

Donor-Acceptor-Donor based π -Conjugated Oligomers for Nonlinear Optics and Near IR Emission

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Supporting Information

Experimental Section

Synthesis:

All reagents and starting materials were purchased from commercial sources and used without further purification unless otherwise noted. The solvents were distilled and dried using known methods^[1]. 2-(6-bromhexyloxy)tetrahydro-2*H*-pyran¹ (**1**), 4,7-bis(5-brom-thiophen-2-yl)benzo [c][1,2,5]thiadiazole² (**13**), 4,7-bis(7-bromo-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo [c][1,2,5]thiadiazole² (**14**), 6,7-dihexyl-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline³ (**21**) and 4,8-bis(2,3-dihydrothieno [3,4-*b*][1,4]dioxin-5-yl)benzo[1,2-*c*;4,5-*c'*]bis[1,2,5]thiadiazole⁴ (**25**) were prepared according to the literature. All reactions were done under argon atmosphere if not otherwise mentioned. ¹H NMR and ¹³C NMR spectra were collected on a Mercury 300 MHz using CDCl₃ or C₂D₂Cl₄ and were referenced to the solvent residual peak (CDCl₃: ¹H: δ= 7.26 ppm, ¹³C: δ= 77.23 ppm; C₂D₂Cl₄: ¹H: δ= 6.00 ppm). Elemental analyses were carried out by Robertson Microanalytical Laboratories, Inc. or Atlantic Microlab, Inc. High resolution mass spectrometry was performed by the spectroscopic services at the Department of Chemistry of University of Florida with a Finnigan MAT 96Q mass spectrometer.

Spectroscopy:

Absorption spectroscopy was performed using a Varian Cary 500 Scan UV-Vis-near-IR spectrophotometer. Both the measurements performed at the University of Florida and the University of Central Florida were performed on this same spectrophotometer model. Fluorescence spectroscopy was performed using a Horiba, Fluoro Max 3 for spectra up to 800 nm. Spectra with λ_{max em} greater than 800 nm were collected with a Photon Technology International Quantamaster near-IR spectrophotometer equipped with an InGaAs photodiode detector, optical chopper, and lock in amplifier.

Electrochemistry:

Electrochemistry was performed using a three-electrode cell with a platinum wire or a Pt flag as the counter electrode, a silver wire pseudo-reference electrode calibrated using a 5 mM solution of Fc/Fc⁺ in 0.1 M electrolyte solution, and a platinum button as the working electrode. The measurements were done in solution (CH₂Cl₂) and all potentials were reported vs. Fc/Fc⁺. An EG&G Princeton Applied Research model 273 potentiostat was used under the control of Corrware II software from Scribner and Associates.

Nonlinear optical spectroscopy:

Two different experimental techniques, Z-scan^{5, 6} and two-photon fluorescence (2PF)⁷ were used for measuring the frequency-degenerate two-photon absorption (2PA) spectra. Both experiments were performed using a femtosecond OPG/OPA source tunable from 270 nm to 2.2 μm. The OPG/OPA is pumped by a Ti:Sapphire regenerative amplifier, Clark-MXR

CPM-2010, which generates ~ 2 mJ per pulse, ~ 140 fs (FWHM) pulsewidth at 775 nm with a pulse repetition rate of 1 kHz. All compounds were prepared in chloroform for the linear and nonlinear optical characterization by saturating the liquid solution, filtering with 200 nm PTFE filters followed by a $\sim 20\%$ dilution and stirred to allow for any aggregates to dissolve. Concentrations were then measured from the previously measured molar absorptivity in 100 μm and 1 mm cells and compared in shape to low concentration spectra to further ensure no aggregation remains.

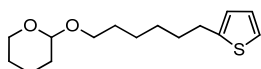
In general, the 2PF technique is more sensitive for measuring samples with relatively large fluorescence quantum yields ($>1\%$), and it is normally used to measure the weak 2PA band close to the 2PA edge. For each wavelength measured, the 2PA cross-section is calculated based on known reference samples Rhodamine B in methanol and the quadratic dependence of the fluorescence on the pump irradiance is also verified to avoid any possible influence of one-photon excited fluorescence. It was not possible to obtain the absolute values of the 2PA cross-sections via 2PF for samples with a significant portion of their fluorescence beyond 800 nm, as this is beyond the calibrated detection limit of our 2PF system. In this event, only the shape of the spectrum was obtained by 2PF and open-aperture Z-scan was performed to measure the absolute value of the cross-sections. For every wavelength, the femtosecond Z-scan is aligned and calibrated by measuring the 2PA and nonlinear refractive index of semiconductors, ZnSe (for $\lambda < 900$ nm) and CdTe (for $\lambda > 900$ nm), and the nonlinear refractive index of carbon disulfide.

Device Fabrication and Characterization:

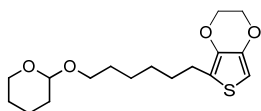
PLEDs were fabricated on prepatterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of $\sim 20 \Omega/\square$. The ITO substrates were cleaned sequentially with a sodium dodecyl sulfate solution, acetone, and isopropyl alcohol. The substrates were then exposed to an oxygen plasma followed by spin coating with a layer of PEDOT:PSS (Baytron P VP Al4083) and annealing at 120°C under vacuum. The active layer solutions were prepared and spin coated from chlorobenzene in an argon atmosphere glovebox (<0.1 ppm oxygen and water). The cathode of LiF (1 nm), Ca (10 nm) and Al (80 nm) was deposited in a thermal evaporator at a pressure of 1×10^{-6} mbar. The electroluminescence spectra were measured inside the argon atmosphere glovebox with an Ocean Optics USB 4000 fiber optic spectrometer. Radiometric measurements were performed in ambient atmosphere with a UDT optometer (Model S471) coupled with a calibrated Si photodiode (350-1100 nm range).

Morphology Characterization:

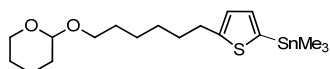
Film morphology was characterized through AFM and TEM. A Veeco Innova scanning probe microscope with MikroMasch NSC 15 tapping mode silicon probes (~300 kHz resonant frequency) was used in tapping mode for the AFM height measurements. TEM imaging was carried out on a JEOL 200CX TEM at an accelerating voltage of 120 kV in the Major Analytical Instrumentation Center at the University of Florida.



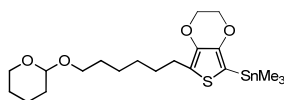
2-(6-(Thiophen-2-yl)hexyloxy)tetrahydro-2H-pyran (2): To a solution of thiophene (15.7 mL, 172 mmol) in THF cooled at -78°C was added n-butyllithium (21 mL, 52 mmol). The reaction mixture was allowed to warm up and was stirred for 1h at room temperature. Then 2-(6-bromohexyloxy)tetrahydro-2H-pyran (**1**) (8.5 g 32 mmol) in 15 mL THF was added and the mixture was stirred at 50°C for 12 h. The reaction poured on to ice and extracted with diethyl ether, the combined organic layers were washed with water and dried over magnesium sulfate. After removing the solvent, column chromatography (SiO_2 hexane:ethylacetate 8:1) afforded the title compound as a colorless oil 5.3 g (62%). Anal. calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{S}$: C 67.12, H 9.01, found C 67.29, H 9.34, N 0.00; HRMS (ESI TOF) m/z calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{SNa}$: 291.1389 (MNa^+) found 291.1379 (MNa^+); ^1H NMR (CDCl_3): δ 7.10 (d, 1H), 6.91 (t, 1H), 6.77 (d, 1H), 4.57 (t, 1H), 3.87 (m, 1H), 3.74 (dt, 1H), 3.50 (m, 1H), 3.39 (dt, 1H), 2.86 (t, 2H), 1.85-1.35 (m, 14H); ^{13}C NMR (CDCl_3): δ 145.67, 126.59, 123.88, 122.69, 98.82, 67.52, 62.31, 31.69, 30.75, 29.62, 28.89, 25.974, 25.47, 19.67.



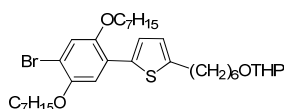
5-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin (3): To a solution of 2,3-dihydrothieno[3,4-b][1,4]dioxine (21 g, 147 mmol) in THF cooled at -78°C was added n-butyllithium (26 mL, 65 mmol). The reaction mixture was stirred for 1h at -78°C before 2-(6-bromohexyloxy)tetrahydro-2H-pyran (**1**) (12.5 g 47 mmol) in 15 mL THF was added. Then the mixture was allowed to warm up to rt and was stirred for additionally 12 h. The reaction poured in to water and extracted with diethyl ether, the combined organic layers were washed with water and dried over magnesium sulfate. After removing the solvent, column chromatography (SiO_2 hexane:diethylether 3:1) afforded compound (**3**) as a light yellow oil 8.57 g (55%). Anal. calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_4\text{S}$: C 62.55, H 8.03, N 0.00 found C 62.52, H 8.26, N 0.33; HRMS (ESI TOF) m/z calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_4\text{S}$: 326.1546 (M^+) found 326.1564 (M^+); ^1H NMR (CDCl_3): δ 6.09 (s, 1H), 4.56 (t, 1H), 4.15 (s, 4H), 3.85 (m, 1H), 3.74 (dt, 1H), 3.50 (m, 1H), 3.39 (dt, 1H), 2.61 (t, 2H), 1.85-1.35 (m, 14H); ^{13}C NMR (CDCl_3): δ 144.70, 137.64, 118.53, 99.06, 95.27, 67.81, 64.93, 64.77, 62.55, 31.00, 30.61, 29.89, 29.19, 26.18, 25.74, 19.92, 18.09.



Trimethyl-(5-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)thiophene-2-yl)-stannane (4): 2-(6-(thiophen-2-yl)-hexyloxy)tetrahydro-2H-pyran (**2**) (340 mg, 1.27 mmol) was dissolved in dry THF at room temperature and (1.2 mL, 1.9 mmol) butyllithium was slowly added. After stirring the solution for one hour (1.9 mL, 1.9 mmol) trimethyltinchloride was added and the solution was allowed to stir for 14 h. Then the solvent was evaporated which afforded a yellowish oil 509 mg (93%) that was used without further purification for the next step. ^1H NMR (CDCl_3): δ 6.98 (d, 1H), 6.87 (d, 1H), 4.54 (t, 1H), 3.87 (m, 1H), 3.74 (dt, 1H), 3.50 (m, 1H), 3.39 (dt, 1H), 2.86 (t, 2H), 1.85-1.35 (m, 14H), 0.32 (s, 9H).

