**Electronic Supplementary Information**

# Efficient and readily tuneable near-infrared photodetection up to 1500 nm enabled by thiadiazoloquinoxaline-based push-pull type conjugated polymers

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## 1. Materials and methods

NMR chemical shifts (δ, in ppm) were determined relative to the residual $CHCl_3$ (7.26 ppm) or DMSO (2.50 ppm) absorption or the $^{13}C$ resonance shift of $CDCl_3$ (77.16 ppm) or DMSO (39.52 ppm). Polymer molar mass distributions were estimated by SEC (size exclusion chromatography) at 160 °C on an Agilent 1260 Infinity II high temperature GPC system using a PL-GEL 10 µm MIXED-B column with 1,2,4-trichlorobenzene (TCB) as the eluent and using polystyrene internal standards. UV-VIS-NIR absorption spectroscopy measurements were performed on a VARIAN Cary 5000 UV-VIS-NIR spectrophotometer at a scan rate of 600 nm $min^{-1}$. The films for the UV-VIS-NIR absorption measurements were prepared by spin-coating a solution of the respective polymer in *o*-dichlorobenzene on a glass substrate. Absorption coefficients were determined using the DRA 2500 internal diffuse reflectance accessory. By measuring both the transmission (T) and reflectance (R), the absorption coefficient was calculated as α = -1/d ln (T/100%-R), hereby neglecting weak interference effects. Three different films thicknesses were used for all polymers and average values were determined. The solid-state UV-VIS-NIR absorption spectra were used to estimate the optical gaps (from the wavelength at the intersection of the tangent line drawn at the low energy side of the absorption spectrum with the baseline: $E_g$ (eV) = 1240/(wavelength in nm)). Electrochemical measurements (cyclic voltammetry, CV) were performed with an Eco Chemie Autolab PGSTAT 30 potentiostat/galvanostat using a three-electrode microcell with a platinum working electrode, a platinum counter electrode and a $Ag/AgNO_3$ reference electrode (silver wire dipped in a solution of 0.01 M $AgNO_3$ and 0.1 M $NBu_4PF_6$ in anhydrous acetonitrile). The reference electrode was calibrated against ferrocene/ferrocenium as external standard. Sample preparation was done by dip-coating the platinum working electrode in the respective polymer solutions. The CV measurements were done on the resulting films with 0.1 M $NBu_4PF_6$ in anhydrous acetonitrile as electrolyte solution. The experiments were carried out under a curtain of argon to prevent air from entering the system. Cyclic voltammograms were recorded at a scan rate of 100 mV $s^{-1}$. For the conversion of V to eV, the onset potentials of the first oxidation/reduction peaks were used and referenced to ferrocene/ferrocenium, which has an ionization potential of −4.98 eV vs. vacuum. This correction factor is based on a value of 0.31 eV for $Fc/Fc^+$ vs. SCE[1] and a value of 4.68 eV for SCE vs. vacuum[2]: $E_{HOMO/LUMO}$ (eV) = −4.98 − $E_{onset\ ox/red}^{Ag/AgNO3}$ (V) + $E_{onset\ Fc/Fc+}^{Ag/AgNO3}$ (V). The accuracy of measuring redox potentials by CV is about 0.01−0.02 V. Reproducibility issues can occur due to the dependence of the potentials on concentration and temperature.

## 2. Synthesis of precursors and monomers

All reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried by a solvent purification system (MBraun, MB-SPS-800) equipped with alumina columns. 2,5-Bis(trimethylstannyl)thiophene,[3] bis(trimethylstannyl)thieno[3,2-*b*]thiophene,[4] and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene[5] were synthesized according to literature procedures.

**1-iodo-2-butyloctane (1 BO).** The synthesis of 1-iodo-2-butyloctane (**1 BO**) was carried out according to a literature procedure.[6] Yield = 95%, $^1H$-NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.26 (d, *J* = 4.6 Hz, 2H), 1.35−1.20 (m, 16H), 1.15−1.07 (m, 1H), 0.92−0.85 (m, 6H).

**1-iodo-2-hexyldecane (1 HD).** The synthesis of 1-iodo-2-hexyldecane (**1 HD**) was carried out according to a literature procedure.[6] Yield = 98%, $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.25 (d, *J* = 4.6 Hz, 2H), 1.34−1.20 (m, 24H), 1.12−1.06 (m, 1H), 0.90−0.84 (m, 6H).

**1-iodo-2-octyldodecane (1 OD).** The synthesis of 1-iodo-2-octyldodecane (**1 OD**) was carried out according to a literature procedure.[6] Yield = 83%, $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.26 (d, *J* = 4.6 Hz, 2H), 1.30−1.20 (m, 32H), 1.14−1.06 (m, 1H), 0.87 (t, *J* = 6.8 Hz, 6H).

**2-(2-butyloctyl)thiophene (2 BO).** The synthesis of 2-(2-butyloctyl)thiophene was carried out according to a literature procedure.[7] Yield = 52%, $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.11 (dd, *J* = 5.1 Hz, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.1 Hz, 3.4 Hz, 1H), 6.75 (dd, *J* = 3.4 Hz, 1.1 Hz, 1H), 2.75 (d, *J* = 6.7 Hz, 2H), 1.63−1.57 (m, 1H), 1.33−1.19 (m, 16H), 0.91−0.84 (m, 6H).

**2-(2-hexyldecyl)thiophene (2 HD).** The synthesis of 2-(2-hexyldecyl)thiophene was carried out according to a literature procedure.[7] Yield = 67%, $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.10 (dd, *J* = 5.1 Hz, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.1 Hz, 3.4 Hz, 1H), 6.74 (dd, *J* = 3.4 Hz, 1.0 Hz, 1H), 2.74 (d, *J* = 6.7 Hz, 2H), 1.65−1.57 (m, 1H), 1.32−1.20 (m, 24H), 0.90−0.84 (m, 6H).

**2-(2-octyldodecyl)thiophene (2 OD).** The synthesis of 2-(2-octyldodecylthiophene was carried out according to a literature procedure.[7] Yield = 50% (due to purification issues, some minor impurities remain present), $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.10 (dd, *J* = 5.1 Hz, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.1 Hz, 3.4 Hz, 1H), 6.74 (dd, *J* = 3.4 Hz, 1.2 Hz, 1H), 2.74 (d, *J* = 6.7 Hz, 2H), 1.64−1.57 (m, 1H), 1.32−1.19 (m, 16H), 0.90−0.84 (m, 6H).

**1,2-bis(5-(2-butyloctyl)thiophen-2-yl)ethane-1,2-dione (3 BO).** The synthesis of 1,2-bis(5-(2-butyloctyl)thiophen-2-yl)ethane-1,2-dione (**3 BO**) was carried out according to a literature procedure.[8] Yield = 53%, $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.86 (d, *J* = 3.8 Hz, 2H), 6.85 (d, *J* = 3.9 Hz, 2H), 2.81 (d, *J* = 6.7 Hz, 4H), 1.72−1.64 (m, 2H), 1.31−1.19 (m, 32H), 0.92−0.82 (m, 12H).

**1,2-bis(5-(2-hexyldecyl)thiophen-2-yl)ethane-1,2-dione (3 HD).** The synthesis of 1,2-bis(5-(2-hexyldecyl)thiophen-2-yl)ethane-1,2-dione (**3 HD**) was carried out according to a literature procedure.[8] Yield = 70%, $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.86 (d, *J* = 3.8 Hz, 2H), 6.85 (d, *J* = 3.9 Hz, 2H), 2.81 (d, *J* = 6.7 Hz, 4H), 1.73−1.65 (m, 2H), 1.34−1.17 (m, 48H), 0.90−0.80 (m, 12H).

**1,2-bis(5-(2-octyldodecyl)thiophen-2-yl)ethane-1,2-dione (3 OD).** The synthesis of 1,2-bis(5-(2-octyldodecyl)thiophen-2-yl)ethane-1,2-dione (**3 OD**) was carried out according to a literature procedure.[8] Yield = 66%, $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.86 (d, *J* = 3.9 Hz, 2H), 6.84 (d, *J* = 3.9 Hz, 2H), 2.81 (d, *J* = 6.7 Hz, 4H), 1.72−1.64 (m, 2H), 1.32−1.18 (m, 64H), 0.89−0.84 (t, *J* = 6.8 Hz, 12H).

**4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (4).** The synthesis of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (**4**) was carried out according to a literature procedure.[9] Yield = 71%, $^{13}$C-NMR (100 MHz, DMSO): δ (ppm) = 151.7, 143.8, 111.5

**5,6-dinitro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (5).** The synthesis of 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**5**) was carried out according to a literature procedure.[10] Yield = 70%, $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.73 (dd, *J* = 5.1 Hz, 1.1 Hz, 2H), 7.51 (dd, *J* = 3.7 Hz, 1.1 Hz, 2H), 7.23 (dd, *J* = 5.1 Hz, 3.8 Hz, 2H).

**5,6-diamino-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (6).** The synthesis of 5,6-diamino-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**6**) was carried out according to a literature procedure.[11]

Yield = quantitative, $^{1}$H-NMR (400 MHz, DMSO): δ (ppm) = 7.68 (dd, *J* = 5.2 Hz, 1.2 Hz, 2H), 7.27 (dd, *J* = 3.5 Hz, 1.2 Hz, 2H), 7.20 (dd, *J* = 5.2 Hz, 3.5 Hz, 2H), 5.77 (br, 4H).

**6,7-bis(5-(2-butyloctyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (7 BO)** – General synthesis procedure

5,6-Diamino-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**6**) (0.22 g, 0.67 mmol) and 1,2-bis(5-(2-butyloctyl)thiophen-2-yl)ethane-1,2-dione (**3 BO**) (0.37 g, 0.67 mmol) were combined in 10 mL glacial acetic acid and heated to reflux overnight. The reaction mixture was then poured into a saturated aqueous $K_2CO_3$ solution and extracted with $CHCl_3$. The aqueous layer was extracted twice with $CHCl_3$ and the combined organic layers were subsequently washed twice, dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude material was purified by column chromatography (silica, eluent petroleum ether:methylene chloride 3:1), affording the pure product as a dark purple oil (0.53 g, 93%). $^{1}$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.89 (dd, *J* = 3.9 Hz, 1.0 Hz, 2H), 7.69 (dd, *J* = 5.1 Hz, 1.0 Hz, 2H), 7.48 (d, *J* = 3.7 Hz, 2H), 7.32 (dd, *J* = 5.1 Hz, 3.9 Hz, 2H), 6.72 (d, *J* = 3.7 Hz, 2H), 2.85 (d, *J* = 6.7 Hz, 4H), 1.78−1.69 (m, 2H), 1.44−1.23 (m, 32H), 0.96−0.83 (m, 12H). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 152.1, 151.6, 146.3, 139.5, 135.9, 134.4, 133.0, 132.0, 130.9, 126.9, 126.0, 120.5, 40.0, 35.0, 33.4, 33.1, 32.0, 29.8, 29.0, 26.7, 23.1, 22.8, 14.3, 14.2.

**6,7-bis(5-(2-hexyldecyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (7 HD)** – Synthesized according to the general procedure

5,6-Diamino-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**6**) (2.54 g, 7.68 mmol) and 1,2-bis(5-(2-hexyldecyl)thiophen-2-yl)ethane-1,2-dione (**3 HD**) (5.16 g, 7.68 mmol) were combined in glacial acetic acid (135 mL). The crude material was purified by column chromatography (silica, eluent petroleum ether:methylene chloride 2:1), affording the pure product as a dark purple oil (6.85 g, 92%). $^{1}$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.89 (dd, *J* = 3.9 Hz, 1.1 Hz, 2H), 7.69 (dd, *J* = 5.1 Hz, 1.1 Hz, 2H), 7.48 (d, *J* = 3.7 Hz, 2H), 7.31 (dd, *J* = 5.1 Hz, 3.9 Hz, 2H), 6.72 (d, *J* = 3.8 Hz, 2H), 2.85 (d, *J* = 6.7 Hz, 4H), 1.75−1.68 (m, 2H), 1.37−1.22 (m, 48H), 0.90−0.83 (m, 12H). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 152.1, 151.6, 146.3, 139.5, 135.9, 134.4, 133.1, 132.0, 131.0, 126.9, 126.0, 120.4, 40.1, 35.0, 34.8, 34.6, 33.4, 32.0, 31.7, 30.1, 29.8, 29.5, 27.0, 26.8, 26.7, 25.4, 22.8, 14.3.

**6,7-bis(5-(2-octyldodecyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (7 OD)** – Synthesized according to the general procedure

5,6-Diamino-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**6**) (0.31 g, 0.96 mmol) and 1,2-bis(5-(2-octyldodecyl)thiophen-2-yl)ethane-1,2-dione (**3 OD**) (0.75 g, 0.96 mmol) were combined in glacial acetic acid (30 mL). The crude material was purified by column chromatography (silica, eluent petroleum ether:methylene chloride 4:1), affording the product as a dark purple oil (0.70 g, 68%). $^{1}$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.86 (dd, *J* = 3.9 Hz, 1.0 Hz, 2H), 7.64 (dd, *J* = 5.1 Hz, 1.0 Hz, 2H), 7.48 (d, *J* = 3.7 Hz, 2H), 7.27 (dd, *J* = 5.1 Hz, 3.9 Hz, 2H), 6.73 (d, *J* = 3.8 Hz, 2H), 2.86 (d, *J* = 6.7 Hz, 4H), 1.79−1.72 (m, 2H), 1.41−1.21 (m, 64H), 0.91−0.85 (m, 12H). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.9, 151.5, 146.1, 139.5, 135.9, 134.3, 133.0, 132.0, 131.0, 126.8, 126.0, 120.3, 40.1, 35.1, 33.5, 32.1, 30.2, 29.9, 29.8, 29.5, 26.8, 22.8, 14.3.

