Supporting Information for

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

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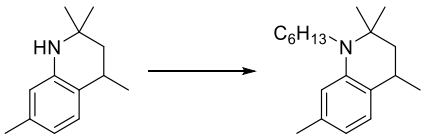
1. Synthetic Part

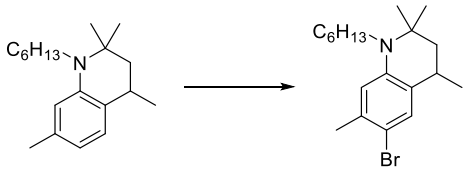
1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline



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_2Cl_2 (2x 100 mL). The combined organic extracts were dried over Na_2SO_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, $CDCl_3$): δ (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, $CDCl_3$): δ (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.

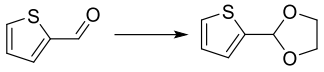
6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline



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_2Cl_2 (3x, 50 mL). The combined organic extracts were dried over Na_2SO_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, $CDCl_3$): δ (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, $CDCl_3$): δ (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.

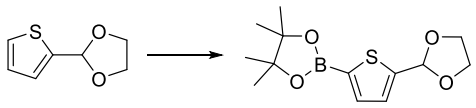
2-(thiophen-2-yl)-1,3-dioxolane



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.

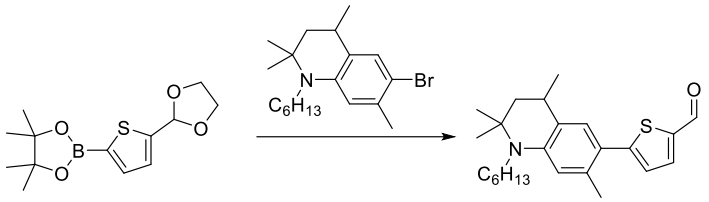
2-(5-(1,3-dioxolane-2-yl)thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane



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-isopropoxy-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_2Cl_2 (4x 50 mL). The combined organic extracts were dried over Na_2SO_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



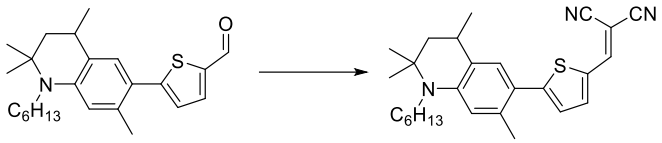
A solution of 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (500 mg, 1.42 mmol), Aliquat 336 (1 mL), Na_2CO_3 (2 M, 3.8 mL, 3.80 mmol) and 2-(5-(1,3-dioxolan-2-yl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (400 mg, 1.42 mmol) in THF/Toluene (50:50, 30 mL) was degassed for 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 CH_2Cl_2 (2x, 50 mL). The combined organic extracts were dried over Na_2SO_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 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 $NaHCO_3$ (sat., 30 mL) and brine (30 mL). The aqueous phase was extracted with CH_2Cl_2 (4x, 20 mL). The combined organic extracts were dried over Na_2SO_4. Removal of the solvent under reduced pressure yielded the deprotected product as an orange oil (94 mg, 0.25, 99%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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-yl)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_2Cl_2 (5x, 20 mL). The combined organic extracts were dried over Na_2SO_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, $CDCl_3$): δ (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, $CDCl_3$): δ (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 $C_{27}H_{33}N_3S$ $[M+H]^+$: 432.2468, found: 432.2453.

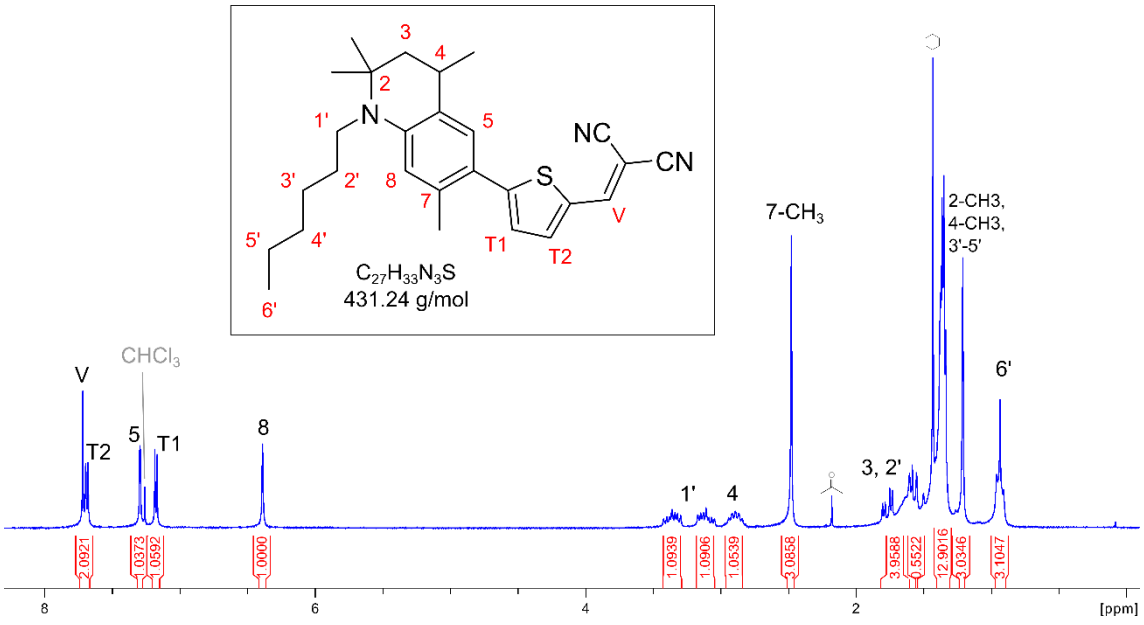


Figure S 1. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of 1T-DCV. [1]

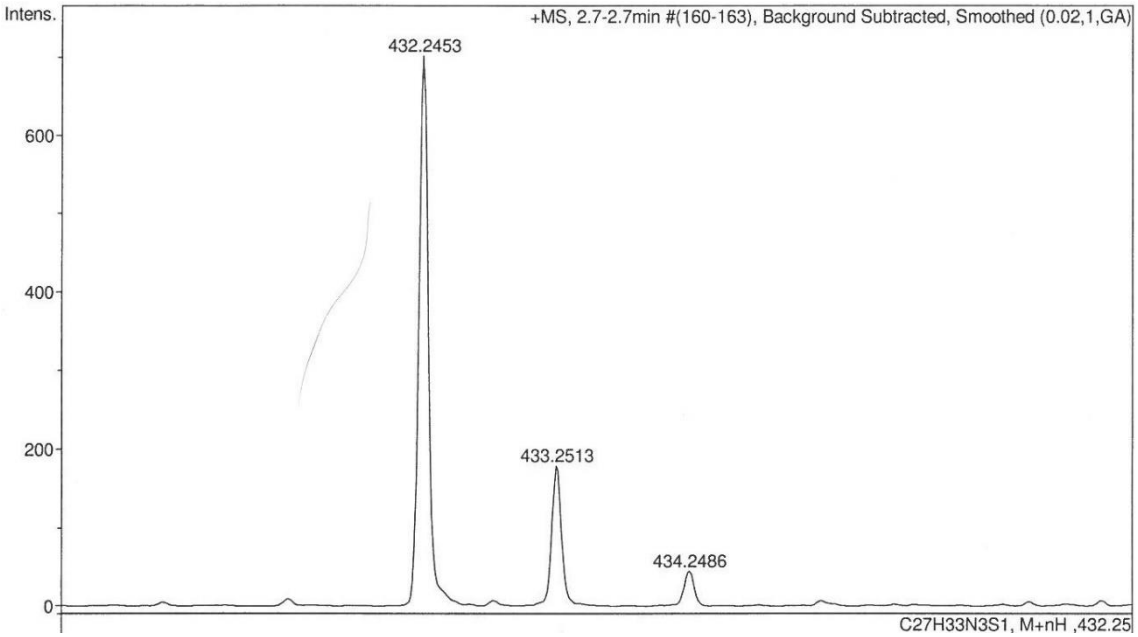
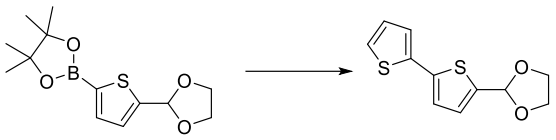


Figure S 2. Mass spectrum of **1T-DCV**. [1]

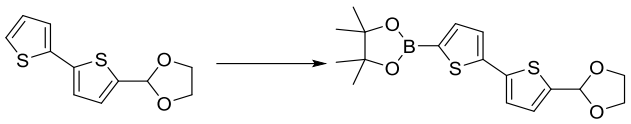
2-([2,2'-bithiophene]-5-yl)-1,3-dioxolane



A solution of 2-bromothiophene (867 mg, 5.32 mmol), Aliquat 336 (1.10 mL), Na_2CO_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_2Cl_2 (100 mL). The combined organic extracts were dried over Na_2SO_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, $CDCl_3$): δ (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).

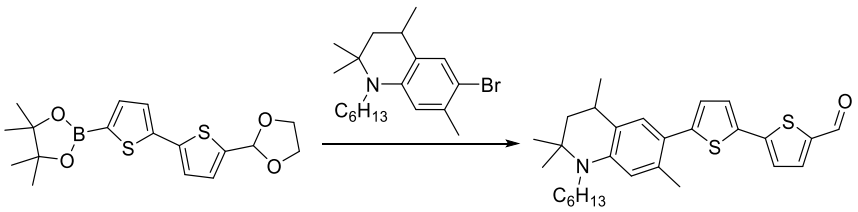
2-(5'-(1,3-dioxolane-2-yl)-[2,2'-bithiophene]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



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 $NaHCO_3$ (100 mL). The aqueous phase was extracted with CH_2Cl_2 (3x 50 mL). The combined organic extracts were dried over Na_2SO_4. 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.

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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



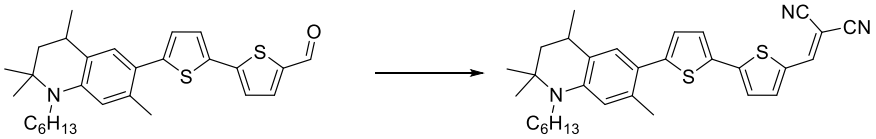
A solution of 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (242 mg, 0.69 mmol), Aliquat 336 (0.70 mL), Na_2CO_3 (2 M, 1.8 mL, 3.6 mmol) and 2-(5'-(1,3-dioxolane-2-yl)-[2,2'-bithiophene]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (250 mg, 0.69 mmol) in THF/toluene (50:50, 20 mL) was degassed for 60 minutes. A solution of tetrakis(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 CH_2Cl_2 (3x, 50 mL). The combined organic extracts were dried over Na_2SO_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 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 Na_2CO_3 (sat., 50 mL) and brine (50 mL). The aqueous phase was extracted with CH_2Cl_2 (2x, 30 mL). Removal of the solvent under reduced pressure gave the product as an orange solid (63.0 mg, 0.14 mmol, 99%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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:

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



5-(1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline-6-yl)thiophene-2-carbaldehyde (199.5 mg, 42.8 mmol), $CH_2(CN)_2$ (81.0 mg, 1.23 mmol) and β-alanine (5 mg, 0.06 mmol) were dissolved in a mixture of CH_2Cl_2/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 Et_2O (3x, 30 mL). The combined organic extracts were dried over $MgSO_4$, 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%)

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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 $C_{31}H_{35}N_3S_2$ [M+H]+: 514.2345, found: 514.2334.

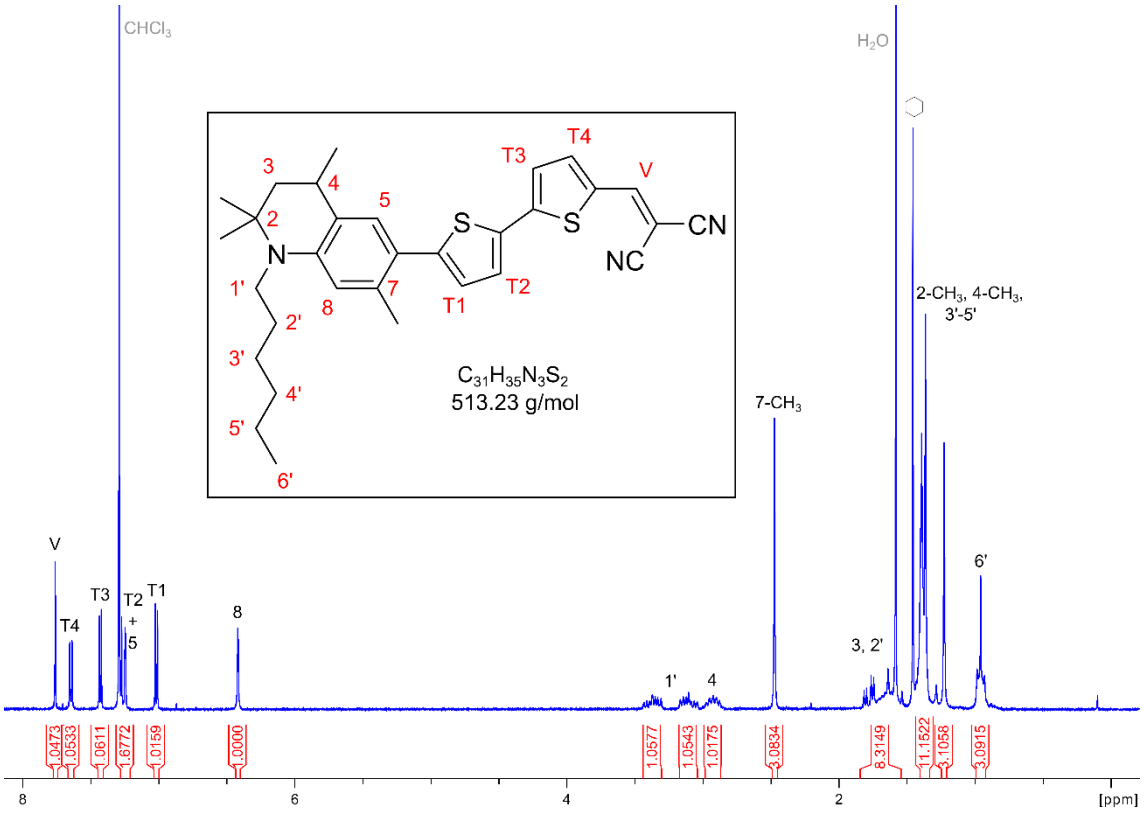


Figure S 3. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **2T-DCV**. [1]