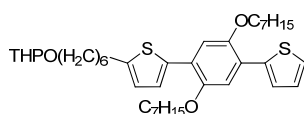


Trimethyl-(7-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-stannane (5): 5-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,3-dihydrothieno [3,4-b][1,4]dioxine (**3**) (234 mg, 0.72 mmol) was dissolved in dry THF at -78°C and (0.5 mL, 1.25 mmol) butyllithium was slowly added. After stirring the solution for one hour at -78°C (1.25 mL, 1.25 mmol) trimethyltinchloride was added and the solution was allowed to stir for 14 h by reaching room temperature. Then the solvent was evaporated which afforded a yellowish oil 327 mg (93%) that was used without further purification for the next step. ^1H NMR (CDCl_3): δ 4.55 (t, 1H), 4.12 (s, 4H), 3.87 (m, 1H), 3.74 (dt, 1H), 3.49 (m, 1H), 3.40 (dt, 1H), 2.61 (t, 2H), 1.82-1.35 (m, 14H), 0.31 (s, 9H).

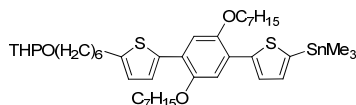


2-(6-(5-(4-bromo-2,5-bis(heptyloxy)phenyl)thiophen-2-yl)hexyloxy)tetrahydro-2H-pyran (6): A solution of **4** (0.5 g, 0.9 mmol), 1,4-dibromo-2,5-bis(heptyloxy)benzene (0.46 g, 1.0 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (0.052 g, 0.1 mmol) in toluene (25 mL) was degassed three times by successive freeze-pump-thaw cycles and heated at 120°C for 12 h in a silicone oil bath. The solvent was evaporated and the residue was a yellowish oil, which was purified by column chromatography (hexane/ethyl acetate 19/1) to afford the title compound (0.3 g, 0.46 mmol, 51%) as a pale yellow oil. Anal. calcd for $\text{C}_{35}\text{H}_{55}\text{O}_4\text{SBr}$: C 64.50, H 8.51, N 0.00 found C 64.55, H 8.63, N 0.00; HRMS (ESI-FTICR): m/z calcd for $\text{C}_{35}\text{H}_{55}\text{O}_4\text{SBr}$ (M^+) 650.3004 found 650.3002; ^1H NMR (CDCl_3): δ 7.30 (d, 1H), 7.12 (s, 1H), 7.08 (s, 1H), 6.72 (d, 1H),

4.57 (t, 1H), 4.03 (q, 4H), 3.86 (m, 1H), 3.74 (dt, 1H), 3.50 (m, 1H), 3.38 (dt, 1H), 2.82 (t, 2H), 1.82–1.26 (m, 34H), 0.90 (t, 6H). ^{13}C NMR (CDCl_3): δ 149.65, 149.41, 146.01, 136.21, 125.30, 123.97, 123.57, 117.76, 113.32, 110.65, 98.78, 70.19, 69.65, 67.49, 62.21, 31.82, 31.79, 31.60, 30.78, 30.03, 29.69, 29.31, 29.07, 28.99, 26.17, 26.06, 26.00, 25.54, 22.64, 22.62, 19.68, 14.12.

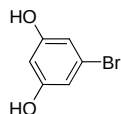


2-(6-(5-(2,5-bis(heptyloxy)-4-(thiophen-2-yl)phenyl)thiophen-2-yl)hexyloxy)tetrahydro-2H-pyran (7): A solution of **6** (0.652 g, 1 mmol), 2-(tributylstannyl)thiophene (0.56 g, 1.5 mmol), PdCl_2 (3.6 mg, 0.02 mmol), $[(\text{tBu})_3\text{PH}]\text{BF}_4$ (11.6 mg, 0.04 mmol), CuI (19.2 mg, 0.1 mmol), CsF (304 mg, 2 mmol) in DMF (20 mL) was degassed three times by successive freeze-pump-thaw cycles and heated at 80°C for 12 h in a silicone oil bath. After dilution with ethyl acetate, the organic phase was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate 19/1) to afford the title compound (0.5 g, 0.76 mmol, 76%) as a yellow oil. Anal. calcd for $\text{C}_{39}\text{H}_{58}\text{O}_4\text{S}_2$: C 71.51, H 8.93, N 0.00 found C 71.59, H 8.95, N 0.00; HRMS (ESI-FTICR): m/z calcd for $\text{C}_{39}\text{H}_{58}\text{O}_4\text{S}_2\text{Na}$ ($\text{M}+\text{Na}^+$) 677.3669 found 677.3686; ^1H NMR (CDCl_3): δ 7.52 (d, 1H), δ 7.36 (d, 1H), δ 7.31 (d, 1H), 7.22 (s, 1H), 7.19 (s, 1H), 7.09 (dd, 1H), 6.76 (d, 1H), 4.57 (t, 1H), 4.07 (t, 4H), 3.86 (m, 1H), 3.74 (dt, 1H), 3.50 (m, 1H), 3.38 (dt, 1H), 2.86 (t, 2H), 1.82–1.26 (m, 34H), 0.92 (t, 6H). ^{13}C NMR (CDCl_3): δ 149.26, 149.15, 145.98, 139.44, 136.76, 126.66, 125.45, 125.19, 124.98, 124.02, 123.44, 122.44, 112.85, 112.53, 98.86, 69.67, 67.58, 62.33, 31.80, 31.77, 31.63, 30.78, 30.08, 29.70, 29.46, 29.11, 29.08, 29.01, 26.23, 26.20, 26.06, 25.52, 22.62, 19.71, 14.11.

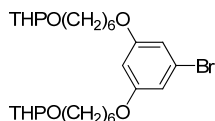


(5-(2,5-bis(heptyloxy)-4(5-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)thiophen-2-yl)phenyl)thiophen-2-yl)trimethylstannane (8): To a solution containing **7** (2.8 g, 4.28 mmol) in anhydrous THF (15 mL) at -78°C , $n\text{BuLi}$ (1.52M, 3.4 mL, 5.1 mmol) was added dropwise. The mixture was stirred for 3 h at -78°C and then a solution of trimethyltin chloride (1.0M in THF, 5.1 mL, 5.1 mmol) was added dropwise and the mixture was stirred at the same

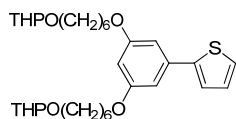
temperature for 2 h before allowing it to warm to room temperature. After dilution with ethyl acetate, the organic phase was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was a brown oil and used without further purification. Crude yield was 87%, which was determined by ^1H NMR. ^1H NMR (CDCl_3): δ 7.65 (d, 1H), 7.36 (d, 1H), 7.22 (s, 1H), 7.19 (m, 2H), 6.75 (d, 2H), 4.57 (t, 1H), 4.08 (t, 4H), 3.86–3.37 (m, 4H), 3.50 (m, 1H), 2.86 (t, 2H), 1.88–1.23 (m, 41H), 0.92 (t, 3H), 0.39 (s, 9H).



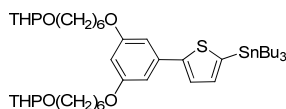
5-Bromobenzene-1,3-diol (9): To a solution containing 1-bromo-3,5-dimethoxybenzene (3.0 g, 13.8 mmol) in methylene chloride (50 mL) at -78°C , BBr_3 (5.2 mL, 55.3 mmol) was added dropwise. The mixture was stirred at the same temperature for 4 h and then at room temperature for another 12 h before quenched with ice-water. The organic phase was extracted with ethyl acetate and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was purified by recrystallization from chloroform/ethanol to afford the title compound (2.3 g, 12.4 mmol, 90%) as a white solid. ^1H NMR (CDCl_3): δ 6.60 (d, 2H), δ 6.29 (t, 1H), δ 4.96 (s, 2H). ^{13}C NMR (CDCl_3): δ 157.29, 122.94, 111.71, 102.08.



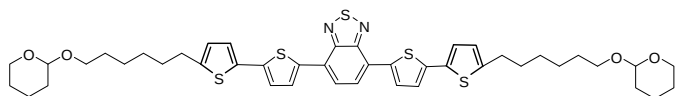
1-Bromo-3,5-di(6-(tetrahydro-2H-pyran-2-yloxy)hexyloxy)benzene (10): A solution of **9** (2 g, 10 mmol), 2-(6-bromohexyloxy)tetrahydro-2H-pyran (6.9 g, 26 mmol), K_2CO_3 (8.3 g, 60 mmol) and KI (0.664 g, 4 mmol) in DMF (50 mL) was stirred at 60°C for 12 h. After dilution with ethyl acetate, the organic phase was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate 19/1) to afford the title compound (3.41 g, 6.12 mmol, 61%) as a pale yellow oil. Anal. calcd for $\text{C}_{28}\text{H}_{45}\text{BrO}_6$: C 60.32, H 8.14, N 0.00 found C 60.51, H 8.41, N 0.34; HRMS (ESI-FTICR): m/z calcd for $\text{C}_{28}\text{H}_{45}\text{BrO}_6\text{Na}$ ($\text{M}+\text{Na}^+$) 579.2297 found 579.2255; ^1H NMR (CDCl_3): δ 6.61 (dd, 2H), δ 6.33 (t, 1H), δ 4.55 (t, 2H), δ 3.90 (t, 4H), δ 3.85–3.70 (m, 4H), δ 3.50–3.33 (m, 4H), δ 1.85–1.34 (m, 28H). ^{13}C NMR (CDCl_3): δ 160.73, 122.81, 110.25, 100.60, 98.86, 68.17, 67.44, 62.32, 30.78, 29.67, 29.07, 26.01, 25.86, 25.52, 19.70.



