,3-dioxolane

A solution of 2,3-dibromothiophene (2.0 g, 8.27 mmol), 2-(5-(1,3-dioxolane-2-yl)thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.57 g, 9.09 mmol) and Na2CO3 (2 M, 16.5 mL, 33 mmol) in 1,4-dioxane (100 mL) was degassed for 90 minutes. Pd(PPh3)4 (763 mg, 0.66 mmol) was suspended in degassed 1,4-dioxane (35 mL) and added to the reaction mixture. The reaction mixture was stirred at 100 °C for four hours. After cooling down the solution was diluted with water (100 mL) and washed with brine (100 mL). The aqueous phase was extracted with Et2O (5x 80 mL). The combined organic phases were dried over Na2SO4 and the solvent removed under reduced pressure. Purification via column chromatography (eluent cyclohexane to cyclohexane/EE 30 : 1) and filtration gave the product as orange liquid (1.27 g, 4.0 mmol, 48%).

1H-NMR (250 MHz, CDCl3): δ (ppm) = 7.30 (d, J = 3.8 Hz, 1H), 7.19 (d, J = 5.4 Hz, 1H), 7.12 (d, J = 3.8 Hz, 1H), 7.01 (d, J = 5.4 Hz, 1H), 6.11 (s, 1H), 4.20-4.00 (m, 4H).

2-(5"-octyl-[2,2':3',2"-terthiophene]-5-y1)-1,3-dioxolane

A solution of 2-(3'-bromo-[2,2'-bithiophene]-5-y1)-1,3-dioxolane (599 mg, 1.89 mmol), Aliquat 336 (0.5 mL), Na2CO3 (2 M, 4.2 mL, 8.40 mmol) and 4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane (600 mg, 1.86 mmol) in THF/toluene (50 : 50, 60 mL) was degassed for 60 minutes. A solution of tetrakis(triphenylphosphine)palladium (135 mg, 117 µmol) in degassed THF (10 mL) was added and the reaction mixture refluxed for 18 hours. The mixture was washed with brine (80 mL). The organic phase was dried over Na2SO4 and the solvent removed under reduced pressure. Purification via column chromatography (eluent cyclohexane/EE 10 : 1) gave the product as yellow solid (491 mg, 1.13 mmol, 61%).

1H-NMR (250 MHz, CDCl3): δ (ppm) = 7.25 (d, J = 5.3 Hz, 1H), 7.12 (d, J = 5.3 Hz, 1H), 7.06 (d, J = 3.7 Hz, 1H), 7.00 (d, J = 3.7 Hz, 1H), 6.85 (d, J = 3.5 Hz, 1H), 6.64 (d, J = 3.5 Hz, 1H), 6.08 (s, 1H), 4.16-3.98 (m, 4H), 2.76 (t, J = 7.7 Hz, 2H), 1.72-1.58 (m,
2H), 1.41-1.23 (m, 10H), 0.93-0.84 (m, 3H). \(^{13}\)C-NMR (62.5 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 182.9, 147.6, 145.9, 143.3, 136.5, 134.3, 133.6, 131.2, 130.5, 127.9, 127.2, 126.0, 124.6, 63.9, 32.0, 31.7, 30.3, 29.5, 29.4, 29.3, 22.8, 14.3.

**5'-(1,3-dioxolane-2-yl)-5''-octyl-[2,2':3',2''-terthiophene]-5'-yl)tri-butylstannane**

![Chemical structure]

To a solution of 2-(5''-octyl-[2,2':3',2''-terthiophene]-5'-yl)-1,3-dioxolane (480 mg, 1.11 mmol) in THF (dry, 20 mL), LDA (1 M in THF, 1.11 mL, 1.11 mmol) was added slowly at -78 °C. The solution was stirred for 60 minutes at -78 °C and tributyltin chloride (379 mg, 0.32 mL, 1.17 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 18 hours. The solution was diluted with water (40 mL) and CH\(_2\)Cl\(_2\) (40 mL). The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (1x 40 mL). The combined organic phases were washed with a saturated solution of Na\(_2\)CO\(_3\) (40 mL), dried over Na\(_2\)SO\(_4\) and the solvent removed under reduced pressure. The product was isolated as yellow liquid (861 mg, 85% product, determined from \(^1\)H-NMR). The product also contained educt and tin organyl resulting in a yield of over 100 %. The product was used without further purification.

\(^1\)H-NMR (250 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.12 (s, 1H), 7.04 (d, \(J = 3.7\) Hz, 1H), 6.97 (d, \(J = 3.7\) Hz, 1H), 6.86 (d, \(J = 3.5\) Hz, 1H), 6.65 (d, \(J = 3.5\) Hz, 1H), 6.07 (s, 1H), 4.16-3.97 (m, 4H), 2.77 (t, \(J = 7.7\) Hz, 2H), 1.75-1.53 (m, 8H), 1.43-1.26 (m, 16H), 1.17-1.07 (m, 6H), 0.95-0.86 (m, 12H).

**5''-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-5''-octyl-[2,2':3',2''-terthiophene]-5'-carbaldehyde**

![Chemical structure]

Pd(PPh\(_3\))\(_4\) (71.5 mg, 61 \(\mu\)mol) was added to a solution of (5-(1,3-dioxolane-2-yl)-5''-octyl-[2,2':3',2''-terthiophene]-5'-yl)tributylstannane (715 mg, 0.99 mmol) and 6-bromo-
1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (275 mg, 0.78 mmol) in degassed toluene (25 mL). The solution was refluxed for 42 hours. After cooling down the reaction mixture was washed with brine (40 mL). The aqueous phase was extracted with CH₂Cl₂ (5x 30 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via column chromatography (eluent cyclohexane/EE 10 : 1) gave the product as yellow oil (172 mg, 0.24 mmol, 32%).

To deprotect the aldehyde the isolated product (166 mg, 236 µmol) was dissolved in p-TsOH (41.5 mg, 236 µmol) and water (0.5 mL) in acetone (10 mL) and refluxed for 3.5 hours. The mixture was washed with saturated NaHCO₃ solution (20 mL) and brine (20 mL). The aqueous phase was extracted with CH₂Cl₂ until no color was left. The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via column chromatography (eluent cyclohexane/EE 20 : 1) gave the product as orange oil (138 mg, 209 µmol, 89%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 9.82 (s, 1H), 7.61 (d, J = 4.0 Hz, 1H), 7.21 (s, 1H), 7.19 (d, J = 4.0 Hz, 1H), 6.98 (s, 1H), 6.92 (d, J = 3.5 Hz, 1H), 6.72 (d, J = 3.5 Hz, 1H), 6.38 (s, 1H), 3.40-3.26 (m, 1H), 3.14-3.00 (m, 1H), 2.96-2.80 (m, 1H), 2.81 (t, J = 7.7 Hz, 2H), 2.45 (s, 3H), 1.79-1.50 (m, 6H), 1.42-1.24 (m, 22), 1.19 (s, 3H), 0.97-0.85 (m, 6H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 182.8, 147.5, 146.7, 145.6, 145.3, 142.4, 136.7, 134.5, 134.2, 134.1, 129.6, 128.0, 127.3, 126.9, 125.5, 124.6, 119.4, 113.3, 54.6, 45.9, 32.0, 31.8, 31.8, 31.1, 30.4, 29.8, 29.5, 29.4, 29.3, 29.2, 27.0, 25.3, 22.87, 22.83, 21.9, 20.2, 14.28, 14.20.

2Tβ-DCV:

2-((5'-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-5''-octyl-[2,2':3',2''-terthiophene-5-yl)methylene]malononitrile

5'-1-Hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-5''-octyl-[2,2':3',2''-terthiophene]-5-carbaldehyde (131 mg, 198 µmol), CH₂(CN)₂ (18 mg, 272 µmol) and five droplets of a solution of NaOH (0.1 M in water) were dissolved in EtOH (dry, 25 mL) and refluxed for 2.5 hours. The reaction mixture was washed with brine (40 mL) and the aqueous phase was extracted with CH₂Cl₂ until no color was left. The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via column chromatography (eluent cyclohexane/EE 20 : 1) gave the product as violet solid (50 mg, 70.6 µmol, 36%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.63 (s, 1H), 7.62 (d, J = 4.2 Hz, 1H), 7.23 (s, 1H), 7.20 (d, J = 4.2 Hz, 1H), 7.00 (s, 1H), 6.95 (d, J = 3.5 Hz, 1H), 6.77 (d, J = 3.5 Hz, 1H), 6.39 (s, 1H), 3.42-3.26 (m, 1H), 3.16-3.00 (m, 1H), 2.96-2.82 (m, 1H), 2.84 (t, J =
7.7 Hz, 2H), 2.46 (s, 3H), 1.79-1.50 (m, 6H), 1.42-1.24 (m, 22H), 1.20 (s, 3H), 0.96-0.85 (m, 6H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 149.9, 149.3, 148.3, 147.0, 145.4, 138.6, 135.5, 134.5, 133.9, 133.4, 129.6, 128.7, 127.89, 127.87, 126.9, 125.7, 124.7, 119.1, 114.8, 113.8, 113.4, 75.3, 54.7, 46.8, 45.3, 32.0, 31.76, 31.72, 30.4, 29.8, 29.47, 29.39, 29.33, 29.18, 26.99, 26.96, 25.3, 22.84, 22.81, 22.0, 20.2, 14.27, 14.19. MS (ESI-TOF): Calculated for C$_{43}$H$_{53}$N$_3$S$_3$ [M+H]$^+$: 708.3474, found: 708.3452.