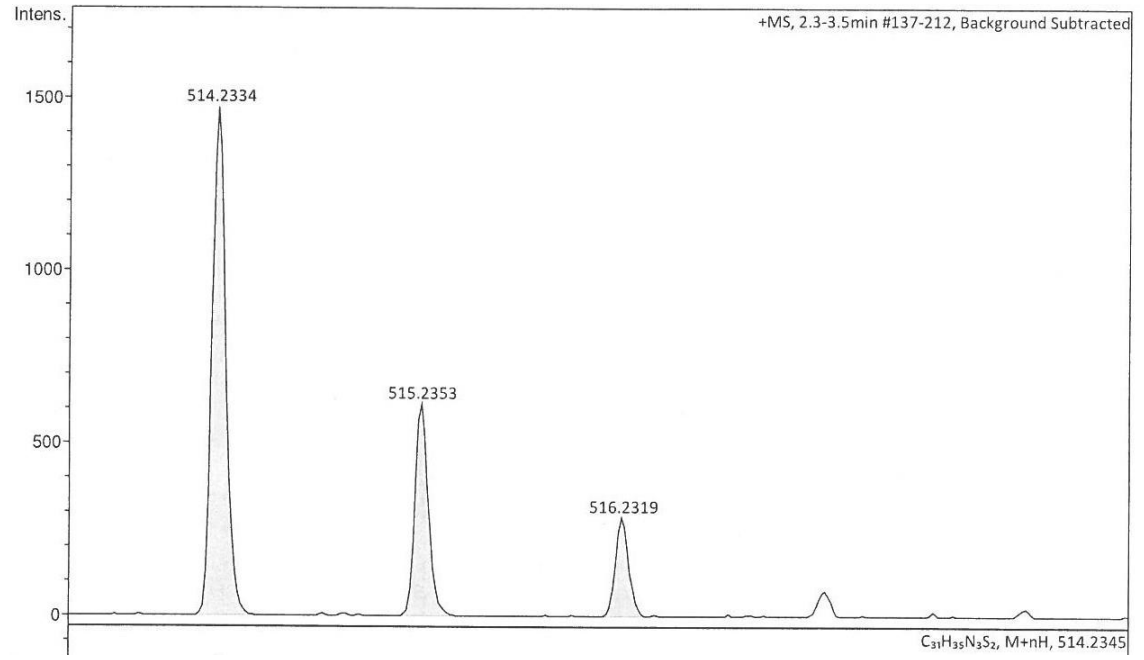
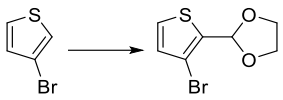


Figure S 4. Mass spectrum of **2T-DCV**. [1]

2-(3-bromothiophene-2-yl)-1,3-dioxolane

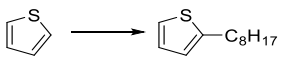


To a solution of LDA (2 M in THF, 12.3 mL, 24.5 mmol) in THF (dry, 40 mL) 3-bromothiophene (4.00 g, 2.30 mL, 24.5 mmol) was added slowly at 0 °C. The reaction mixture was stirred at 0 °C for one hour. After adding DMF (1.79 g, 1.9 mL, 24.5 mmol) the ice bath was removed and the solution was stirred for 3.5 hours. The reaction was terminated by pouring into water (25 mL). The aqueous phase was extracted with CH_2Cl_2 (50 mL). The organic phase was dried over Na_2SO_4 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 $NaHCO_3$ (40 mL) and water (40 mL). The organic phase was dried over Na_2SO_4 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, $CDCl_3$): 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, $CDCl_3$): δ (ppm) = 136.1, 130.5, 126.6, 110.4, 99.7, 65.6.

2-octylthiophene

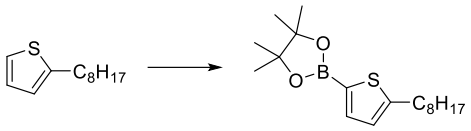


To a solution of thiophene (6.00 g, 5.70 mL, 71.32 mmol) in THF (dry, 60 mL), *n*-BuLi (1.6 M in hexane, 34.30 mL, 54.86 mmol) was added slowly at -78 °C. The cooling bath was removed and the solution stirred for one hour. 1-Bromooctane (10.59 g, 9.50 mL, 54.86 mmol) was added at room temperature and the reaction mixture refluxed for 90 hours. The reaction mixture was washed with brine (60 mL) and the aqueous phase was extracted with Et_2O (2x 50 mL). The combined organic phases were dried over $MgSO_4$ 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, $CDCl_3$): 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,

$CDCl_3$): 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.

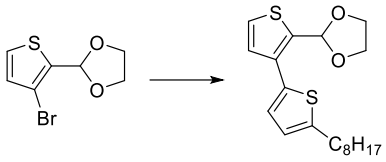
4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane



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 Et_2O (100 mL) and washed with a saturated solution of Na_2CO_3 (2x 50 mL). The organic phase was dried over Na_2SO_4 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.

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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

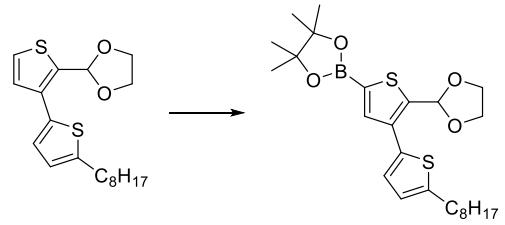


A solution of 2-(3-bromothiophene-2-yl)-1,3-dioxolane (1.00 g, 4.25 mmol), Aliquat 336 (0.8 mL), Na_2CO_3 (1 M, 11.0 mL, 11.0 mmol) and 4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane (1.37 g, 4.25 mmol) in THF/toluene (50:50, 60 mL) was degassed for 60 minutes. A solution of tetrakis(triphenyl-phosphine)palladium (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 Na_2SO_4 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%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-

NMR (62.5 MHz, $CDCl_3$): 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.

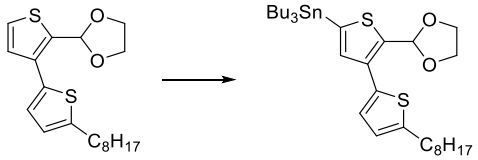
2-(2'-(1,3-dioxolane-2-yl)-5-octyl-[2,3'-bithiophene]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



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 Na_2CO_3 (40 mL). The organic phase was dried over Na_2SO_4 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.

^{1}H-NMR (250 MHz, $CDCl_3$): 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), 1.34 (s, 12H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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

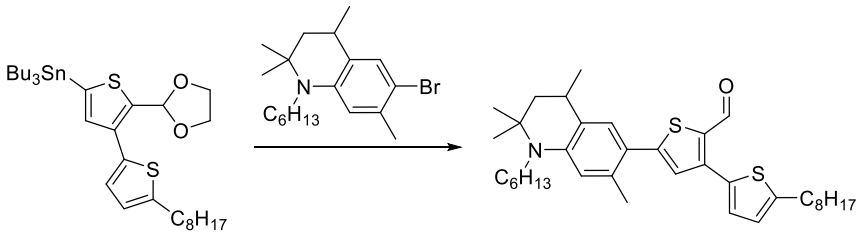


To a solution of 2-(5-octyl-[2,3'-bithiophene]-2'-yl)-1,3-dioxolane (830 mg, 2.37 mmol) in THF (dry, 25 mL) *n*-BuLi (1.6 M in hexane, 1.55 mL, 2.48 mmol) was added slowly at -78 °C. The solution was stirred for 15 minutes at -78 °C and heated to room temperature over a period of one hour. After cooling 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 Na_2CO_3 (40 mL). The organic phase was dried over Na_2SO_4 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, $CDCl_3$): δ (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



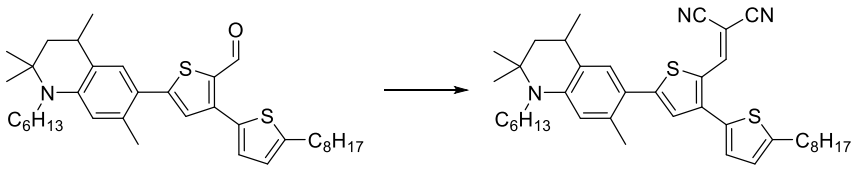
$Pd(PPh_3)_4$ (80 mg, 69 µmol) was added to a solution of (2'-(1,3-dioxolane-2-yl)-5-octyl-[2,3'-bithiophene]-5'-yl)tributylstannane (800 mg, 1.25 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (292 mg, 0.83 mmol) in degassed toluene (40 mL). The solution was refluxed for 16 hours. After cooling down the reaction mixture was washed with brine (80 mL). The aqueous phase was extracted with CH_2Cl_2 (1x 40 mL). The combined organic phases were dried over Na_2SO_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 µmol) 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_2Cl_2 until no color was left. The combined organic phases were dried over Na_2SO_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 µmol, 21%).

^{1}H-NMR (250 MHz, $CDCl_3$): δ (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, $CDCl_3$): δ (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), $CH_2(CN)_2$ (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 CH_2Cl_2 (30 mL). The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. Multiple purification steps via column chromatography (eluent cyclohexane/EE 30 : 1), reverse phase silica gel (C_{18}, eluent THF/water 3 : 1) and size exclusion chromatography gave the product as violet solid (16 mg, 25.6 µmol, 10%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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 $C_{39}H_{51}N_3S_2$ [M+Na]+: 648.3417, found: 648.3397.

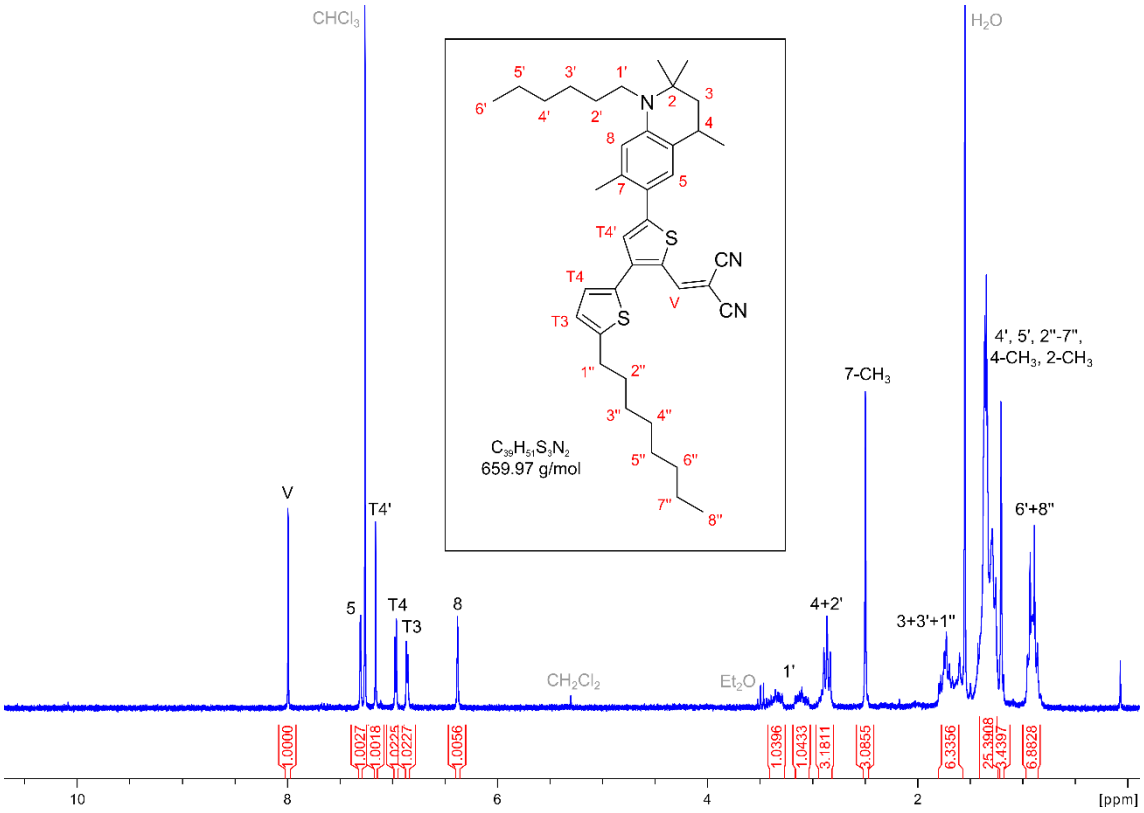


Figure S 5. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **1Tβ-DCV**. [1]

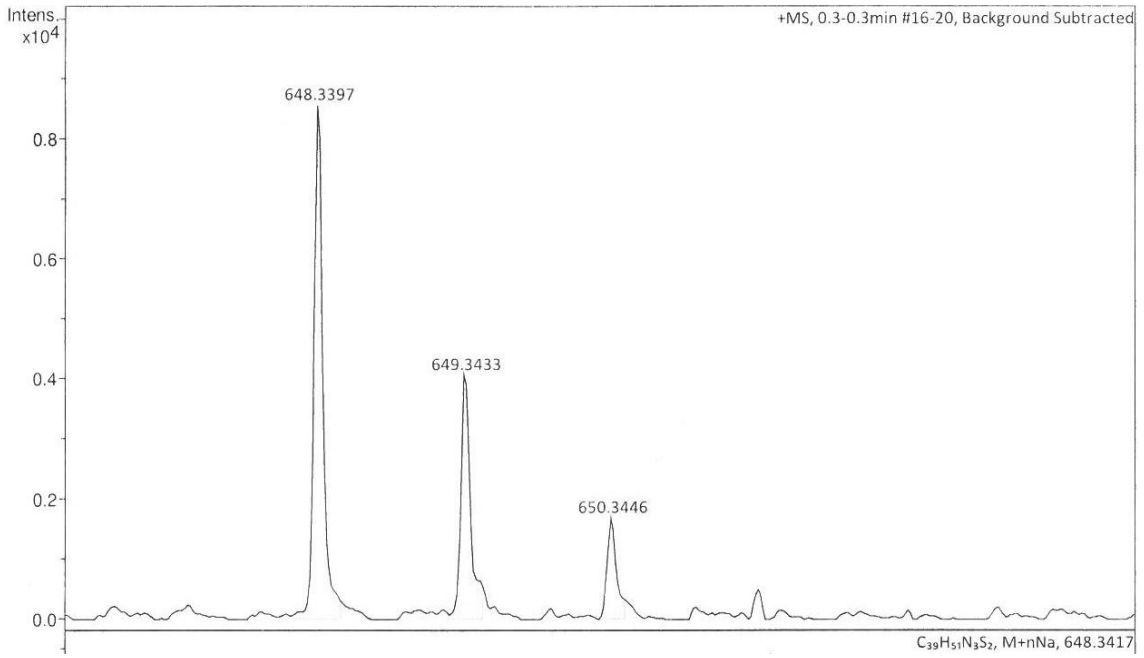
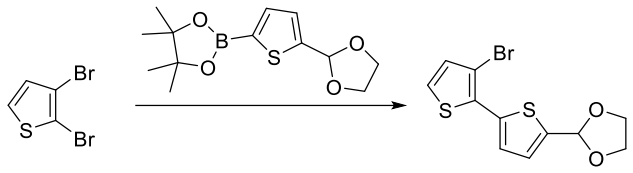


Figure S 6. Mass spectrum of **1Tβ-DCV**. [1]

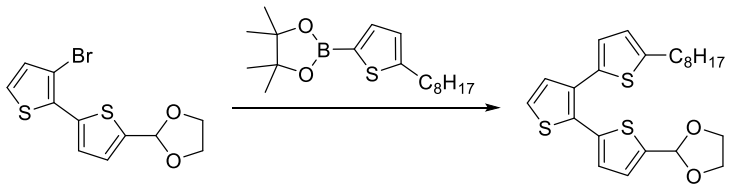
2-(3'-bromo-[2,2'-bithiophene]-5-yl)-1,3-dioxolane



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) und Na_2CO_3 (2 M, 16.5 mL, 33 mmol) in 1,4-dioxane (100 mL) was degassed for 90 minutes. $Pd(PPh_3)_4$ (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 Et_2O (5x 80 mL). The combined organic phases were dried over Na_2SO_4 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%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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-yl)-1,3-dioxolane

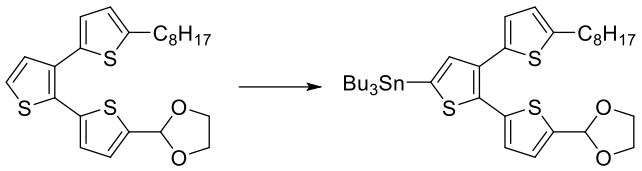


A solution of 2-(3'-bromo-[2,2'-bithiophene]-5-yl)-1,3-dioxolane (599 mg, 1.89 mmol), Aliquat 336 (0.5 mL), Na_2CO_3 (2 M, 4.2 mL, 8.40 mmol) and 4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane (600 mg, 1.86 mmol) in THF/toluene (50 : 50, 60 mL) was degassed for 60 minutes. A solution 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 Na_2SO_4 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%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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, $CDCl_3$): δ (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.