**4,9-bis(5-bromothiophen-2-yl)-6,7-bis(5-(2-butyloctyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (8 BO)** – General synthesis procedure

6,7-Bis(5-(2-butylocyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (**7 BO**) (2.25 g, 2.64 mmol) was dissolved in $CHCl_3$ (44 mL). The solution was cooled down to 0 °C after which NBS (0.94 g, 5.3 mmol) was added portion wise. The mixture was allowed to stir at room temperature,

protected from light, during 3 h. Then, a saturated aq. $NaHCO_3$ was added, the aqueous phase was extracted once with $CHCl_3$ and the combined organic phases were washed twice, dried over $MgSO_4$ and filtered. After removal of the solvent *in vacuo*, the crude product was purified by column chromatography (silica, eluent petroleum ether:methylene chloride 85:15), affording the product as a dark purple oil (2.56 g, 96%). $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.68 (d, *J* = 4.2 Hz, 2H), 7.43 (d, *J* = 3.7 Hz, 2H), 7.15 (d, *J* = 4.2 Hz, 2H), 6.74 (d, *J* = 3.7 Hz, 2H), 2.88 (d, *J* = 6.6 Hz, 4H), 1.82−1.75 (m, 2H), 1.42−1.24 (m, 32H), 0.95−0.84 (m, 12H). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.9, 151.0, 146.2, 140.0, 137.4, 137.3, 133.5, 133.1, 129.3, 126.0, 120.0, 119.0, 40.2, 35.1, 33.5, 33.1, 32.0, 29.8, 29.0, 26.8, 23.1, 22.8, 14.34, 14.27.

**4,9-bis(5-bromothiophen-2-yl)-6,7-bis(5-(2-hexyldecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (8 HD)** – Synthesized according to the general procedure

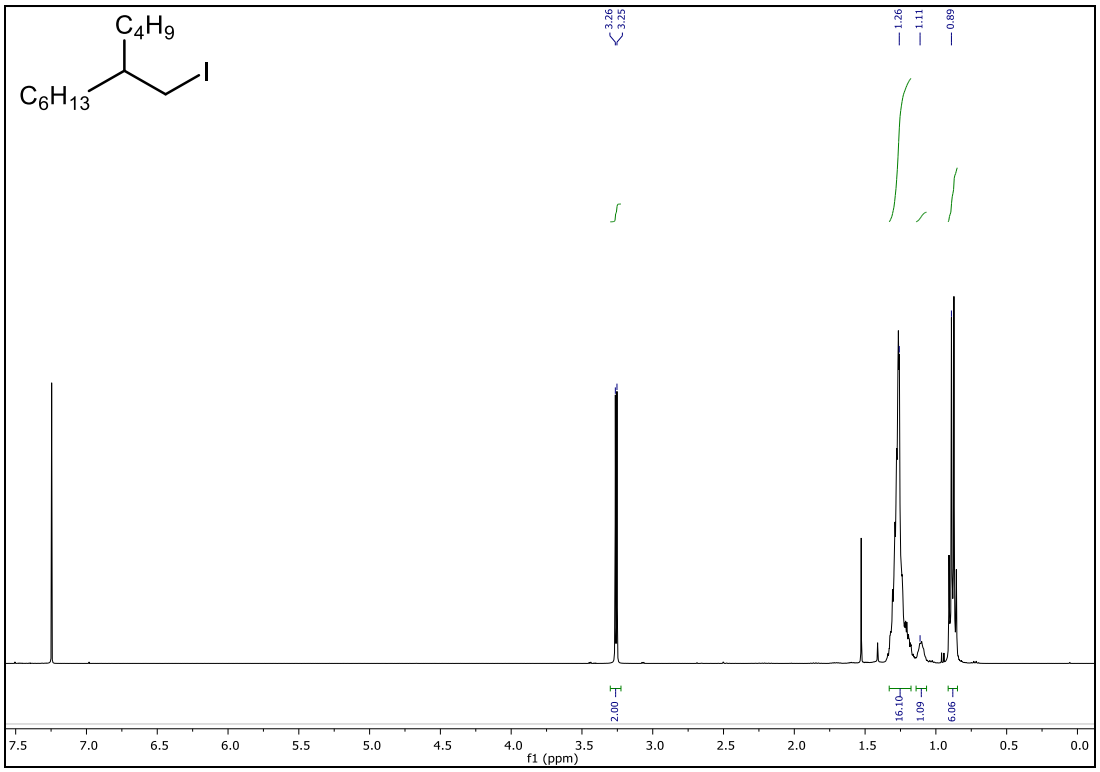
6,7-Bis(5-(2-hexyldecyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (**7 HD**) (5.70 g, 5.90 mmol) and NBS (2.10 g, 11.81 mmol) were dissolved in $CHCl_3$ (80 mL). The crude product was purified by column chromatography (silica, eluent petroleum ether:methylene chloride 17:3) affording the product as a dark purple oil (6.65 g, quant.). $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.79 (d, *J* = 4.2 Hz, 2H), 7.47 (d, *J* = 3.8 Hz, 2H), 7.24 (d, *J* = 4.2 Hz, 2H), 6.74 (d, *J* = 3.8 Hz, 2H), 2.87 (d, *J* = 6.6 Hz, 4H), 1.81−1.73 (m, 2H), 1.41−1.20 (m, 48H), 0.89−0.81 (m, 12H). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.9, 151.1, 146.2, 139.0, 137.4, 133.5, 133.2, 132.3, 129.5, 126.0, 120.0, 119.0, 40.2, 35.1, 33.5, 32.1, 30.1, 29.8, 29.5, 26.9, 26.8, 22.84, 22.82, 14.27, 14.25.

**4,9-bis(5-bromothiophen-2-yl)-6,7-bis(5-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (8 OD)** – Synthesized according to the general procedure

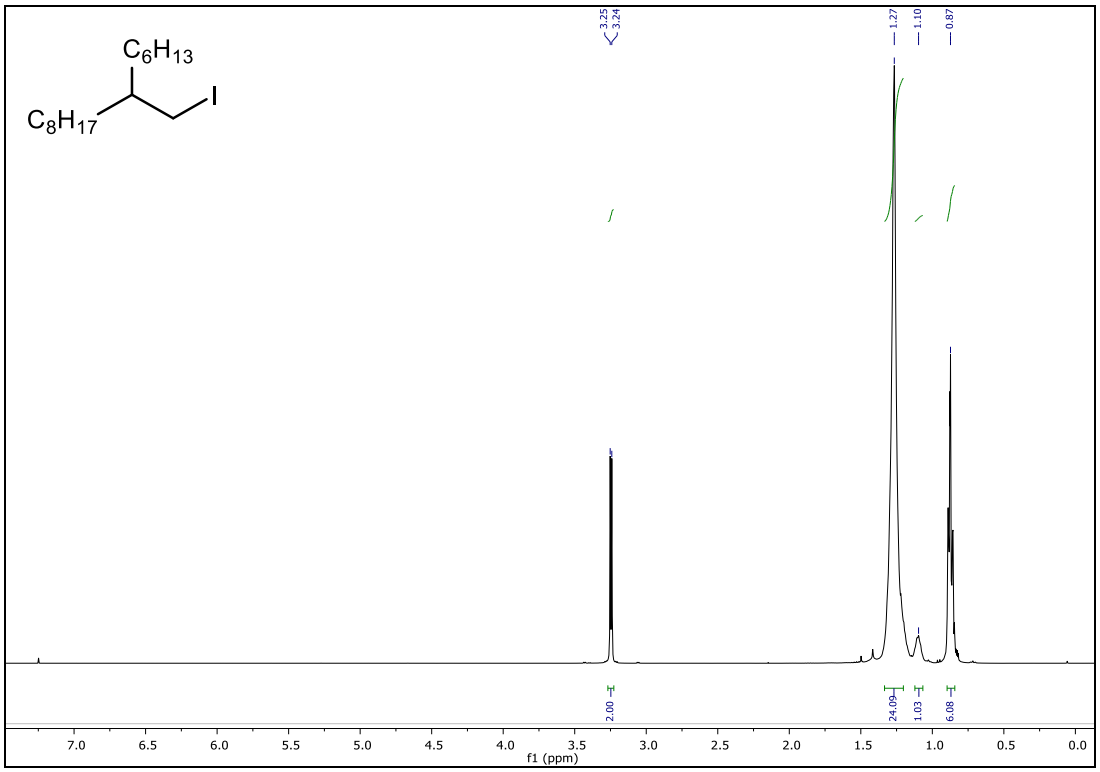
6,7-Bis(5-(2-octyldodecyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (**7 OD**) (1.39 g, 1.29 mmol) and NBS (0.46 g, 2.58 mmol) were dissolved in $CHCl_3$ (20 mL). The crude product was purified by column chromatography (silica, eluent petroleum ether:methylene chloride 93:7), affording the product as a dark purple oil (1.34 g, 84%). $^1$H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.78 (d, *J* = 4.2 Hz, 2H), 7.47 (d, *J* = 3.8 Hz, 2H), 7.22 (d, *J* = 4.2 Hz, 2H), 6.74 (d, *J* = 3.8 Hz, 2H), 2.87 (d, *J* = 6.6 Hz, 4H), 1.82−1.72 (m, 2H), 1.42−1.16 (m, 64H), 0.90−0.80 (m, 12H). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.9, 151.1, 146.2, 138.9, 137.3, 133.5, 133.1, 132.2, 129.4, 126.0, 119.9, 119.1, 53.3, 40.1, 35.0, 33.4, 32.0, 31.9, 30.0, 29.74, 29.70, 29.4, 26.7, 22.71, 22.69, 14.1.

## 3. $^{1}H$ and $^{13}C$-NMR spectra

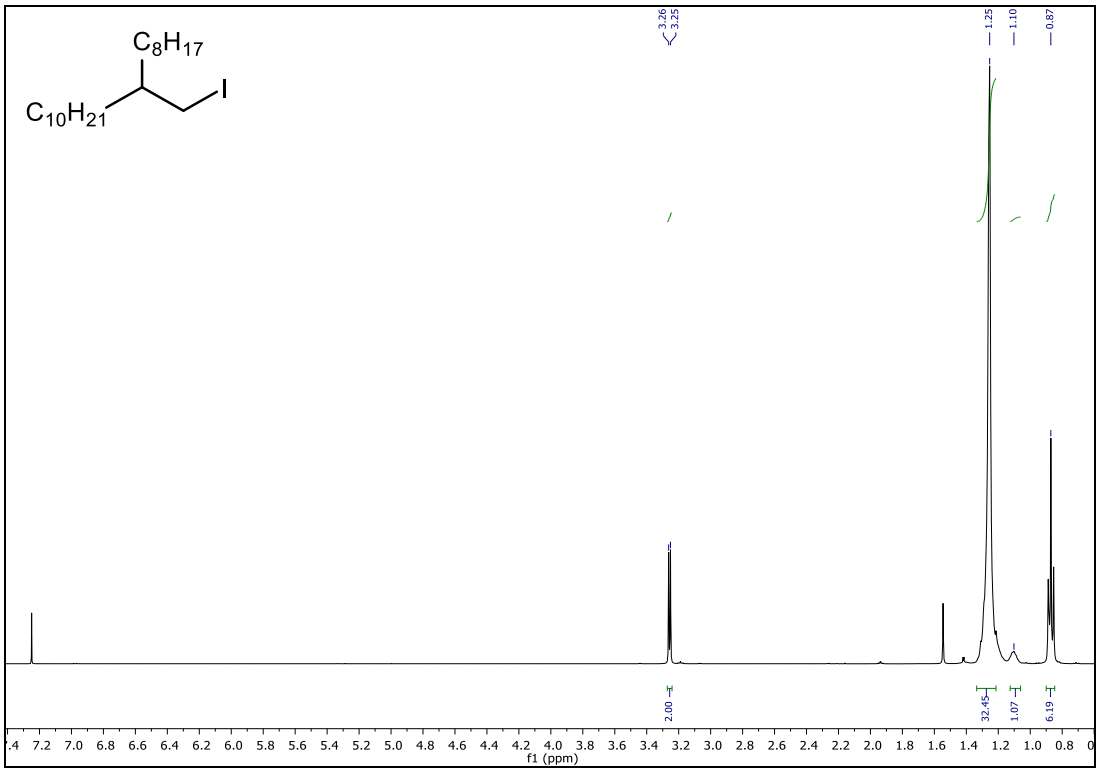
### 1-iodo-2-butyloctane (1 BO)