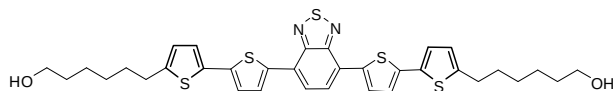
1-Thiophene-yl-3,5-di(6-(tetrahydro-2H-pyran-2-yloxy)hexyloxy)benzene (11): A solution of **10** (0.5 g, 0.90 mmol), 2-(tributylstannyl)thiophene (0.5 g, 1.3 mmol), PdCl₂(PPh₃)₂ (12.6 mg, 0.018 mmol) in THF (20 mL) was degassed three times by successive freeze-pump-thaw cycles and heated at 70°C for 12 h in a silicone oil bath. The solvent was evaporated and the residue was a yellowish oil, which was purified by column chromatography (hexane/ethyl acetate 19/1) to afford the title compound (0.32 g, 0.57 mmol, 63%) as a pale yellow oil. Anal. calcd for C₃₂H₄₈O₆S: C 68.65, H 8.63, N 0.00 found C 68.59, H 8.77, N 0.00; HRMS (ESI-FTICR): *m/z* calcd for C₃₂H₄₈O₆SNa (M+Na⁺) 583.3064 found 583.3053; ¹H NMR (Acetone-*d*₆): δ 7.46 (m, 2H), δ 7.11 (dd, 1H), δ 6.80 (d, 2H), δ 6.46 (t, 1H), δ 4.57 (t, 2H), δ 4.07 (t, 4H), δ 3.82-3.67 (m, 4H), δ 3.45-3.32 (m, 4H), δ 1.83-1.36 (m, 28H). ¹³C NMR (CDCl₃): δ 160.56, 144.47, 136.08, 127.80, 124.73, 123.28, 104.84, 100.45, 98.86, 68.00, 67.48, 62.33, 30.78, 29.70, 29.24, 26.06, 25.94, 25.51, 19.70.



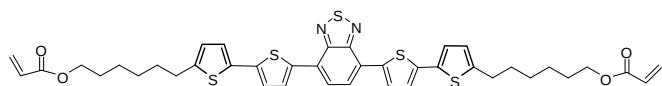
5-(3,5-Bis(6-(tetrahydro-2H-pyran-2-yloxy)hexyloxy)phenyl)-2-(tributylstannyl)-thiophene (12): To a solution containing **11** (0.910 g, 1.62 mmol) in anhydrous THF at -78°C, *n*BuLi (1.56M, 1.14 mL, 1.785 mmol) was added dropwise in 3 h. The mixture was stirred for another 2 h at -78°C and then tributyltin chloride (0.581 g, 1.785 mmol) was added dropwise and the mixture was stirred at the same temperature for 2 h before allowing it to warm to room temperature. After dilution with ethyl acetate, the organic phase was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was a yellow oil and used without further purification. Crude yield was >95%, which was determined by ¹H NMR. ¹H NMR (Acetone-*d*₆): δ 7.54 (d, 1H), 7.19 (d, 1H), 6.80 (d, 2H), 6.44 (t, 1H), δ 4.57 (t, 2H), δ 4.06 (t, 4H), δ 3.82-3.67 (m, 4H), δ 3.45-3.32 (m, 4H), δ 1.83-0.85 (m, 55H).



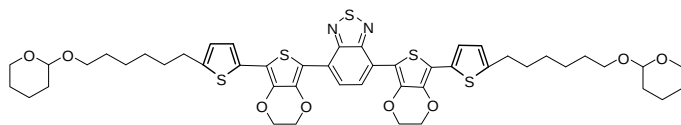
4,7-bis(5'-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazole, TT-BTD-TT (15): Trimethyl-(5-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)thiophene-2-yl)-stannane (**4**) (705 mg, 1.63 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole (**13**) (150 mg, 0.32 mmol) and Pd(PPh₃)₂Cl₂ (40 mg, 4 mol%) are dissolved in 25 mL of dry and degassed THF. Then the mixture is stirred for 14 h at 60 °C, the solvent was evaporated and the product was purified by column chromatography (SiO₂/diethyl ether:hexane [1:1]) followed by a second column (SiO₂/DCM ethylacetate [1:1]) to obtain 176 mg (66 %) of a red solid. Mp: 135 °C -137 °C; Anal. calcd. for C₄₄H₅₂N₂O₄S₅: C 63.43, H 6.29, N 3.36 found C 63.35, H 6.22, N 3.33; HRMS (ESI TOF) *m/z* calcd. for C₄₄H₅₂N₂O₄S₅: 832.243 (MH⁺) found 832.2461 (MH⁺); ¹H NMR (CDCl₃): δ 8.01 (d, 2H), 7.80 (s, 2H), 7.17 (d, 2H), 7.09 (d, 2H), 6.70 (d, 2H), 4.57 (t, 2H), 3.87 (m, 2H), 3.74 (dt, 2H), 3.50 (m, 2H), 3.39 (dt, 2H), 2.83 (t, 4H), 1.82-1.25 (m, 28H); ¹³C NMR (CDCl₃): δ 152.71, 146.09, 139.56, 137.69, 134.91, 128.47, 125.71, 125.27, 125.23, 124.03, 123.98, 99.11, 67.77, 62.58, 31.72, 31.02, 30.38, 29.87, 29.12, 26.11, 25.73, 19.93.



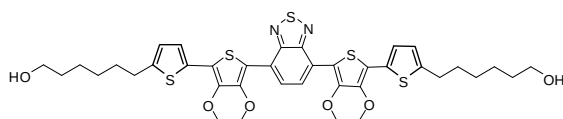
6,6'-(5',5'')bis(2,2'-bithiophene-5',5'-diyl)bis(2,2'-bithiophene-5',5'-diyl)dihexan-1-ol, TT-BTD-TT-diol: To 4,7-bis(5'-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazole (**15**) (250 mg, 0.30 mmol) dissolved in 50 mL CH₂Cl₂ 2 mL of conc. HCl and 10 mL of methanol are added and the mixture is stirred for 16 h at room temperature. Then the solvent was evaporated. The solid was dissolved in THF and was precipitated two times by adding an excess of Methanol to the solution. Then the solid was filtered and dried to obtain 177 mg (89 %) of a brown-black solid. Mp: 199 °C - 202 °C; Anal. calcd. for C₃₄H₃₆N₂O₂S₅: C 61.41, H 5.46, N 4.21 found C 60.97, H 5.37, N 4.15; HRMS (ESI TOF) *m/z* calcd. for C₃₄H₃₆N₂O₂S₅: 665.1453 (MH⁺) found 665.1438 (MH⁺); ¹H NMR (C₂D₂Cl₄, 100 °C): δ 8.05 (d, 2H), 7.85 (s, 2H), 7.22 (d, 2H), 7.13 (d, 2H), 6.76 (d, 2H), 3.64 (t, 4H), 2.84 (t, 4H), 1.82-1.25 (m, 18H); ¹³C NMR (CDCl₃): could not be determined because of poor solubility.



6,6'-(5',5''(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(2,2'-bithiophene-5',5-diyl))bis(hexan-6,1-diyl) diacrylate, TT-BTD-TT-diacrylate: 6,6'-(5',5''(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(2,2'-bi-thiophene-5',5-diyl))dihexan-1-ol (**15a**) (150 mg, 0.22 mmol) is dissolved in 100 mL of dry THF, then acryloyl chloride (6 mL, 60 mmol) is added via syringe and the mixture was stirred for 24 h. Water and CH₂Cl₂ is added and the organic phases were separated, dried over MgSO₄ and the solvent evaporated. The residue was mixed with water and methanol, which afforded a precipitate. The precipitate is centrifuged and washed several times with water and dried under vacuum. This afforded 151 mg (86%) of a red solid. Mp: 129 °C - 132 °C; Anal. calcd. for C₄₀H₄₀N₂O₄S₅: C 62.14, H 5.22, N 3.62 found C 61.55, H 5.17, N 3.51; HRMS (ESI TOF) *m/z* calcd. for C₄₀H₄₀N₂O₄S₅: 773.1664 (MH⁺) found 773.1671 (MH⁺); ¹H NMR (CDCl₃): δ 8.04 (d, 2H), 7.83 (s, 2H), 7.25 (d, 2H), 7.10 (d, 2H) 6.72 (d, 2H), 6.41 (d, 2H), 6.13 (dd, 2H), 5.82 (d, 2H) 4.16 (t, 4H), 2.80 (t, 4H), 1.72-1.42 (m, 16H); ¹³C NMR (CDCl₃): δ 164.87, 152.71, 148.03, 139.07, 137.69, 134.91, 128.69, 126.64, 125.27, 125.12, 124.53, 123.98, 99.01, 67.97, 62.49, 31.78, 31.12, 30.38, 29.87, 29.12, 25.83.

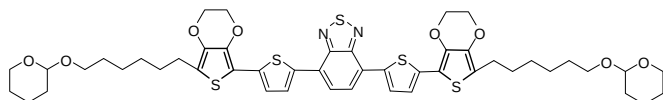


4,7-bis(7-(5-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)thiophen-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole, TE-BTD-ET (16**):** Trimethyl-(5-(6-(tetrahydro-2H-pyran-2-yloxy) hexyl)thiophene-2-yl)-stannane (**4**) (1.03 g, 2.4 mmol), 4,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole (**14**) (545 mg, 0.95 mmol) and Pd(PPh₃)₂Cl₂ (40 mg, 4 mol%) are dissolved in 25 mL of dry and degassed THF. Then the mixture is stirred for 14 h at 60 °C, the solvent was evaporated and the product was purified by column chromatography (SiO₂/hexane:DCM [2:1]) to obtain 633 mg (70 %) of a dark black-brown solid. Mp: 160 °C -163 °C; Anal. calcd. for C₄₈H₅₆N₂O₈S₅: C 60.73, H 5.95, N 2.95 found C 60.93, H 5.95, N 2.95; HRMS (ESI TOF) *m/z* calcd. for C₄₈H₅₆N₂O₈S₅: 971.2532 (M+Na⁺) found 971.2451 (M+Na⁺); ¹H NMR (CDCl₃): δ 8.37 (s, 2H), 7.17 (d, 2H), 6.70 (d, 2H), 4.56 (t, 2H), 4.42 (m, 8H), 3.84 (m, 2H), 3.73 (dt, 2H), 3.50 (m, 2H), 3.36 (dt, 2H), 2.81 (t, 4H), 1.82-1.40 (m, 28H); ¹³C NMR (CDCl₃): δ 152.36, 145.31, 140.73, 137.02, 132.39, 126.50, 124.57, 123.40, 123.27, 115.26, 111.06, 99.09, 67.79, 64.84, 62.58, 31.79, 31.02, 30.31, 29.89, 29.16, 26.25, 25.74, 19.93.