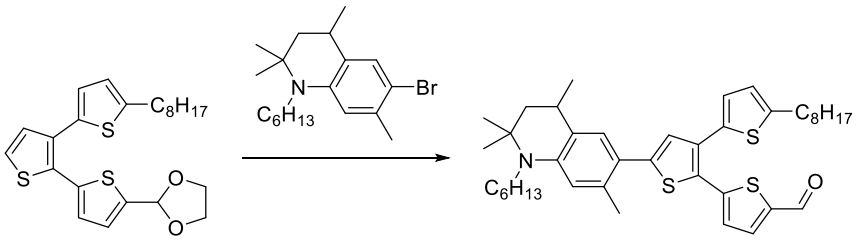
(5-(1,3-dioxolane-2-yl)-5''-octyl-[2,2':3',2''-terthiophene]-5'-yl)tri-butylstannane



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_2Cl_2 (40 mL). The aqueous phase was extracted with CH_2Cl_2 (1x 40 mL). The combined organic phases were washed with a saturated solution of Na_2CO_3 (40 mL), dried over Na_2SO_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, $CDCl_3$): δ (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



$Pd(PPh_3)_4$ (71.5 mg, 61 µmol) 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-

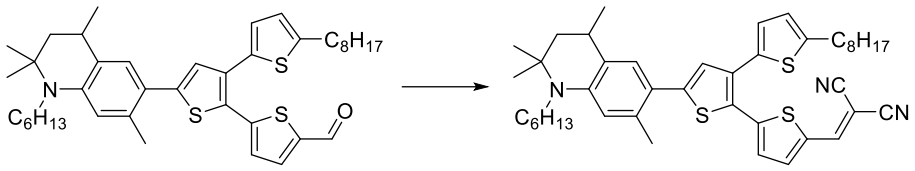
1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (275 mg, 0.78 mmol) in degassed toluene (25 mL). The solution was refluxed for 42 hours. After cooling down the reaction mixture was washed with brine (40 mL). The aqueous phase was extracted with CH_2Cl_2 (5x 30 mL). The combined organic phases were dried over Na_2SO_4 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 $NaHCO_3$ solution (20 mL) and brine (20 mL). The aqueous phase was extracted with CH_2Cl_2 until no color was left. The combined organic phases were dried over Na_2SO_4 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%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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), $CH_2(CN)_2$ (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 CH_2Cl_2 until no color was left. The combined organic phases were dried over Na_2SO_4 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%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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 $C_{43}H_{53}N_3S_3$ $[M+H]^+$: 708.3474, found: 708.3452.

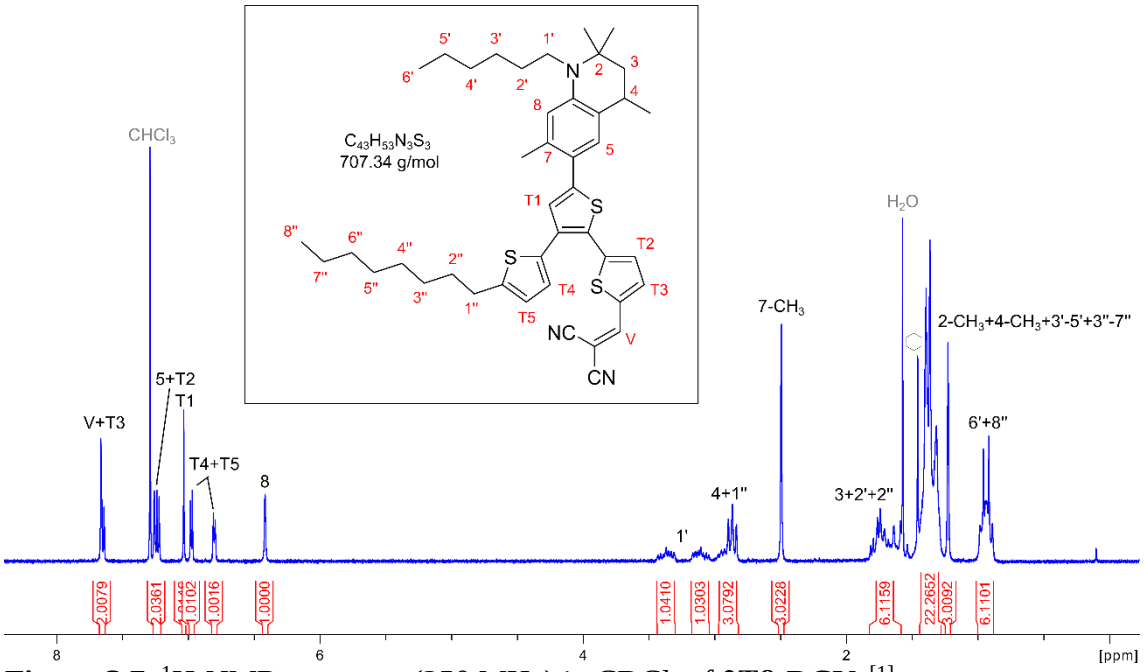


Figure S 7. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **2Tβ-DCV**. [1]

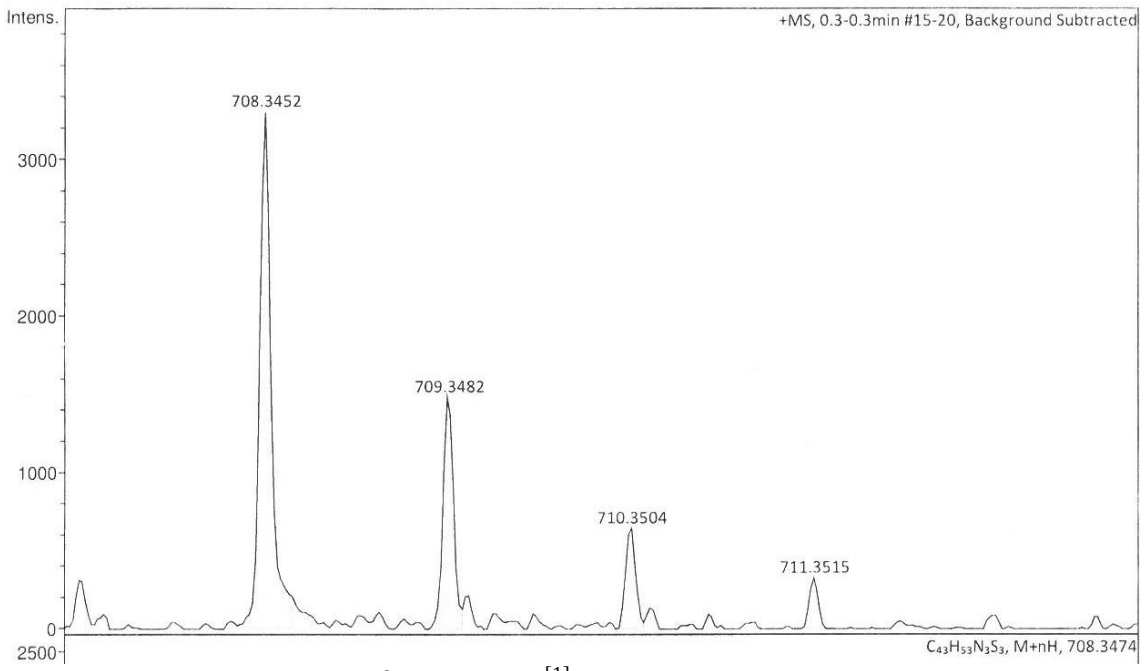
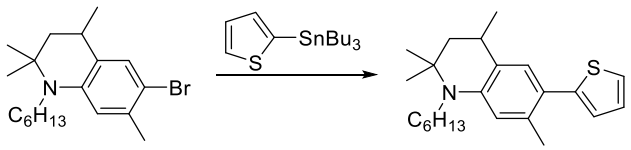


Figure S 8. Mass spectrum of **2Tβ-DCV**. [1]

1-hexyl-2,2,4,7-tetramethyl-6-(thiophene-2-yl)-1,2,3,4-tetrahydro-quinoline

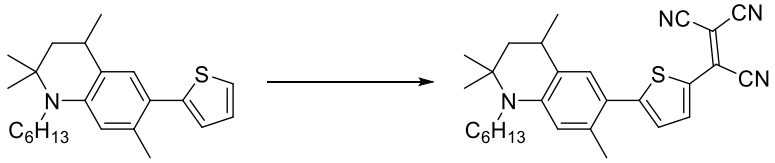


$Pd(PPh_3)_4$ (170 mg, 147 µmol) was added to a solution of trimethyl(5''-octyl-5'-(tributylstannyl)-[2,2':3',2''-terthiophene]-5-yl)silane (1.59 g, 1.35 mL, 4.26 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (1.0 g, 2.84 mmol) in degassed toluene (50 mL). The solution was refluxed for 16 hours. After cooling down the reaction mixture was washed with brine (40 mL). The aqueous phase was extracted with $CHCl_3$ (3x 40 mL). The combined organic phases were dried over Na_2SO_4 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 ^{1}H-NMR) of contamination in form of tin organyl (product: ~500 mg, 1.40 mmol, 50%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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-tetrahydro-quinoline (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 $CHCl_3$ (3x 20 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. Purification via column chromatography gave the product as green solid (101 mg, 0.22 mmol, 79%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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),

2.53 (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 $C_{28}H_{32}N_4S$ $[M+Na]^+$: 479.2240, found: 479.2231.

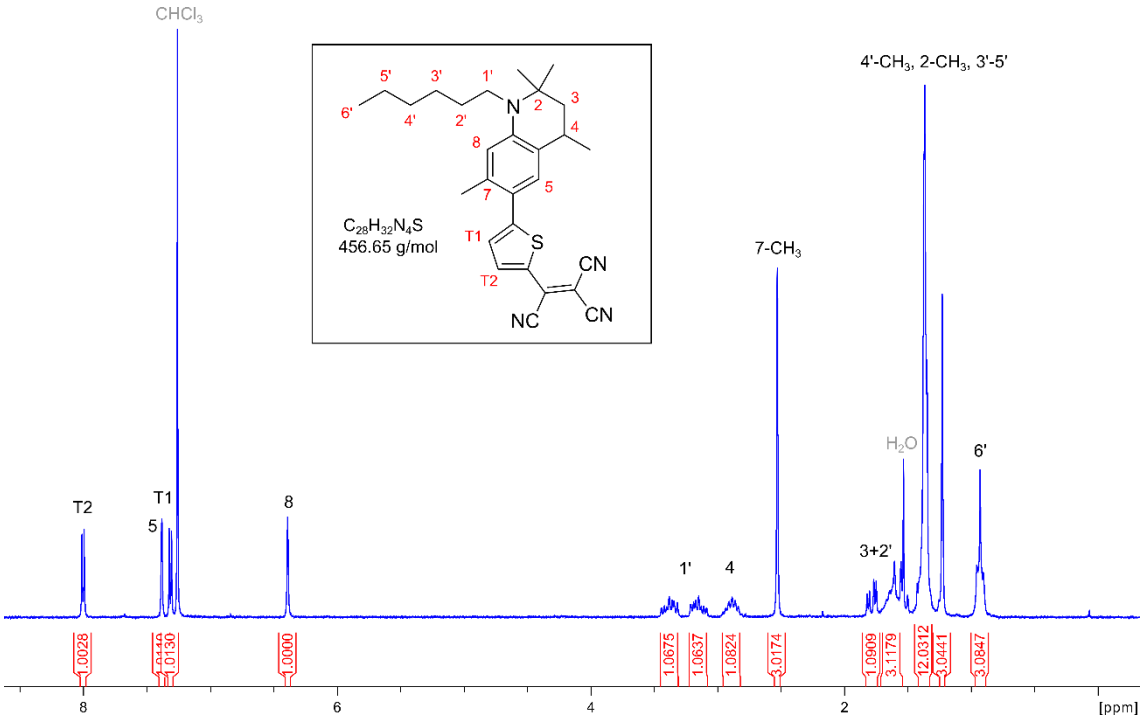


Figure S 9. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **1T-TCV**. [1]

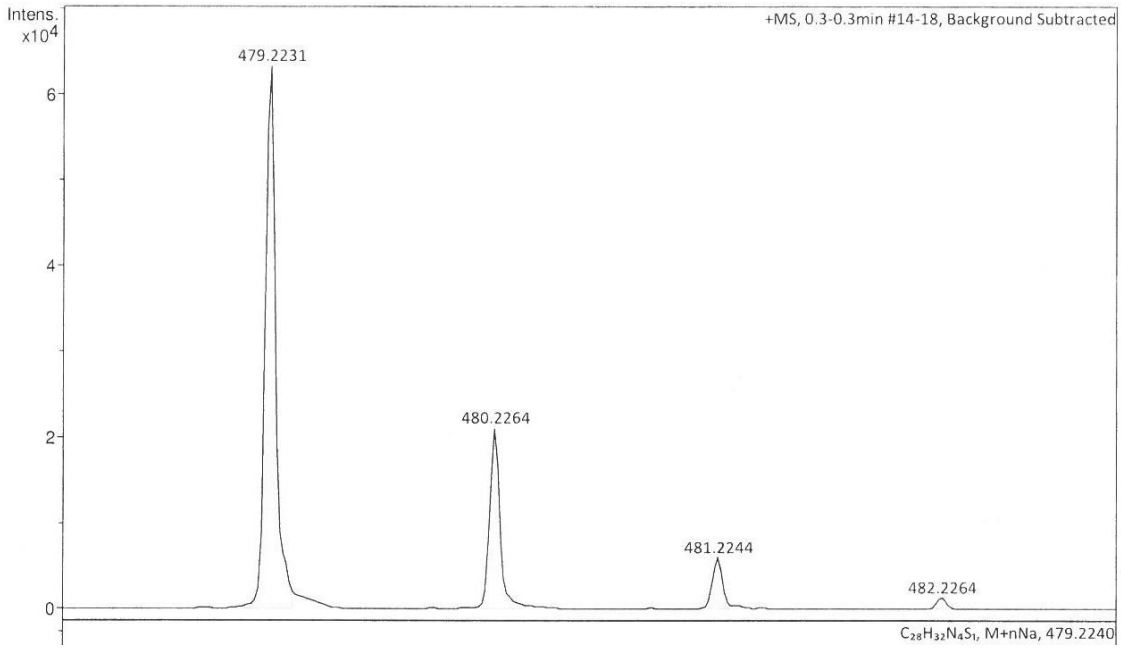
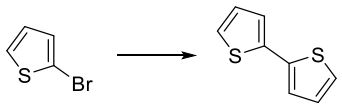


Figure S 10. Mass spectrum of **1T-TCV**. [1]

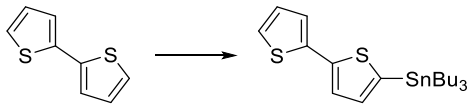
2,2'-bithiophene



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 Et_2O (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)Cl_2 (950 mg, 1.8 mmol) und 2-bromothiophene (14.6 g, 8.7 mL, 89.5 mmol) in Et_2O (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 $CHCl_3$ (4x 50 mL). The combined organic phases were dried over Na_2SO_4 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%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 137.5, 127.9, 124.5, 123.9.