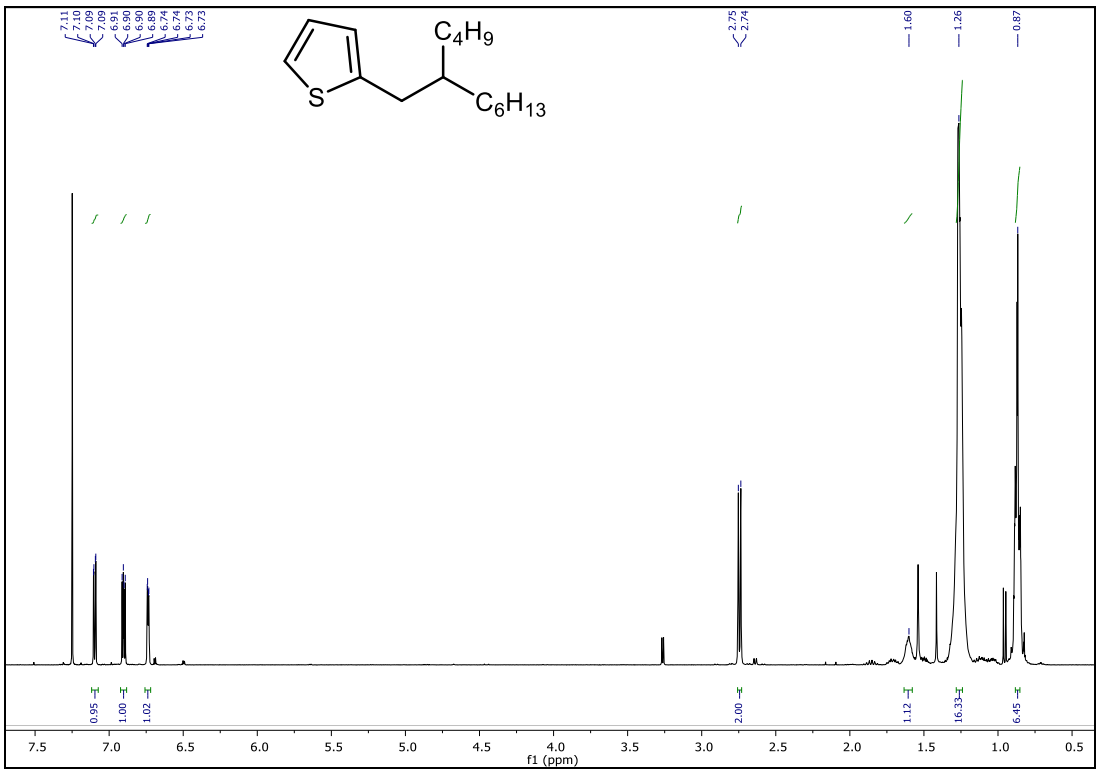

### 1-iodo-2-hexyldecane (1 HD)



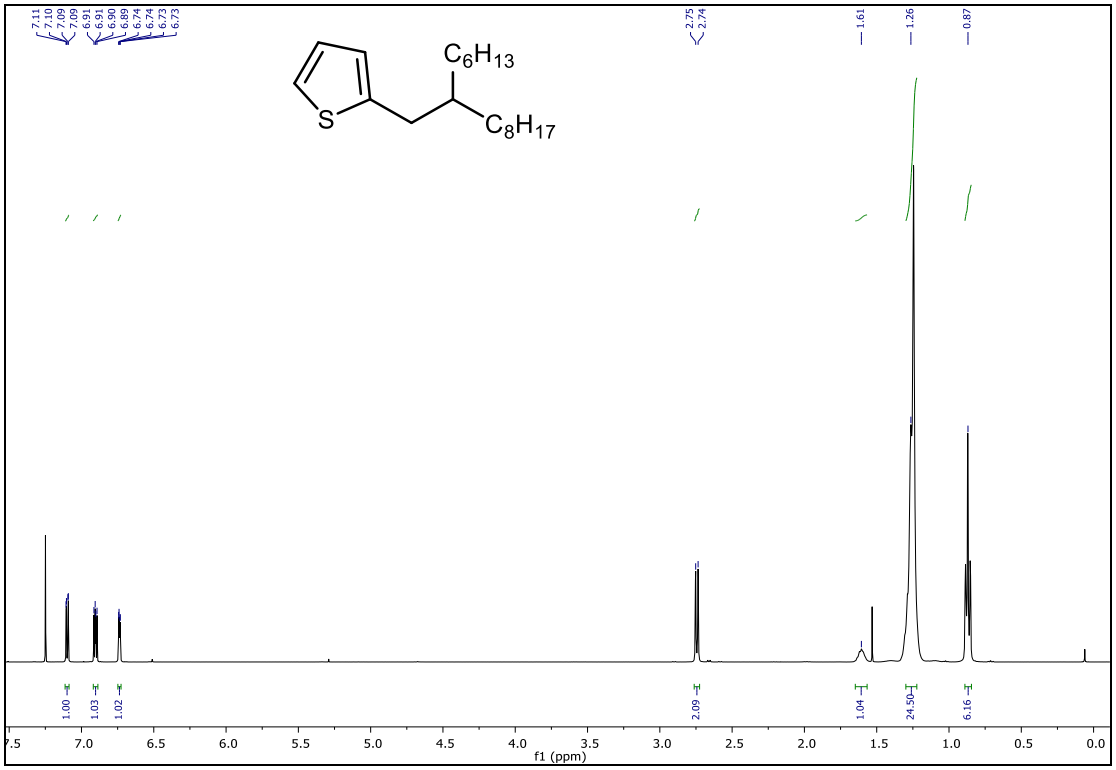
**1-iodo-2-octyldodecane (1 OD)**



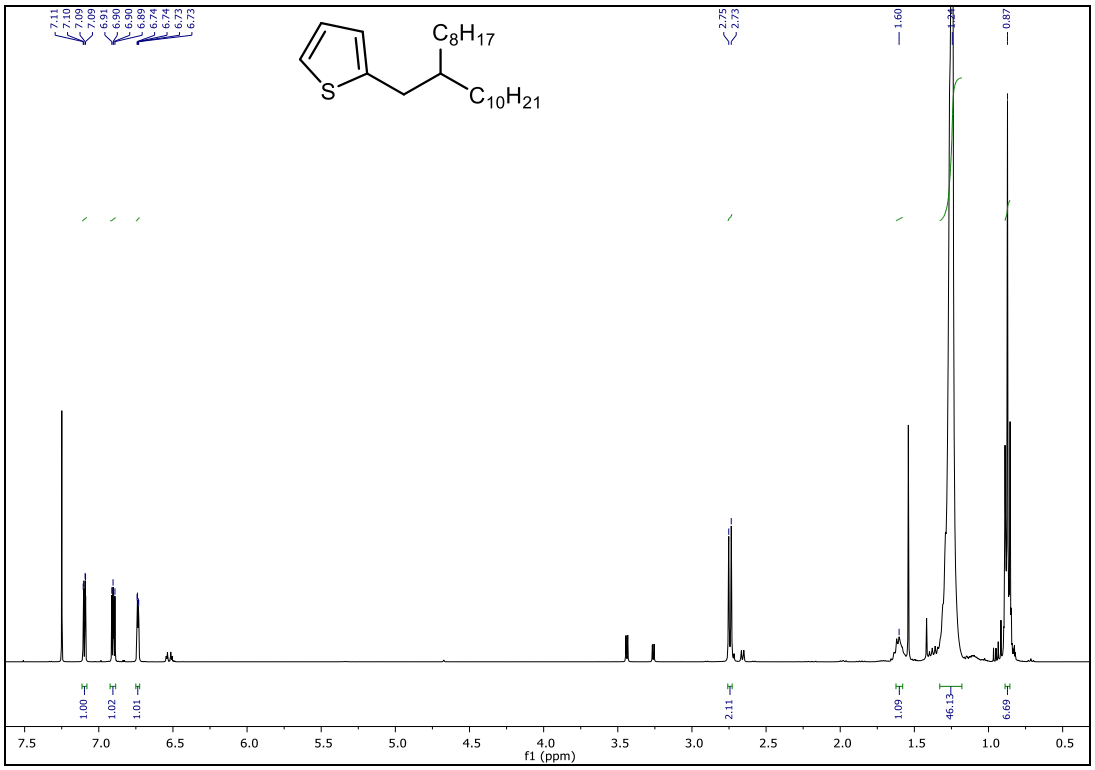

**2-(2-butyloctyl)thiophene (2 BO)**



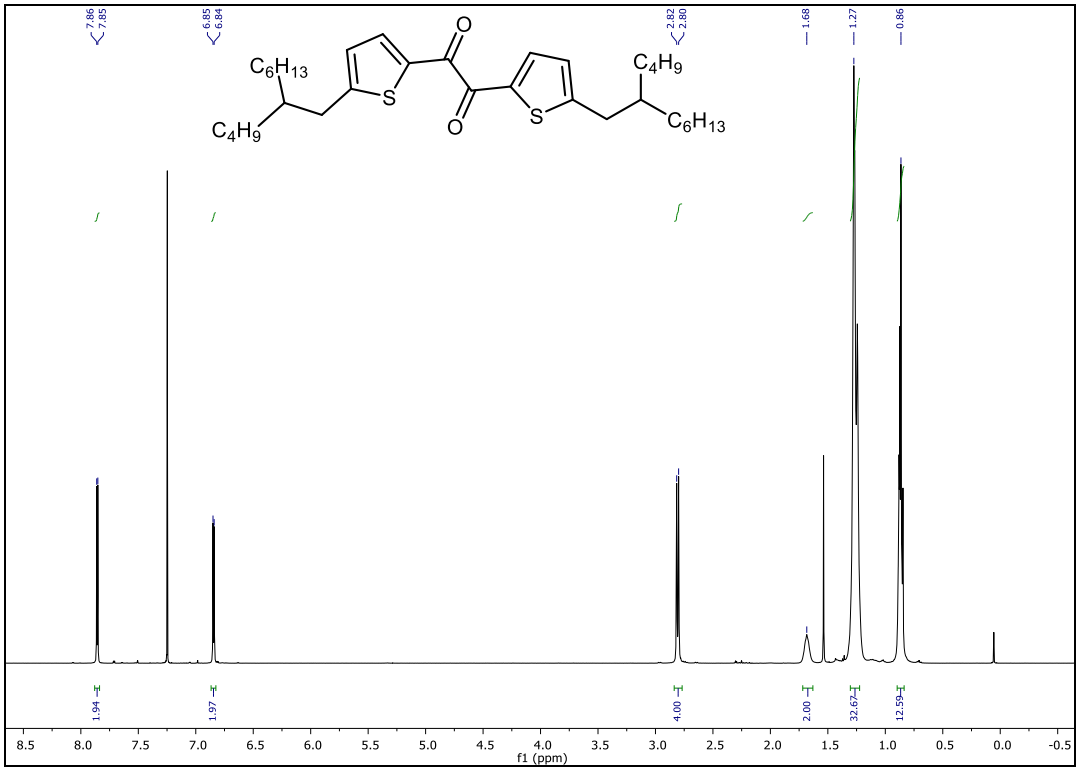
## 2-(2-hexyldecyl)thiophene (2 HD)