Figure S 7. $^1$H-NMR spectrum (250 MHz) in CDCl$_3$ of 2Tβ-DCV.$^1$

Figure S 8. Mass spectrum of 2Tβ-DCV.$^1$
1-hexyl-2,2,4,7-tetramethyl-6-(thiophene-2-yl)-1,2,3,4-tetrahydro-quinoline

Pd(PPh₃)₄ (170 mg, 147 μmol) was added to a solution of trimethyl(5''-octyl-5'-(tributylstannyl)-[2,2':3',2''-terthiophene]-5-yl)silane (1.59 g, 1.35 mL, 4.26 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (1.0 g, 2.84 mmol) in degassed toluene (50 mL). The solution was refluxed for 16 hours. After cooling down the reaction mixture was washed with brine (40 mL). The aqueous phase was extracted with CHCl₃ (3x 40 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Multiple purification steps via column chromatography (eluent cyclohexane/EE 10:1 and cyclohexane) gave a product mixture as yellow liquid which contained 50 % (determined from ¹H-NMR) of contamination in form of tin organyl (product: ~500 mg, 1.40 mmol, 50%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.23 (dd, J = 1.2 Hz, 5.2 Hz, 1H), 7.17 (s, 1H), 7.05 (dd, J = 3.5 Hz, 5.2 Hz, 1H), 6.96 (dd, J = 1.2 Hz, 3.5 Hz, 1H), 6.38 (s, 1H), 3.40-3.25 (m, 1H), 3.13-2.98 (m, 1H), 2.97-2.81 (m, 1H), 2.37 (s, 3H), 1.77-1.52 (m, 4H), 1.41-1.29 (m, 12H), 1.18 (s, 3H), 0.93 (m, 3H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 144.8, 144.7, 134.5, 128.4, 127.0, 125.3, 125.2, 123.8, 120.8, 113.0, 54.4, 47.0, 45.3, 31.7, 29.9, 29.3, 27.0, 25.1, 22.9, 21.6, 20.2, 14.2.

1T-TCV:

2-(5-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-thiophene-2-yl)ethene-1,1,2-tricarbonitrile

To a solution of 1-hexyl-2,2,4,7-tetramethyl-6-(thiophene-2-yl)-1,2,3,4-tetrahydroquinoline (100 mg, 0.28 mmol) in DMF (dry, 5 mL) tetracyanoethylene (149 mg, 1.16 mmol) was added. The solution was stirred at room temperature for 90 minutes. The reaction was terminated by pouring into brine (40 mL). The aqueous phase was extracted with CHCl₃ (3x 20 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via column chromatography gave the product as green solid (101 mg, 0.22 mmol, 79%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 8.00 (d, J = 4.5 Hz, 1H), 7.38 (s, 1H), 7.32 (d, J = 4.5 Hz, 1H), 6.39 (s, 1H), 3.45-3.30 (m, 1H), 3.23-3.07 (m, 1H), 2.97-2.82 (m, 1H), 2.07-1.87 (m, 4H), 1.41-1.29 (m, 12H), 1.18 (s, 3H), 0.93 (m, 3H).
2.53 (s, 3H), 1.83-1.74 (m, 1H), 1.64-1.50 (m, 3H) 1.43-1.32 (m, 12H), 1.23 (s, 3H), 0.93 (t, J = 6.7 Hz, 3H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 162.8, 147.7, 140.9, 136.6, 131.6, 130.7, 128.4, 126.7, 126.6, 118.3, 114.4, 113.6, 113.4, 113.3, 55.5, 46.3, 45.4, 31.6, 29.7, 29.0, 27.0, 26.8, 25.7, 23.2, 22.8, 20.0, 14.2. MS(ESI-TOF): Calculated for C$_{28}$H$_{32}$N$_4$S [M+Na]$^+$: 479.2240, found: 479.2231.

**Figure S 9.** $^1$H-NMR spectrum (250 MHz) in CDCl$_3$ of 1T-TCV. [1]

**Figure S 10.** Mass spectrum of 1T-TCV. [1]
2,2'-bithiophene

Magnesium (2.40 g, 98.7 mmol) and 2-bromothiophene (14.6 g, 8.7 mL, 89.5 mmol) were transferred to the corresponding Grignard reagent in Et₂O (dry, 30 mL). Therefore, the reaction was stirred for 15 hours at room temperature. The Grignard solution was added slowly to a suspension of Ni(dppe)Cl₂ (950 mg, 1.8 mmol) and 2-bromothiophene (14.6 g, 8.7 mL, 89.5 mmol) in Et₂O (dry, 30 mL). The reaction mixture was refluxed for 16 hours and terminated by pouring into water (200 mL). The solution was washed with brine (100 mL) and the aqueous phase extracted with CHCl₃ (4x 50 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via vacuum distillation (p = 0.18 mbar) gave the product as green liquid (8.88 g, 53.4 mmol, 60%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.22 (dd, J = 1.2 Hz, 5.1 Hz, 2H), 7.18 (dd, J = 1.2 Hz, 3.7 Hz, 2H), 7.02 (dd, J = 3.7 Hz, 5.1 Hz, 2H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 137.5, 127.9, 124.5, 123.9.

[2,2'-bithiophene]-5-yltributylstannane

To a solution of 2,2'-bithiophene (2.00 g, 12.03 mmol) in THF (dry, 50 mL) n-BuLi (2.5 M in hexane, 5.30 mL, 13.23 mmol) was added slowly at -78 °C. The solution was stirred for 40 minutes at -78 °C and tributyltin chloride (4.31 g, 3.60 mL, 13.23 mmol) was added slowly. After stirring the mixture for 40 minutes at -78 °C, the cooling bath was removed and the reaction mixture was stirred at room temperature for 17 hours. The solution was diluted with a saturated solution of NH₄Cl (30 mL). The aqueous phase was extracted with CH₂Cl₂ (2x 50 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. The product was isolated as orange liquid (6.06 g, 80%, determined from ¹H-NMR). The product also contained ~10% side product and tin organyl resulting in a yield of over 100%. The product was used without further purification.

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.29 (d, J = 3.4 Hz, 1H), 7.21-7.16 (m, 2H), 7.06 (d, J = 3.4 Hz, 1H), 7.00 (dd, J = 3.8 Hz, 5.0 Hz, 1H), 1.68-1.51 (m, 6H), 1.42-1.29 (m, 6H), 1.16-1.07 (m, 6H), 0.95-0.87 (m, 9H).
6-([2,2'-bithiophene]-5-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline

\[
\begin{array}{c}
\text{N} \\
\text{C}_{6} \text{H}_{13} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{SnBu}_{3}
\end{array}
\begin{array}{c}
\text{N} \\
\text{C}_{6} \text{H}_{13}
\end{array}
\]

Pd(PPh\(_{3}\))\(_{4}\) (175 mg, 151 µmol) was added to a solution of [2,2'-bithiophene]-5-yl-tributylstannane (1.90 g, 4.17 mmol) und 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (0.98 g, 2.78 mmol) in degassed toluene (50 mL). The solution was refluxed for 16 hours. After cooling down the reaction mixture was washed with brine (40 mL). The aqueous phase was extracted with CHCl\(_{3}\) (5x 50 mL). The combined organic phases were dried over Na\(_{2}\)SO\(_{4}\) and the solvent removed under reduced pressure. Multiple purification steps via column chromatography (eluent cyclohexane/EE 20 : 1) gave the product as yellow liquid (705 mg, 1.61 mmol, 58%).

\(^1\)H-NMR (250 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) = 7.22-7.14 (m, 3H), 7.12 (d, \(J = 3.7\) Hz, 1H), 7.01 (dd, \(J = 3.7\) Hz, 5.0 Hz, 1H), 6.87 (d, \(J = 3.7\) Hz, 1H), 6.39 (s, 1H), 3.41-3.25 (m, 1H), 3.14-2.99 (m, 1H), 2.98-2.82 (m, 1H), 2.42 (s, 3H), 1.79-1.52 (m, 4H), 1.40-1.30 (m, 12H), 1.19 (s, 3H), 0.93 (t, \(J = 6.7\) Hz, 3H).

2T-TCV:

2-([5'-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl]-[2,2'-bithiophene]-5-yl)ethene-1,1,2-tricarbonitrile

\[
\begin{array}{c}
\text{N} \\
\text{C}_{6} \text{H}_{13} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{NC} \\
\text{CN}
\end{array}
\begin{array}{c}
\text{N} \\
\text{C}_{6} \text{H}_{13}
\end{array}
\]

To a solution of 6-([2,2'-bithiophene]-5-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (140 mg, 320 µmol) in THF (dry, 15 mL) n-BuLi (2.5 M in hexane, 130 µL, 336 µmol) was added slowly at -15 °C. The cooling bath was removed and the solution was stirred at room temperature for 90 minutes. After cooling the solution to -15 °C, tetracyanoethylene (120 mg, 937 µmol) was added in two steps (50 mg at the beginning followed by 70 mg after 40 minutes) and the solution was stirred for 17 hours at room temperature. The reaction was terminated by diluting with brine (30 mL). The aqueous phase was extracted with CHCl\(_{3}\) (3x 50 mL). The combined organic phases were dried over Na\(_{2}\)SO\(_{4}\) and the solvent removed under reduced pressure. Purification via column chromatography (eluent PE/EE 20 : 1) gave the product as black green solid (59 mg, 161 µmol, 34%).