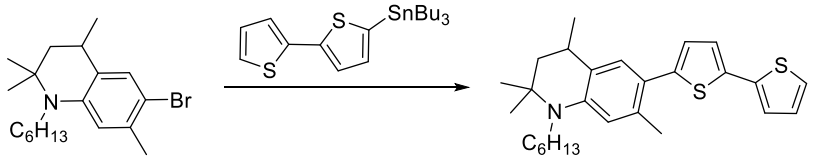
[2,2'-bithiophene]-5-yltributylstannane



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 NH_4Cl (30 mL). The aqueous phase was extracted with CH_2Cl_2 (2x 50 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. The product was isolated as orange liquid (6.06 g, 80%, determined from ^{1}H-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.

^{1}H-NMR (250 MHz, $CDCl_3$): 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

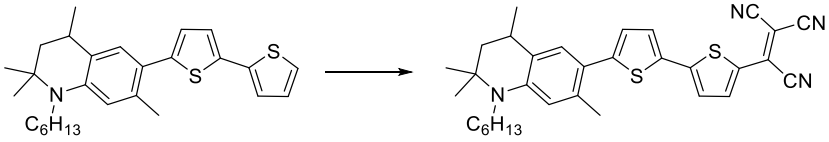


$Pd(PPh_3)_4$ (175 mg, 151 µmol) was added to a solution of [2,2'-bithiophene]-5-yl-tributylstannane (1.90 g, 4.17 mmol) und 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (0.98 g, 2.78 mmol) in degassed toluene (50 mL). The solution was refluxed for 16 hours. After cooling down the 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_2SO_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, $CDCl_3$): δ (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



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_2SO_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, 110 µmol, 34%).

^{1}H-NMR (250 MHz, $CDCl_3$): δ (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, $CDCl_3$): δ (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 $C_{32}H_{34}N_4S_2$ [M+H]+: 561.2117, found: 561.2101.

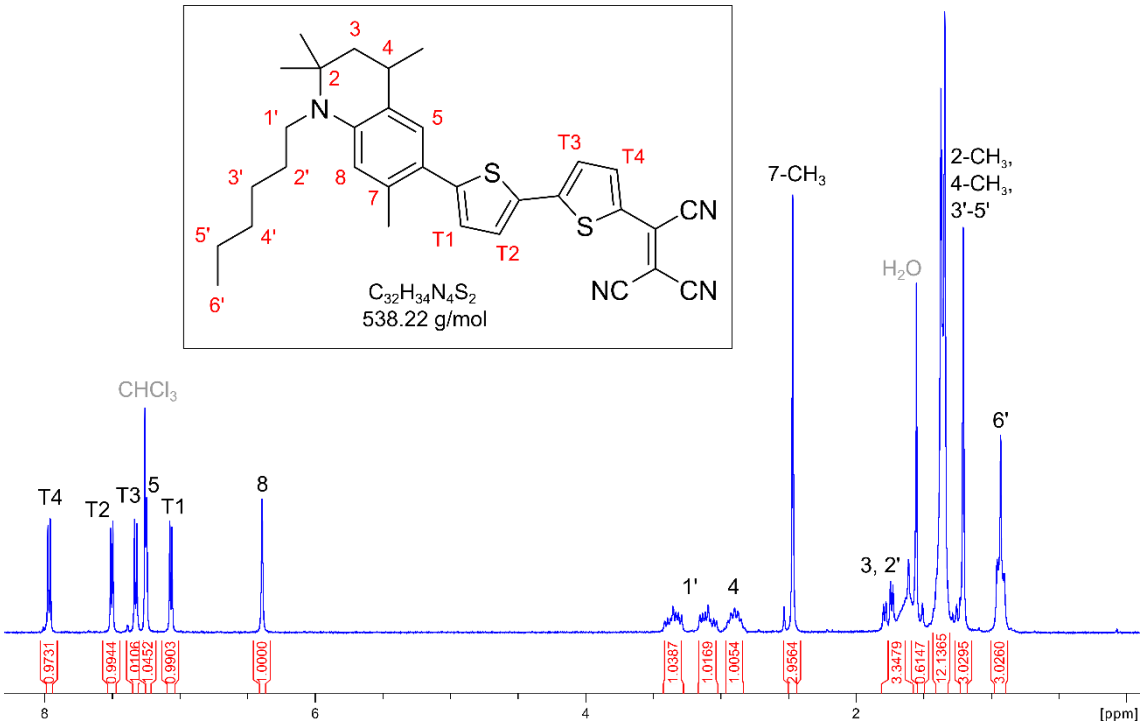


Figure S 11. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **2T-TCV**. [1]

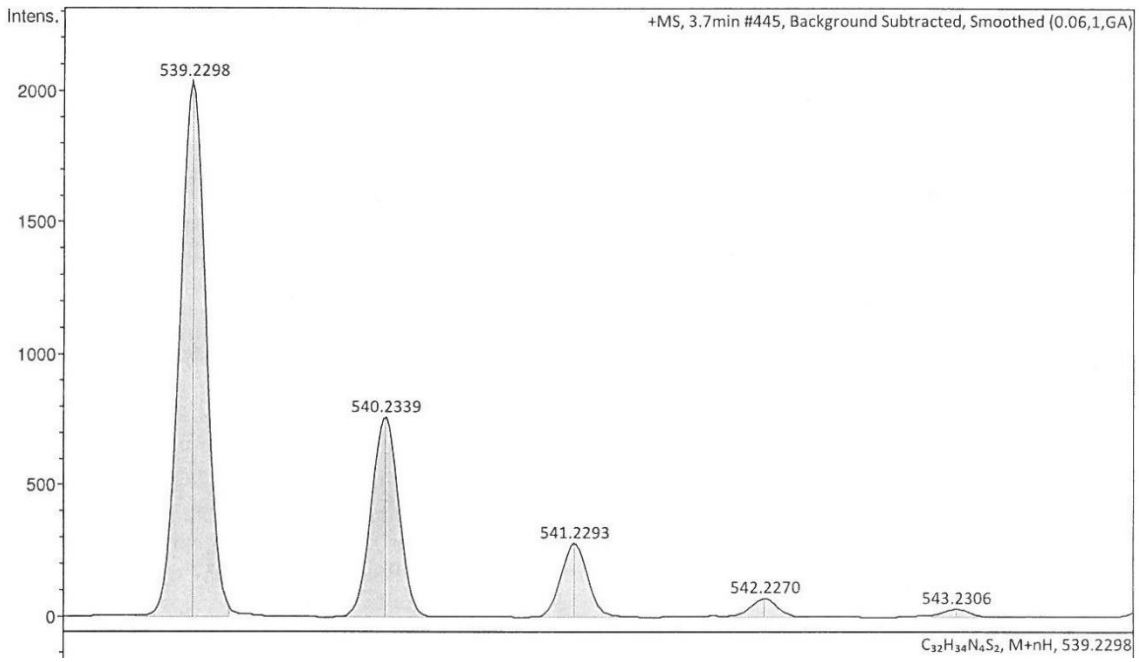
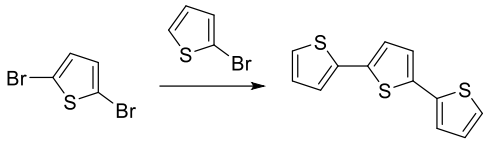


Figure S 12. Mass spectrum of **2T-TCV**. [1]

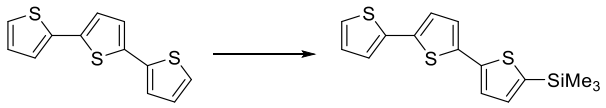
2,2':5',2''-terthiophene



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 Et_2O (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)Cl_2 (850 mg, 1.61 mmol) and 2,5-dibromothiophene (9.68 g, 4.50 mL, 40.0 mmol) in Et_2O (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 CH_2Cl_2 (800 mL in total). The combined organic phases were dried over Na_2SO_4 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 %).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 137.2, 136.3, 128.0, 124.6, 124.4, 123.8.

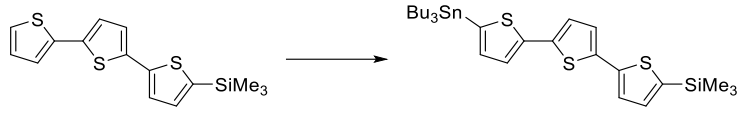
[2,2':5',2''-terthiophene]-5-yl-trimethylsilane



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 CH_2Cl_2 (50 mL). The combined organic phases were dried over Na_2SO_4 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%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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).

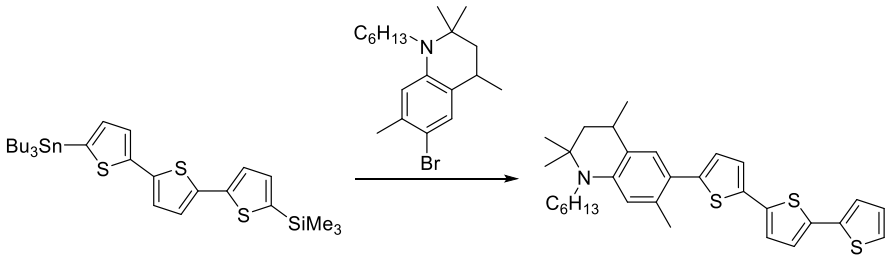
trimethyl-(5''-(tributylstannyl)-[2,2':5',2''-terthiophene]-5-yl)silane



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 NH_4Cl (30 mL). The aqueous phase was extracted with Et_2O (3x 20 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. The product was isolated as colorless oil (1.40 g, 80%, determined from ^{1}H-NMR). The product further contained ~20% educt and tin organyl. The product was used without further purification.

^{1}H-NMR (250 MHz, $CDCl_3$): 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



$Pd(PPh_3)_4$ (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 CH_2Cl_2 (3x 30 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification via column chromatography (eluent PE/EE 15 : 1) and size exclusion chromatography (eluent $CHCl_3$) 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.

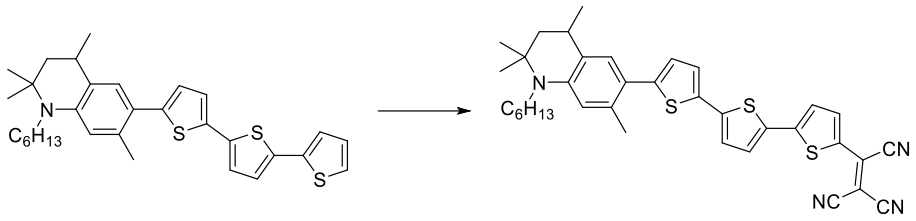
A solution of 1-hexyl-2,2,4,7-tetramethyl-6-(5''-(trimethylsilyl)-[2,2':5',2''-terthiophene]-5-yl)-1,2,3,4-tetrahydroquinoline (333 mg, 560 µmol) and TBAF (1 M in THF, 840 µL, 840 µmol) in THF (dry, 40 mL) was stirred for one hour at room temperature. The reaction mixture was poured into water (50 mL) and the aqueous phase extracted

with CH_2Cl_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



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 cooling bath was removed and 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 (eluent PE/EE 10 : 1, 5 : 1 and $CHCl_3$) followed by size exclusion chromatography (eluent $CHCl_3$) 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 $C_{36}H_{36}N_4S_3$ [M+H]+: 621.2175, found: 621.2163.

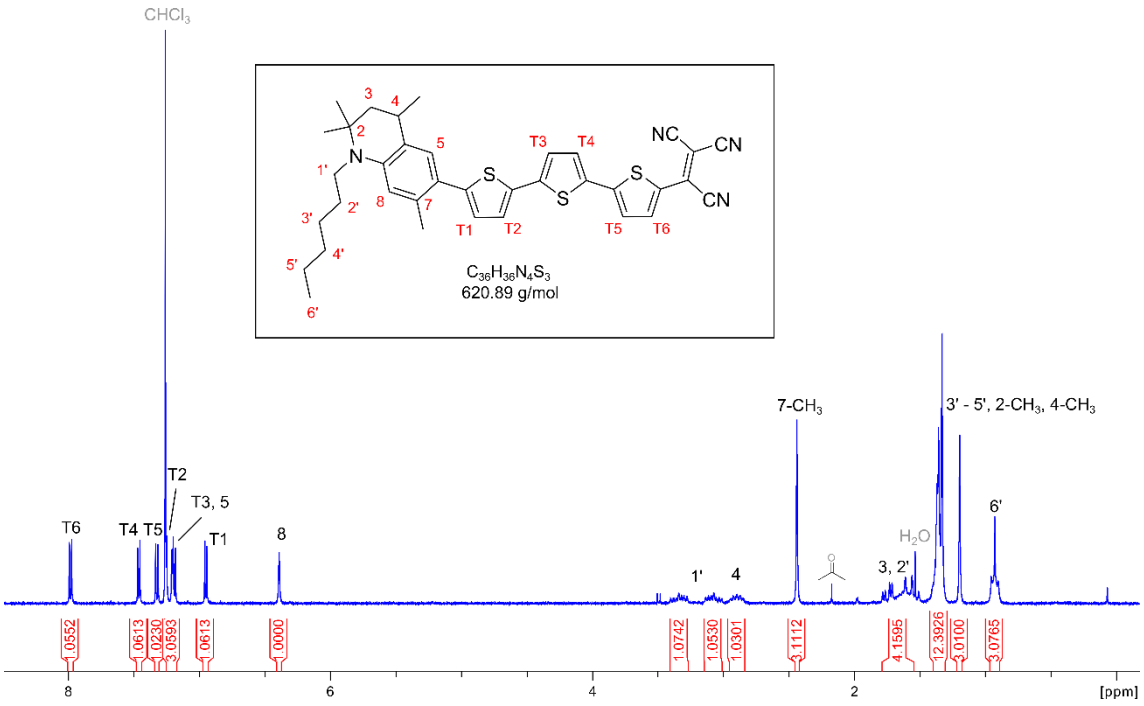


Figure S 13. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **3T-TCV**. [1]