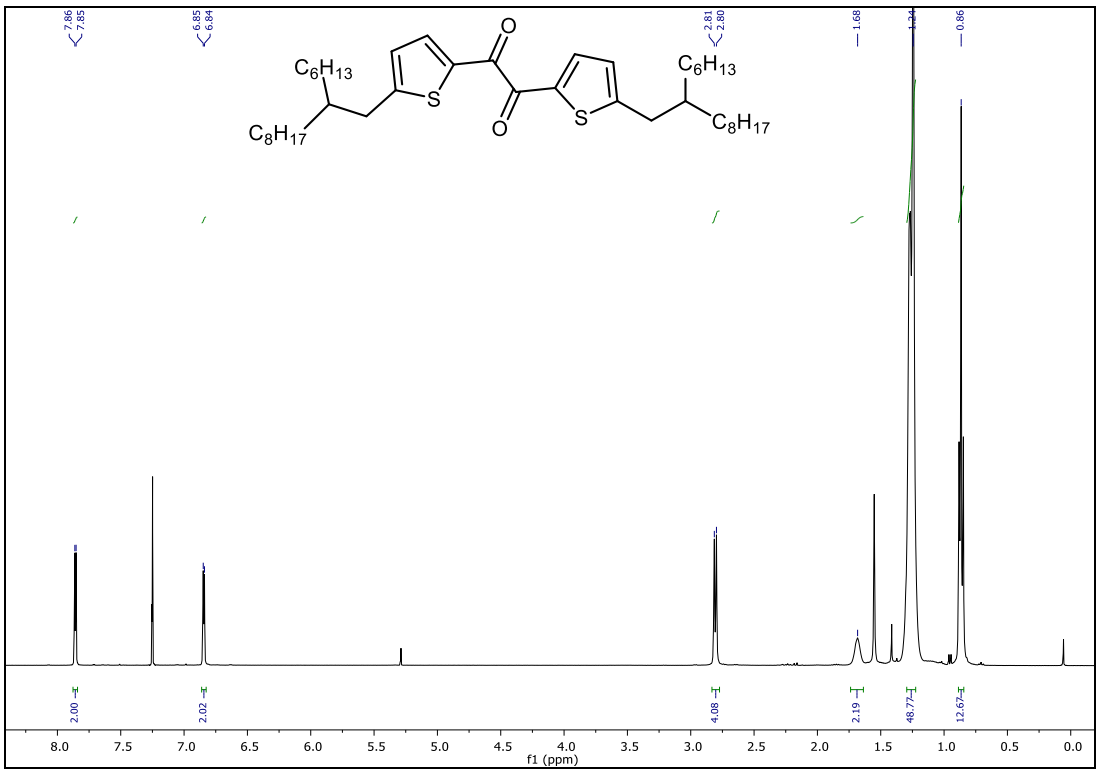

## 2-(2-octyldodecyl)thiophene (2 OD)



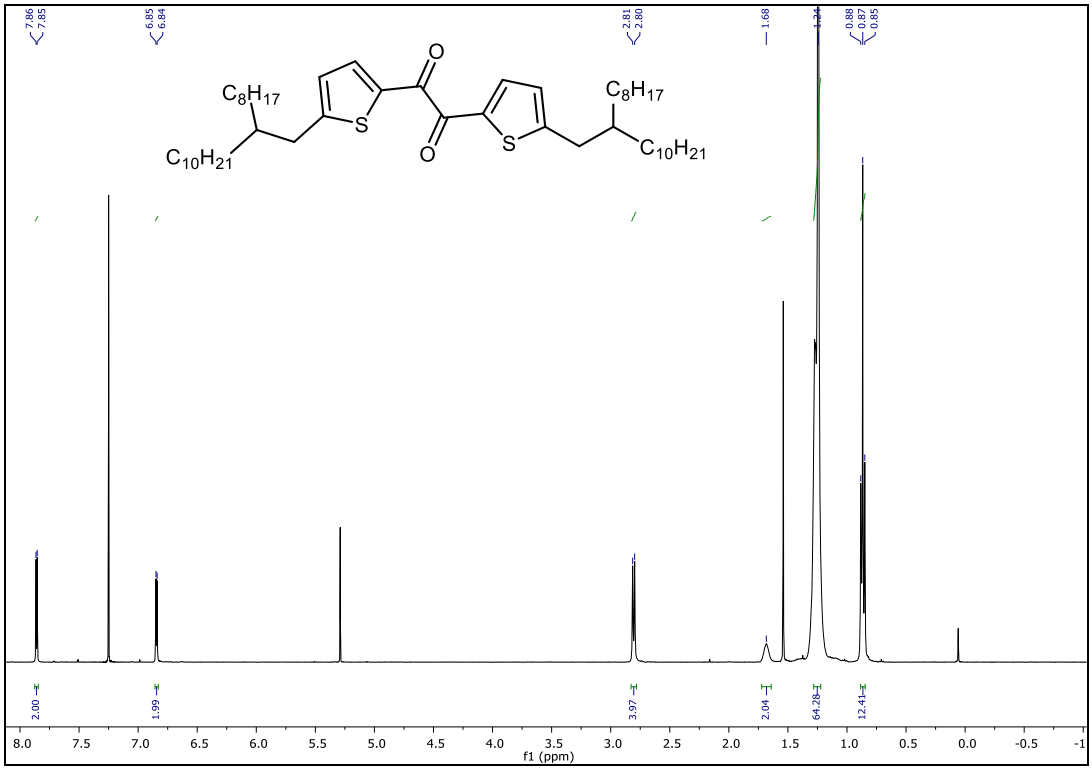
**1,2-bis(5-(2-butyloctyl)thiophen-2-yl)ethane-1,2-dione (3 BO)**



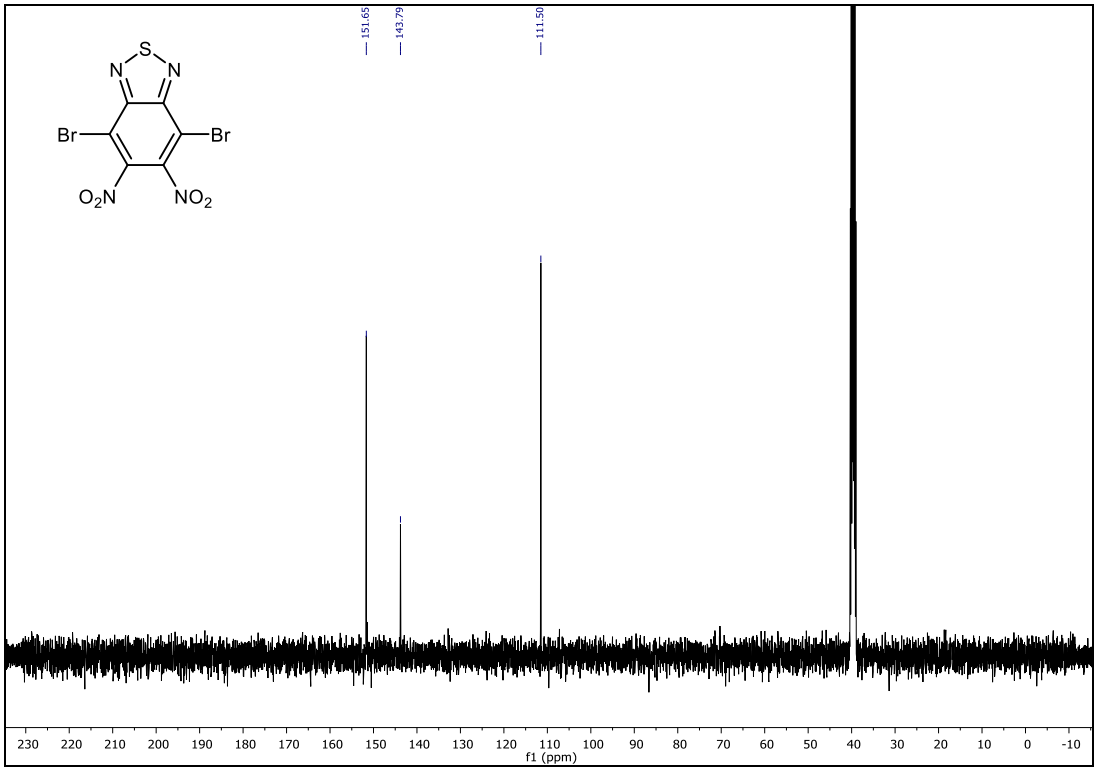

**1,2-bis(5-(2-hexyldecyl)thiophen-2-yl)ethane-1,2-dione (3 HD)**



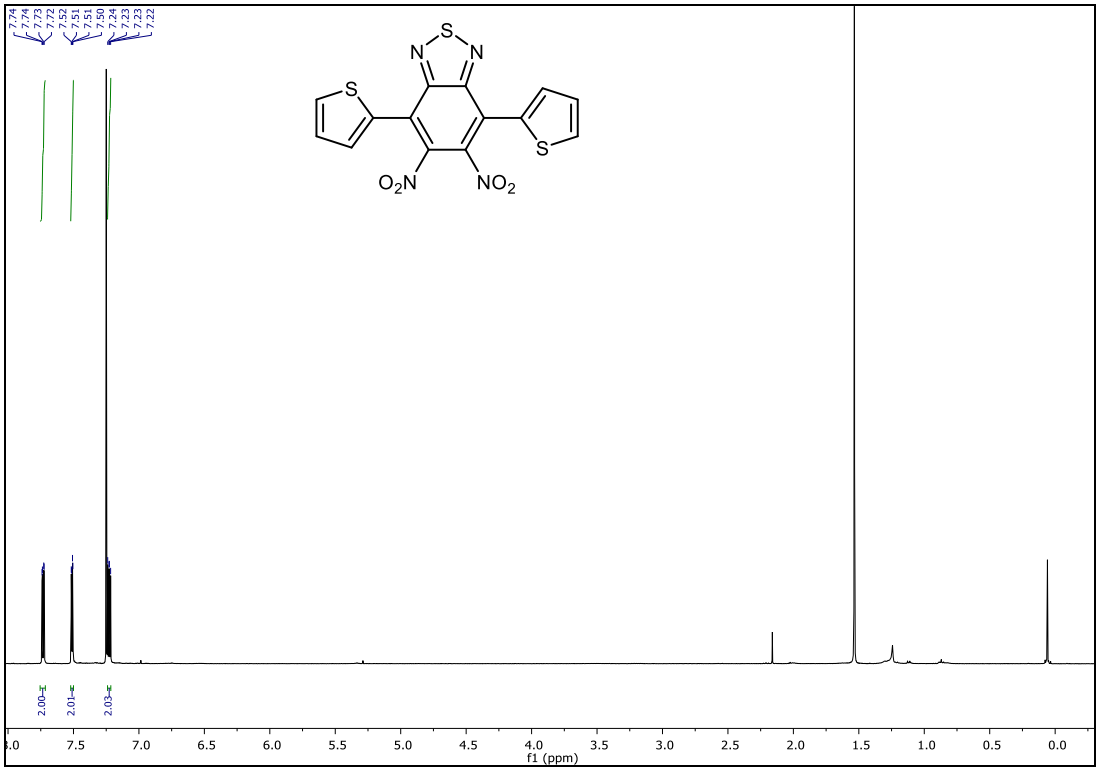
**1,2-bis(5-(2-octyldodecyl)thiophen-2-yl)ethane-1,2-dione (3 OD)**



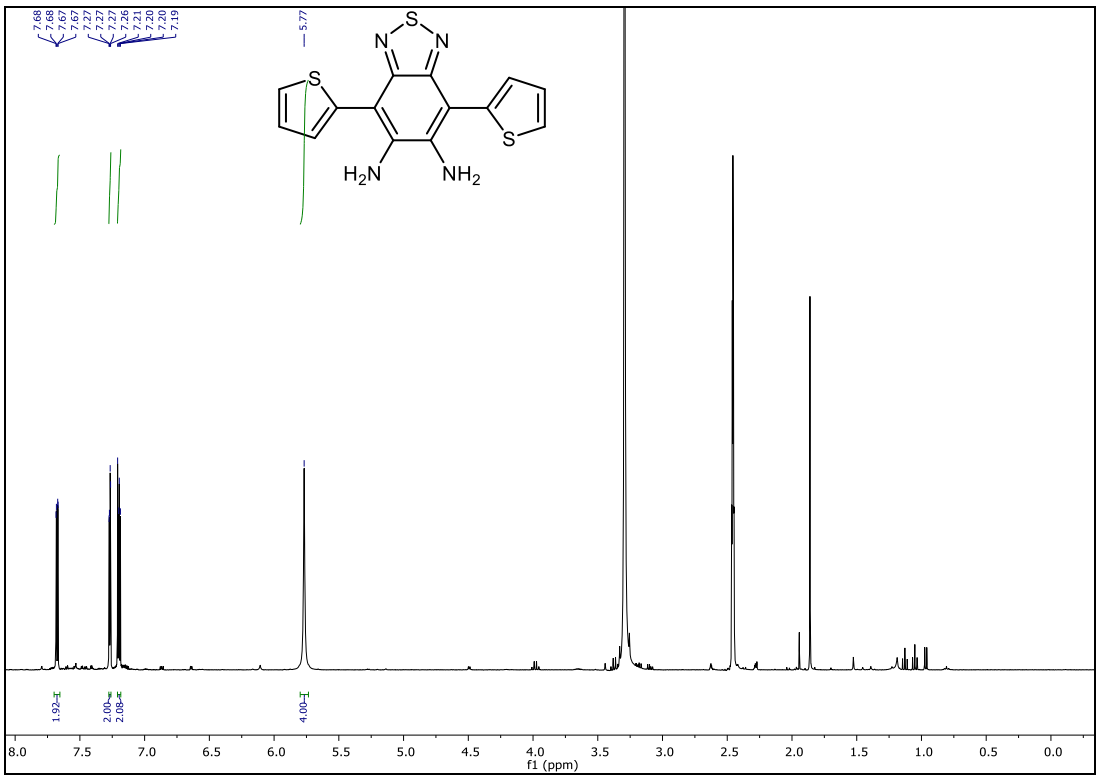

**4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (4)**



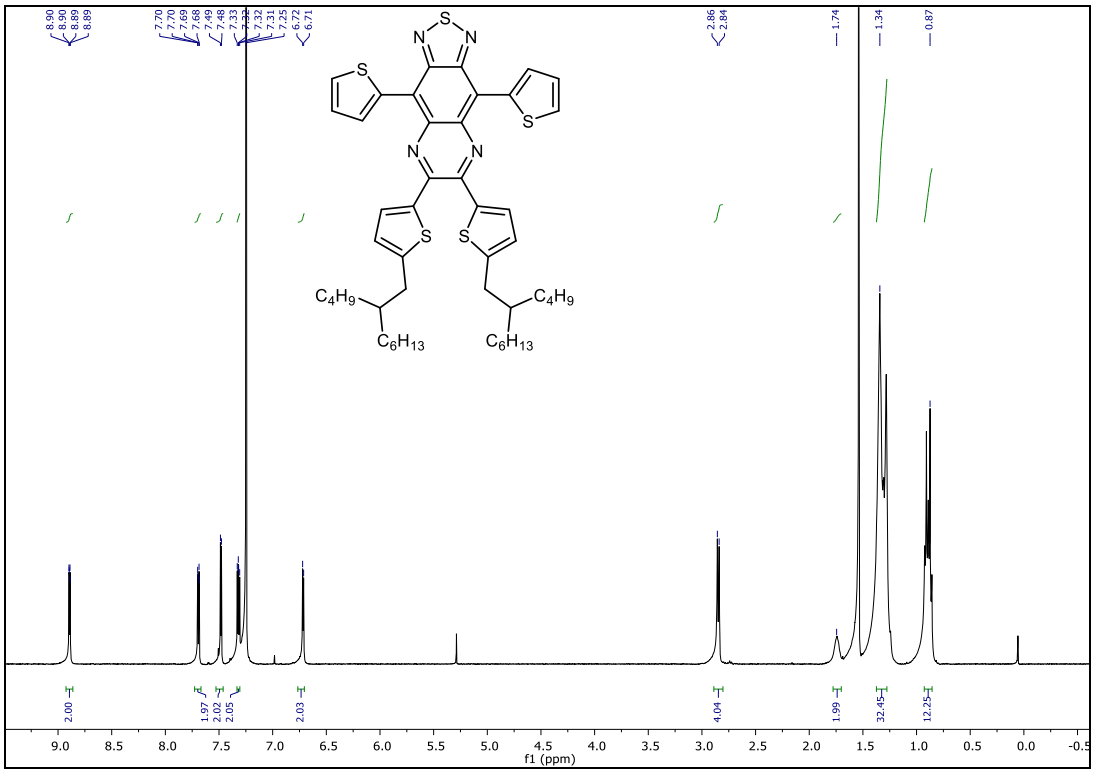
**5,6-dinitro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (5)**