\(^1\)H-NMR (250 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) = 7.97 (d, \(J = 4.4\) Hz, 1H), 7.50 (d, \(J = 4.0\) Hz, 1H), 7.33 (d, \(J = 4.4\) Hz, 1H), 7.25 (s, 1H), 7.07 (d, \(J = 4.0\) Hz, 1H), 6.39 (s, 1H), 3.43-3.27 (m, 1H), 3.17-3.02 (m, 1H), 2.97-2.82 (m, 1H), 2.47 (s, 3H), 1.82-1.51 (m, 4H),
1.44-1.31 (m, 12H), 1.21 (s, 3H), 0.93 (t, \( J = 6.7 \) Hz, 3H). \(^{13}\)C-NMR (62.5 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 153.7, 152.3, 145.8, 141.9, 134.7, 131.9, 131.6, 131.1, 129.9, 127.9, 127.0, 125.9, 124.7, 119.2, 113.6, 113.11, 113.07, 112.8, 79.1, 54.8, 46.7, 45.3, 31.7, 29.8, 29.1, 26.99, 26.94, 25.4, 22.8, 22.3, 20.1, 14.2. MS(ESI-TOF): Calculated for C\(_{32}\)H\(_{34}\)N\(_4\)S\(_2\) \([\text{M+H}]^+\): 561.2117, found: 561.2101.

**Figure S 11.** \(^1\)H-NMR spectrum (250 MHz) in CDCl\(_3\) of 2T-TCV. \(^{[1]}\)

**Figure S 12.** Mass spectrum of 2T-TCV. \(^{[1]}\)
**2,2':5',2''-terthiophene**

![Diagram](image)

Magnesium (3.62 g, 148.91 mmol) and 2-bromothiophene (13.04 g, 7.75 mL, 89.5 mmol) were transferred to the corresponding Grignard reagent in Et₂O (dry, 30 mL). Therefore, the reaction was stirred for two hours at room temperature. The Grignard solution was added slowly to a suspension of Ni(dppe)Cl₂ (850 mg, 1.61 mmol) and 2,5-dibromothiophene (9.68 g, 4.50 mL, 40.0 mmol) in Et₂O (dry, 45 mL). The reaction mixture was refluxed for 16 hours and terminated by pouring into a mixture of ice and 4N HCl. The aqueous phase was extracted with CH₂Cl₂ (800 mL in total). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via recrystallization from MeOH gave the product as copper red solid (6.40 g, 25.77 mmol, 64%).

**1H-NMR** (250 MHz, CDCl₃): δ (ppm) = 7.23 (dd, J = 1.2 Hz, 5.1 Hz, 2H), 7.18 (dd, J = 1.2 Hz, 3.7 Hz, 2H), 7.09 (s, 2H), 7.03 (dd, J = 3.7 Hz, 5.1 Hz, 2H).

**13C-NMR** (62.5 MHz, CDCl₃): δ (ppm) = 137.2, 136.3, 128.0, 124.6, 124.4, 123.8.

**[2,2':5',2''-terthiophene]-5-yl-trimethylsilane**

![Diagram](image)

To a solution of 2,2':5',2''-terthiophene (6.00 g, 12.03 mmol) in THF (dry, 140 mL) n-BuLi (2.5 M in hexane, 10.20 mL, 25.50 mmol) was added slowly at -78°C. The cooling bath was removed and the solution stirred for 75 minutes at room temperature. After cooling to -78°C chlorotrimethylsilane (2.89 g, 3.38 mL, 26.57 mmol) was added slowly. The cooling bath was removed and the solution stirred for 22 hours at room temperature. The reaction was terminated by adding water (40 mL) and washed with brine (40 mL). The aqueous phase was extracted with CH₂Cl₂ (50 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via multiple recrystallization steps from MeOH gave the product as yellow solid (1.20 g, 3.74 mmol, 16%).

**1H-NMR** (250 MHz, CDCl₃): δ (ppm) = 7.24-7.20 (m, 2H), 7.17 (dd, J = 1.2 Hz, 3.7 Hz, 1H), 7.14 (d, J = 3.5 Hz, 1H), 7.10-7.07 (m, 2H), 7.02 (dd, J = 3.7 Hz, 5.2 Hz, 1H), 0.34 (s, 9H).
To a solution of [2,2':5',2''-terthiophene]-5-yltrimethylsilane (0.90 g, 2.81 mmol) in THF (dry, 30 mL) n-BuLi (1.6 M in hexane, 1.95 mL, 3.12 mmol) was added slowly at -78 °C. The solution was stirred for 30 minutes at -78 °C and tributyltin chloride (1.01 g, 0.84 mL, 3.09 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature overnight. The reaction was terminated by adding a saturated solution of NH₄Cl (30 mL). The aqueous phase was extracted with Et₂O (3x 20 mL). The combined organic phases were dried over MgSO₄ and the solvent removed under reduced pressure. The product was isolated as colorless oil (1.40 g, 80%, determined from ¹H-NMR). The product further contained ~20% educt and tin organyl. The product was used without further purification.

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.30 (d, J = 3.4 Hz, 1H), 7.23 (d, J = 3.5 Hz, 1H), 7.15 (d, J = 3.5 Hz, 1H), 7.11-7.07 (m, 3H), 1.70-1.53 (m, 6H), 1.44-1.28 (m, 6H), 1.19-1.08 (m, 6H), 0.96-0.88 (m, 9H), 0.34 (s, 9H).

6-([2,2':5',2''-terthiophene]-5-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline

Pd(PPh₃)₄ (108 mg, 941 µmol) was added to a solution of trimethyl(5''-(tributylstannyl)-[2,2':5',2''-terthiophene]-5-yl)silane (1.71 g, 2.81 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (659 mg, 1.87 mmol) in degassed toluene (50 mL). The solution was refluxed overnight. After cooling down the reaction mixture was washed with brine (3x 15 mL). The aqueous phase was extracted with CH₂Cl₂ (3x 30 mL). The combined organic phases were dried over MgSO₄ and the solvent removed under reduced pressure. Purification via column chromatography (eluent PE/EE 15 : 1) and size exclusion chromatography (eluent CHCl₃) gave the product as yellow solid (0.84 g, 1.47 mmol, 76%). The obtained product still contained the TMS protection group and was used for the following deprotection step.

A solution of 1-hexyl-2,2,4,7-tetramethyl-6-(5''-trimethylsilyl)-[2,2':5',2''-terthiophene]-5-yl)-1,2,3,4-tetrahydroquinoline (333 mg, 560 µmol) and TBAF (1 M in THF, 840 µL, 840 µmol) in THF (dry, 40 mL) was stirred for one hour at room temperature. The reaction mixture was poured into water (50 mL) and the aqueous phase extracted...
with CH$_2$Cl$_2$ (3x 40 mL). The combined organic phases were washed with an aqueous solution of NaOH (0.1 M, 20 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure and the product was obtained as orange solid (241 mg, 464 μmol, 83%).

$^1$H-NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.23-7.15 (m, 3H), 7.12 (d, J = 3.7 Hz, 1H), 7.09-7.00 (m, 3H), 6.88 (d, J = 3.7 Hz, 1H), 6.39 (s, 1H), 3.41-3.25 (m, 1H), 3.14-2.99 (m, 1H), 2.96-2.83 (m, 1H), 2.43 (s, 3H), 1.78-1.51 (m, 4H), 1.40-1.30 (m, 12H), 1.19 (s, 3H), 0.96-0.89 (m, 3H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 144.8, 144.4, 137.0, 135.6, 135.1, 134.5, 128.1, 128.0, 127.8, 126.0, 125.4, 124.5, 124.4, 123.9, 123.7, 123.6, 120.4, 113.2, 54.5, 47.0, 45.3, 31.8, 29.9, 29.3, 27.0, 25.2, 22.9, 21.8, 20.2, 14.2.

3T-TCV:

2-(5''-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-[2,2':5',2''-terthiophene]-5-yl)ethene-1,1,2-tricarbonitrile

![Chemical structure](attachment:image.png)

To a solution of 6-([2,2':5',2''-terthiophene]-5-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (100 mg, 180 μmol) in THF (dry, 15 mL) n-BuLi (1.6 M in hexane, 130 μL, 202 μmol) was added slowly at -15 °C. The solution was stirred at room temperature for 60 minutes. After cooling the solution to -15 °C, tetracyanoethylene (100 mg, 781 μmol) was added and the solution was stirred for 17 hours at room temperature. The reaction was terminated by diluting with a saturated solution of NaHCO$_3$ (25 mL). The aqueous phase was extracted with CHCl$_3$ (2x 30 mL). The combined organic phases were dried over MgSO$_4$ and the solvent removed under reduced pressure. Multiple purification steps via column chromatography (eluents PE/EE 10:1, 5:1 and CHCl$_3$) followed by size exclusion chromatography (eluents CHCl$_3$) gave the product as black green solid (21 mg, 34 μmol, 18%).

$^1$H-NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.98 (d, J = 4.4 Hz, 1H), 7.46 (d, J = 4.0 Hz, 1H), 7.33 (d, J = 4.4 Hz, 1H), 7.25 (d, J = 3.8 Hz, 1H), 7.21 (s, 1H), 7.19 (d, J = 4.0 Hz, 1H), 6.95 (d, J = 3.8 Hz, 1H), 6.39 (s, 1H), 3.41-3.27 (m, 1H), 3.15-3.00 (m, 1H), 2.96-2.82 (m, 1H), 2.44 (s, 3H), 1.79-1.51 (m, 4H), 1.40-1.31 (m, 12H), 1.20 (s, 3H), 0.93 (t, J = 6.7 Hz, 3H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 152.6, 147.4, 145.2, 144.1, 141.7, 134.5, 133.5, 132.0, 131.3, 130.3, 128.0, 126.3, 126.1, 125.6, 125.0, 124.7, 119.7, 113.4, 113.0, 112.9, 112.5, 80.2, 54.6, 45.9, 45.3, 31.7, 29.8, 29.2, 27.00, 26.97, 25.3, 22.9, 22.0, 20.2, 14.2. MS (ESI-TOF): Calculated for C$_{38}$H$_{36}$N$_4$S$_3$ [M+H]+: 621.2175, found: 621.2163.
Figure S 13. $^1$H-NMR spectrum (250 MHz) in CDCl$_3$ of 3T-TCV.\textsuperscript{[1]}

Figure S 14. Mass spectrum of 3T-TCV.\textsuperscript{[1]}
5-octyl-2,3'-bithiophene

A solution of 3-bromothiophene (2.22 g, 13.62 mmol), Aliquat 336 (2.30 mL), Na$_2$CO$_3$ (2 M, 36 mL, 72 mmol) and 4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane (4.39 g, 13.62 mmol) in THF/toluene (50 : 50, 200 mL) was degassed for three hours. A solution of tetakis(triphenylphosphine)palladium (945 mg, 817 μmol) in degassed THF was added and the reaction mixture refluxed for 24 hours. The mixture was extracted with CH$_2$Cl$_2$ (3x 100 mL). The combined organic phases were washed with brine (2x 75 mL), dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. Purification via column chromatography (eluent PE) gave the product as colorless oil (2.53 g, 9.09 mmol, 67%).