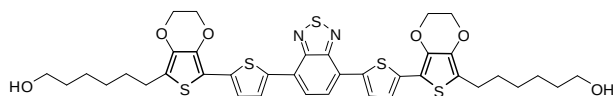
6,6'-(5,5'-(7,7'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(2,3-dihydrothieno[3,4-b]

[1,4]dioxin-7,5-diyl))bis(thiophene-5,2-diyl)dihexan-1-ol, TE-BTD-ET-diol: To 4,7-bis(7-(5-(6-(tetrahydro-2*H*-pyran-2-yloxy)hexyl)thiophen-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-yl)-benzo[c][1,2,5]thiadiazole (**16**) (550 mg, 0.58 mmol) dissolved in 50 mL THF 2 mL of conc. HCl and 10 mL of methanol are added and the mixture is stirred for 16 h at room temperature. Then the solvent was evaporated. The solid was dissolved in THF and was precipitated two times by adding an excess of Methanol to the solution. Then the solid was filtered and dried to obtain 376 mg (83 %) of a black solid. Mp: 215 °C -216 °C; Anal. calcd. for C₃₈H₄₀N₂O₆S₅: C 58.43, H 5.16, N 3.59 found C 58.43, H 5.14, N 3.47; HRMS (ESI TOF) *m/z* calcd. for C₃₈H₄₀N₂O₆S₅: 781.1563 (MH⁺) found 781.1587 (MH⁺); ¹H NMR (C₂D₂Cl₄, 100 °C): δ 8.44 (s, 2H), 7.21 (d, 2H), 6.77 (d, 2H), 4.46 (m, 8H), 3.63 (t, 4H), 2.84 (t, 4H), 1.75-1.26 (m, 16H); ¹³C NMR (CDCl₃): could not be determined because of poor solubility

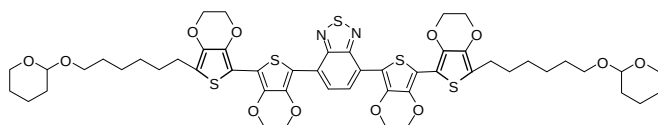


4,7-bis(5-(7-(6-(tetrahydro-2*H*-pyran-2-yloxy)hexyl)-2,3-dihydrothieno[3,4-b]

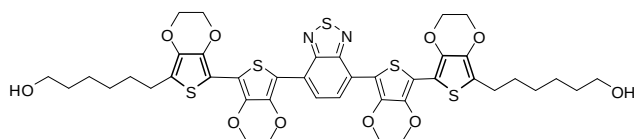
[1,4]dioxin-5-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole, ET-BTD-TE (17**):** Trimethyl-(7-(6-(tetrahydro -2*H*-pyran-2-yloxy)hexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5yl)-stannane (**5**) (837 mg, 1.72 mmol), 4,7-dibrombenzo [c][1,2,5]-thiadiazole (**13**) (303 mg, 0.66 mmol) and Pd(PPh₃)₂Cl₂ (30 mg, 6 mol%) are dissolved in 40 mL of dry and degassed THF. Then the mixture is stirred for 16 h at 60 °C, the solvent was evaporated and the product was purified by column chromatography (SiO₂/hexane:DCM [1:1]) to obtain 356 mg (56 %) of compound **17** as a brown solid. Mp: 129 °C - 132 °C; Anal. calcd. for C₄₈H₅₆N₂O₈S₅: C 60.73, H 5.95, N 2.95 found C 60.73, H 5.80, N 2.92; HRMS (ESI TOF) *m/z* calcd. for C₄₈H₅₆N₂O₈S₅: 948.2634 (M⁺) found 948.2635 (M⁺); ¹H NMR (CDCl₃): δ 8.08 (d, 2H), 7.81 (s, 2H), 7.22 (d, 2H), 4.58 (t, 2H), 4.38-4.26 (m, 8H), 3.87 (m, 2H), 3.74 (dt, 2H), 3.50 (m, 2H), 3.40 (dt, 2H), 2.67 (t, 4H), 1.85-1.42 (m, 28H); ¹³C NMR (CDCl₃): δ 152.76, 138.16, 137.97, 137.02, 136.81, 128.02, 125.56, 125.00, 123.11, 117.16, 108.47, 67.82, 65.43, 64.74, 62.56, 31.02, 30.52, 29.89, 29.18, 26.21, 25.99, 25.74.



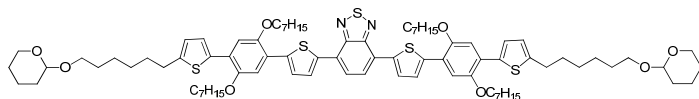
6,6'-(7,7'-(5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(thiophen-5,2-diyl))bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-7,5-diyl)) dihexan-1-ol, ET-BTD-TE-diol: 4,7-bis(5-(7-(6-(tetrahydro-2*H*-pyran-2-yloxy)hexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)benzo[c][1,2,5] thiadiazole (**17**) (100 mg, 0.11 mmol) dissolved in 25 mL CH₂Cl₂ 2 mL of conc. HCl and 8 mL of methanol are added and the mixture is stirred for 16 h at room temperature. Then the precipitated solid was filtered and dried to obtain 73 mg (89 %) of a blue-green solid. Mp: 169 °C -170; Anal. calcd. for C₃₈H₄₀N₂O₆S₅: C 58.48, H 5.16, N 3.59 found C 58.09, H 5.16, N 3.56; HRMS (ESI TOF) *m/z* calcd. for C₃₈H₄₀N₂O₆S₅: 781.1563 (MH⁺) found 781.1474 (MH⁺); ¹H NMR (C₂D₂Cl₄, 100 °C): δ 8.08 (d, 2H), 7.83 (s, 2H), 7.26 (d, 2H), 4.39 (m, 8H), 3.69 (t, 4H), 2.69 (t, 4H), 1.82-1.25 (m, 16H); ¹³C NMR (CDCl₃): could not be determined because of poor solubility



4,7-bis(7'-(6-(tetrahydro-2*H*-pyran-2-yloxy)hexyl)2,2'3,3'-tetrahydro-5,5'bithieno[3,4-b][1,4]dioxin-7-yl)benzo[c][1,2,5]thiadiazole, EE-BTD-EE (18**):** Trimethyl-(7-(6-(tetrahydro-2*H*-pyran-2-yloxy) hexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5yl)-stannane (**5**) (1.04 g, 2.12 mmol), 4,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole (**14**) (468 mg, 0.81 mmol) and Pd(PPh₃)₂Cl₂ (63 mg, 4 mol%) are dissolved in 20 mL of dry and degassed THF. Then the mixture is stirred for 24 h at 60 °C, the solvent was evaporated and the product was purified by column chromatography (SiO₂/EtAc:DCM [1:1]) to obtain 472 mg (55 %) of a blue-black solid. Mp: 202 °C -206 °C; Anal. calcd. for C₅₂H₆₀N₂O₁₂S₅: C 58.62, H 5.69, N 2.63 found C 58.61, H 5.69, N 2.64; HRMS (ESI TOF) *m/z* calcd. for C₅₂H₆₀N₂O₁₂S₅: 1064.2744 (MH⁺) found 1064.2741 (MH⁺); ¹H NMR (CDCl₃): δ 8.37 (s, 2H), 4.57 (t, 2H), 4.42-4.25 (m, 16H), 3.87 (m, 2H), 3.74 (dt, 2H), 3.50 (m, 2H), 3.40 (dt, 2H), 2.65 (t, 4H), 1.85-1.42 (m, 28H); ¹³C NMR (CDCl₃): δ 152.50, 140.26, 137.80, 137.46, 136.45, 126.34, 123.34, 117.59, 113.22, 111.52, 106.20, 99.08, 67.85, 65.54, 65.19, 64.91 64.81, 62.56, 31.02, 30.60, 29.90, 29.26, 26.22, 26.06, 25.74, 19.95.

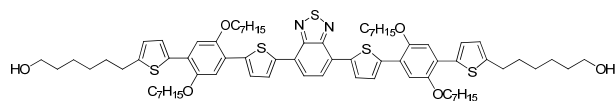


6,6'-(7',7''-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxin-7',7'-diyl)) dihexan-1-ol, EE-BTD-EE-diol: 4,7-bis(7'-(6-(tetrahydro-2H-pyran-2-yloxy)-hexyl)-2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxin-7-yl)benzo[c][1,2,5]thiadiazole (**18**) (30 mg, 0.03 mmol) is dissolved in 10 mL CH₂Cl₂, then 2 mL of conc. HCl and 4 mL of methanol are added and the mixture is stirred for 12 h at room temperature. The resulting solid was filtered off, washed with methanol (3x 5mL) and dried in vacuo to obtain 22 mg (87 %) of a black solid. Mp: 246 °C -251 °C; Anal. calcd. for C₄₂H₄₄N₂O₁₀S₅: C 56.23, H 4.94, N 3.12 found C 56.21, H 4.77, N 3.08; HRMS (ESI TOF) *m/z* calcd. for C₄₂H₄₄N₂O₁₀S₅: 896.1594 (MH⁺) found 896.1575 (MH⁺); ¹H NMR (C₂D₂Cl₄, 100 °C): δ 8.39 (s, 2H), 4.46 (m, 8H), 3.63 (t, 4H), 2.69 (t, 4H), 1.75-1.26 (m, 16H); ¹³C NMR (CDCl₃): could not be determined because of poor solubility.



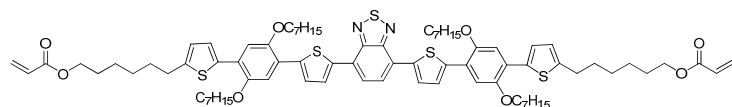
4,7-Bis(5-(2,5-bis(heptyloxy)-4-(5-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)thiophen-2-yl)phenyl)thiophen-2-yl)benzothiadiazole, TPT-BTD-TPT (19**):** A solution of **8** (3.15 g, 3.85 mmol), 4,7-dibromobenzothiadiazole (0.514 g, 1.75 mmol), PdCl₂ (13.6 mg, 0.08 mmol), [(tBu)₃PH]BF₄ (44.7 mg, 0.15 mmol), CuI (73.3 mg, 0.38 mmol), CsF (1.169 g, 7.67 mmol) in DMF (40 mL) was degassed three times by successive freeze-pump-thaw cycles and heated at 80 °C for 12 h in a silicone oil bath. After dilution with ethyl acetate, the organic phase was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate 49/1) to afford the title compound (1.65 g, 1.14 mmol, 65%) as a red solid. Anal. calcd for C₈₄H₁₁₆N₂O₈S₅: C 69.96, H 8.11, N 1.94 found C 69.76, H 8.12, N 1.92; HRMS (ESI-FTICR): *m/z* calcd for C₈₄H₁₁₆N₂O₈S₅ (M⁺) 1440.7329 found 1440.7292; ¹H NMR (CDCl₃): δ 8.16 (d, 1H), δ 7.89 (s, 1H), δ 7.65 (d, 1H), δ 7.40 (d, 1H), 7.31 (s, 1H), 7.23 (s, 1H), 6.78 (d, 1H), 4.58 (t, 1H), 4.16 (t, 4H), 3.86 (m, 1H), 3.74 (dt, 1H), 3.50 (m, 1H), 3.38 (dt, 1H), 2.86 (t, 2H), 1.82–1.26 (m, 34H), 0.92 (t, 6H). ¹³C NMR (CDCl₃): δ 152.85, 149.60, 149.26, 146.22, 140.81, 139.11, 136.74, 127.68, 126.21, 125.93, 125.37, 125.27, 124.10, 123.89, 122.20, 112.51, 112.44,

98.90, 69.82, 69.77, 67.61, 62.37, 31.89, 31.84, 31.65, 30.82, 30.11, 29.71, 29.56, 29.50, 29.25, 29.15, 29.03, 26.38, 26.27, 26.08, 25.54, 22.70, 22.65, 19.73, 14.14.