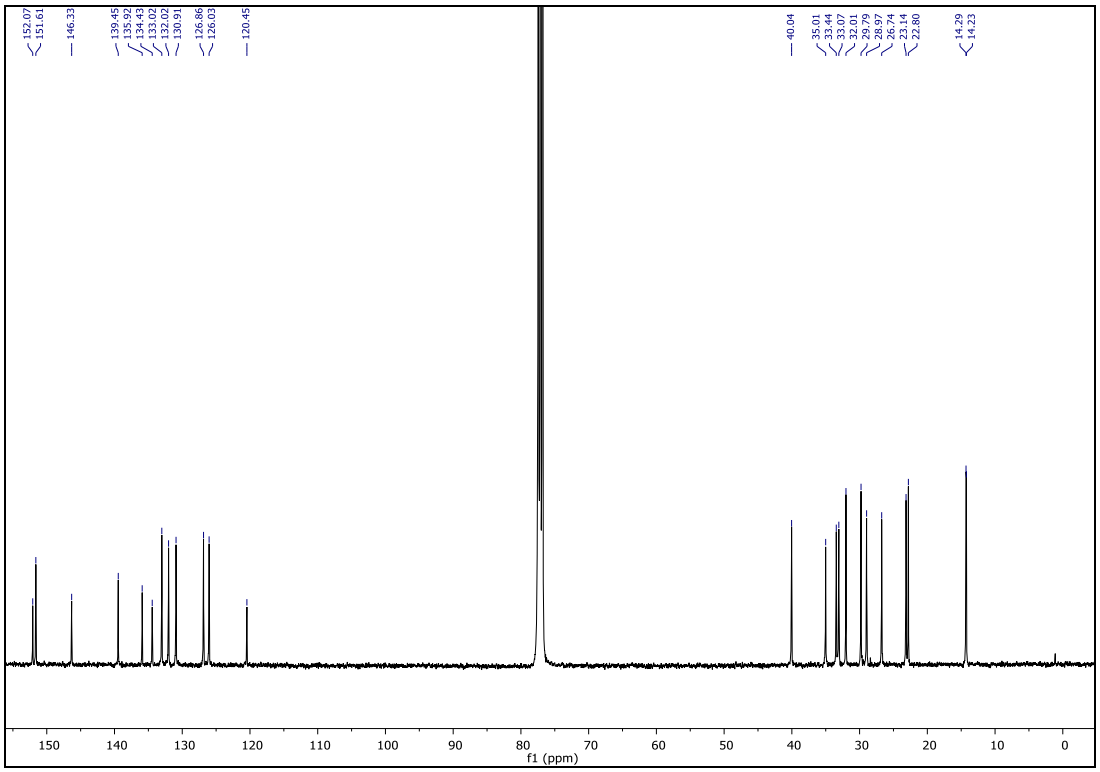



**5,6-diamino-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (6)**

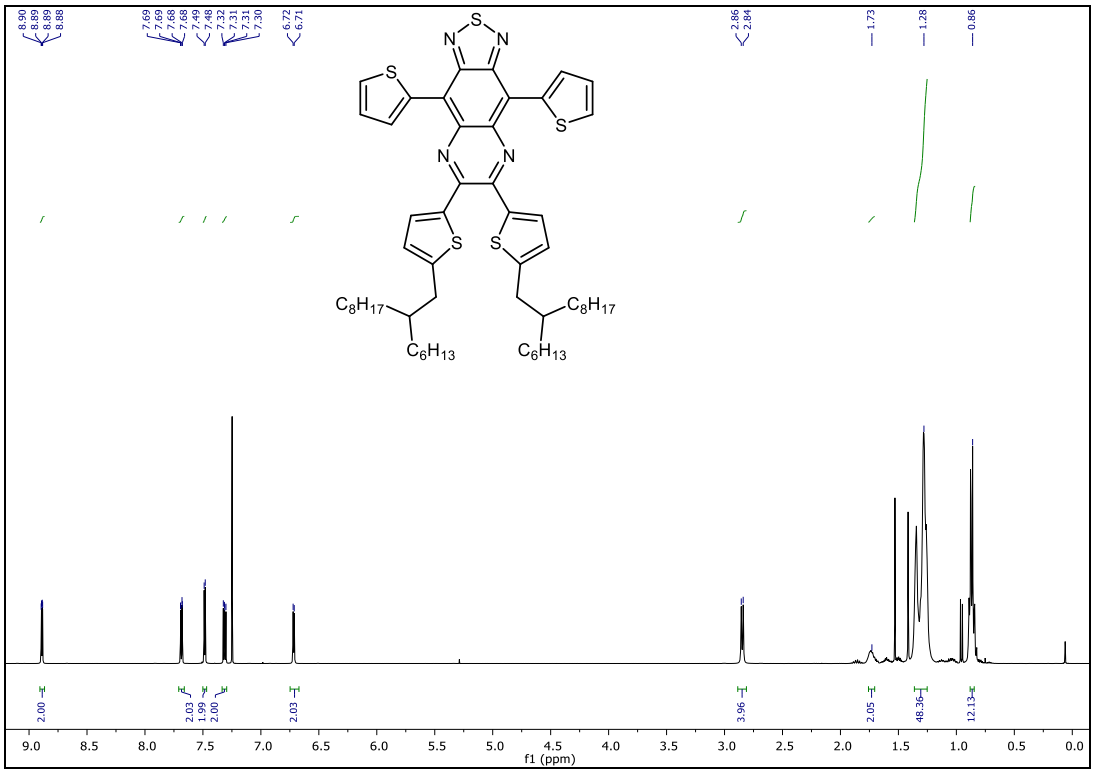


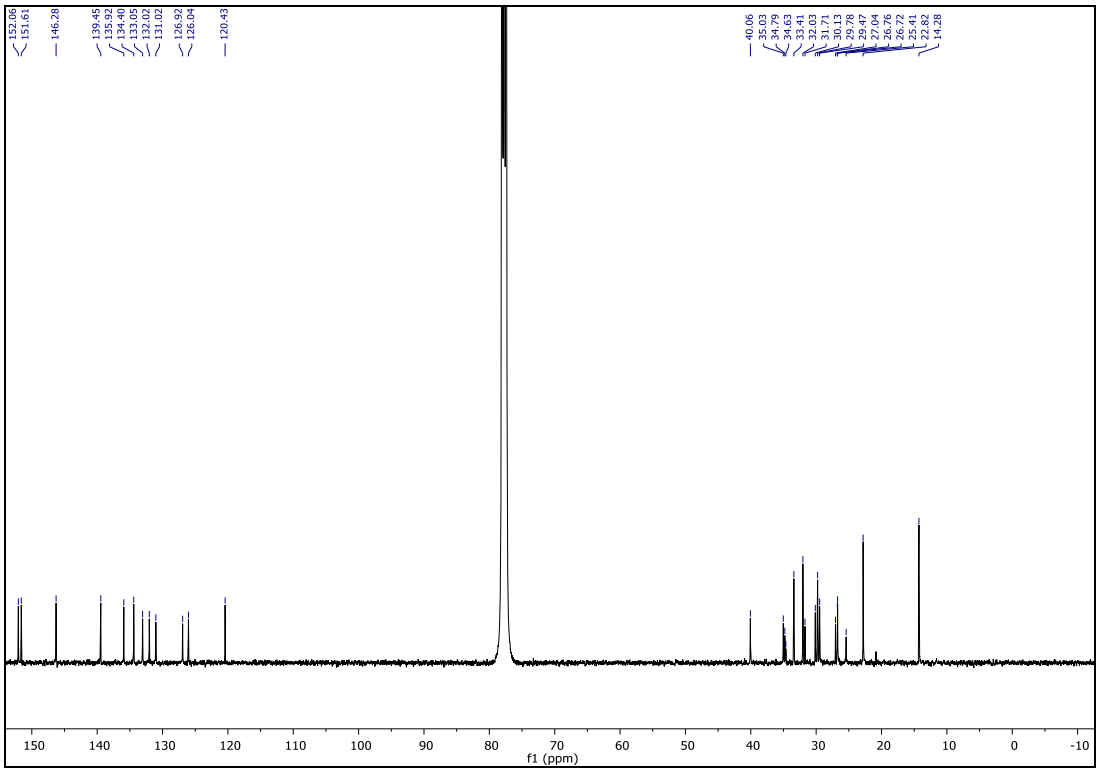
**6,7-bis(5-(2-butyloctyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (7 BO)**



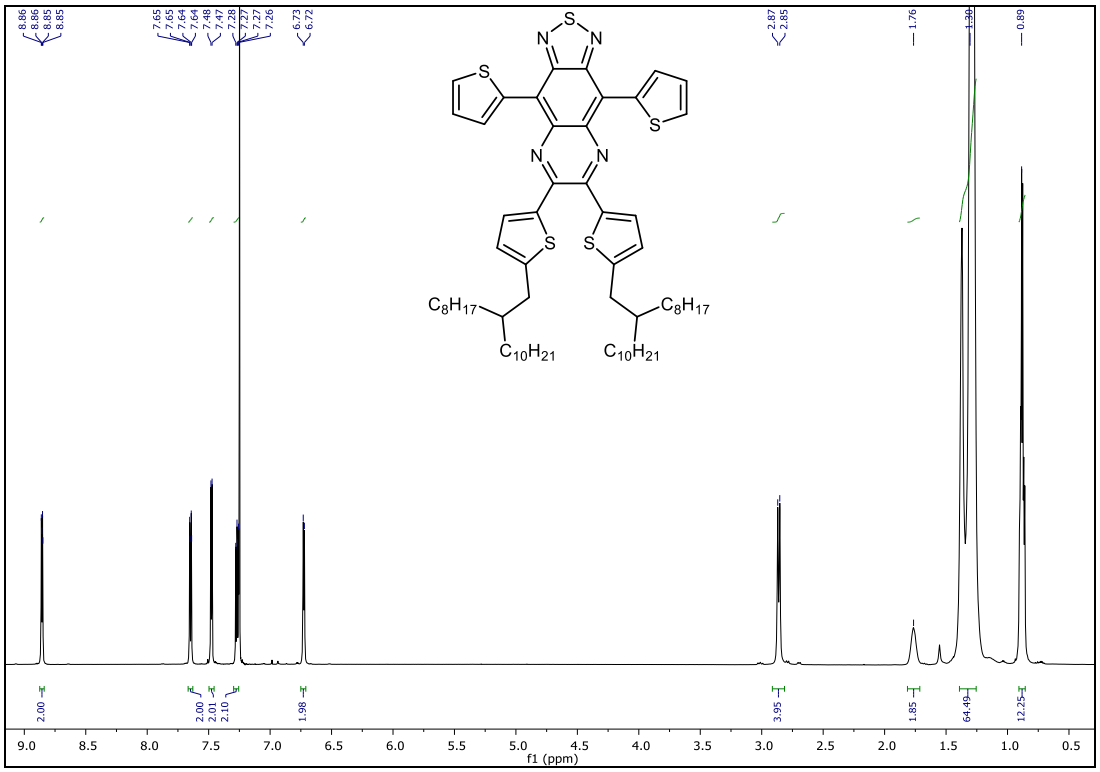



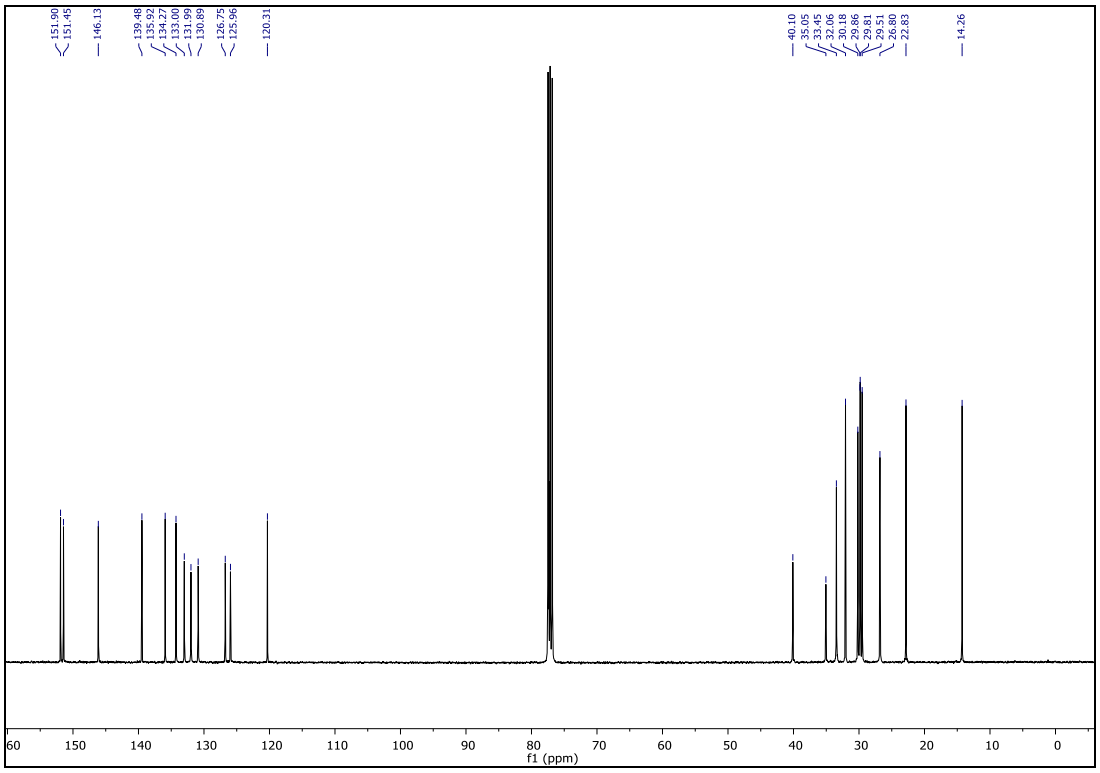
**6,7-bis(5-(2-hexyldecyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (7 HD)**