$^1$H-NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.34-7.23 (m, 3H), 6.99 (d, $J = 3.5$ Hz, 1H), 6.69 (d, $J = 3.5$ Hz, 1H), 2.79 (t, $J = 7.4$ Hz, 2H), 1.75-1.62 (m, 2H), 1.40-1.24 (m, 10H), 0.88 (t, $J = 6.7$ Hz, 3H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 144.9, 137.7, 136.6, 126.2, 126.1, 124.7, 122.8, 118.8, 32.0, 31.8, 30.3, 29.5, 29.4, 29.2, 22.8, 14.3.

trimethyl(5-octyl-[2,3'-bithiophene]-2'-yl)silane

To a solution of LDA (2 M in THF, 4.5 mL, 8.98 mmol) in THF (dry, 40 mL) 5-octyl-2,3'-bithiophene (2.5 g, 8.98 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for one hour at room temperature. After TMSCl (975 mg, 1.14 mL, 8.98 mmol) was added, the ice bath was removed and the solution stirred for 66 hours at room temperature. The aqueous phase was extracted with CH$_2$Cl$_2$ (3x 75 mL). The combined organic phases were dried over MgSO$_4$ and the solvent removed under reduced pressure. Purification via column chromatography (eluent cyclohexane/TEA 99 : 1) gave the product as colorless oil (1.32 g, 3.76 mmol, 42%).

$^1$H-NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.52 (d, $J = 4.7$ Hz, 1H), 7.20 (d, $J = 4.7$ Hz, 1H), 6.82 (d, $J = 3.4$ Hz, 1H), 6.69 (d, $J = 3.4$ Hz, 1H), 2.81 (t, $J = 7.5$ Hz, 2H), 1.75-1.62 (m, 2H), 1.41-1.24 (m, 10H), 0.88 (t, $J = 6.7$ Hz, 3H), 0.25 (s, 9H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 144.9, 136.7, 136.2, 126.2, 126.1, 124.7, 122.9, 118.8, 32.0, 31.8, 30.3, 29.5, 29.4, 29.3, 22.8, 14.3, 2.1.
trimethyl(5-octyl-5′-(tributylstannyl)-[2,3′-bithiophene]-2′-yl)silane

To a solution of trimethyl(5-octyl-[2,3′-bithiophene]-2′-yl)silane (1.28 g, 3.65 mmol) in THF (dry, 20 mL) n-BuLi (2.5 M in hexane, 1.55 mL, 3.83 mmol) was added slowly at -78 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature for 15 minutes. After cooling to -78 °C tributyltin chloride (1.31 g, 1.09 mL, 4.02 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 66 hours. The reaction was terminated by adding a saturated solution of Na₂CO₃ (2x 75 mL) and water (2x 75 mL). The aqueous phase was extracted with CH₂Cl₂ (3x 75 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. The product was isolated as yellow liquid (2.02 g, 80%, determined from ¹H-NMR). The product further contained ~20% contaminations in the aromatic region and tin organyl. The product was used without further purification.

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.23 (s, 1H), 6.83 (d, J = 3.4 Hz, 1H), 6.69 (d, J = 3.4 Hz, 1H), 2.81 (t, J = 7.5 Hz, 2H), 1.75-1.51 (m, 8H), 1.40-1.26 (m, 16H), 1.15-1.06 (m, 6H), 0.94-0.86 (m, 12H), 0.25 (s, 9H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 145.6, 143.5, 142.3, 141.7, 139.8, 137.8, 125.9, 123.9, 32.0, 31.9, 30.3, 29.5, 29.43, 29.42, 29.2, 29.1, 28.0, 27.6, 27.4, 27.0, 22.8, 17.7, 14.3, 13.9, 13.82, 13.78, 11.0, 8.9, 0.8.

1-hexyl-2,2,4,7-tetramethyl-6-(5-octyl-[2,3′-bithiophene]-5′-yl)-1,2,3,4-tetrahydroquinoline

A solution of Pd(PPh₃)₄ (195 mg, 167 μmol) in degassed THF was added to a solution of trimethyl(5-octyl-5′-(tributylstannyl)-[2,3′-bithiophene]-2′-yl)silane (2.0 g, 3.13 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (740 mg, 2.09 mmol) in degassed toluene (100 mL). The solution was refluxed for 19 hours. After cooling down the reaction mixture was washed with brine (2x 75 mL). The aqueous phase was extracted with CH₂Cl₂ (3x 100 mL). The combined organic phases were dried over MgSO₄ and the solvent removed under reduced pressure. Purification via
column chromatography (eluent PE/EE 10 : 1) and size exclusion chromatography (eluent CHCl₃) gave the product as yellow oil (523 mg, 948 μmol, 45%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.19 (m, 2H), 7.11 (s, 1H), 6.99 (d, J = 3.5 Hz, 1H), 6.69 (d, J = 3.5 Hz, 1H), 6.39 (s, 1H), 3.41-3.24 (m, 1H), 3.13-2.98 (m, 1H), 2.96-2.84 (m, 1H), 2.79 (t, J = 7.6 Hz, 2H), 2.39 (s, 3H), 1.78-1.50 (m, 6H), 1.41-1.24 (m, 22H), 1.19 (s, 3H), 0.96-0.84 (m, 6H).

**1Tb-TCV:**

2-(5'-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-5-octyl-[2,3'-bithiophene]-2'-yl)ethene-1,1,2-tricarbonitrile

To a solution of 1-hexyl-2,2,4,7-tetramethyl-6-(5-octyl-[2,3'-bithiophene]-5'-yl)-1,2,3,4-tetrahydroquinoline (165 mg, 300 μmol) in THF (dry, 15 mL) n-BuLi (2.5 M in hexane, 130 μL, 315 μmol) was added slowly at -15 °C. The cooling bath was removed and the solution was stirred at room temperature for 90 minutes. After cooling the solution to -15 °C, tetracyanoethylene (122 mg, 952 μmol) was added in two steps (47 mg at the beginning followed by 75 mg as solid after 40 minutes) and the solution was stirred for 17 hours at room temperature. The reaction was terminated by adding brine (30 mL). The aqueous phase was extracted with CH₂Cl₂ (3x 50 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Multiple purification steps via column chromatography (eluent PE/EE 20 : 1, 15 : 1 and CHCl₃) followed by size exclusion chromatography (eluent CHCl₃) gave the product as copper red solid (89 mg, 137 μmol, 46%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.33 (s, 1H), 7.20 (s, 1H), 7.02 (d, J = 3.6 Hz, 1H), 6.87 (d, J = 3.6 Hz, 1H), 6.39 (s, 1H), 3.45-3.30 (m, 1H), 3.22-3.06 (m, 1H), 2.96-2.82 (m, 3H), 2.53 (s, 3H), 1.81-1.51 (m, 6H), 1.44-1.25 (m, 22H), 1.23 (s, 3H), 0.97-0.85 (m, 6H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 157.5, 151.9, 147.3, 136.1, 132.2, 131.8, 128.5, 128.3, 126.3, 125.8, 124.7, 117.9, 114.1, 113.2, 113.1, 112.2, 83.1, 55.2, 46.3, 45.3, 32.0, 31.7, 31.6, 30.5, 29.7, 29.4, 29.3, 29.2, 29.0, 27.0, 26.8, 25.6, 22.82, 22.80, 22.76, 20.1, 14.3, 14.2. MS (ESI-TOF): Calculated for C₄₀H₅₀N₄S₂ [M+Na]⁺: 673.3369, found: 673.3365.
Figure S 15. $^1$H-NMR spectrum (250 MHz) in CDCl$_3$ of 1Tβ-TCV. $^{[1]}$

Figure S 16. Mass spectrum of 1Tβ-TCV. $^{[1]}$
trimethyl(thiophene-2-yl)silane

To a solution of thiophene (4.00 g, 3.80 mL, 47.55 mmol) in THF (dry, 70 mL) n-BuLi (1.6 M in hexane, 31.20 mL, 49.92 mmol) was added slowly at 0 °C. The cooling bath was removed and the reaction stirred at room temperature for 3.5 hours. After cooling to 0 °C chlorotrimethylsilane (5.70 g, 6.70 mL, 52.47 mmol) was added slowly. The cooling bath was removed and the reaction mixture stirred for 12 hours at room temperature. The reaction was terminated by adding water (50 mL). The organic phase was washed with NaOH (0.2 M, 20 mL) and brine (30 mL). The aqueous phase was extracted with Et₂O (40 mL). The combined organic phases were dried over MgSO₄ and the solvent removed under reduced pressure. Fractional distillation gave the product as a colorless liquid (5.16 g, 33.03 mmol, 69%).

1H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.60 (dd, J = 0.8 Hz, 4.6 Hz, 1H), 7.27 (dd, J = 0.8 Hz, 3.3 Hz, 1H), 7.20 (dd, J = 3.3 Hz, 4.6 Hz, 1H), 0.33 (s, 9H).