4,7-Bis(5-(2,5-bis(heptyloxy)-4-(5-(6-hydroxyhexyl)-thiophen-2-yl)phenyl)-

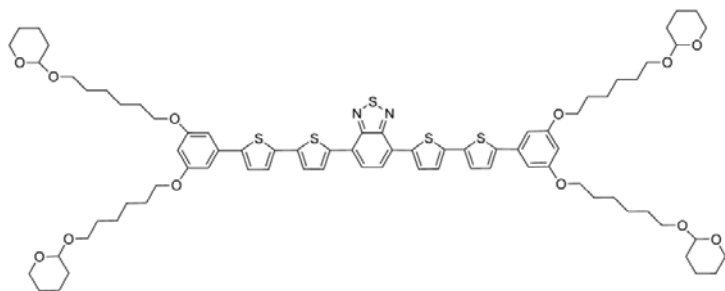
thiophen-2-yl)benzothiadiazole, TPT-BTD-TPT-diol: A solution of **19** (1.65 g, 1.14 mmol) and 12 M hydrochloric acid (1 mL) in methanol (30 mL) and dichloromethane (50 mL) was stirred at room temperature for 24 h. After removing the solvent, the residue was precipitated from dichloromethane into methanol three times to afford the title compound (1.26 g, 0.99 mmol, 87%) as a red solid. Anal. calcd for $C_{74}H_{100}N_2O_6S_5$: C 69.77, H 7.91, N 2.20 found C 69.67, H 7.99, N 2.27; HRMS (ESI-FTICR): m/z calcd for $C_{74}H_{100}N_2O_6S_5$ (M^+) 1272.6179 found 1272.6135; ^1H NMR ($CDCl_3$): δ 8.10 (d, 1H), δ 7.79 (s, 1H), δ 7.59 (d, 1H), δ 7.38 (d, 1H), 7.26 (s, 1H), 7.19 (s, 1H), 6.76 (d, 1H), 4.09 (t, 4H), 3.66 (t, 2H), 2.84 (t, 2H), 1.82–1.26 (m, 28H), 0.93 (t, 6H). ^{13}C NMR ($CDCl_3$): δ 152.74, 149.55, 149.19, 146.01, 140.65, 139.07, 136.78, 127.62, 126.10, 125.78, 125.29, 125.11, 124.08, 123.73, 122.16, 112.33, 112.23, 69.76, 69.72, 62.96, 32.71, 31.90, 31.85, 31.62, 30.08, 29.58, 29.52, 29.29, 29.18, 28.97, 26.39, 26.29, 25.55, 22.71, 22.66, 14.14.



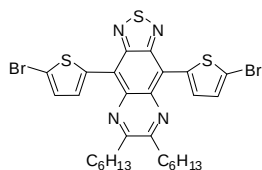
4,7-bis(5-(2,5-bis(heptyloxy)-4-(5-(6-acryloyloxyhexyl)-thiophen-2-yl)phenyl)-

thiophen-2-yl)benzothiadiazole, TPT-BTD-TPT-diacrylate: A solution of **19a** (900 mg, 0.65 mmol) in THF (50 mL) was cooled to 0 °C; acryloyl chloride (5 mL, 61.6 mmol) was added and the reaction mixture was allowed to warm to room temperature over night. The reaction mixture was concentrated and then reprecipitated from THF into methanol and purified by column chromatography (hexane/ethyl acetate 9/1) to afford the title compound (345 mg, 0.25 mmol, 35%) as a red solid. Anal. calcd for $C_{80}H_{104}N_2O_8S_5$: C 69.53, H 7.58, N 2.03 found C 69.21, H 7.96, N 1.83; HRMS (ESI-FTICR): m/z calcd for $C_{80}H_{105}N_2O_8S_5$ ($M+H^+$) 1381.6469 found 1381.6429; ^1H NMR ($CDCl_3$): δ 8.15 (d, 1H), 7.88 (s, 1H), 7.65 (d, 1H), 7.40 (d, 1H), 7.30 (s, 1H), 7.24 (s, 1H), 6.78 (d, 1H), 6.44 (dd, 1H), 6.17 (dd, 1H), 5.84 (dd, 1H), 4.19 (m, 6H), 2.88 (t, 2H), 2.00–1.26 (m, 28H), 0.93 (t, 6H). ^{13}C NMR ($CDCl_3$): δ 166.54, 153.03, 149.79, 149.44, 146.19, 140.97, 139.31, 137.00, 130.66, 128.84, 127.87, 126.41, 126.11, 125.54, 125.45, 124.34, 124.02, 122.43, 112.68, 112.61, 70.01, 69.96, 64.82,

32.09, 32.03, 31.75, 30.26, 29.76, 29.67, 29.45, 29.34, 28.99, 28.78, 26.58, 26.47, 25.97, 22.90, 22.84, 14.34.

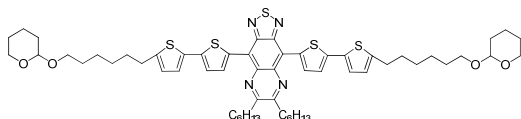


4,7-Bis(5-(3,5-bis(6-(tetrahydro-2H-pyran-2-yloxy)hexyloxy)phenyl)-thiophene-2-yl)benzothiadiazole, PTT-BTD-TTP (20): A solution of **12** (0.2 g, 0.235 mmol), 4,7-bis(5-bromothiophen-2-yl)benzothiadiazole (47 mg, 0.1 mmol), PdCl₂ (2 mg, 0.01 mmol), [(tBu)₃PH]BF₄ (6.4 mg, 0.02 mmol), CuI (10.7 mg, 0.06 mmol), CsF (169 mg, 1.11 mmol) in DMF (15 mL) was degassed three times by successive freeze-pump-thaw cycles and heated at 80°C for 12 h in a silicone oil bath. After dilution with ethyl acetate, the organic phase was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography (hexane/ethyl acetate 19/1) to afford the title compound (50 mg, 0.035 mmol, 30%) as a red solid. Anal. calcd for C₇₈H₁₀₀N₂O₁₂S₅: C 66.07, H 7.11, N 1.98 found C 65.72, H 7.48, N 1.83; HRMS (ESI-FTICR): *m/z* calcd for C₇₈H₁₀₀N₂O₁₂S₅Na (M+Na⁺) 1439.5772 found 1439.5774; ¹H NMR (CDCl₃): δ 8.03 (d, 1H), δ 7.81 (s, 1H), δ 7.26-7.22 (m, 3H), δ 6.74 (d, 2H), δ 6.40 (t, 1H), δ 4.60 (t, 2H), δ 4.01 (t, 4H), δ 3.88-3.73 (m, 4H), δ 3.52-3.38 (m, 4H), δ 1.86-1.25 (m, 28H). ¹³C NMR (CDCl₃): δ 160.66, 152.45, 143.70, 138.85, 138.07, 135.60, 128.32, 125.47, 125.13, 124.74, 124.39, 124.13, 104.48, 100.79, 98.91, 68.01, 67.52, 62.37, 30.81, 29.72, 29.27, 26.09, 25.96, 25.53, 19.72.

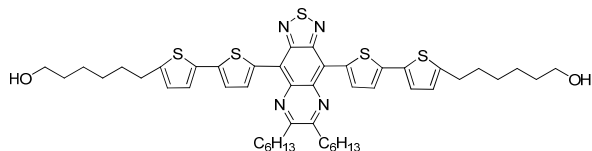


4,9-bis(5-bromothiophen-2-yl)-6,7-dihexyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline (22): 6,7-di-hexyl-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (**21**) (1.09 g, 2.09 mmol) is dissolved in 170 mL DMF and NBS (783 mg, 4.39 mmol) are added in the absence of light. The solution is stirred for 10 h, then methanol is added and the precipitate is filtered off,

washed with cold methanol and dried, to obtain 1.08 g (76 %) of a blue solid. Mp: 140 °C - 143 °C; Anal. calcd. for C₂₈H₃₀Br₂N₄S₃: C 49.56, H 4.46, N 8.26 found C 49.64, H 4.44, N 8.23; HRMS (ESI TOF) *m/z* calcd. for C₂₈H₃₀Br₂N₄S₃: 676.0049 (M⁺) found 675.9999 (M⁺); ¹H NMR (C₂D₂Cl₄): δ 8.82 (d, 2H), 7.23 (d, 2H), 3.01 (t, 4H), 2.02 (t, 4H), 1.60-1.36 (m, 12H) 0.97 (t, 6H); ¹³C NMR (C₂D₂Cl₄): δ 159.27, 152.37, 139.11, 136.09, 134.63, 131.13, 121.93, 121.45, 36.99, 33.31, 30.80, 29.59, 24.09, 15.66.