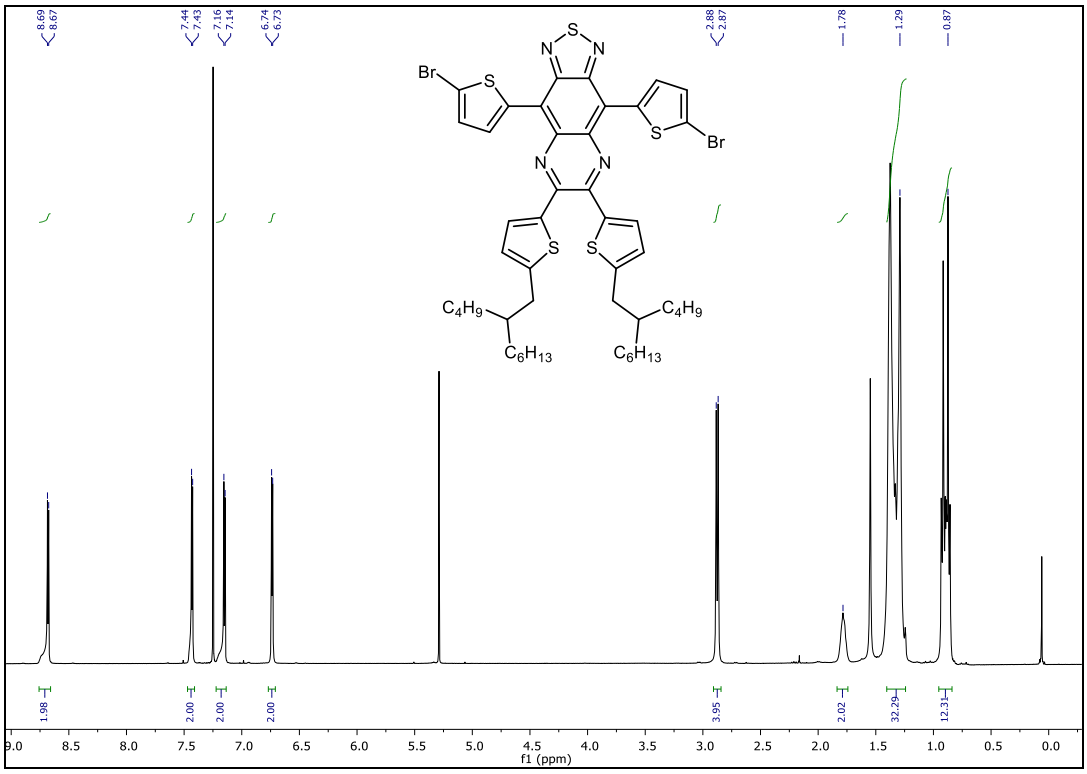



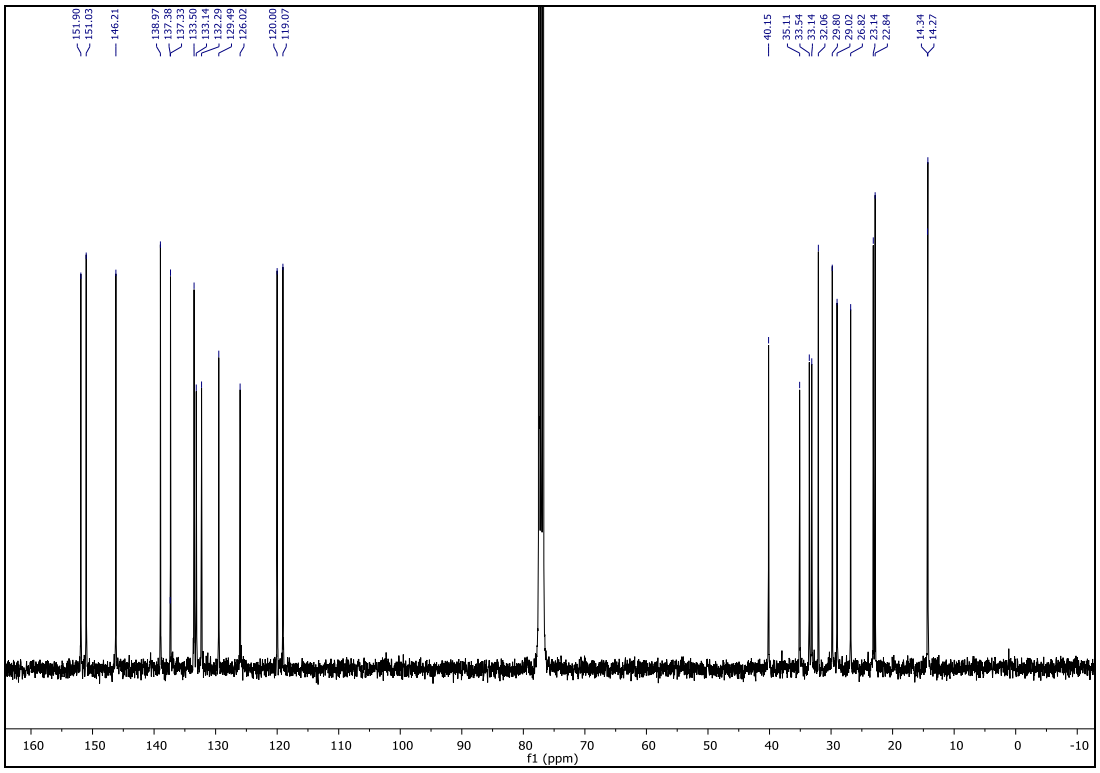
**6,7-bis(5-(2-octyldodecyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (7 OD)**



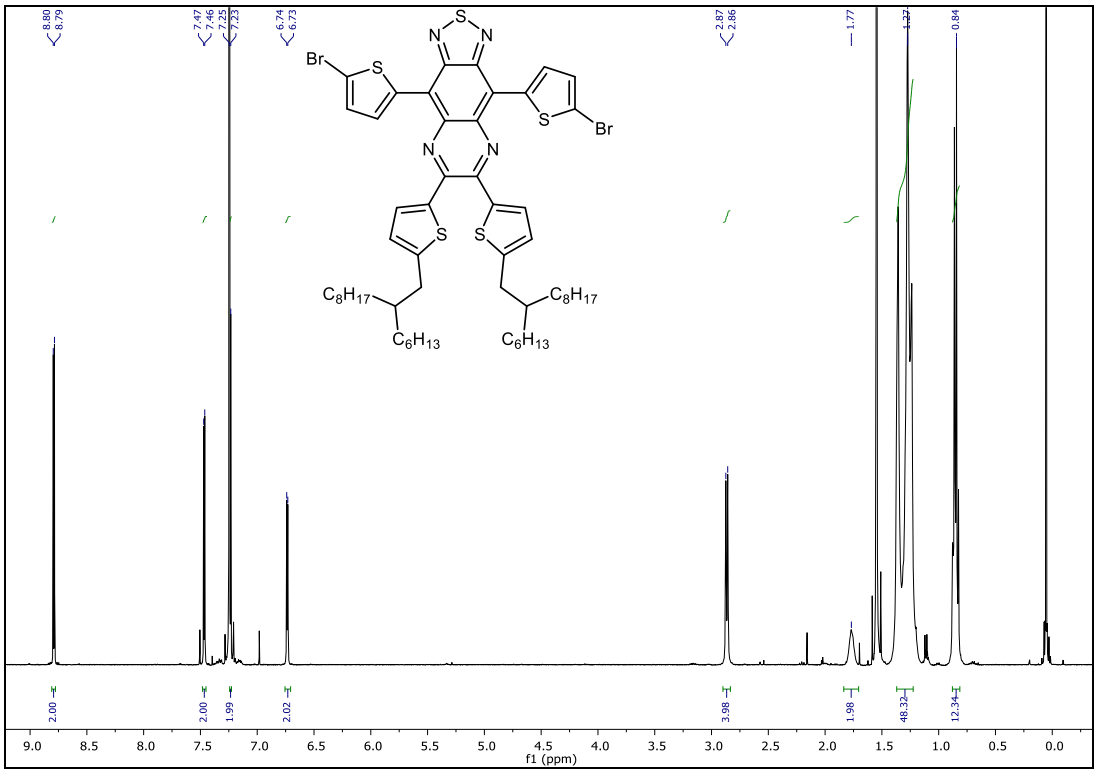



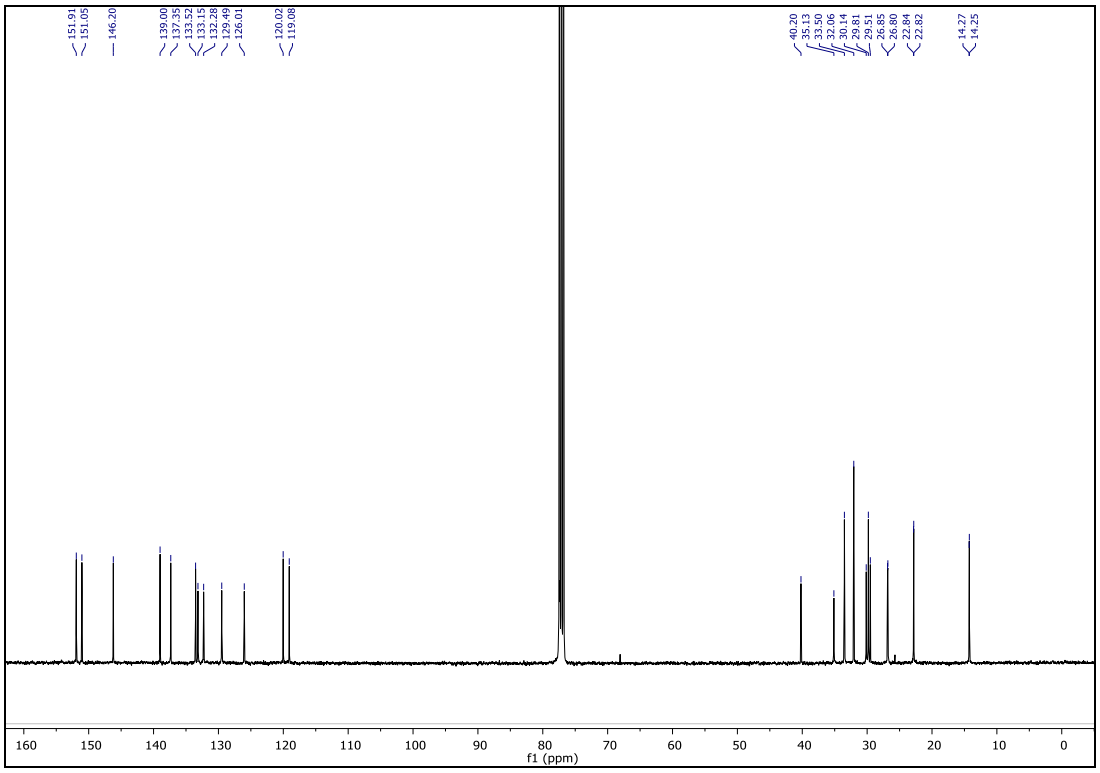
**4,9-bis(5-bromothiophen-2-yl)-6,7-bis(5-(2-butyloctyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (8 BO)**