13C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 140.2, 134.1, 130.5, 128.2, 0.2.

trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)thiophene-2-yl)silane

To a solution of trimethyl(thiophene-2-yl)silane (4.60 g, 29.43 mmol) in THF (dry, 60 mL) n-BuLi (1.6 M in hexane, 19.3 mL, 30.90 mmol) was added slowly at -78 °C. The solution was stirred for 10 minutes at -78 °C and subsequently heated to room temperature over a period of one hour. After cooling the solution to -78 °C 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.02 g, 6.60 mL, 32.37 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 90 hours. The solution was washed with a saturated solution of Na₂CO₃ (40 mL). The aqueous phase was extracted with Et₂O (50 mL). The organic phase was dried over MgSO₄ and the solvent removed under reduced pressure. The product was isolated as colorless solid (8.30 g, 29.14 mmol, 99%) and was used without further purification.

1H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.69 (d, J = 3.3 Hz, 1H), 7.33 (d, J = 3.3 Hz, 1H), 1.34 (s, 12H), 0.32 (s, 9H). 13C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 148.6, 138.0, 135.2, 84.2, 24.9, 0.1.
tributyl(5-octylthiophene-2-yl)stannane

To a solution of 2-octylthiophene (7.00 g, 35.65 mmol) in THF (dry, 70 mL) n-BuLi (1.6 M in hexane, 23.4 mL, 37.43 mmol) was added slowly at -78 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature for 80 minutes. After cooling to -78 °C tributyltin chloride (12.18 g, 10.20 mL, 37.43 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 25 hours. The reaction was terminated by adding water (80 mL). The aqueous phase was extracted with CHCl₃ (2x 50 mL). The combined organic phases were dried over MgSO₄ and the solvent removed under reduced pressure. The product was isolated as yellow liquid (15.75 g, 32.44 mmol, 91% determined from ¹H-NMR). The product further contained 9% educt and tin organyl leading to a yield above 100%. The product was used without further purification.

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 6.98 (d, J = 3.1 Hz, 1H), 6.90 (d, J = 3.1 Hz, 1H), 2.85 (t, J = 7.7 Hz, 2H), 1.74-1.63 (m, 2H), 1.62-1.49 (m, 6H), 1.41-1.24 (m, 16H), 1.10-1.04 (m, 6H), 0.92-0.85 (m, 12H).

(3'-bromo-[2,2'-bithiophene]-5-yl)trimethylsilane

A solution of 2,3-dibromothiophene (4.00 g, 16.53 mmol), trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)thiophene-2-yl)silane (5.13 g, 18.19 mmol) and Na₂CO₃ (2 M, 33 mL, 66 mmol) in 1,4-dioxane (200 mL) was degassed for 70 minutes. Pd(PPh₃)₄ (1.54 g, 1.33 mmol) was suspended in degassed 1,4-dioxane (75 mL) and added to the reaction mixture. The reaction mixture was stirred at 100 °C for 3.5 hours. After cooling down the solution was diluted with water (80 mL) and washed with brine (80 mL). The aqueous phase was extracted with Et₂O (2x 50 mL). The combined organic phases were dried over MgSO₄ and the solvent removed under reduced pressure. Purification via column chromatography (eluent PE/TEA 100 : 1) gave the product as yellow liquid (3.51 g, 11.06 mmol, 67%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.49 (d, J = 3.5 Hz, 1H), 7.20 (d, J = 3.5 Hz, 1H), 7.18 (d, J = 5.3 Hz, 1H), 7.01 (d, J = 5.3 Hz, 1H), 0.35 (s, 9H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 141.7, 139.5, 134.3, 132.6, 132.0, 128.0, 124.5, 107.9, 0.1.
Pd(PPh$_3$)$_4$ (570 mg, 49.3 mmol) was added to a solution of tributyl(5-octylthiophene-2-yl)stannane (7.1 g, 14.65 mmol) and (3′-bromo-[2,2′-bithiophene]-5-yl)trimethylsilane (3.1 g, 9.77 mmol) in degassed toluene (100 mL). The solution was refluxed for 16 hours. After cooling down the reaction mixture was washed with water (80 mL). The aqueous phase was extracted with CHCl$_3$ (3x 50 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was removed under reduced pressure. Purification via column chromatography (eluent PE/TEA 100 : 1) gave the product as yellow liquid (4.06 g, 9.38 mmol, 96%).

$^1$H-NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.24 (d, $J = 5.3$ Hz, 1H), 7.16 (d, $J = 3.4$ Hz, 1H), 7.13 (d, $J = 5.3$ Hz, 1H), 7.12 (d, $J = 3.4$ Hz, 1H), 6.85 (d, $J = 3.5$ Hz, 1H), 6.65 (d, $J = 3.5$ Hz, 1H), 2.77 (t, $J = 7.7$ Hz, 2H), 1.72-1.53 (m, 2H), 1.38-1.24 (m, 10H), 1.1 (t, $J = 6.6$ Hz, 3H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): δ (ppm) = 146.2, 142.0, 140.5, 135.0, 134.3, 132.3, 131.1, 130.0, 128.9, 126.1, 124.4, 124.2, 31.8, 30.2, 29.4, 29.2, 22.8, 14.3, 14.1.

To a solution of trimethyl(5″-octyl-[2,2′:3′,2″-terthiophene]-5-yl)stannane (3.80 g, 8.78 mmol) in THF (dry, 75 mL) n-BuLi (1.6 M in hexane, 5.80 mL, 9.28 mmol) was added slowly at -78 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature for one hour. After cooling to -78 °C tributyltin chloride (3.00 g, 2.50 mL, 37.43 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 89 hours. The reaction was terminated by adding water (75 mL). The aqueous phase was extracted with CHCl$_3$ (2x 50 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was removed under reduced pressure. The product was isolated as yellow liquid (5.70 g, 7.90 mmol, 90%, determined from $^1$H-NMR). The product further contained 10% educt and tin organyl leading to a yield above 100%. The product was used without further purification.

$^1$H-NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.14 (d, $J = 3.4$ Hz, 1H), 7.13 (s, 1H), 7.10 (d, $J = 3.4$ Hz, 1H), 6.86 (d, $J = 3.5$ Hz, 1H), 6.66 (d, $J = 3.5$ Hz, 1H), 2.78 (t, $J = 7.6$ Hz, 2H),

trimethyl(5″-octyl-[2,2′:3′,2″-terthiophene]-5-yl)silane

To a solution of trimethyl(5″-octyl-[2,2′:3′,2″-terthiophene]-5-yl)silane (3.80 g, 8.78 mmol) in THF (dry, 75 mL) n-BuLi (1.6 M in hexane, 5.80 mL, 9.28 mmol) was added slowly at -78 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature for one hour. After cooling to -78 °C tributyltin chloride (3.00 g, 2.50 mL, 37.43 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 89 hours. The reaction was terminated by adding water (75 mL). The aqueous phase was extracted with CHCl$_3$ (2x 50 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was removed under reduced pressure. The product was isolated as yellow liquid (5.70 g, 7.90 mmol, 90%, determined from $^1$H-NMR). The product further contained 10% educt and tin organyl leading to a yield above 100%. The product was used without further purification.

$^1$H-NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.14 (d, $J = 3.4$ Hz, 1H), 7.13 (s, 1H), 7.10 (d, $J = 3.4$ Hz, 1H), 6.86 (d, $J = 3.5$ Hz, 1H), 6.66 (d, $J = 3.5$ Hz, 1H), 2.78 (t, $J = 7.6$ Hz, 2H),
1.72-1.53 (m, 8H), 1.40-1.24 (m, 16H), 1.16-1.09 (m, 6H), 0.95-0.86 (m, 12H), 0.30 (s, 9H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): $\delta$ (ppm) = 146.0, 141.3, 141.1, 138.4, 137.1, 136.6, 135.4, 134.3, 133.3, 128.1, 126.0, 124.2, 32.0, 31.9, 30.3, 29.5, 29.4, 29.3, 29.1, 27.4, 22.8, 14.3, 13.8, 11.0, 0.1.

1-hexyl-2,2,4,7-tetramethyl-6-(5''-octyl-[2,2':3',2''-terthiophene]-5'-yl)-1,2,3,4-tetrahydroquinoline

Pd(PPh$_3$)$_4$ (108 mg, 941 µmol) was added to a solution of trimethyl(5''-octyl-5'-tributylstannyl-[2,2':3',2''-terthiophene]-5-yl)silane (1.07 g, 1.45 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (3.46 g, 0.98 mmol) in degassed toluene (50 mL). The solution was refluxed for 19 hours. After cooling down the reaction mixture was washed with brine (50 mL). The aqueous phase was extracted with CHCl$_3$ (6x 40 mL). The combined organic phases were dried over MgSO$_4$ and the solvent removed under reduced pressure. Purification via column chromatography (eluent PE/EE 40 : 1) gave the product as orange oil (791 mg). The obtained product still contained the TMS protection group and was used for the following deprotection step.

A solution of 1-hexyl-2,2,4,7-tetramethyl-6-(5''-octyl-5-(trimethylsilyl)-[2,2':3',2''-terthiophene]-5'-yl)-1,2,3,4-tetrahydroquinoline and TBAF (1 M in THF, 1.5 mL, 1.5 mmol) in THF (dry, 40 mL) was stirred for two hours at room temperature. The reaction mixture was poured into a saturated solution of Na$_2$CO$_3$ (30 mL) and the aqueous phase was extracted with CHCl$_3$ (3x 25 mL). The combined organic phases were washed with water (2x 30 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure and the product was purified by size exclusion chromatography (eluent CHCl$_3$). The deprotected product was obtained as orange oil (467 mg, 0.75 mmol, 78%).