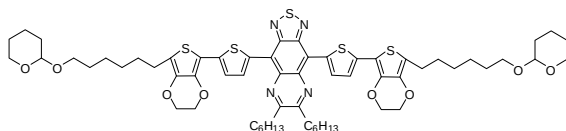


6,7-dihexyl-4,9-bis(5'-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,2'-bithiophen-5-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline, TT-TQ-TT (23): Trimethyl-(5-(6-(tetrahydro-2H-pyran-2-yloxy) hexyl)thiophene-2-yl)-stannane (**4**) (747 mg, 1.7 mmol), 4,9-bis(5-bromothiophen-2-yl)-6,7-dihexyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline (**22**) (489 mg, 0.72 mmol) and Pd(PPh₃)₂Cl₂ (25 mg, 4 mol%) are dissolved in 55 mL of dry and degassed THF. Then the mixture is stirred for 13 h at 55 °C, the solvent was evaporated and the product was purified by column chromatography (SiO₂/EtAc:hexane [2:5]) to obtain 337 mg (44 %) of a black-green solid. Mp: 146 °C -148 °C; Anal. calcd. for C₅₈H₇₆N₄O₄S₅: C 66.12, H 7.27, N 5.32 found C 65.61, H 7.01, N 5.39; HRMS (ESI TOF) *m/z* calcd. for C₅₈H₇₆N₄O₄S₅: 1052.4465 (M⁺) found 1052.4386 (M⁺); ¹H NMR (CDCl₃): δ 8.70 (d, 2H), 7.06 (d, 2H), 7.02 (d, 2H), 6.80 (d, 2H) 4.60 (t, 2H), 3.89 (m, 2H), 3.78 (dt, 2H), 3.53 (m, 2H), 3.43 (dt, 2H), 2.85 (t, 4H) 2.52 (t, 4H), 1.83-1.34 (m, 44H), 0.94 (t, 6H); ¹³C NMR (CDCl₃): δ 156.17, 150.46, 145.46, 142.44, 135.98, 134.59, 133.99, 133.72, 125.10, 123.24, 122.44, 119.28, 101.89, 100.12, 99.13, 67.83, 64.31, 62.61, 36.14, 32.81, 31.82, 31.05, 30.51, 29.97, 29.31, 27.90, 26.31, 25.77, 23.29, 19.96, 14.52.

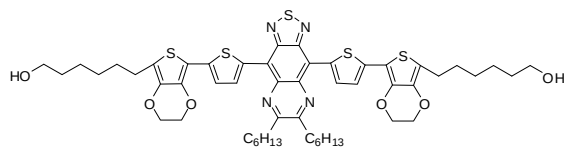


6,6'-(5,5'-(6,7-dihexyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline-4,9-diyl)bis(2,2'-bithiophene-5',5'-diyl))dihexan-1-ol, TT-TQ-TT-diol: 6,7-dihexyl-4,9-bis(5'-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,2'-bithiophen-5-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (**23**) (60 mg, 0.06 mmol) is dissolved in CH₂Cl₂ and MeOH. Conc. HCl (0.5 mL, 47 %) is added and the mixture is stirred for 12h, the precipitate is filtered off and dried to obtain (37 mg, 73 %) of a

dark-green solid. Mp: 162 °C -165 °C; Anal. calcd. for C₄₈H₆₀N₄O₂S₅: C 65.12, H 6.83, N 6.33 found C 64.31, H 6.58, N 6.31; HRMS (ESI TOF) *m/z* calcd. for C₄₈H₆₀N₄O₂S₅: 884.3314 (M⁺) found 884.3291 (M⁺); ¹H NMR (C₂D₂Cl₄, 100 °C): δ 8.93 (d, 2H), 7.19 (d, 2H), 7.17(d, 2H), 6.69 (d, 2H), 3.65 (t, 4H), 3.14 (t, 4H), 2.93 (t, 4H) 2.83 (t, 4H), 2.05 (t, 4H), 1.72-1.35 (m, 26H), 0.90 (t, 6H); ¹³C NMR (CDCl₃): could not be determined because of poor solubility.

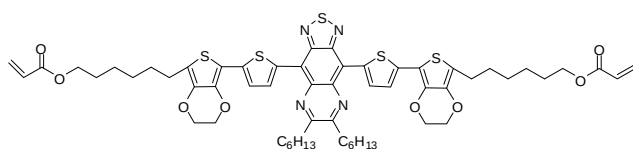


6,7-dihexyl-4,9-bis(5-(7-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl) [1,2,5]thiadiazolo[3,4-g]quinoxaline, ET-TQ-TE (24): Trimethyl-(7-(6-(tetrahydro-2H-pyran-2-yloxy)-hexyl)-2,3-dihydrothieno[3,4-b][1,4] dioxine-5-yl)-stannane (**5**) (1.06 g, 2.18 mmol), 4,9-bis(5-bromothiophen-2-yl)-6,7-dihexyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline (**22**) (520 mg, 0.76 mmol) and Pd(PPh₃)₂Cl₂ (30 mg, 4 mol%) are dissolved in 60 mL of dry and degassed THF. Then the mixture is stirred for 24 h at 55 °C, the solvent was evaporated and the product was purified by column chromatography (SiO₂/EtAc:hexane [1:6]) to obtain 397 mg (45 %) of a dark-green solid. Mp: 103 °C -107 °C; Anal. calcd. for C₆₂H₈₀N₄O₈S₅: C 63.67, H 6.89, N 4.79 found C 63.61, H 6.98, N 4.75; HRMS (ESI TOF) *m/z* calcd. for C₆₂H₈₀N₄O₈S₅: 1169.4652 (MH⁺) found 1169.4662 (MH⁺); ¹H NMR (CDCl₃): δ 8.98 (d, 2H), 7.35 (d, 2H), 4.58 (t, 2H), 4.36-4.27 (m, 8H), 3.87 (m, 2H), 3.74 (dt, 2H), 3.48 (m, 2H), 3.40 (dt, 2H), 3.06 (t, 4H) 2.68 (t, 4H), 2.12 (t, 4H) 1.67-1.29 (m, 40H), 0.94 (t, 6H); ¹³C NMR (CDCl₃): δ 156.15, 151.13, 150.87, 138.34, 134.43, 122.56, 119.59, 116.96, 99.15, 67.87, 65.33, 64.8, 62.61, 35.24, 31.04, 30.75, 30.10, 29.98, 29.34, 27.81, 26.27, 25.75, 23.26, 19.96, 14.47.

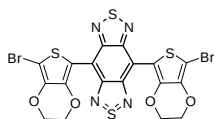


6,6'-(7,7'-(5,5'-(6,7-dihexyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline-4,9-diyl)bis(thiophen-5,2-diyl))bis(2,3-dihydrothieno[3,4-b][1,4]dioxine-7,5-diyl))dihexan-1-ol, ET-TQ-TE-diol: 6,7-dihexyl-4,9-bis(5-(7-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) thiophen-2-yl) [1,2,5]thiadiazolo[3,4-g]quinoxaline (**24**) (50 mg, 0.04

mmol) is dissolved in CH₂Cl₂ and MeOH (10 mL, 7:3). Conc. HCl (0.5 mL, 47 %) is added and the mixture is stirred for 12h, the precipitate is filtered off and dried to obtain (41 mg, 96 %) of a green solid. Mp: 162 °C -165 °C; Anal. calcd. for C₅₂H₆₄N₄O₆S₅: C 62.37, H 6.44, N 5.59 found C 62.31, H 6.44, N 5.59; HRMS (ESI TOF) *m/z* calcd. for C₅₂H₆₄N₄O₆S₅: 1001.3502 (MH⁺) found 1001.3505 (MH⁺); ¹H NMR (C₂D₂Cl₄, 100 °C): δ 9.03 (d, 2H), 7.38 (d, 2H), 4.36-4.28 (m, 8H), 3.66 (t, 4H), 3.14 (t, 4H), 2.69 (t, 4H), 2.18 (t, 4H), 1.67-1.29 (m, 30H), 0.94 (t, 6H); ¹³C NMR (CDCl₃): could not be determined because of poor solubility.

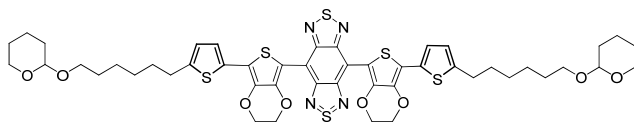


6,6'-(7,7'-(5,5'-(6,7-dihexyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline-4,9-diyl)bis(thiophen-5,2-diyl))bis(2,3-dihydrothieno[3,4-b][1,4]dioxine-7,5-diyl))bis(hexane-6,1-diyl) di-acrylate, ET-TQ-TE-diacrylate: 6,7-dihexyl-4,9-bis(5-(7-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)-2,3-dihydrothieno [3,4-b][1,4]dioxin-5-yl) thiophen-2-yl) [1,2,5]thiadiazolo[3,4-g]quinoxaline (**24a**) (50 mg, 0.05 mmol) is dissolved in 30 mL of dry THF, then acryloyl chloride (4 mL, 39 mmol) is added and the mixture was stirred for 24 h at rt. Then water and methanol was added to the mixture, which afforded a green-black precipitate. The precipitate is centrifuged, washed several times with water and dried under vacuum to afforded 13 mg (23%) of a black solid. Mp: 87 °C -93 °C; Anal. calcd. for C₅₈H₆₈N₄O₈S₅: C 62.79, H 6.18, N 5.05 found C 62.05, H 6.23, N 5.75; HRMS (ESI TOF) *m/z* calcd. for C₅₈H₆₈N₄O₈S₅: 1108.3635 (MH⁺) found 1108.3631 (MH⁺); ¹H NMR (CDCl₃): δ 9.08 (d, 2H), 7.32 (d, 2H), 6.43 (d,2H), 6.15 (dd, 2H), 5.83 (d, 2H), 4.39 - 4.28 (m, 8H), 4.16 (t, 4H), 3.40 (t,2H), 2.69 (t, 4H), 2.31 (t, 4H), 1.67-1.29 (m, 28H), 0.84 (t, 6H)

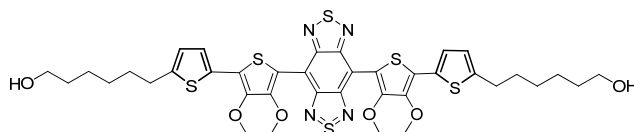


4,8-dibrom-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2-c;4,5-c'] bis [1,2,5]thiadiazole (26): 4,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2-c;4,5-c']bis [1,2,5]thiadiazole (**25**) (430 mg, 0.9 mmol) is dissolved in 200 mL CHCl₃ and NBS (480 mg, 2.72 mmol) are added in the absence of light. The solution is stirred for 10 h, then methanol is added and the precipitate is filtered off, washed with cold acetone and dried, to obtain 530 mg (93 %) of a dark purple/blue solid. Anal. calcd. for C₁₈H₈Br₂N₄O₄S₄: C 34.19, H 1.28, N 8.86 found C C, 34.15; H, 1.23; N, 8.76; HRMS (ESI TOF) *m/z* calcd. for C₁₈H₈Br₂N₄O₄S₄:

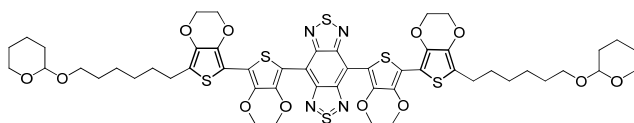
652.7687 ($M+Na^+$) found 652.7642. ($M+Na^+$); ^1H NMR ($CDCl_3$): δ , 4.36-4.28 (m, 8H); ^{13}C NMR ($CDCl_3$): could not be determined because of poor solubility.