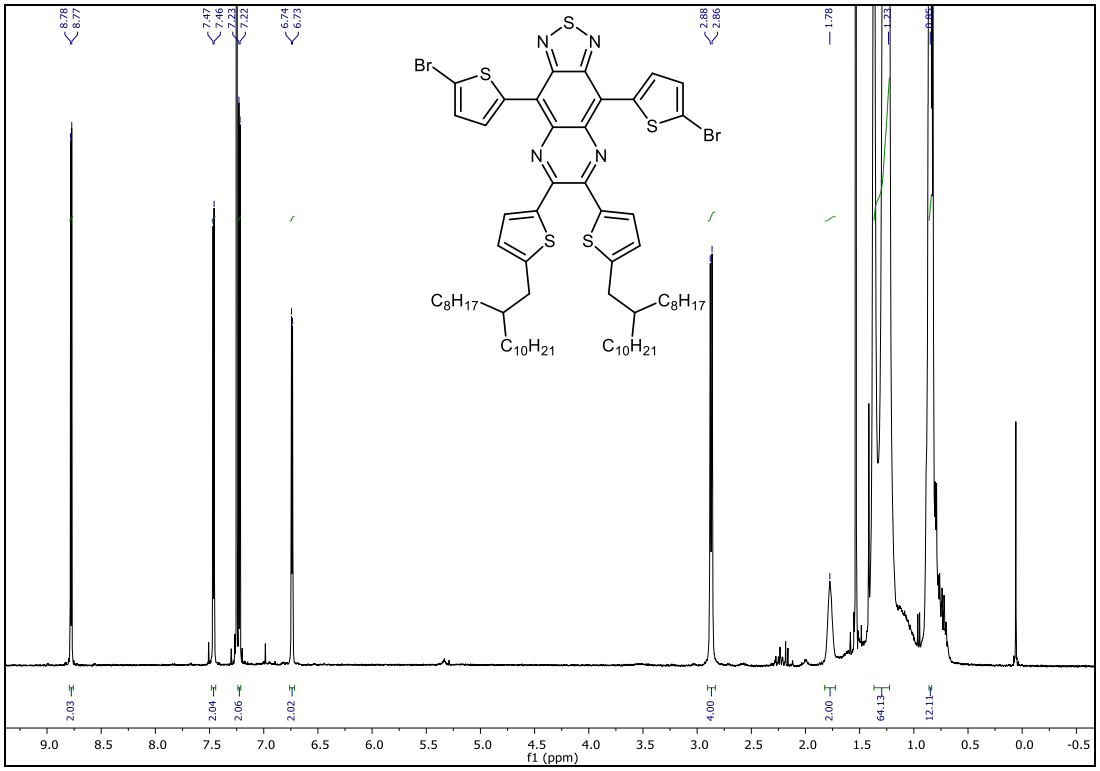



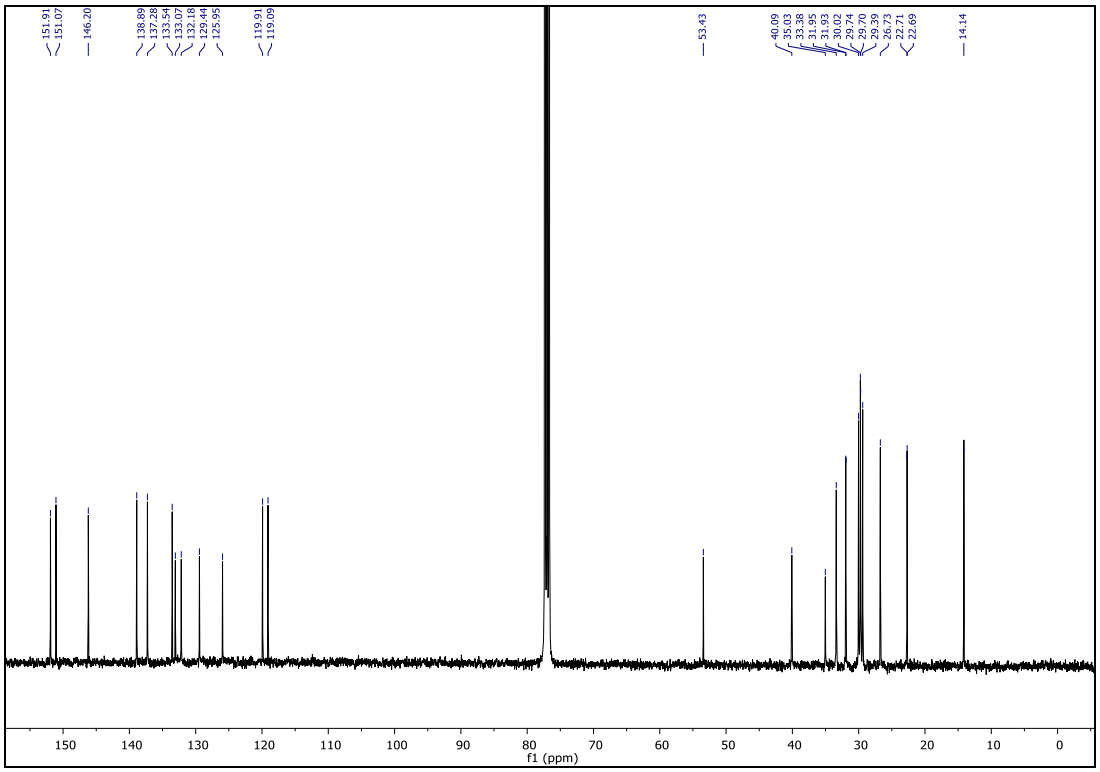
**4,9-bis(5-bromothiophen-2-yl)-6,7-bis(5-(2-hexyldecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (8 HD)**



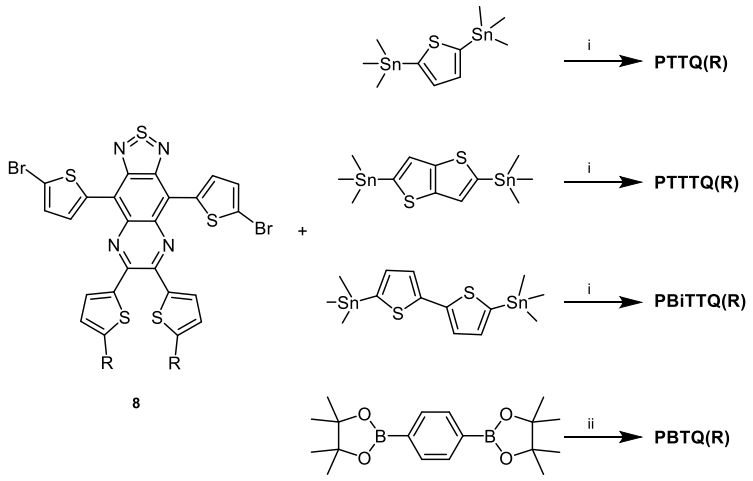



**4,9-bis(5-bromothiophen-2-yl)-6,7-bis(5-(2-octyldodecyl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (8 OD)**



## 4. Polymer synthesis




**Scheme S1.** *Synthetic pathway towards the TQ-based polymers: i) $Pd_2(dba)_3$, P(o-tolyl)$_3$, toluene/DMF, 125 °C; ii) $Pd_2(dba)_3$, $PPh_3$, aq. $K_3PO_4$, toluene, 115 °C.*

**PBTQ(OD).** TQ monomer **8 OD** (131.5 mg, 0.106 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (35.1 mg, 0.106 mmol), triphenylphosphine (3.3 mg, 12.6 µmol) and $Pd_2(dba)_3$ (2.9 mg, 3.2 µmol ) were dissolved in a mixture of $N_2$ purged toluene (1.5 mL) and a 2M aqueous $K_3PO_4$ solution (0.26 mL). The reaction was heated to 115 °C overnight after which the mixture was diluted in chlorobenzene. A scoop of diethylammonium diethyldithiocarbamate was added and the resulting mixture was stirred at 100 °C for 1 h. The mixture was then added dropwise to methanol, filtered in a thimble and purified by repetitive Soxhlet extractions using methanol, acetone, *n*-hexane, methylene chloride, chloroform and chlorobenzene. After concentrating the polymer containing fraction *in vacuo*, the target polymer was precipitated in methanol, filtered and dried, yielding a red/orange solid (38 mg, 31%). SEC (1,2,4-TCB, 160 °C, PS standards): $M_n$ = 33.1 kDa, $Đ$ = 3.2. UV-VIS-NIR: $\lambda_{max\ IR,film}$ = 942 nm.

**General polymerization procedure for PTQ(x)T, BiT and TT.** The dibrominated monomer **8** (1 equiv.), the distannylated donor monomer (1 equiv.), $Pd_2(dba)_3$ (0.03 equiv.) and P(*o*-tolyl)$_3$ (0.12 equiv.) were combined in a Schlenk tube and dissolved in dry toluene and DMF, which were degassed with $N_2$ for 15 min prior to the addition. The Schlenk tube was put under nitrogen, heated to 120 °C and the polymerization mixture was allowed to stir overnight. Then, the viscous solution was diluted in chlorobenzene after which a scoop of diethylammonium diethyldithiocarbamate was added and the mixture was stirred at 100 °C for 1 h. The resulting mixture was then added dropwise to methanol, filtered in a thimble and purified by repetitive Soxhlet extractions using methanol, acetone, *n*-hexane, methylene chloride, chloroform and chlorobenzene. After concentrating the polymer containing fraction *in vacuo*, the target polymer was precipitated in methanol, filtered and dried. All polymerizations were conducted according to this general procedure with minor modifications as listed below.

**PTTQ(BO).** TQ monomer **8 BO** (95.0 mg, 0.0940 mmol), 2,5-bis(trimethylstannyl)thiophene (38.5 mg, 0.0940 mmol), $Pd_2(dba)_3$ (2.6 mg, 2.8 µmol) and P(*o*-tolyl)$_3$ (3.4 mg, 11.2 µmol) were dissolved in a mixture of dry toluene (3.0 mL) and DMF (0.8 mL). The chloroform fraction obtained from Soxhlet extraction was precipitated in methanol and filtered, yielding a red solid (50 mg, 57%). SEC (1,2,4-TCB, 160 °C, PS standards): $M_n$ = 36.6 kDa, $Đ$ = 2.6. UV-VIS-NIR: $\lambda_{max\ IR,film}$ = 1145 nm.

**PTTQ(HD).** TQ monomer **8 HD** (109.7 mg, 0.0976 mmol), 2,5-bis(trimethylstannyl)thiophene (40.0 mg, 0.0976 mmol), $Pd_2(dba)_3$ (2.7 mg, 2.9 µmol) and P(*o*-tolyl)$_3$ (3.5 mg, 11.5 µmol) were dissolved in a mixture of dry toluene (2.0 mL) and DMF (0.5 mL). The chloroform fraction obtained from Soxhlet extraction was precipitated in methanol and filtered, yielding a red solid (91 mg, 89%). SEC (1,2,4-TCB, 160 °C, PS standards): $M_n$ = 52.8 kDa, $Đ$ = 2.7. UV-VIS-NIR: $\lambda_{max\ IR,film}$ = 1117 nm.

**PTTQ(OD).** TQ monomer **8 OD** (147.8 mg, 0.120 mmol), 2,5-bis(trimethylstannyl)thiophene (49.0 mg, 0.120 mmol), $Pd_2(dba)_3$ (3.3 mg, 3.6 µmol) and P(*o*-tolyl)$_3$ (4.4 mg, 14.4 µmol) were dissolved in a mixture of dry toluene (3.0 mL) and DMF (0.8 mL). The methylene chloride fraction obtained from Soxhlet extraction was precipitated in methanol and filtered, yielding a red/orange solid (98 mg, 73%). SEC (1,2,4-TCB, 160 °C, PS standards): $M_n$ = 21.9 kDa, $Đ$ = 2.0. UV-VIS-NIR: $\lambda_{max\ IR,film}$ = 1111 nm.

**PTTTQ(OD).** TQ monomer **8 OD** (94.6 mg, 0.0765 mmol), bis(trimethylstannyl)thieno[3,2-*b*]thiophene (35.7 mg, 0.0765 mmol), $Pd_2(dba)_3$ (2.1 mg, 2.3 µmol) and P(*o*-tolyl)$_3$ (2.8 mg, 9.2 µmol) were dissolved in a mixture of dry toluene (0.9 mL) and DMF (0.3 mL). The chloroform fraction obtained from Soxhlet extraction was precipitated in methanol and filtered, yielding a red/orange solid (86 mg, 92%). SEC (1,2,4-TCB, 160 °C, PS standards): $M_n$ = 64.6 kDa, $Đ$ = 1.8. UV-VIS-NIR: $\lambda_{max\ IR,film}$ = 1053 nm.

**PBiTTQ(HD).** TQ monomer **8 HD** (92.3 mg, 0.0822 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (40.4 mg, 0.0822 mmol), $Pd_2(dba)_3$ (2.3 mg, 2.4 µmol) and P(*o*-tolyl)$_3$ (3.0 mg, 10.3 µmol) were dissolved in a mixture of dry toluene (2.7 mL) and DMF (0.7 mL). The chlorobenzene fraction obtained from Soxhlet extraction was precipitated in methanol and filtered, yielding a red solid (40 mg, 43%). SEC (1,2,4-TCB, 160 °C, PS standards): $M_n$ = 11.1 kDa, $Đ$ = 2.1. UV-VIS-NIR: $\lambda_{max\ IR,film}$ = 1015 nm.

**PBiTTQ(OD).** TQ monomer **8 OD** (146.0 mg, 0.118 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (58.1 mg, 0.118 mmol), $Pd_2(dba)_3$ (3.2 mg, 3.5 µmol) and P(*o*-tolyl)$_3$ (4.3 mg, 14.1 µmol) were dissolved in a mixture of dry toluene (1.2 mL) and DMF (0.4 mL). The chlorobenzene fraction obtained from Soxhlet extraction was precipitated in methanol and filtered, yielding a red/orange solid (120 mg, 82%). SEC (1,2,4-TCB, 160 °C, PS standards): $M_n$ = 37.2 kDa, $Đ$ = 2.3. UV-VIS-NIR: $\lambda_{max\ IR,film}$ = 1018 nm.