$^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ (ppm) = 7.27 (dd, $J = 1.2$ Hz, 5.2 Hz, 1H), 7.21 (s, 1H), 7.14 (dd, $J = 1.2$ Hz, 3.6 Hz, 1H), 7.00 (dd, $J = 3.6$ Hz, 5.2 Hz, 1H), 6.99 (s, 1H), 6.87 (d, $J = 3.5$ Hz, 1H), 6.66 (d, $J = 3.5$ Hz, 1H), 6.39 (s, 1H), 3.41-3.25 (m, 1H), 3.14-2.99 (m, 1H), 2.96-2.83 (m, 1H), 2.77 (t, $J = 7.7$ Hz, 2H), 2.45 (s, 3H), 1.78-1.50 (m, 6H), 1.41-1.25 (m, 22H), 1.19 (s, 3H), 0.96-0.85 (m, 6H). $^{13}$C-NMR (62.5 MHz, CDCl$_3$): $\delta$ (ppm) = 146.2, 144.9, 143.6, 135.8, 135.4, 134.5, 132.4, 129.1, 128.1, 127.9, 127.4, 127.2, 126.21, 126.19, 125.4, 124.1, 120.0, 113.2, 54.5, 47.0, 45.3, 32.0, 31.8, 31.7, 30.3, 29.9, 29.5, 29.4, 29.3, 27.0, 25.2, 22.9, 22.8, 21.8, 20.2, 14.3, 14.2.
2Tβ-TCV:  

2-(5'-((1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)-5''-octyl-[2,2':3',2''-terthiophene]-5-yl)ethene-1,1,2-tricarbonitrile

To a solution of 1-hexyl-2,2,4,7-tetramethyl-6-(5''-octyl-[2,2':3',2''-terthiophene]-5'-yl)-1,2,3,4-tetrahydroquinoline (79 mg, 125 μmol) in THF (dry, 15 mL) n-BuLi (1.6 M in hexane, 90 μL, 144 μmol) was added slowly at -15 °C. The cooling bath was removed and the solution was stirred at room temperature for 90 minutes. Tetracyanoethylene (66 mg, 515 μmol) was added and the solution was stirred for 3 hours at room temperature. The reaction was terminated by adding brine (25 mL). The aqueous phase was extracted with CHCl3 (30 mL). The combined organic phases were dried over MgSO4 and the solvent removed under reduced pressure. Purification via column chromatography (eluent CHCl3) gave the product as black green solid (25 mg, 23 μmol, 28%).

1H-NMR (250 MHz, CDCl3): δ (ppm) = 7.86 (d, J = 4.5 Hz, 1H), 7.27 (d, J = 4.5 Hz, 1H), 7.26 (s, 1H), 7.06 (s, 1H), 6.98 (d, J = 3.5 Hz, 1H), 6.82 (d, J = 3.5 Hz, 1H), 6.39 (s, 1H), 3.42-3.28 (m, 1H), 3.16-3.02 (m, 1H), 2.96-2.82 (m, 1H), 2.85 (t, J = 7.7 Hz, 2H), 2.48 (s, 3H), 1.80-1.51 (m, 6H), 1.42-1.26 (m, 22H), 1.21 (s, 3H), 0.96-0.85 (m, 6H). 13C-NMR (62.5 MHz, CDCl3): δ (ppm) = 152.6, 149.5, 149.3, 145.9, 140.4, 137.9, 134.7, 132.5, 132.5, 131.1, 130.2, 128.8, 128.6, 127.9, 126.9, 125.9, 125.1, 118.7, 113.6, 113.1, 112.94, 112.89, 54.8, 46.7, 45.3, 32.0, 31.73, 31.71, 30.4, 29.8, 29.5, 29.4, 29.1, 26.99, 26.94, 25.4, 22.8, 22.2, 20.2, 14.3, 14.2. MS (ESI-TOF): Calculated for C44H52N4S3 [M+Na]+: 755.3246, found: 755.3255.
Figure S 17. $^1$H-NMR spectrum (250 MHz) in CDCl$_3$ of 2T$\beta$-TCV. [1]

Figure S 18. Mass spectrum of 2T$\beta$-TCV. [1]
trimethyl(5'-{(tributylstanny])-{2,2'-bithiophene}-5-yl)silane

To a solution of [2,2'-bithiophene]-5-yltrimethylsilane (5.00 g, 20.97 mmol) in THF (dry, 75 mL) n-BuLi (2.5 M in hexane, 9.25 mL, 23.07 mmol) was added slowly at -78 °C. The reaction mixture was stirred at -78 °C for one hour. Tributyltin chloride (4.31 g, 3.60 mL, 13.23 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 20 hours. The reaction was terminated by adding a saturated solution of NH₄Cl (50 mL). The aqueous phase was extracted with Et₂O (2x 50 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. The product was isolated as orange liquid (11.49 g, 90%, determined from ¹H-NMR). The product further contained 10% educt and tin organyl leading to a yield above 100 %. The product was used without further purification.

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.30 (d, J = 3.3 Hz, 1H), 7.22 (d, J = 3.4 Hz, 1H), 7.12 (d, J = 3.4 Hz, 1H), 7.06 (d, J = 3.3 Hz, 1H), 1.63-1.50 (m, 6H), 1.40-1.29 (m, 6H), 1.16-1.07 (m, 6H), 0.94-0.86 (m, 9H), 0.32 (s, 9H).

(5'″-hexadecyl-[2,2':5',2'″:3',2'″]-quaterthiophene]-5-yl)trimethyl-silane

Pd(PPh₃)₄ (108 mg, 941 μmol) was added to a solution of von trimethyl(5'-(tributylstanny])-{2,2'-bithiophene}-5-yl)silane (6.67 g, 12.78 mmol) and 2'-bromo-5-hexadecyl-2,3'-'-bithiophene (4.00 g, 8.52 mmol) in degassed toluene (200 mL). The solution was refluxed for 64 hours. After cooling down the reaction mixture was washed with brine (100 mL). The aqueous phase was extracted with CH₂Cl₂ (4x 80 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via recrystallization from MeOH/CHCl₃/THF 200 : 50 : 50 mL gave the product as green solid (3.44 g, 5.49 mmol, 64 %).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.24 (d, J = 5.3 Hz, 1H), 7.18 (d, J = 3.5 Hz, 1H), 7.12 (d, J = 5.3 Hz, 1H), 7.11 (d, J = 3.5 Hz, 1H), 7.08 (d, J = 3.8 Hz, 1H), 7.02 (d, J = 3.8 Hz, 1H), 6.89 (d, J = 3.5 Hz, 1H), 6.67 (d, J = 3.5 Hz, 1H), 2.77 (t, J = 7.7 Hz, 2H), 1.73-1.56 (m, 2H), 1.40-1.21 (m, 26H), 0.88 (t, J = 6.7 Hz, 3H), 0.32 (s, 9H).
(5''-hexadecyl-5''-(tributylstannyl)-[2,2':5',2'':3'',2'''-quaterthiophene]-5-yl)trimethylsilane

To a solution of (5''-hexadecyl-[2,2':5',2'':3'',2'''-quaterthiophene]-5-yl)trimethylsilane (2.61 g, 4.15 mmol) in THF (dry, 50 mL) n-BuLi (2.5 M in hexane, 1.85 mL, 4.57 mmol) was added slowly at -78 °C. The cooling bath was removed and the reaction mixture was stirred for 75 minutes at room temperature. After cooling down to -78 °C tributyltin chloride (1.49 g, 1.25 mL, 4.57 mmol) was added slowly. The cooling bath was removed and the reaction mixture was stirred at room temperature for 15 hours. The reaction was terminated by adding a saturated solution of NH₄Cl (50 mL). The aqueous phase was extracted with CH₂Cl₂ (5x 80 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. The product was isolated as orange liquid (11.49 g, 7.90 mmol, 90%, determined from ¹H-NMR). The product further contained 10% educt and tin organyl leading to a yield above 100%. The product was used without further purification.

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.17 (d, J = 3.5 Hz, 1H), 7.12 (s, 1H), 7.10 (d, J = 3.5 Hz, 1H), 7.06 (d, J = 3.8 Hz, 1H), 7.00 (d, J = 3.8 Hz, 1H), 6.90 (d, J = 3.5 Hz, 1H), 6.68 (d, J = 3.5 Hz, 1H), 2.78 (t, J = 7.5 Hz, 2H), 1.72-1.52 (m, 8H), 1.42-1.22 (m, 34H), 1.18-1.09 (m, 6H), 0.95-0.87 (m, 12H), 0.32 (s, 9H).

6-(5''-hexadecyl-[2,2':5',2'':3'',2'''-quaterthiophene]-5''-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline

Pd(PPh₃)₄ (130 mg, 0.11 mmol) was added to a solution of (5''-hexadecyl-5''-(tributylstannyl)-[2,2':5',2'':3'',2'''-quaterthiophene]-5-yl)trimethylsilane (3.00 g, 3.27 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (770 mg, 2.18 mmol) in degassed toluene (60 mL). The solution was refluxed for 64 hours. After cooling down the reaction mixture was washed with brine (60 mL). The aqueous phase was extracted with CH₂Cl₂ (5x 50 mL). The combined organic phases were dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification via column
chromatography (eluent PE/EE 40 : 1) gave the product as red oil (2.0 g). The obtained product still contained the TMS protection group and was used for the following deprotection step.