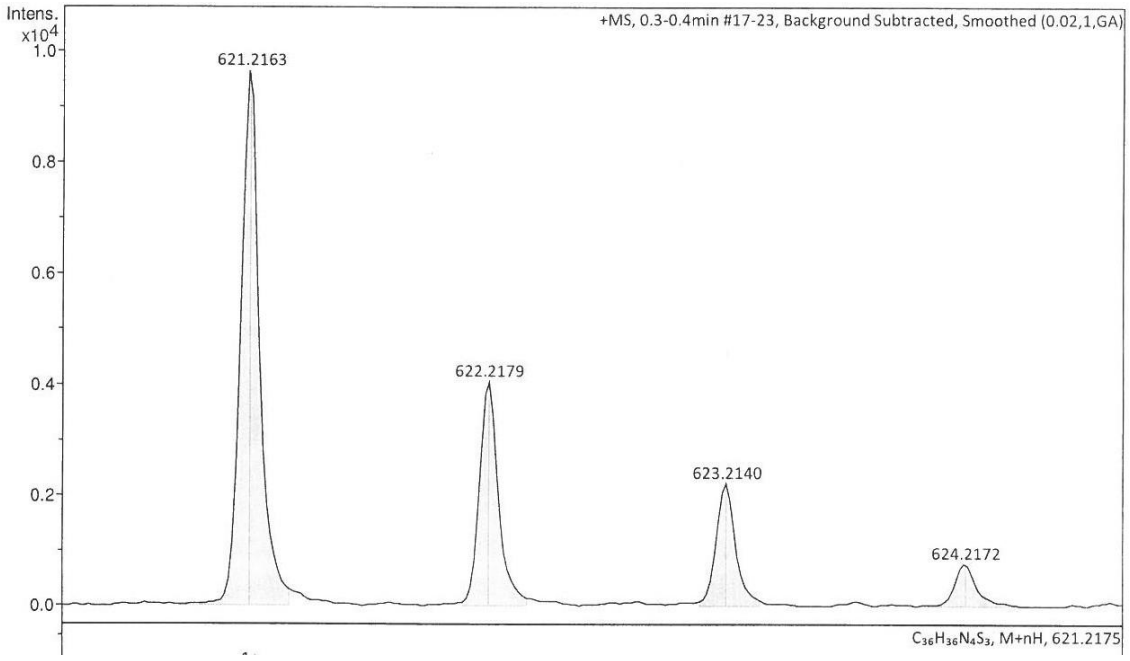
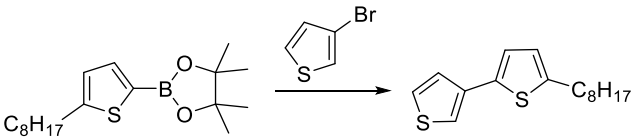


Figure S 14. Mass spectrum of **3T-TCV**. [1]

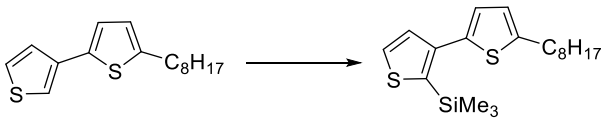
5-octyl-2,3'-bithiophene



A solution of 3-bromothiophene (2.22 g, 13.62 mmol), Aliquat 336 (2.30 mL), Na_2CO_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 tetrakis(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_2Cl_2 (3x 100 mL). The combined organic phases were washed with brine (2x 75 mL), dried over Na_2SO_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.

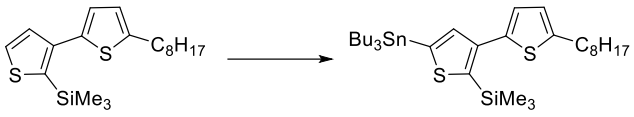
trimethyl(5-octyl-[2,3'-bithiophene]-2'-yl)silane



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_2Cl_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.

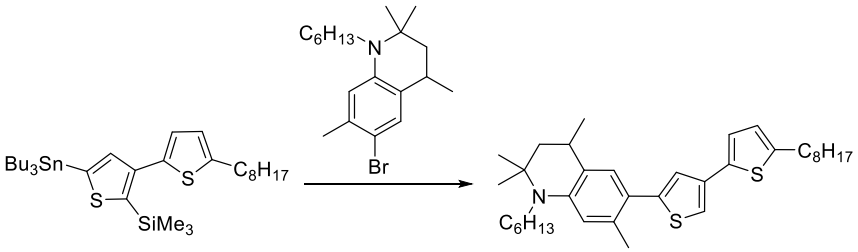
trimethyl(5-octyl-5'-(tributylstannyl)-[2,3'-bithiophene]-2'-yl)silane



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 Na_2CO_3 (2x 75 mL) and water (2x 75 mL). The aqueous phase was extracted with CH_2Cl_2 (3x 75 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. The product was isolated as yellow liquid (2.02 g, 80%, determined from ^{1}H-NMR). The product further contained ~20% contaminations in the aromatic region and tin organyl. The product was used without further purification.

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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



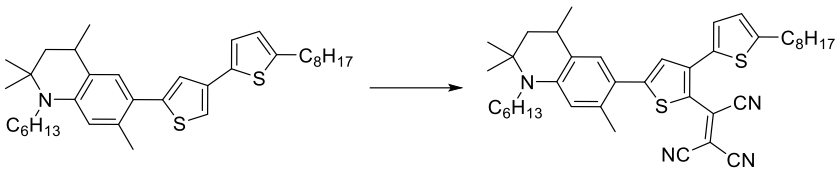
A solution of $Pd(PPh_3)_4$ (195 mg, 167 µmol) in degassed THF was added to a solution of trimethyl(5-octyl-5'-(tributylstannyl)-[2,3'-bithiophene]-2'-yl)silane (2.0 g, 3.13 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (740 mg, 2.09 mmol) in degassed toluene (100 mL). The 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 CH_2Cl_2 (3x 100 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification via

column chromatography (eluent PE/EE 10 : 1) and size exclusion chromatography (eluent $CHCl_3$) gave the product as yellow oil (523 mg, 948 µmol, 45%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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).

1Tβ-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 CH_2Cl_2 (3x 50 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. Multiple purification steps via column chromatography (eluent PE/EE 20 : 1, 15 : 1 and $CHCl_3$) followed by size exclusion chromatography (eluent $CHCl_3$) gave the product as copper red solid (89 mg, 137 µmol, 46%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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), 1.18-1.51 (m, 6H), 1.44-1.25 (m, 22H), 1.23 (s, 3H), 0.97-0.85 (m, 6H). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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 $C_{40}H_{50}N_4S_2$ $[M+Na]^+$: 673.3369, found: 673.3365.

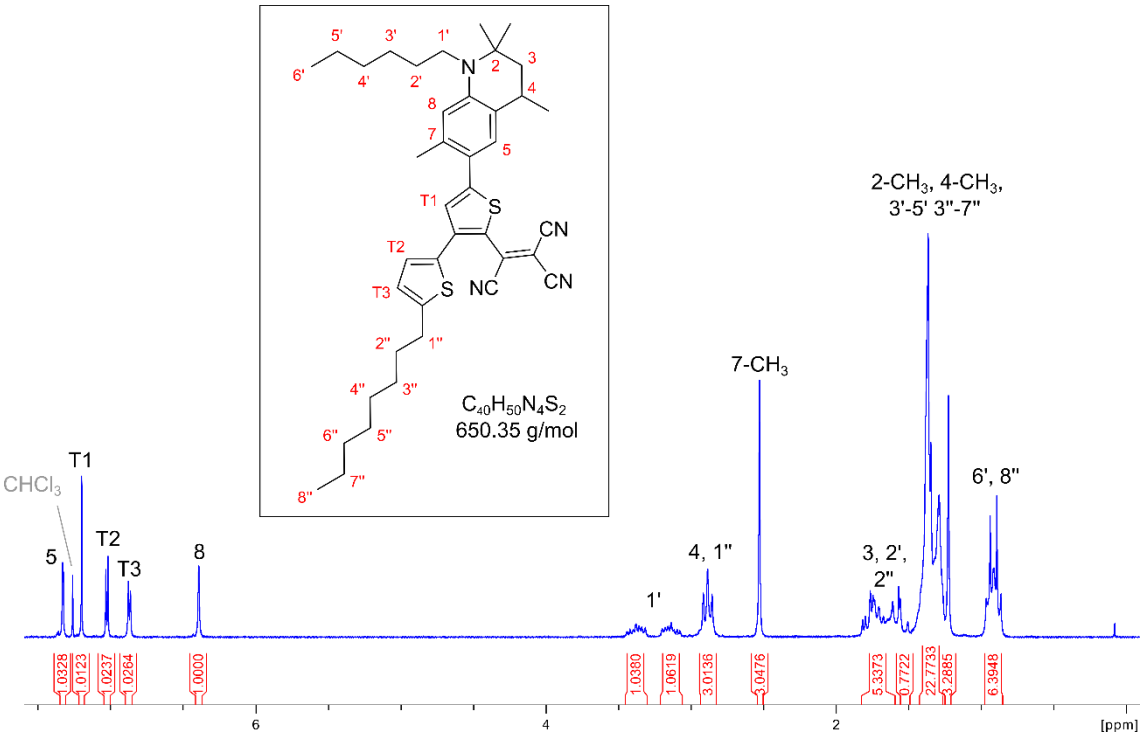


Figure S 15. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **1Tβ-TCV.** [1]

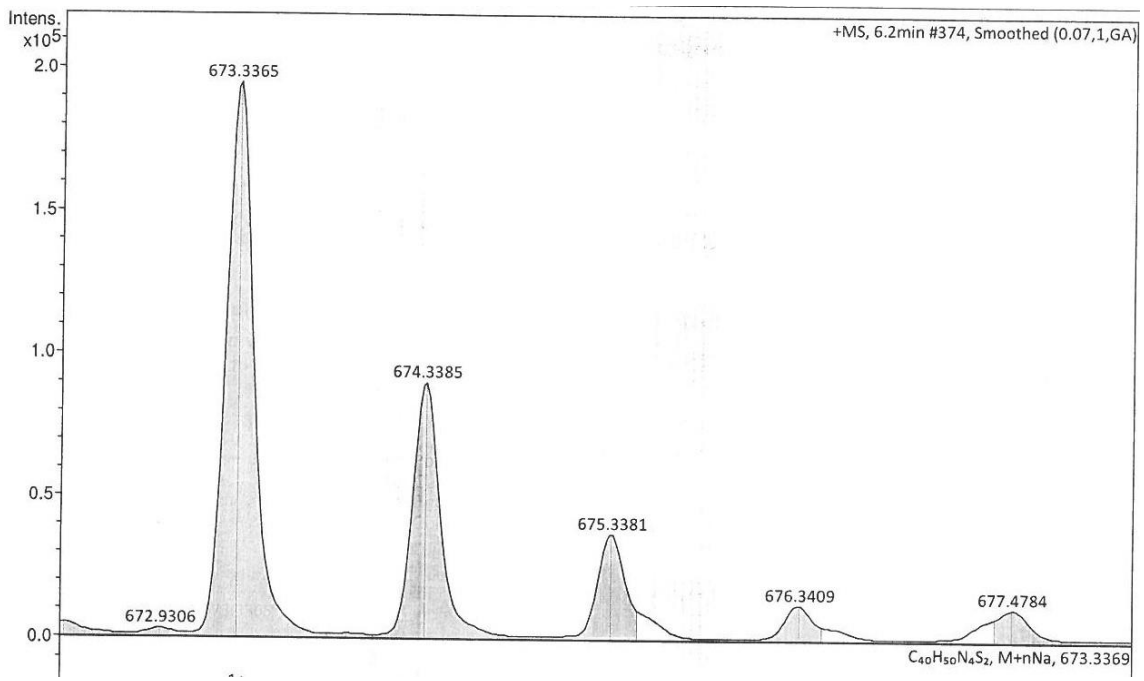
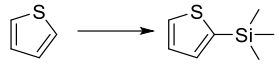


Figure S 16. Mass spectrum of **1Tβ-TCV**. [1]

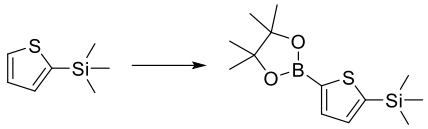
trimethyl(thiophene-2-yl)silane



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 Et_2O (40 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. Fractional distillation gave the product as a colorless liquid (5.16 g, 33.03 mmol, 69%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 140.2, 134.1, 130.5, 128.2, 0.2.

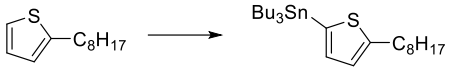
trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)thiophene-2-yl)silane



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 Na_2CO_3 (40 mL). The aqueous phase was extracted wit Et_2O (50 mL). The organic phase was dried over $MgSO_4$ 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.

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 148.6, 138.0, 135.2, 84.2, 24.9, 0.1.

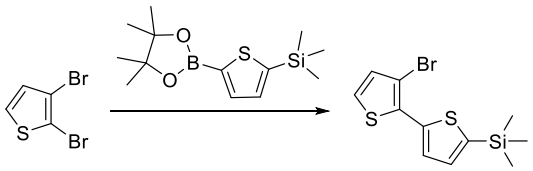
tributyl(5-octylthiophene-2-yl)stannane



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 $CHCl_3$ (2x 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. The product was isolated as yellow liquid (15.75 g, 32.44 mmol, 91%(determined from ^{1}H-NMR)). The product further contained 9% 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) = 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).

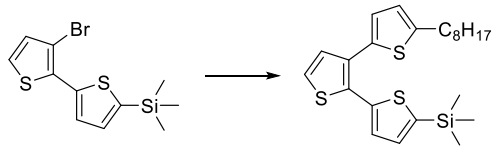
(3'-bromo-[2,2'-bithiophene]-5-yl)trimethylsilane



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 Na_2CO_3 (2 M, 33 mL, 66 mmol) in 1,4-dioxane (200 mL) was degassed for 70 minutes. $Pd(PPh_3)_4$ (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 Et_2O (2x 50 mL). The combined organic phases were dried over $MgSO_4$ 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%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 141.7, 139.5, 134.3, 132.6, 132.0, 128.0, 124.5, 107.9, 0.1.