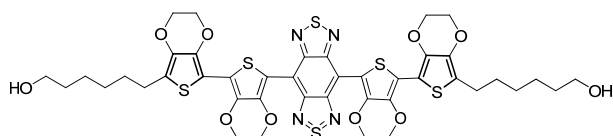
Compound TE-BBT-ET (27): To a flame dried 100 mL 3-neck r.b. flask was added (190 mg, 0.30 mmol) of compound (26) plus (10 mg, 4mol%) of the $Pd(PPh_3)_2Cl_2$ catalyst. The reaction was then subjected to evacuation and backfill with argon 6 times. Then a degassed solution of (4) (290 mg, 0.67 mmol) in 25 mL of THF was added via canula. The solution was then refluxed overnight. Purification by column chromatography (5 % EtOAc/DCM) yielded 0.19 g (63 %) of a dark green solid. Dp: 195 °C -198 °C; Anal. calcd. for $C_{48}H_{54}N_4O_8S_6$: C 57.23, H 5.40, N 5.56 found C 57.38, H 5.41, N 5.53; HRMS (ESI TOF) m/z calcd. for $C_{48}H_{54}N_4O_8S_6$: 1029.2158 ($M+Na^+$) found 1029.2204 ($M+Na^+$); ^1H NMR ($CDCl_3$): δ 7.20 (d, 2H), 6.72 (d, 2H), 4.56 (t, 2H), 4.48 - 4.31 (m, 8H), 3.87 (m, 2H), 3.75 (dt, 2H), 3.48 (m, 2H), 3.40 (dt, 2H), 2.80 (t, 4H), 1.81-1.42 (m, 28H), ^{13}C NMR ($CDCl_3$): δ 152.51, 145.89, 141.60, 137.33, 131.95, 124.57, 123.82, 98.97, 67.70, 64.98, 64.80, 62.50, 31.68, 30.93, 30.25, 29.79, 29.07, 26.15, 25.64, 19.84.



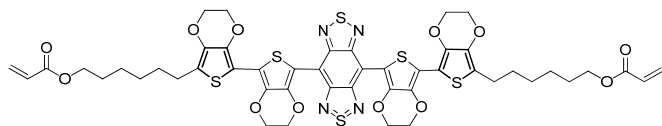
Compound TE-BBT-ET-diol: (30 mg, 0.030 mmol) of compound (27) was dissolved in 15 mL of CH_2Cl_2 , 2 mL of conc. HCl and 8 mL of methanol are added and the mixture is stirred for 10 h at room temperature. Then the precipitate was filtered and dried to obtain 22 mg (90 %) of a green solid. Dp: 225 °C; Anal. calcd. for $C_{38}H_{38}N_4O_6S_6$: C 54.39, H 4.56, N 6.68 found C 54.26, H 4.54, N 6.58; HRMS (ESI TOF) m/z calcd. for $C_{38}H_{38}N_4O_6S_6$: 839.1188 ($M+H^+$) found 839.1142 ($M+H^+$); ^1H NMR ($C_2D_2Cl_4$, 100 °C): δ 7.23 (d, 2H), 6.78 (d, 2H), 4.49 - 4.36 (m, 8H), 3.63 (t, 4H), 2.85 (t, 4H), 1.73-1.26 (m, 18H); ^{13}C NMR ($CDCl_3$): could not be determined because of poor solubility.



Compound EE-BBT-EE (28): To a flame dried 100 mL 3-neck r.b. flask was added (400 mg, 0.63 mmol) of compound (26) plus (20 mg, 4 mol%) Pd(PPh₃)₂Cl₂ catalyst. The reaction was then subjected to evacuation and backfill with argon 6 times. Then a degassed solution of compound (5) (690 mg, 1.41 mmol) in 25 mL THF was added via canula followed by another 25 mL of degassed THF. The solution was then refluxed overnight. Purification by column chromatography (5 % EtOAc/DCM) yielded 0.55 g (77 %) of a dark green solid. Anal. calcd. for C₅₂H₅₈N₄O₁₂S₆: C 55.59, H 5.20, N 4.99 found C 55.83, H 4.60, N 4.74; HRMS (ESI TOF) *m/z* calcd. for C₅₂H₅₈N₄O₁₂S₆: 1122.2370 (MH⁺) found 1122.2427 (MH⁺); ¹H NMR (CDCl₃): δ 4.59 (t, 2H), 4.48 - 4.24 (m, 16H), 3.87 (m, 2H), 3.75 (dt, 2H), 3.48 (m, 2H), 3.40 (dt, 2H), 2.68 (t, 4H), 1.85-1.42 (m, 28H); ¹³C NMR (CDCl₃): δ 152.58, 141.07, 138.09, 137.39, 136.75, 118.23, 115.60, 112.84, 108.98, 106.12, 99.00, 67.76, 65.40, 65.04, 64.82, 64.70, 62.49, 30.95, 30.47, 29.17, 26.13, 26.03, 25.68, 25.67, 19.86.



Compound EE-BBT-EE-diol: (50 mg, 0.044 mmol) of compound (28) was dissolved in 15 mL of CH₂Cl₂, 2 mL of conc. HCl and 8 mL of methanol are added and the mixture is stirred for 10 h at room temperature. Then the precipitate was filtered and dried to obtain 38 mg (91 %) of a green solid. Anal. calcd. for C₄₂H₄₂N₄O₁₀S₆: C 52.81, H 4.43, N 5.87 found C 52.99, H 4.44, N 5.93; HRMS (ESI TOF) *m/z* calcd. for C₄₂H₄₂N₄O₁₀S₆: 977.1117 (M+Na⁺) found 977.1133 (M+Na⁺); ¹H NMR (C₂D₂Cl₄, 100 °C): δ 4.46 - 4.26 (m, 16H), 3.63 (t, 4H), 2.71 (t, 4H), 1.79-1.26 (m, 18H); ¹³C NMR (CDCl₃): could not be determined because of poor solubility.



Compound EE-BBT-EE-diacrylate: (30 mg, 0.031 mmol) of compound (28a) is dissolved in 60 mL of dry THF, then acryloyl chloride (4 mL, 40 mmol) is added and the mixture was stirred for 24 h at rt. Then water and methanol was added to the mixture, which afforded a bright green precipitate. The precipitate is centrifuged, washed several times with water and dried under vacuum to afforded 15 mg (45%) of a green solid. Dp: 143 °C; Anal. calcd. for C₄₈H₄₆N₄O₁₂S₆: C 54.22, H 4.36, N 5.27 found C 54.57, H 4.58, N 4.76; HRMS (ESI TOF) *m/z* calcd. for C₄₈H₄₆N₄O₁₂S₆: 1062.1431 (M⁺) found 1062.1481 (M⁺); ¹H NMR (CDCl₃): δ

6.41 (dd, 2H), 6.13 (dd, 2H), 5.82 (dd, 2H), 4.39 - 4.13 (m, 20H), 2.66 (t, 4H), 1.72-1.42 (m, 16H).

Spectroscopy

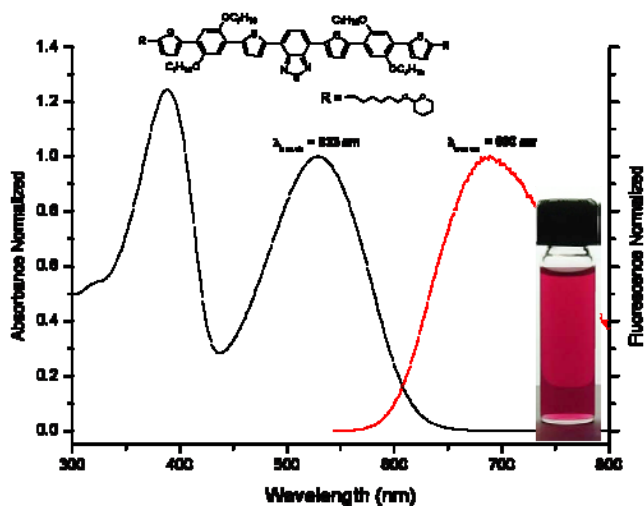


Figure 1. Absorbance and fluorescence of **TPT-BTD-TPT** in CHCl_3 ($c = 5\text{E-}5$ mol/l).

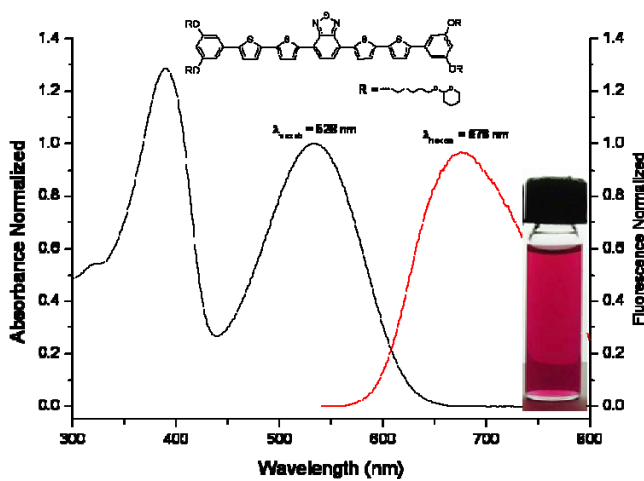


Figure 2. Absorbance and fluorescence of **PTT-BTD-TTP** in CHCl_3 ($c = 5\text{E-}5 \text{ mol/l}$).

Electrochemistry

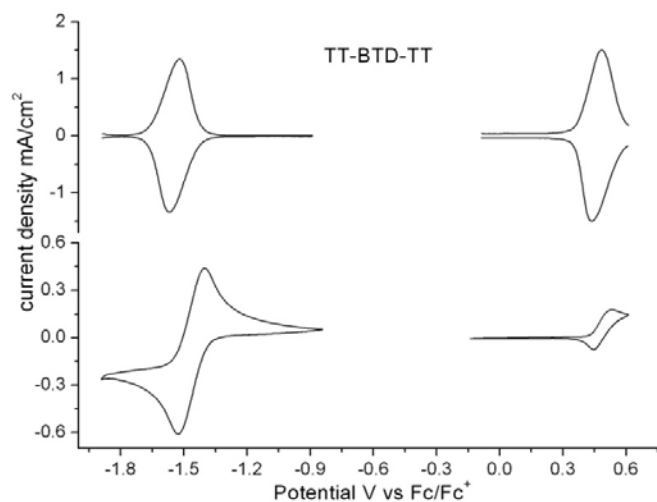


Figure 3. Cyclic voltammetry (bottom) of **TT-BTD-TT** (4 mM) in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (0.1 M) solution at 50 mV s^{-1} . Differential pulse voltammetry (top) for **TT-BTD-TT** (4 mM) in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (0.1 M) with a step time of 0.1 s and a step size of 2 mV.