A solution of 6-(5''-hexadecyl-5-(trimethylsilyl)-[2,2':5',2'':3'',2'''-quaterthiophene]-5'-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (2.0 g, 2.2 mmol) and TBAF (1 M in THF, 3.3 mL, 3.3 mmol) in THF (dry, 50 mL) was stirred for 18 hours at room temperature. The reaction mixture was poured into water (50 mL) and the aqueous phase extracted with Et₂O (3x 40 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. Multiple purification steps via column chromatography (eluent PE und PE/EE 100:1) followed by size exclusion chromatography (eluent CHCl₃) gave the deprotected product as orange oil (1.56 g, 1.89 mmol, 87%).

^H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.22 (s, 1H), 7.20 (dd, J = 1.2 Hz, 5.1 Hz, 1H), 7.13 (dd, J = 1.2 Hz, 3.6 Hz, 1H), 7.07 (d, J = 3.8 Hz, 1H), 7.04 (d, J = 3.8 Hz, 1H), 6.99 (s, 1H), 6.94 (d, J = 3.8 Hz, 1H), 6.69 (d, J = 3.5 Hz, 1H), 6.39 (s, 1H), 3.42-3.25 (m, 1H), 3.15-2.99 (m, 1H), 2.97-2.82 (m, 1H), 2.80 (t, J = 7.5 Hz, 2H), 2.46 (s, 3H), 1.78-1.52 (m, 6H), 1.42-1.23 (m, 38H), 1.20 (s, 3H), 0.97-0.85 (m, 6H).

^13C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 146.4, 144.9, 143.6, 137.7, 137.5, 135.2, 134.9, 134.5, 132.3, 129.1, 128.2, 128.0, 127.9, 127.7, 126.5, 125.4, 124.4, 123.9, 123.7, 119.9, 113.2, 54.5, 46.9, 45.3, 34.4, 32.1, 31.8, 31.7, 30.5, 30.3, 29.85, 29.82, 29.81, 29.7, 29.54, 29.52, 29.3, 27.0, 25.2, 22.87, 22.84, 21.8, 20.2, 14.28, 14.21.

3Tβ-TCV:

\[ \text{2-(5''-hexadecyl-5''-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)} - [2,2':5',2'':3'',2'''-quaterthiophenene]-5'-yl] \text{ethene}-1,1,2-tricarbonitrile \]

To a solution of 6-(5''-hexadecyl-[2,2':5',2'':3'',2'''-quaterthiophenene]-5''-yl)-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (150 mg, 180 μmol) in THF (dry, 20 mL) \( n \)-BuLi (1.6 M in hexane, 120 μL, 191 μmol) was added slowly at -15 °C. The cooling bath was removed and the solution was stirred at room temperature for 90 minutes. After cooling the reaction mixture to -15 °C tetracyanoethylene (67.5 mg, 527 μmol) was added in two steps (37.5 mg at the beginning followed by 75 mg as solid after 40 minutes) and the solution was stirred for 19 hours at room temperature. The reaction was terminated by pouring into a saturated solution of NaHCO₃ (50 mL). The aqueous phase was extracted with CHCl₃ (3x 70 mL). The combined organic phases were dried over MgSO₄ and the solvent removed under reduced pressure. Purification via column
chromatography (eluent PE/EE 50 : 1) followed by size exclusion chromatography (eluent CHCl₃) gave the product as black green solid (52 mg, 56 μmol, 31%).

¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 7.95 (d, J = 4.4 Hz, 1H), 7.40 (d, J = 4.1 Hz, 1H), 7.25 (d, J = 4.4 Hz, 1H), 7.22 (s, 1H), 7.15 (d, J = 4.1 Hz, 1H), 6.99 (s, 1H), 6.95 (d, J = 3.5 Hz, 1H), 6.76 (d, J = 3.5 Hz, 1H), 6.39 (s, 1H), 3.42-3.26 (m, 1H), 3.15-3.00 (m, 1H), 2.98-2.82 (m, 1H), 2.84 (t, J = 7.7 Hz, 2H), 2.47 (s, 3H), 1.79-1.51 (m, 6H), 1.41-1.22 (m, 38H), 1.20 (s, 3H), 0.97-0.84 (m, 6H). ¹³C-NMR (62.5 MHz, CDCl₃): δ (ppm) = 147.7, 145.5, 145.3, 142.6, 141.6, 134.5, 134.1, 133.9, 133.6, 132.0, 131.4, 129.4, 129.1, 128.7, 127.94, 127.90, 127.4, 125.6, 125.2, 124.6, 113.4, 113.3, 112.94, 112.85, 112.5, 80.3, 54.6, 46.8, 45.3, 32.1, 31.9, 31.7, 30.3, 29.9, 29.82, 29.81, 29.7, 29.5, 29.3, 29.2, 26.99, 26.97, 25.3, 22.8, 21.9, 20.2, 14.3, 14.2. MS (ESI-TOF): Calculated for C₅₆H₇₀N₄S₄ [M+H]⁺: 927.4556, found: 927.4538.

Figure S 19. ¹H-NMR spectrum (250 MHz) in CDCl₃ of 3Tβ-TCV. [¹]
Figure S 20. Mass spectrum of 3Tβ-TCV. [1]
2. Thermal Properties

Table S 1. Thermal properties of all synthesized push-pull molecules.

<table>
<thead>
<tr>
<th></th>
<th>$1T$-DCV</th>
<th>$1T\beta$-DCV</th>
<th>$2T$-DCV</th>
<th>$2T\beta$-DCV</th>
<th>$1T$-TCV</th>
<th>$1T\beta$-TCV</th>
<th>$2T$-TCV</th>
<th>$2T\beta$-TCV</th>
<th>$3T$-TCV</th>
<th>$3T\beta$-TCV</th>
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</thead>
<tbody>
<tr>
<td>$T_d$</td>
<td>308</td>
<td>xa</td>
<td>327</td>
<td>357</td>
<td>274</td>
<td>371</td>
<td>310</td>
<td>368</td>
<td>360</td>
<td>419</td>
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* Due to a lack of the necessary amount of substance no data could be acquired for $1T\beta$-DCV (marked by X).
Figure S 21. Thermogravimetry of a) 1T-DCV, b) 2T-DCV, c) 2Tβ-DCV, d) 1T-TCV, e) 1Tβ-TCV, f) 2T-TCV, g) 2Tβ-TCV, h) 3T-DCV and i) 3Tβ-TCV (compare Table S 1).
3. Absorption Properties

Table S 2. Absorption maxima of all chromophores, measured in solvents of different polarity. 1,4-dioxane ($\varepsilon_r = 2.2189$), toluene ($\varepsilon_r = 2.379$), chloroform ($\varepsilon_r = 4.8069$), dichloromethane ($\varepsilon_r = 8.93$), acetone ($\varepsilon_r = 21.01$), acetonitrile ($\varepsilon_r = 36.64$).

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ [nm]</th>
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</thead>
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<tr>
<td></td>
<td>1,4-dioxane</td>
</tr>
<tr>
<td>1T-DCV</td>
<td>502</td>
</tr>
<tr>
<td>1T$\beta$-DCV</td>
<td>519</td>
</tr>
<tr>
<td>2T-DCV</td>
<td>509</td>
</tr>
<tr>
<td>2T$\beta$-DCV</td>
<td>510</td>
</tr>
<tr>
<td>1T-TCV</td>
<td>620</td>
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<tr>
<td>1T$\beta$-TCV</td>
<td>623</td>
</tr>
<tr>
<td>2T-TCV</td>
<td>631</td>
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<tr>
<td>2T$\beta$-TCV</td>
<td>625</td>
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<tr>
<td>3T-TCV</td>
<td>613</td>
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<tr>
<td>3T$\beta$-TCV</td>
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</tr>
</tbody>
</table>
4. Electrochemical Measurements

Figure S 22. Differential pulse voltammograms of the chromophores 2T-DCV (a), 1Tβ-DCV (b) and 2Tβ-DCV (c) recorded in dichloromethane with 0.1 M Bu₄NPF₆ as electrolyte (black: oxidation, red: reduction). $E_{1/2}$ was obtained using $E_{1/2} = E_p + \Delta E/2$; where $\Delta E$ is 25 mV.
Figure S 23. CVs of the chromophores 2T-DCV (a) and 2Tβ-DCV (b) of the first and second oxidation recorded in dichloromethane with 0.1 M Bu₄NPF₆ as electrolyte; 2nd cycles are shown.

Figure S 24. Separate CVs during oxidation (black line) and reduction (red line) of the chromophores 2T-TCV (a), 2Tβ-TCV (b), 3T-TCV (c), 3Tβ-TCV (d) recorded in dichloromethane with 0.1 M Bu₄NPF₆ as electrolyte, 2nd cycles are shown.
5. DFT-Calculations

Computational Details

The molecular geometries of all chromophores were optimized at the framework of the Density Functional Theory (DFT) level using the hybrid meta-GGAs functional of Truhlar and Zhao (M06-2X)\cite{2} and a 6-31G** basis set\cite{3,4}, as implemented in the GAUSSIAN09 program\cite{5}. All geometrical parameters were allowed to vary independently, and no imaginary frequencies were observed, which ensures the finding of the global minimum energy. Note that M06-2X functional is well known to give reliable ground electronic state polarization when compared to X-ray structures\cite{6} and also accurate excited states dipole moments for a large variety of push-pull systems\cite{7}. Interestingly, M06-2X functional was found to predict accurate first hyperpolarizabilities for small molecules by comparison to reference results obtained at the CCSD(T) level\cite{8}.

Furthermore, vertical electronic excitation energies were calculated by using the time-dependent DFT (TD-DFT) approach\cite{9,10} on the resulting optimized molecular geometries, at the same level of theory. Absorption spectra were simulated through convolution of the vertical transition energies and oscillator strengths with Gaussian functions characterized by a half width at half-maximum of 0.3 eV.