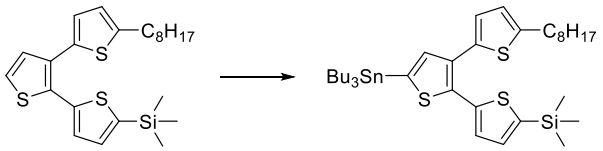
trimethyl(5''-octyl-[2,2':3',2''-terthiophene]-5-yl)silane



$Pd(PPh_3)_4$ (570 mg, 49.3 mmol) was added to a solution of tributyl(5-octylthiophene-2-yl)stannane (7.1 g, 14.65 mmol) und (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 brine (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 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), 0.88 (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, 0.1.

trimethyl(5''-octyl-5'-(tributylstannyl)-[2,2':3',2''-terthiophene]-5-yl)-silane

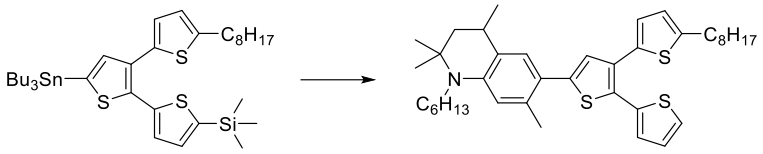


To a solution of trimethyl(5''-octyl-[2,2':3',2''-terthiophene]-5-yl)silane (3.80 g, 8.78 mmol) in THF (dry, 75 mL) *n*-BuLi (1.6 M in hexane, 5.80 mL, 9.28 mmol) was added slowly at -78 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature for one hour. After cooling 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 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, $CDCl_3$): δ (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



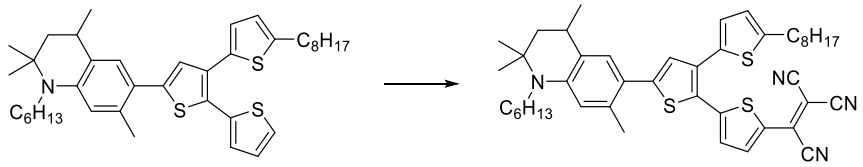
$Pd(PPh_3)_4$ (108 mg, 941 µmol) was added to a solution of trimethyl(5''-octyl-5'-(tributylstannyl)-[2,2':3',2''-terthiophene]-5-yl)silane (1.07 g, 1.45 mmol) and 6-bromo-1-hexyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline (3.46 g, 0.98 mmol) in degassed toluene (50 mL). The solution was refluxed 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_2CO_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, $CDCl_3$): δ (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, $CDCl_3$): δ (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 $CHCl_3$ (30 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification via column chromatography (eluent $CHCl_3$) gave the product as black green solid (25 mg, 23 µmol, 28%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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 $C_{44}H_{52}N_4S_3$ $[M+Na]^+$: 755.3246, found: 755.3255.

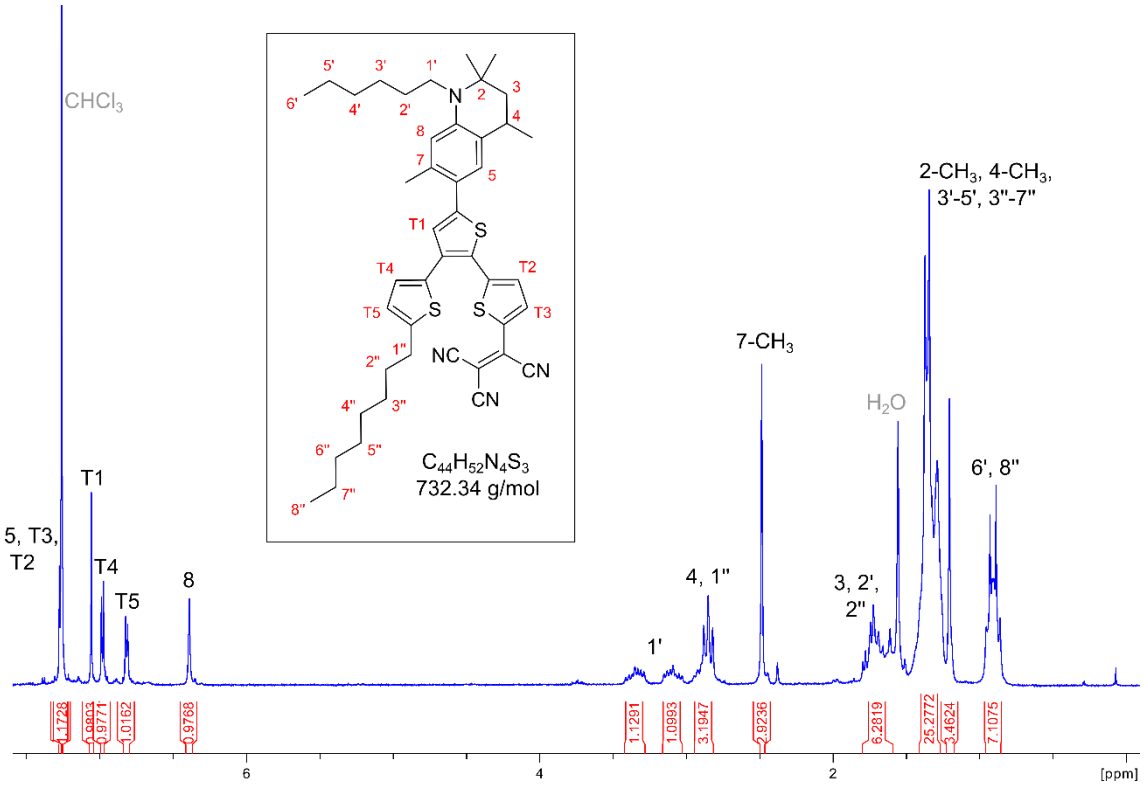


Figure S 17. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **2Tβ-TCV**. [1]

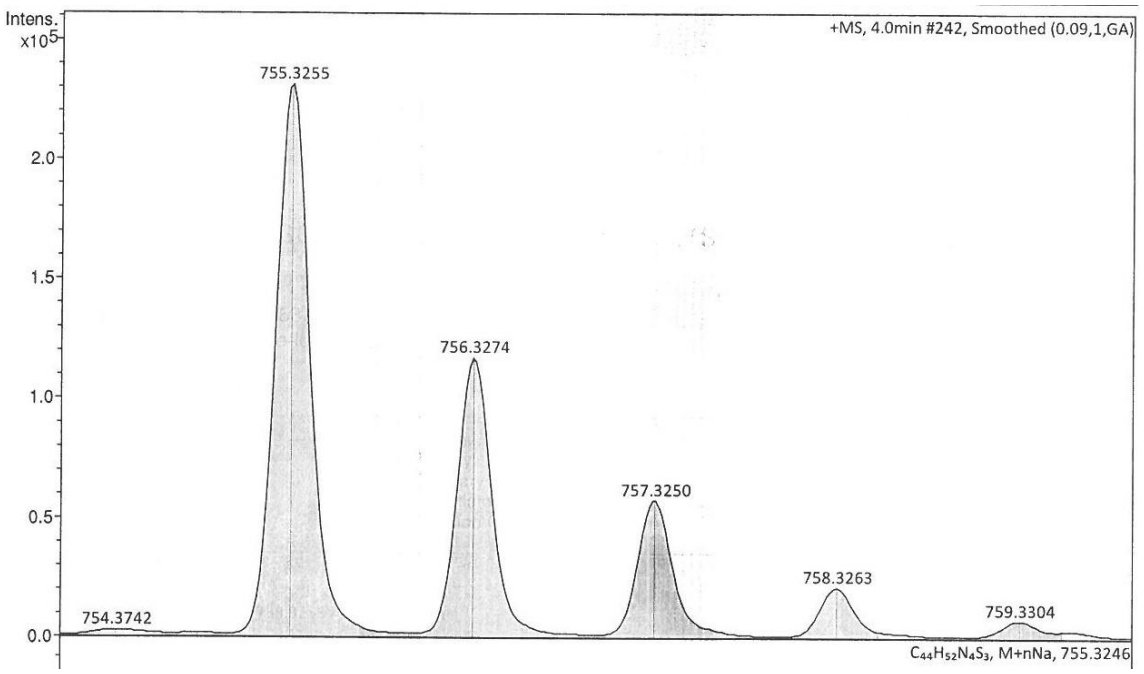


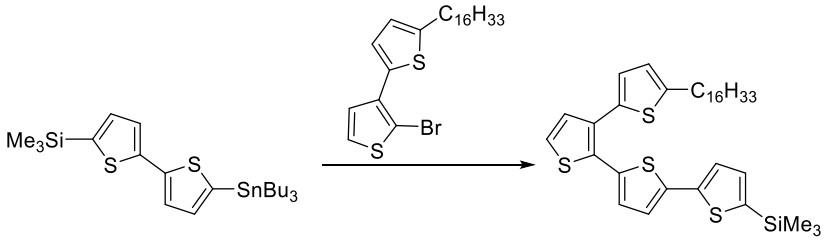
Figure S 18. Mass spectrum of **2Tβ-TCV**. [1]

trimethyl(5'-(tributylstannyl)-[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 NH_4Cl (50 mL). The aqueous phase was extracted with Et_2O (2x 50 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. The product was isolated as orange liquid (11.49 g, 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) = 7.30 (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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 142.87, 142.85, 139.4, 136.8, 136.2, 134.8, 125.1, 124.9, 29.1, 27.4, 13.8, 11.0, 0.1.

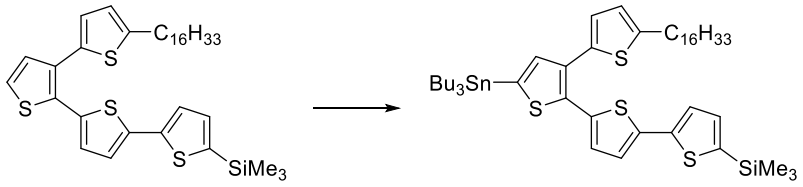
(5'''-hexadecyl-[2,2':5',2'':3'',2'''-quaterthiophene]-5-yl)trimethyl-silane



$Pd(PPh_3)_4$ (108 mg, 941 µmol) was added to a solution of von trimethyl(5'-(tributyl-stannyl)-[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 CH_2Cl_2 (4x 80 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. Purification via recrystallization from MeOH/$CHCl_3$/THF 200 : 50 : 50 mL gave the product as green solid (3.44 g, 5.49 mmol, 64 %).

^{1}H-NMR (250 MHz, $CDCl_3$): 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).

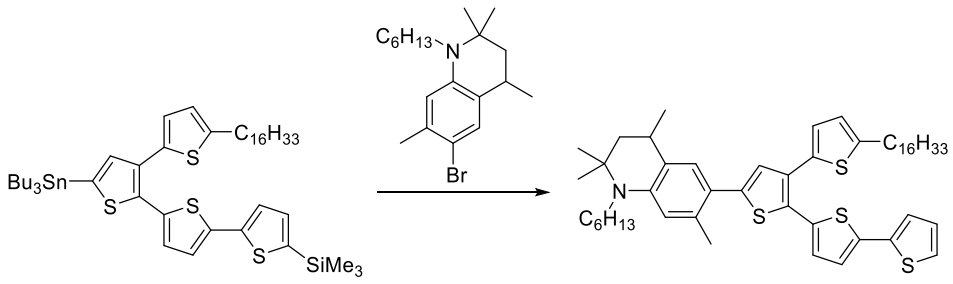
(5'''-hexadecyl-5''-(tributylstannyl)-[2,2':5',2'':3'',2'''-quarterthiophene]-5-yl)trimethylsilane



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 NH_4Cl (50 mL). The aqueous phase was extracted with CH_2Cl_2 (5x 80 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. The product was isolated as orange liquid (11.49 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) = 7.17 (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



$Pd(PPh_3)_4$ (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 CH_2Cl_2 (5x 50 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. Purification via column

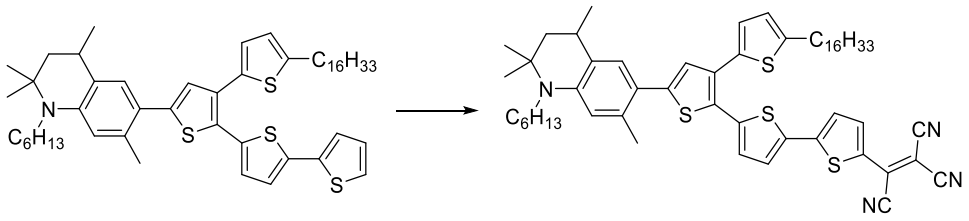
chromatography (eluent PE/EE 40 : 1) gave the product as red oil (2.0 g). The obtained product still contained the TMS protection group and was used for the following deprotection step.

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 Et_2O (3x 40 mL). The combined organic phases were dried over Na_2SO_4 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 $CHCl_3$) gave the deprotected product as orange oil (1.56 g, 1.89 mmol, 87%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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), 7.22 (s, 1H), 7.00 (dd, *J* = 3.6 Hz, 5.1 Hz, 1H), 6.99 (s, 1H), 6.94 (d, *J* = 3.5 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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:

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



To a solution of 6-(5'''-hexadecyl-[2,2':5',2'':3'',2'''-quaterthiophene]-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 $NaHCO_3$ (50 mL). The aqueous phase was extracted with $CHCl_3$ (3x 70 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification via column

chromatography (eluent PE/EE 50 : 1) followed by size exclusion chromatography (eluent $CHCl_3$) gave the product as black green solid (52 mg, 56 µmol, 31%).

^{1}H-NMR (250 MHz, $CDCl_3$): 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). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 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 $C_{56}H_{70}N_4S_4$ [M+H]+: 927.4556, found: 927.4538.

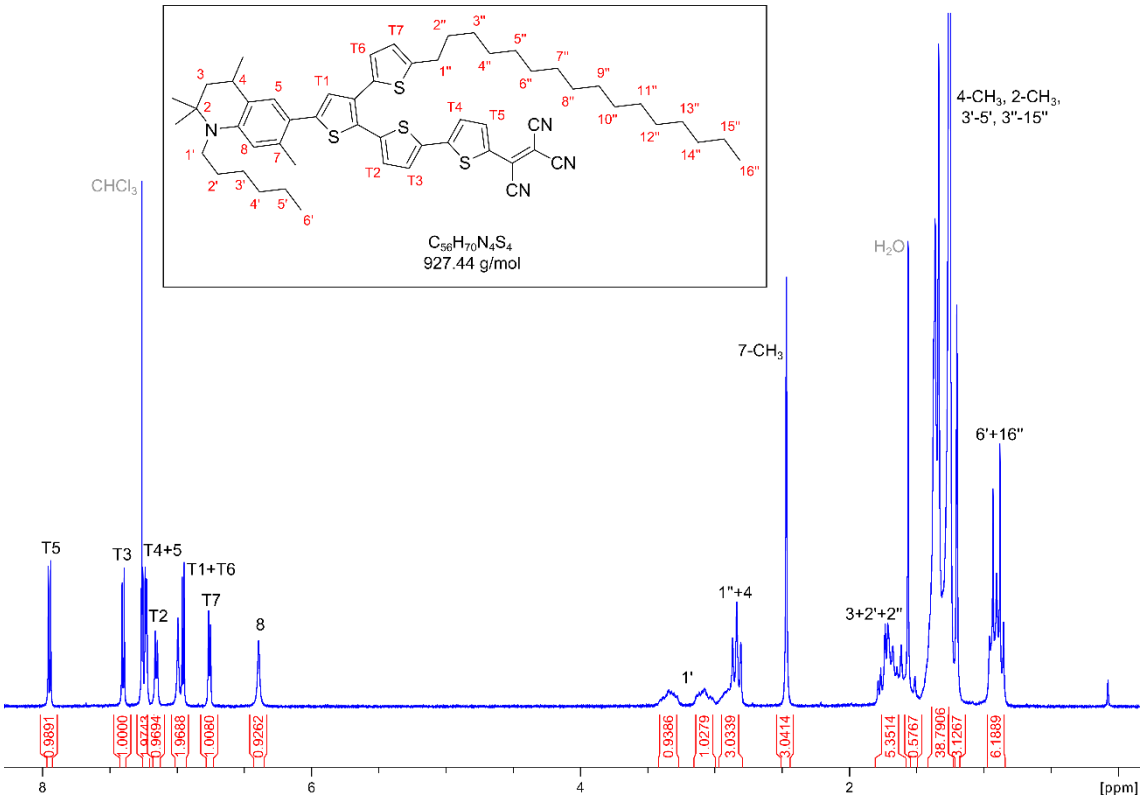


Figure S 19. ^{1}H-NMR spectrum (250 MHz) in $CDCl_3$ of **3Tβ-TCV**. [1]