## 5. Cyclic voltammetry

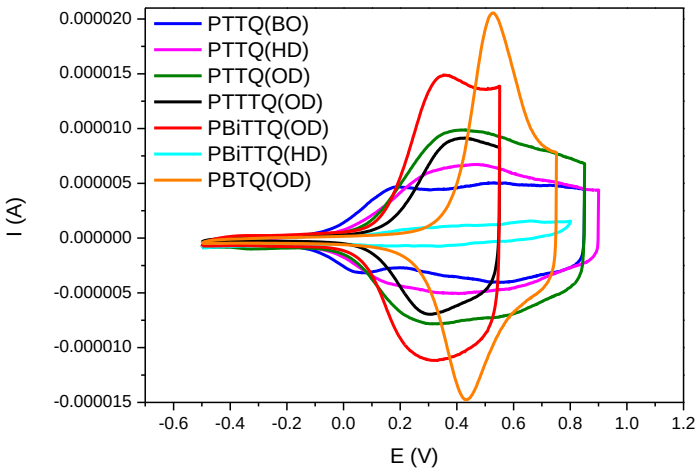



**Figure S1.** *Overlay of the oxidation curves (cyclic voltammetry) for all polymers.*

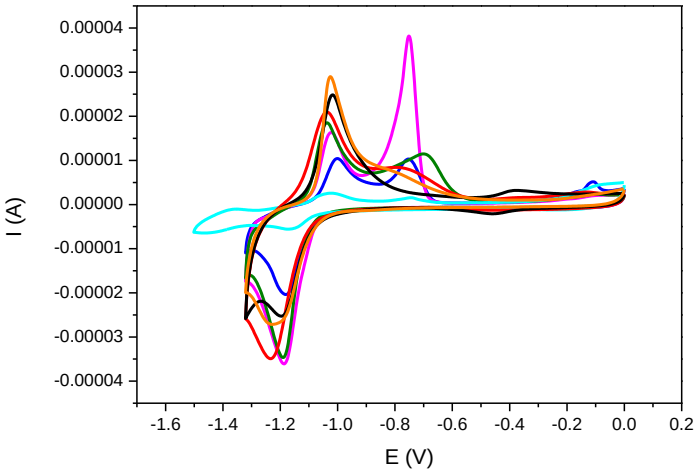



**Figure S2.** *Overlay of the reduction curves (cyclic voltammetry) for all polymers.*

## 6. Gel permeation chromatograms

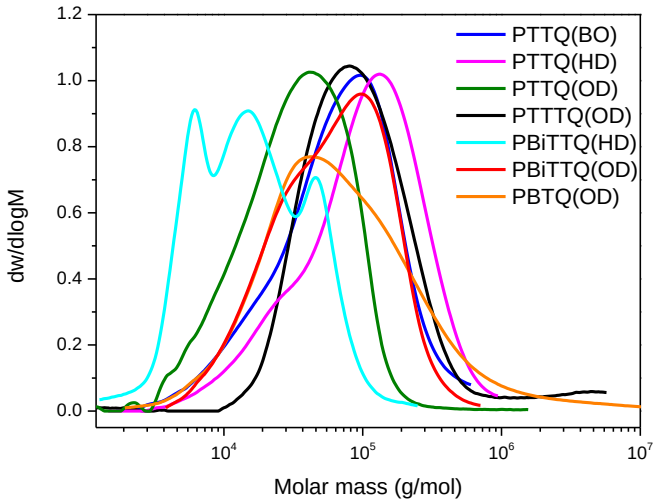



**Figure S3.** *Overlay of the GPC traces for all polymers.*

## 7. Organic photodetector fabrication and characterization

Bulk heterojunction organic photodetectors were prepared using the inverted architecture glass/ITO/ZnO/active layer/$MoO_3$/Ag. Prior to device processing, the ITO-coated substrates (100 nm, Kintec, sheet resistivity 20 Ω $sq^{-1}$) were thoroughly cleaned via sonication in soap water, demineralized water, acetone and isopropanol, followed by a UV/$O_3$ treatment for 30 min. ZnO interlayers were spin-coated from a solution of $Zn(OAc)_2.2H_2O$ (0.5 g, Merck) and ethanolamine (0.14 g, Merck) in 2-methoxyethanol (Merck).[12] The ZnO layers were annealed at 300 °C for 10 min to obtain a layer thickness of ~30 nm. Further processing was performed under nitrogen atmosphere in a glove box (<1 ppm $O_2$/$H_2O$). The photoactive layer solution, consisting of the active polymer and $PC_{71}BM$ (Solenne), was then spin-coated from *o*-dichlorobenzene. The devices were prepared with a blend solution of 1:3 polymer:$PC_{71}BM$, with a total concentration of 48 mg $mL^{-1}$ in *o*-dichlorobenzene with 3 v/v% of 1,8-diiodooctane (DIO) additive (accept for **PTTQ(HD)**, which was spin-coated from chloroform with a total concentration of 32 mg $mL^{-1}$). The solution was stirred overnight at 80 °C to ensure complete

dissolution. The active layer was deposited on top of the ZnO layer by means of spin-coating at room temperature with an optimal layer thickness near 300 nm. Finally, the top electrodes $MoO_3$ (10 nm) and Ag (100 nm) were deposited by vacuum deposition to afford photodetector devices with an active area of 3 mm². The *J-V* characteristics of all photodetectors in darkness were evaluated using a Keithley 2400 source meter, in darkness. EQE measurements were performed using a homebuilt setup, combining a Newport Apex illuminator (100 W Quartz Tungsten Halogen lamp) as light source with a Newport Cornerstone 130° monochromator. The monochromated light was chopped at 123 Hz and the photocurrent measured using a Stanford SR830 lock-in amplifier. A pyro-electric detector was employed as a reference cell. AFM experiments were performed (on the devices used for the *J-V* measurements) with a JPK NanoWizard 3 AFM (JPK Instruments AG, Berlin, Germany) using AC mode in air. Silicon ACTA-50 tips from AppNano with cantilever length ~125 mm, spring constant ~40 N $m^{-1}$ and resonance frequency ~300 kHz were used. The scan angle, set point height, gain values and scan rate were adjusted according to the calibration of the AFM tip. Frequency response measurements were performed using an ENA network analyser (E5061B 5 Hz – 500 MHz) and an Oxxius L6Cc laser source tuned by a Keysight 33600 A series waveform generator to enable the pulsed input signals. The linear dynamic range was determined using an EXA signal analyser (N9010B 10 Hz – 3.6 GHz) and an Oxxius L6Cc laser source attenuated by Thorlabs light attenuators.

## 8. Spectral responsivity

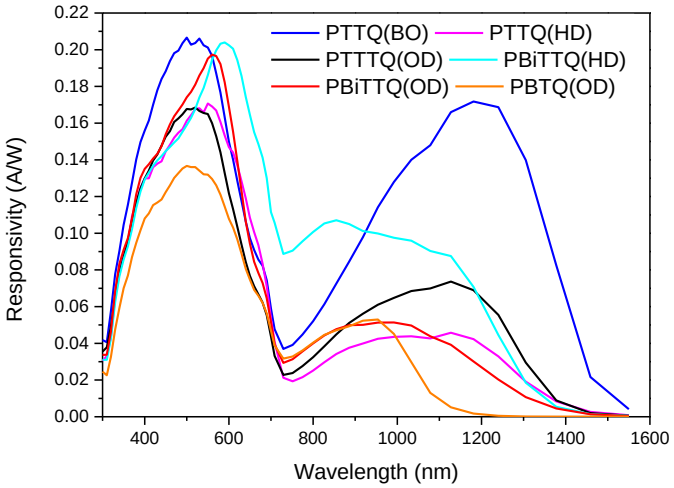



**Figure S4.** *Spectral responsivity for the optimally performing NIR-OPD devices at -2 V bias.*

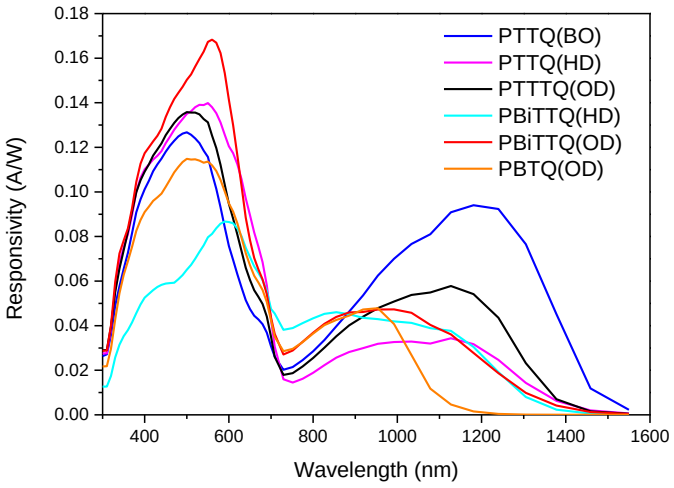



**Figure S5.** *Spectral responsivity for the optimally performing NIR-OPD devices at 0 V bias.*

## 9. Atomic force microscopy

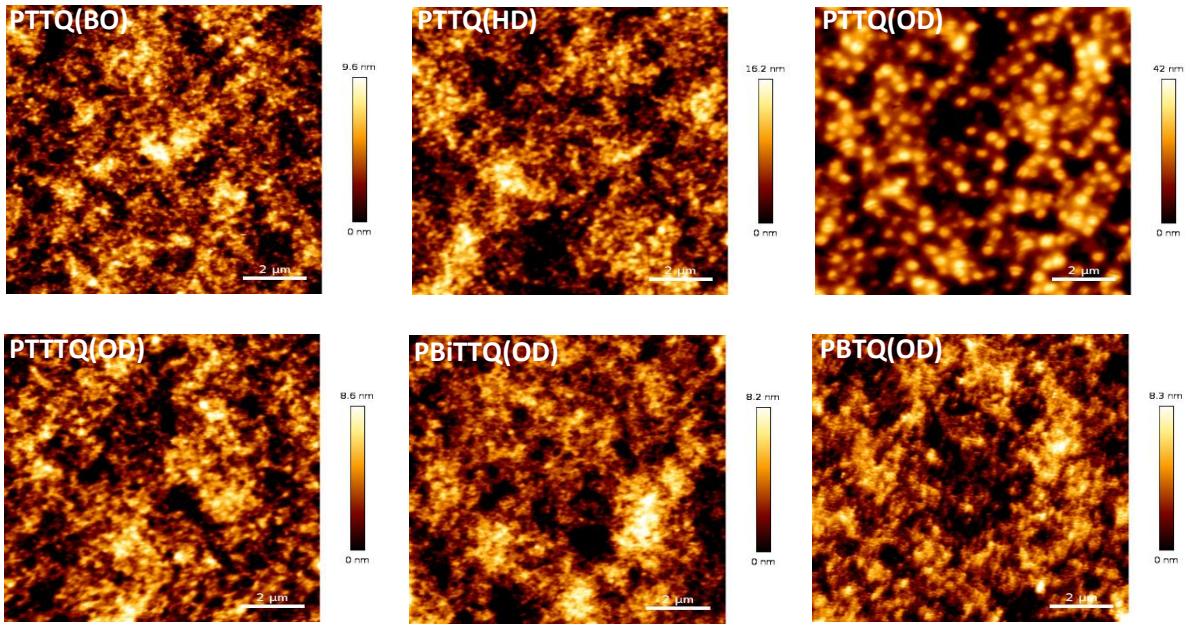



**Figure S6.** *AFM images of the active layer blends from the optimally performing NIR-OPD devices.*

The active layer of the photodiodes prepared from **PBiTTQ(HD)** had a very high roughness and showed visible light scattering and was therefore not analysed by AFM.

## 10. Frequency response

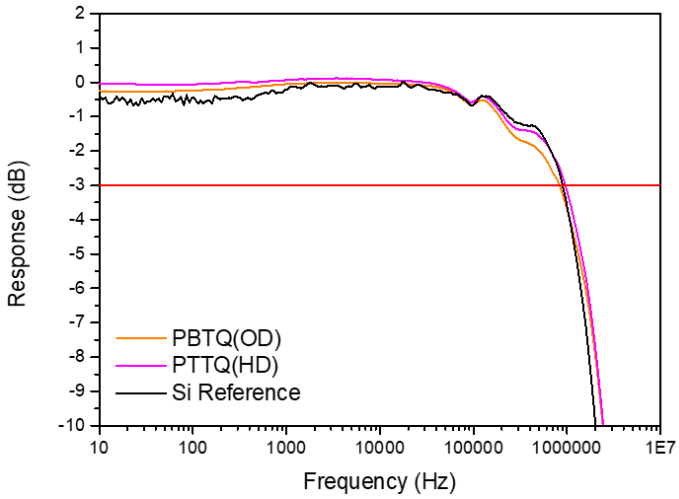



**Figure S7.** *Spectral responsivity for the optimally performing PBTQ(OD) and PTTQ(HD)-based NIR-OPD devices at -2 V bias.*

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