For the NLO properties study, molecular hyperpolarizabilities at zero frequency were calculated at M06-2X/6-31G** level and the default parameters provided by the “polar” keyword. Molecular orbitals distribution were plotted using the GaussView 5.0 molecular modelling software. Solvent effects were considered in all calculations by using the SCRF (self-consistent-reaction-field) theory using the PCM (Polarized Continuum Model) model\cite{11-16} developed by Tomasi to model the interaction between the NLO-phores and the solvent (CH$_2$Cl$_2$).

The Nucleus-Independent Chemical Shifts (NICS) values\cite{17} were calculated for the optimized geometries at the B3LYP/6–311++G(2df, p) level by using the gauge-independent atomic orbital (GIAO) method.
Table S3. B3LYP/6-311++G(2df,p)//PCM-M06-2X/6-31G** NICS(0) values, computed at the geometrical center of the thienyl rings of the linear and branched push-pull systems and their unsubstituted analogue systems. Values are given in ppm.

<table>
<thead>
<tr>
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<th>NICS(0)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ring 1</td>
<td>Ring 2</td>
<td>Ring 3</td>
<td>Ring β</td>
</tr>
<tr>
<td>1T-DCV</td>
<td>-8.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1Tβ-DCV</td>
<td>-7.9</td>
<td>-</td>
<td>-</td>
<td>-9.8</td>
</tr>
<tr>
<td>2T-DCV</td>
<td>-8.3</td>
<td>-8.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2Tβ-DCV</td>
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<td>-8.7</td>
<td>-</td>
<td>-10.4</td>
</tr>
<tr>
<td>1T-TCV</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1Tβ-TCV</td>
<td>-7.8</td>
<td>-</td>
<td>-</td>
<td>-10.1</td>
</tr>
<tr>
<td>2T-TCV</td>
<td>-8.1</td>
<td>-7.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2Tβ-TCV</td>
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<td>-8.3</td>
<td>-</td>
<td>-10.4</td>
</tr>
<tr>
<td>3T-TCV</td>
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<td>-7.5</td>
<td>-8.1</td>
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<tr>
<td>3Tβ-TCV</td>
<td>-7.8</td>
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<td>1T</td>
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<td>2T</td>
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</tr>
<tr>
<td>3T</td>
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</tr>
<tr>
<td>3Tβ</td>
<td>-10.2</td>
<td>-8.8</td>
<td>-10.2</td>
<td>-9.9</td>
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</table>
Table S4. Mülliken atomic charges on various molecular domains for 1T-DCV, 1Tβ-DCV, 1T-TCV, 1Tβ-TCV, 2T-TCV and 2Tβ-TCV systems calculated at the PCM-M06-2X/6-31G** level using CH$_2$Cl$_2$ as solvent.

<table>
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<tr>
<th>Compound</th>
<th>Mülliken atomic charges</th>
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<tbody>
<tr>
<td></td>
<td>Donor Group</td>
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<tr>
<td>1T-DCV</td>
<td>0.229</td>
</tr>
<tr>
<td>1Tβ-DCV</td>
<td>0.235</td>
</tr>
<tr>
<td>1T-TCV</td>
<td>0.283</td>
</tr>
<tr>
<td>1Tβ-TCV</td>
<td>0.255</td>
</tr>
<tr>
<td>2T-TCV</td>
<td>0.197</td>
</tr>
<tr>
<td>2Tβ-TCV</td>
<td>0.201</td>
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</table>
Figure S25. Simulated absorption spectra and main excitations (oscillator strength vs. wavelength) shown as vertical bars for 2T-DCV (a), 2Tβ-DCV (b), 3T-TCV (c) and 3Tβ-TCV (d) calculated at PCM-M06-2X/6-31G** level using CH₂Cl₂ as solvent.

Table S5. TD-DFT/PCM-M06-2X/6-31G**-based electronic transitions for 2T-DCV, 2Tβ-DCV, 3T-TCV and 3Tβ-TCV.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electronic Transitions</th>
<th>Description</th>
<th>Energy (eV)</th>
<th>nm</th>
<th>Oscillator Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>2T-DCV</td>
<td>S₀→S₁</td>
<td>H→L (81%)</td>
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<td>465</td>
<td>1.3280</td>
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<tr>
<td>2T-DCV</td>
<td>S₀→S₂</td>
<td>H→L (77%)</td>
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<tr>
<td>2T-DCV</td>
<td>S₀→S₃</td>
<td>H→L+1 (83%)</td>
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<td>0.2600</td>
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<tr>
<td>2T-DCV</td>
<td>S₀→S₄</td>
<td>H→L+1 (51%)</td>
<td>4.91</td>
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<td>0.2085</td>
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<tr>
<td>2T-DCV</td>
<td>S₀→S₅</td>
<td>H→L (80%)</td>
<td>2.68</td>
<td>463</td>
<td>1.2283</td>
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<tr>
<td>2T-DCV</td>
<td>S₀→S₆</td>
<td>H→L+1 (47%)</td>
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<tr>
<td>2T-DCV</td>
<td>S₀→S₇</td>
<td>H→L+1 (37%)</td>
<td>4.27</td>
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<td>0.1398</td>
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<tr>
<td>2T-DCV</td>
<td>S₀→S₈</td>
<td>H→L+1 (60%)</td>
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<td>252</td>
<td>0.2489</td>
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<tr>
<td>2T-DCV</td>
<td>S₀→S₉</td>
<td>H→L+1 (55%)</td>
<td>5.08</td>
<td>244</td>
<td>0.2058</td>
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</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electronic Transitions</th>
<th>Description</th>
<th>Energy (eV)</th>
<th>nm</th>
<th>Oscillator Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T-TCV</td>
<td>S₀→S₁</td>
<td>H→L (72%)</td>
<td>2.12</td>
<td>559</td>
<td>1.2616</td>
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<tr>
<td>3T-TCV</td>
<td>S₀→S₂</td>
<td>H→L+1 (67%)</td>
<td>2.99</td>
<td>415</td>
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<td>3T-TCV</td>
<td>S₀→S₃</td>
<td>H→L+1 (77%)</td>
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<tr>
<td>3T-TCV</td>
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<td>H→L+2 (50%)</td>
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<td>3T-TCV</td>
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<td>H→L+2 (25%)</td>
<td>4.95</td>
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<td>3T-TCV</td>
<td>S₀→S₆</td>
<td>H→L (68%)</td>
<td>2.24</td>
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<td>3T-TCV</td>
<td>S₀→S₇</td>
<td>H→L+1 (61%)</td>
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<td>420</td>
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<td>3T-TCV</td>
<td>S₀→S₈</td>
<td>H→L+1 (70%)</td>
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<td>3T-TCV</td>
<td>S₀→S₉</td>
<td>H→L+1 (14%)</td>
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<td>3T-TCV</td>
<td>S₀→S₁₀</td>
<td>H→L+4 (68%)</td>
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<td>H→L+4 (38%)</td>
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</table>
Figure S 26. DFT-calculated molecular orbital topologies for 1T-DCV (a), 1Tβ-DCV (b), 2T-DCV (c), 2Tβ-DCV (d), 1T-TCV (e), 1Tβ-TCV (f), 2T-TCV (g) and 2Tβ-TCV (h), chromophores at PCM-M06-2X/6-31G** level using CH$_2$Cl$_2$ as solvent.
Table S6: Experimental and calculated nonlinear optical properties of all chromophores.

<table>
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<tr>
<th>Compound</th>
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<th>Theoretical</th>
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<tbody>
<tr>
<td></td>
<td>Polar M062X/6-31G**[^c]</td>
<td>TD-DFT M062X/6-31G**[^c]</td>
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<td>1T-DCV</td>
<td>1150</td>
<td>730</td>
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<tr>
<td>1T-TCV</td>
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<td>2350</td>
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<td>1Tβ-DCV</td>
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<td>620</td>
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<td>1Tβ-TCV</td>
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<td>1760</td>
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<td>2T-DCV</td>
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<td>2T-TCV</td>
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<td>2Tβ-TCV</td>
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<td>3T-TCV</td>
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<tr>
<td>3Tβ-TCV</td>
<td>7700</td>
<td>3530</td>
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</table>

[^a]: Measured by EFISH in dichloromethane. Experimental uncertainty is ± 10% except for 2Tβ-DCV (± 20%)
[^b]: Calculated using a two level model.
[^c]: Solvent calculations using the PCM model in CH₂Cl₂.
6. NLO measurements

Electric field induced second harmonic generation (EFISH) measurements have been performed using as the fundamental radiation the 1.9 µm output of a H₂ Raman shifter pumped by a Q-switched Nd:YAG laser. This laser operates at 1064 nm, with a repetition rate of 10 Hz and pulse width of 8 ns. A computer controlled NLO spectrometer completes the SHG experimental set-up. In that spectrometer, the 1.9 µm incident light is split in two beams. The less intense one is directed to a N-(4-nitrophenyl)-(L)-prolinol (NPP) powder sample whose SH signal is used as a reference in order to reduce the effects of laser fluctuations. The second one is passed through a linear (vertical) polarizer and focused into the EFISH wedge-shaped liquid cell. Voltage pulses of 5 kV and 3 µs are applied across the cell (2 mm gap between the electrodes) synchronously with the laser pulses. The harmonic signals from both the EFISH cell and the NPP reference are measured with two photomultipliers. Interference filters are used to remove the residual excitation light beyond the sample and the reference.

The molecular µβ values of the reported compounds have been determined in dichloromethane. As a rule, several solutions of concentration in the range 10⁻³ - 3.10⁻⁴ M were measured. The effect of absorption at harmonic wavelength (954 nm) of compounds has been corrected following reference[18]. Static-zero frequency- µβ(0) values were extrapolated using a two-level dispersion model[19] and λmax corresponding to the maximum of the lowest energy absorption band.
7. References