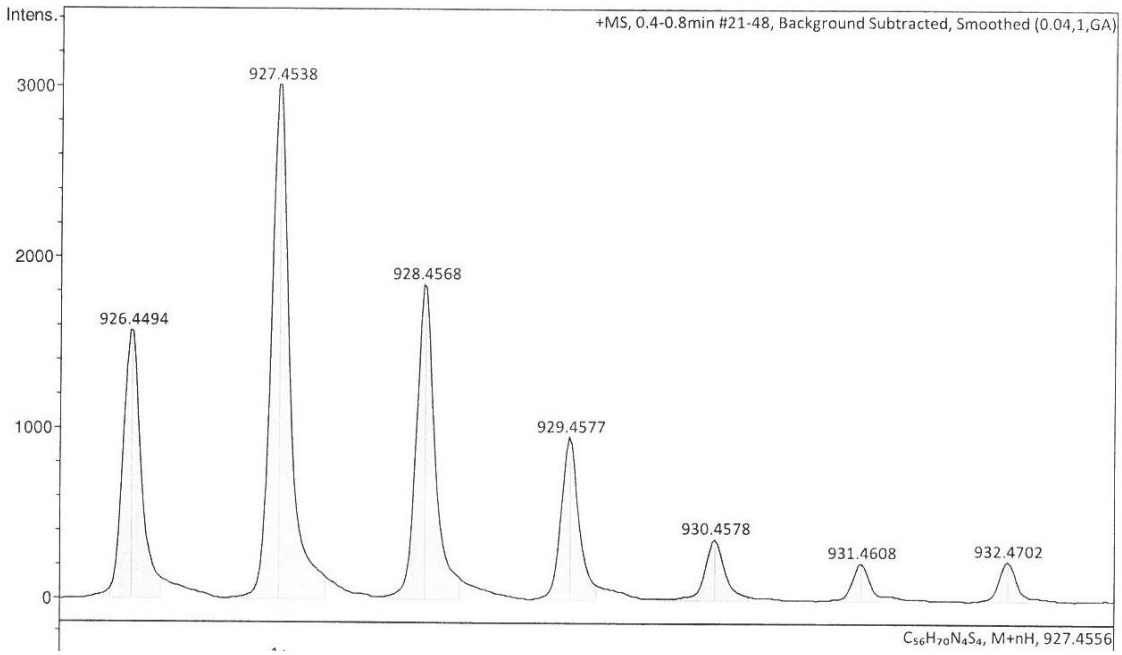


Figure S 20. Mass spectrum of **3Tβ-TCV**. [1]

2. Thermal Properties

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

	1T-DCV	**1Tβ-DCV**	**2T-DCV**	**2Tβ-DCV**	**1T-TCV**	**1Tβ-TCV**	**2T-TCV**	**2Tβ-TCV**	**3T-TCV**	**3Tβ-TCV**
T_d **[°C]**	308	xa	327	357	274	371	310	368	360	419

[a] Due to a lack of the necessary amount of substance no data could be acquired for **1Tβ-DCV** (marked by X).

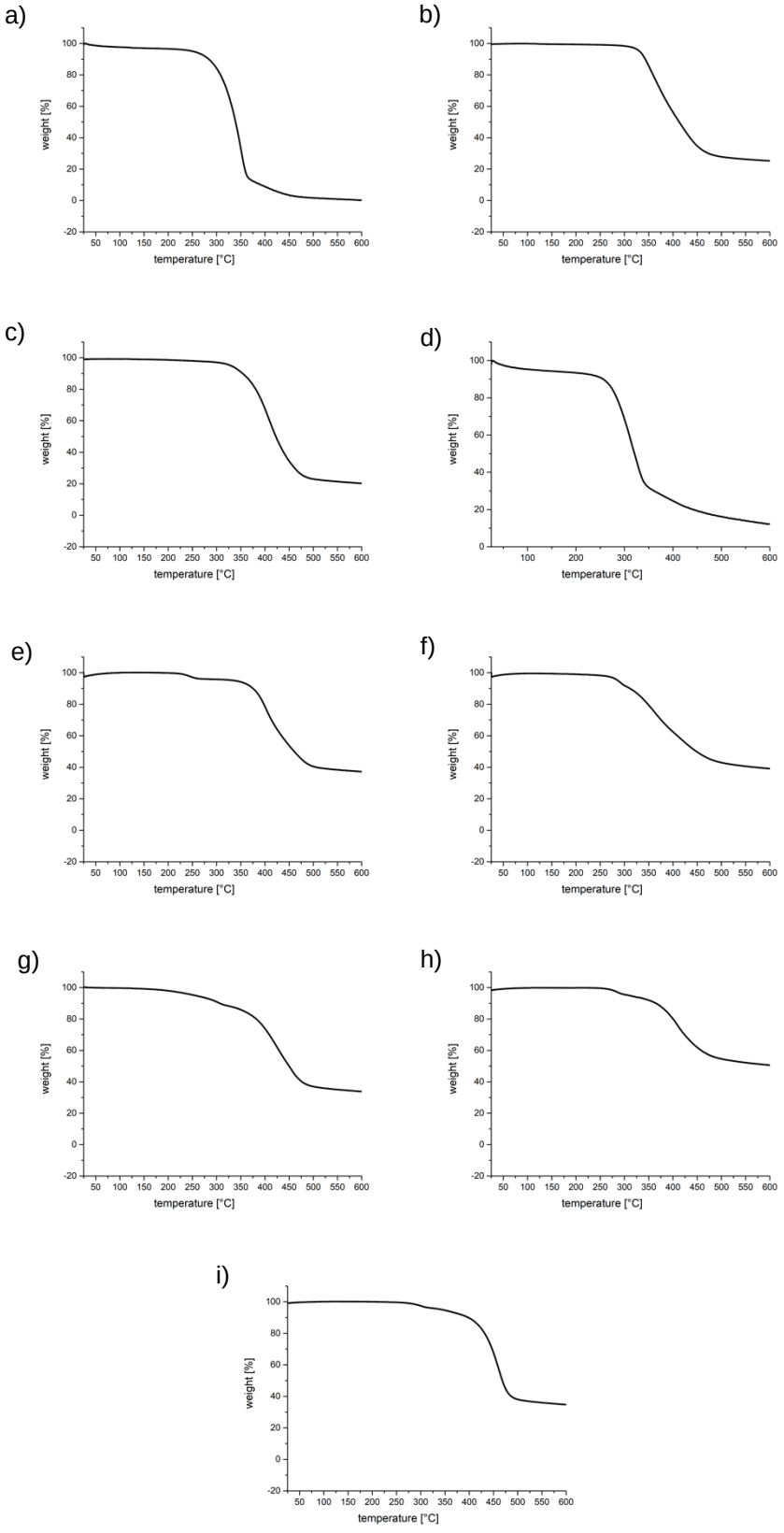


Figure S 21. Thermogravimetry of a) **1T-DCV**, b) **2T-DCV**, c) **2Tβ-DCV**, d) **1T-TCV**, e) **1Tβ-TCV**, f) **2T-TCV**, g) **2Tβ-TCV**, h) **3T-DCV** and i) **3Tβ-TCV** (compare Table S 1).

3. Absorption Properties

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

	λ_{max} [nm]					
	1,4-dioxane	**toluene**	**$CHCl_3$**	**CH_2Cl_2**	**acetone**	**MeCN**
1T-DCV	502	512	530	530	514	516
1Tβ-DCV	519	528	543	543	535	534
2T-DCV	509	521	539	537	516	516
2Tβ-DCV	510	521	539	537	517	517
1T-TCV	620	630	672	675	652	660
1Tβ-TCV	623	641	675	681	654	663
2T-TCV	631	643	689	691	649	655
2Tβ-TCV	625	644	690	689	647	654
3T-TCV	613	629	661	655	611	-
3Tβ-TCV	613	631	668	660	610	-

4. Electrochemical Measurements

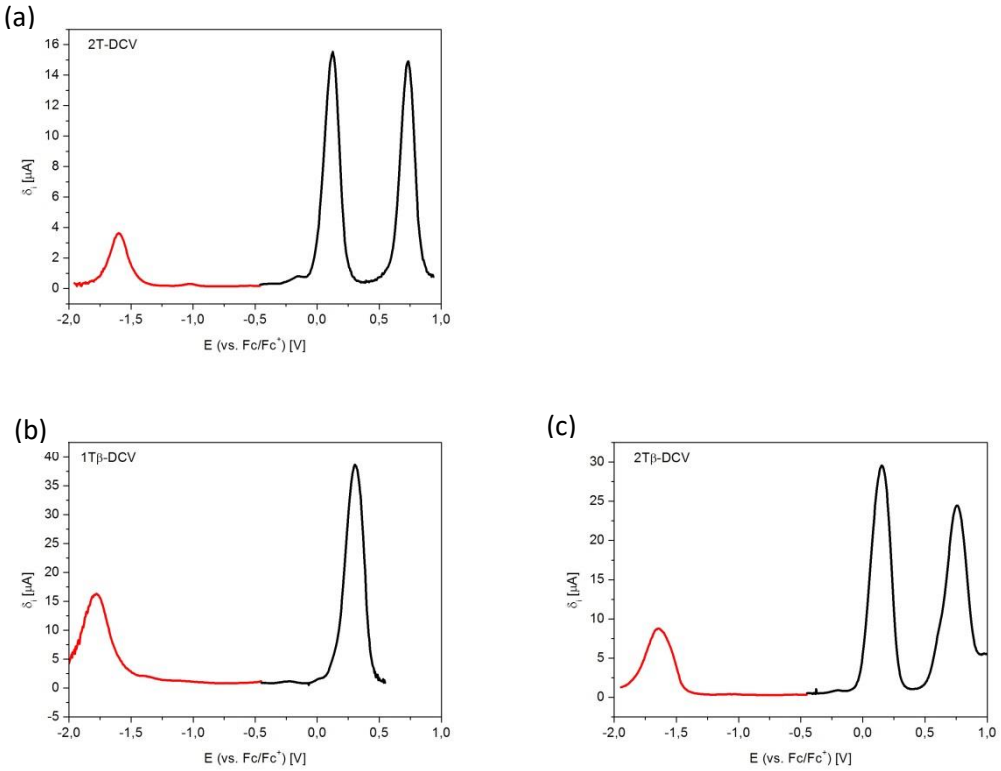


Figure S 22. Differential pulse voltammograms of the chromophores **2T-DCV** (a), **1Tβ-DCV** (b) and **2Tβ-DCV** (c) recorded in dichloromethane with 0.1 M Bu_4NPF_6 as electrolyte (black: oxidation, red: reduction). $E_{1/2}$ was obtained using $E_{1/2} = E_p + \Delta E/2$; where ΔE is 25 mV.

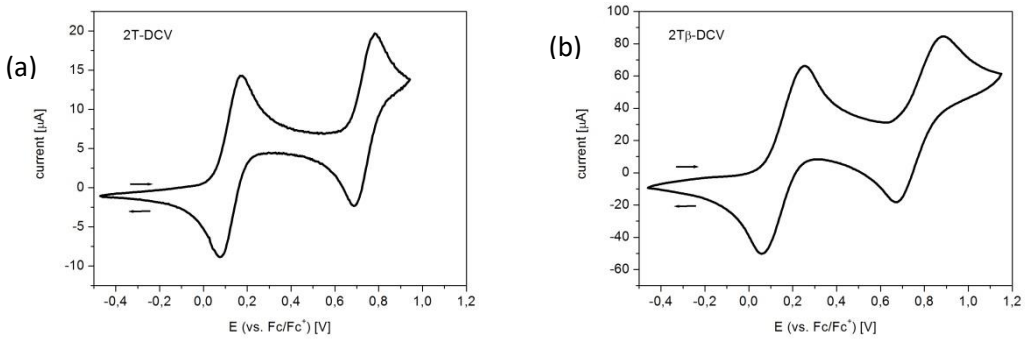


Figure S 23. CVs of the chromophores **2T-DCV** (a) and **2Tβ-DCV** (b) of the first and second oxidation recorded in dichloromethane with 0.1 M Bu_4NPF_6 as electrolyte; 2nd cycles are shown.

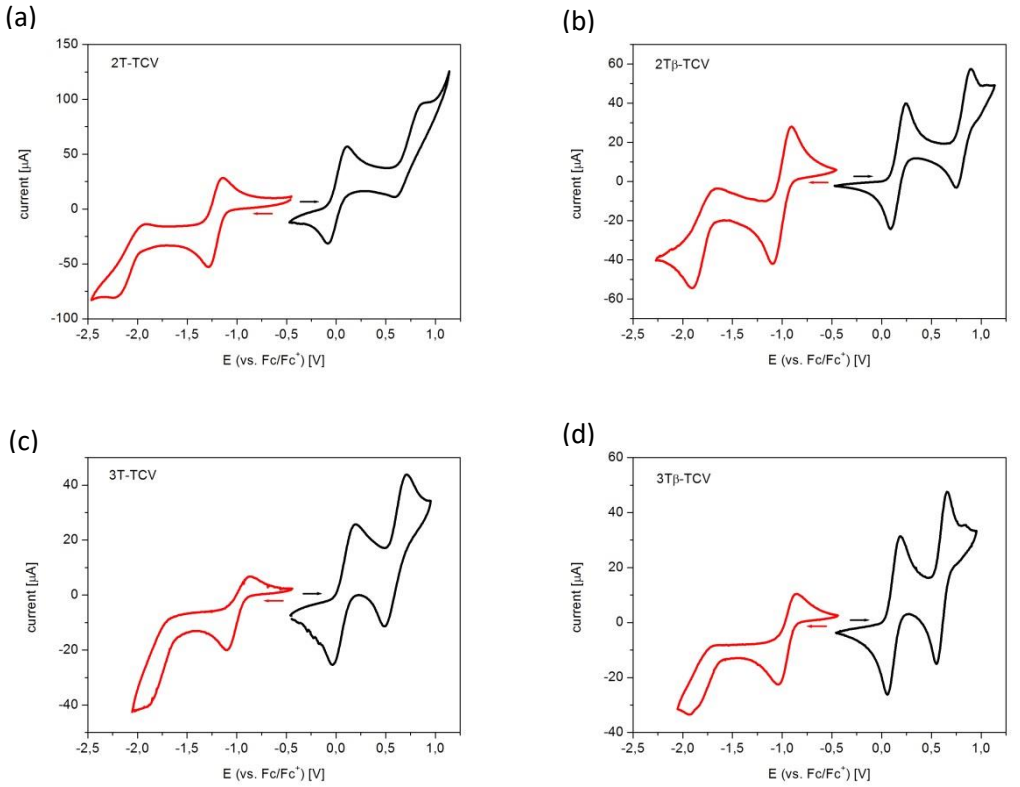


Figure S 24. Separate CVs during oxidation (black line) and reduction (red line) of the chromophores **2T-TCV** (a), **2Tβ-TCV** (b), **3T-TCV** (c), **3Tβ-TCV** (d) recorded in dichloromethane with 0.1 M Bu_4NPF_6 as electrolyte, 2nd cycles are shown.