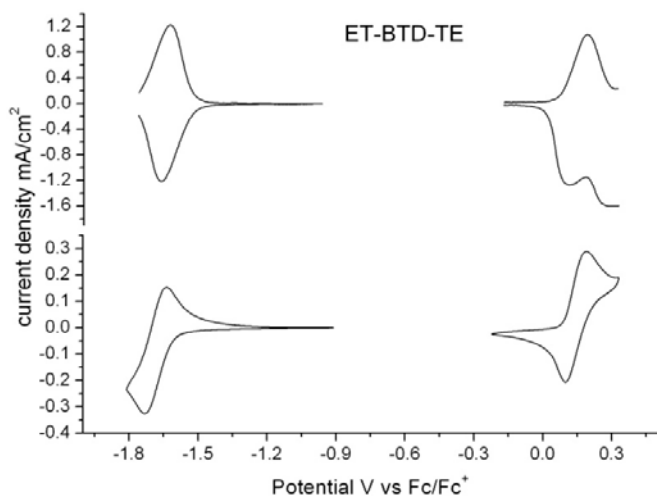


Figure 4. Cyclic voltammetry (bottom) of **ET-BTD-TE** (4 mM) in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (0.1 M) solution at 50 mV s^{-1} . Differential pulse voltammetry (top) for **ET-BTD-TE** (4 mM) in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (0.1 M) with a step time of 0.1 s and a step size of 2 mV.

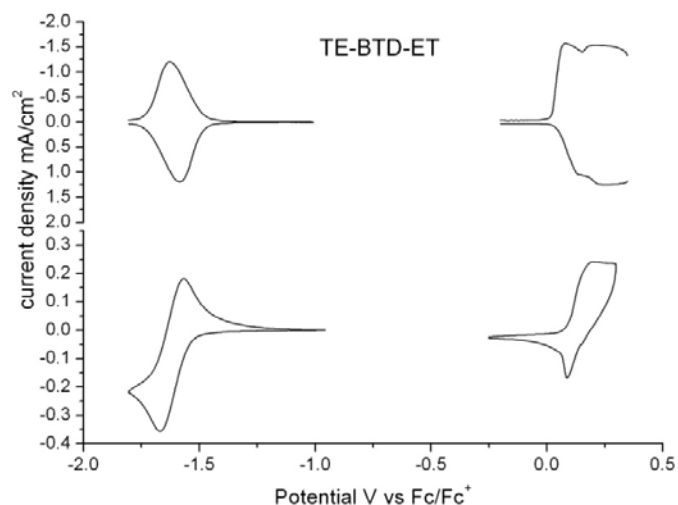


Figure 5. Cyclic voltammetry (bottom) of **TE-BTD-ET** (4 mM) in CH₂Cl₂/TBAP (0.1 M) solution at 50 mV s⁻¹. Differential pulse voltammetry (top) for **TE-BTD-ET** (4 mM) in CH₂Cl₂/TBAP (0.1 M) with a step time of 0.1 s and a step size of 2 mV.

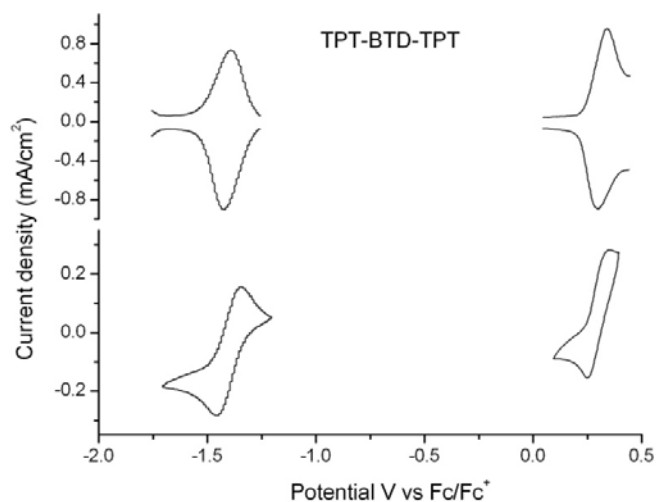


Figure 6. Cyclic voltammetry (bottom) of **TPT-BTD-TPT** (4 mM) in CH₂Cl₂/TBAP (0.1 M) solution at 50 mV s⁻¹. Differential pulse voltammetry (top) for **TPT-BTD-TPT** (4 mM) in CH₂Cl₂/TBAP (0.1 M) with a step time of 0.1 s and a step size of 2 mV.

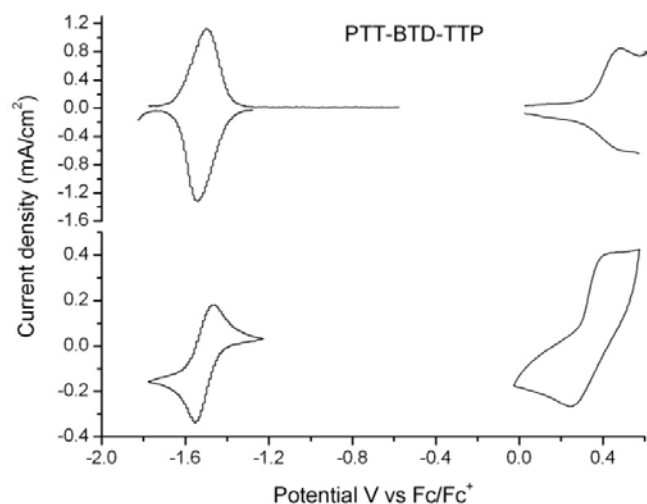


Figure 7. Cyclic voltammetry (bottom) of **PTT-BTD-TTP** (4 mM) in CH₂Cl₂/TBAP (0.1 M) solution at 50 mV s⁻¹. Differential pulse voltammetry (top) for **PTT-BTD-TTP** (4 mM) in CH₂Cl₂/TBAP (0.1 M) with a step time of 0.1 s and a step size of 2 mV.

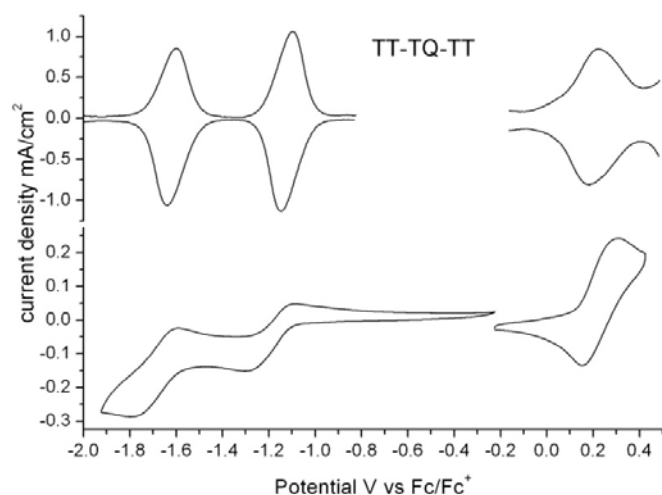


Figure 8. Cyclic voltammetry (bottom) **TT-TQ-TT** (4 mM) in CH₂Cl₂/TBAP (0.1 M) solution at 50 mV s⁻¹. Differential pulse voltammetry (top) for **TT-TQ-TT** (4 mM) in CH₂Cl₂/TBAP (0.1 M) with a step time of 0.1 s and a step size of 2 mV.

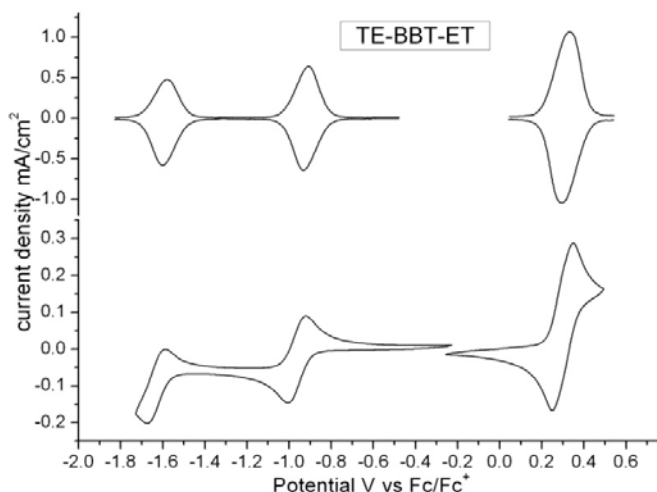


Figure 9. Cyclic voltammetry (bottom) **TE-BBT-ET** (4 mM) in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (0.1 M) solution at 50 mV s^{-1} . Differential pulse voltammetry (top) for **TE-BBT-ET** (4 mM) in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (0.1 M) with a step time of 0.1 s and a step size of 2 mV.

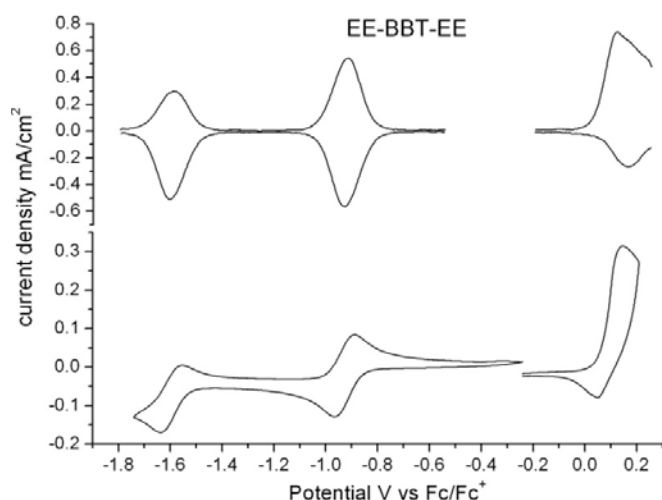


Figure 10. Cyclic voltammetry (bottom) **EE-BBT-EE** (4 mM) in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (0.1 M) solution at 50 mV s^{-1} . Differential pulse voltammetry (top) for **EE-BBT-EE** (4 mM) in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ (0.1 M) with a step time of 0.1 s and a step size of 2 mV.

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