5. DFT-Calculations

Computational Details

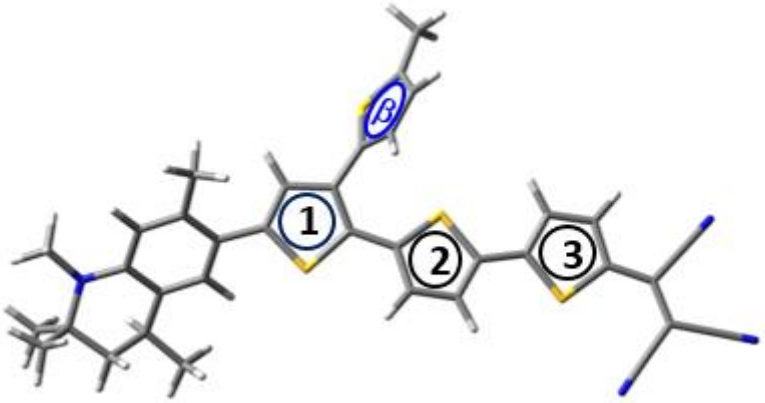
The molecular geometries of all chromophores were optimized at the framework of the Density Functional Theory (DFT) level using the hybrid meta-GGAs functional of Truhlar and Zhao (M06-2X)[2] and a 6-31G** basis set[3,4], as implemented in the GAUSSIAN09 program[5]. All geometrical parameters were allowed 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[6] and also accurate excited states dipole moments for a large variety of push-pull systems[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.[8]

Furthermore, vertical electronic excitation energies were calculated by using the time-dependent DFT (TD-DFT) approach[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[11-16] developed by Tomasi to model the interaction between the NLO-phores and the solvent (CH_2Cl_2).

The Nucleus-Independent Chemical Shifts (NICS) values[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.



	NICS(0)			
	Ring 1	**Ring 2**	**Ring 3**	**Ring β**
1T-DCV	-8.8	-	-	-
1Tβ-DCV	-7.9	-	-	-9.8
2T-DCV	-8.3	-8.3	-	-
2Tβ-DCV	-7.5	-8.7	-	-10.4
1T-TCV	-8.3	-	-	-
1Tβ-TCV	-7.8	-	-	-10.1
2T-TCV	-8.1	-7.9	-	-
2Tβ-TCV	-7.5	-8.3	-	-10.4
3T-TCV	-8.5	-7.5	-8.1	-
3Tβ-TCV	-7.8	-7.9	-8.1	-10.4
1T	-12.6	-	-	-
1Tβ	-11.3	-	-	-9.4
2T	-10.4	-10.4	-	-
2Tβ	-10.2	-11.5	-	-9.8
3T	-10.4	-8.3	-10.4	-
3Tβ	-10.2	-8.8	-10.2	-9.9

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_2Cl_2 as solvent.

Compound	Mülliken atomic charges		
	Donor Group	**π-Spacer**	**Acceptor Group**
1T-DCV	0.229	-0.018	-0.211
1Tβ-DCV	0.235	0.001	-0.236
1T-TCV	0.283	0.040	-0.323
1Tβ-TCV	0.255	0.047	-0.302
2T-TCV	0.197	0.107	-0.304
2Tβ-TCV	0.201	0.098	-0.299

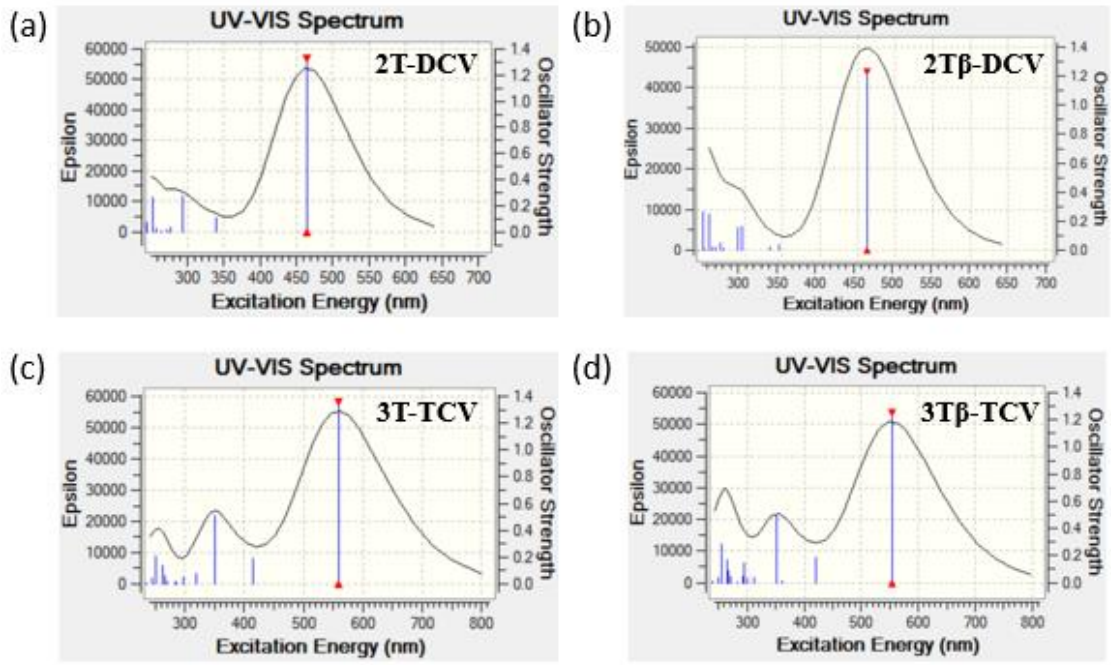


Figure S25. Simulated absorption spectra and main excitations (oscillator strength vs. wavelength) shown as vertical bars for **2T-DCV** (a), **2Tβ-DCV** (b), **3T-TCV** (c) and **3Tβ-TCV** (d) calculated at PCM-M06-2X/6-31G** level using CH_2Cl_2 as solvent.

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

Compound	Electronic Transitions	Description	Energy		*f*
			eV	nm	
2T-DCV	$S_0 \rightarrow S_1$	H→L (81%)	2.67	465	1.3280
	$S_0 \rightarrow S_2$	H-1→L (79%)	3.64	341	0.1077
	$S_0 \rightarrow S_3$	H→L+1 (81%)	4.23	293	0.2690
	$S_0 \rightarrow S_8$	H-4→L (51%) H-5→L (20%)	4.91	253	0.2585
2Tβ-DCV	$S_0 \rightarrow S_1$	H→L (80%)	2.68	463	1.2283
	$S_0 \rightarrow S_4$	H→L+1 (47%) H-4→L (30%)	4.19	296	0.1664
	$S_0 \rightarrow S_5$	H-4→L (47%) H→L+1 (36%)	4.27	290	0.1598
	$S_0 \rightarrow S_{10}$	H-6→L (46%) H-7→L (29%)	4.92	252	0.2489
	$S_0 \rightarrow S_{12}$	H-1→L+1 (55%) H→L+4 (20%)	5.08	244	0.2663

Compound	Electronic Transitions	Description	Energy		*f*
			eV	nm	
3T-TCV	$S_0 \rightarrow S_1$	H→L (73%)	2.22	559	1.3616
	$S_0 \rightarrow S_2$	H-1→L (67%)	2.99	415	0.1925
	$S_0 \rightarrow S_3$	H→L+1 (77%)	3.54	350	0.5105
	$S_0 \rightarrow S_{11}$	H→L+2 (50%)	4.73	262	0.1414
	$S_0 \rightarrow S_{13}$	H-8→L (25%) H-7→L (24%) H-6→L (22%)	4.96	250	0.2109
3Tβ-TCV	$S_0 \rightarrow S_1$	H→L (68%)	2.24	554	1.2505
	$S_0 \rightarrow S_2$	H-1→L (61%)	2.95	420	0.1888
	$S_0 \rightarrow S_4$	H→L+1 (70%)	3.52	352	0.4880
	$S_0 \rightarrow S_7$	H-1→L+1 (68%)	4.21	294	0.1475
	$S_0 \rightarrow S_{14}$	H-2→L+1 (25%) H-6→L (21%)	4.69	264	0.1699
	$S_0 \rightarrow S_{15}$	H→L+4 (33%) H-1→L+2 (12%)	4.87	255	0.2889

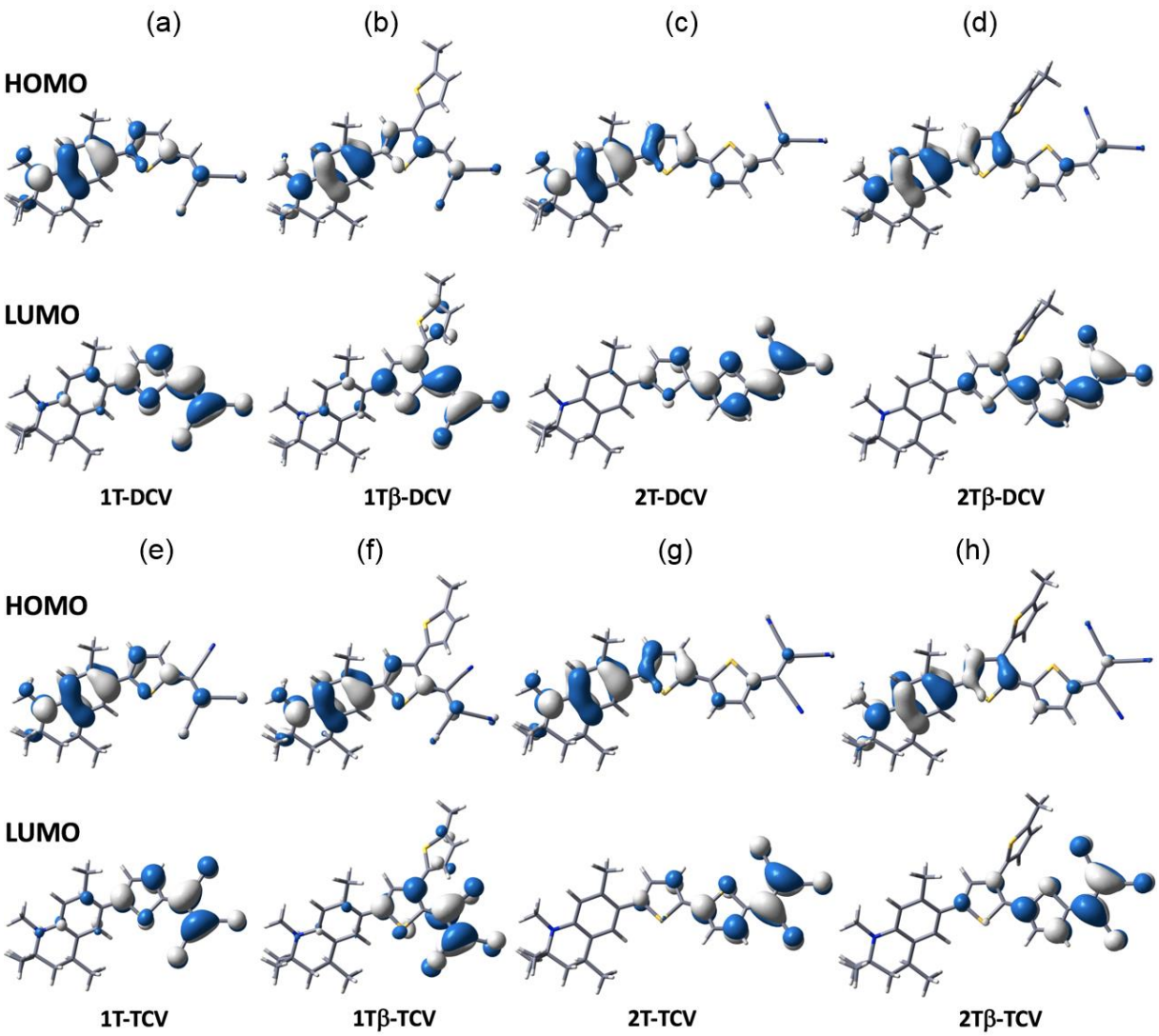


Figure S 26. DFT-calculated molecular orbital topologies for **1T-DCV** (a), **1Tβ-DCV** (b), **2T-DCV** (c), **2Tβ-DCV** (d), **1T-TCV** (e), **1Tβ-TCV** (f), **2T-TCV** (g) and **2Tβ-TCV** (h), chromophores at PCM-M06-2X/6-31G** level using CH_2Cl_2 as solvent.

Table S6: Experimental and calculated nonlinear optical properties of all chromophores.

Compound	Experimental[a]		Theoretical									
			*Polar M062X/6-31G**[c]*			*TD-DFT M062X/6-31G**[c]*						
	$\mu\beta$ [10^{-48} esu]	$\mu\beta_0$ [10^{-48} esu][b]	μ [D]	$\beta_{0,tot}$ [10^{-48} esu]	$\mu\beta_0$ [10^{-48} esu]	μ_g [D]	μ_e [D]	μ_{ge} [D]	$\Delta\mu_{ge}$ [D]	E_{max} [eV]	f osc	Description
1T-DCV	1150	730	10.4	121	1156	12.8	27.3	9.5	15.3	2.82	0.96	H→L (93%)
1T-TCV	5400	2350	12.9	211	2691	16.1	32.2	10.4	16.3	2.33	0.95	H→L (95%)
1Tβ-DCV	1000	620	10.3	114	1012	12.8	26.3	8.8	15.1	2.76	0.81	H→L (92%)
1Tβ-TCV	4100	1760	11.2	168	1816	14.0	31.7	8.6	18.4	2.33	0.65	H→L (93%)
2T-DCV	1490	940	12.0	244	2758	14.2	32.2	11.5	18.6	2.67	1.33	H→L (81%)
2T-TCV	9100	3750	14.0	419	5828	16.8	39.6	11.8	23.0	2.24	1.19	H→L (86%)
2Tβ-DCV	1300	820	10.9	212	2227	13.3	30.4	11.0	17.6	2.68	1.23	H→L (80%)
2Tβ-TCV	7600	3160	16.1	375	4858	16.1	32.0	9.7	22.2	2.24	1.07	H→L (85%)
3T-TCV	10400	4840	13.9	608	8449	16.2	42.0	12.7	25.8	2.22	1.36	H→L (73%)
3Tβ-TCV	7700	3530	13.6	510	6909	15.7	39.6	13.2	24.0	2.24	1.25	H→L (68%)

[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 CH_2Cl_2.

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 H_2 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 λ_{max} corresponding to the maximum of the lowest energy absorption band.

7. References

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