

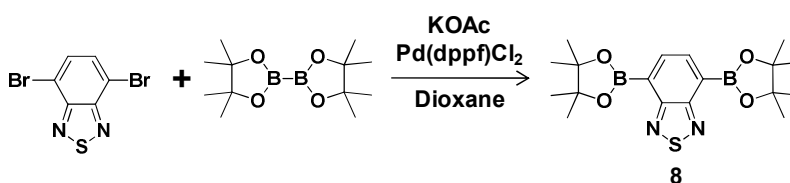
Supporting Information

Conjugated Thiophene-Containing Polymer Zwitterions: Direct Synthesis and Thin Film Electronic Properties

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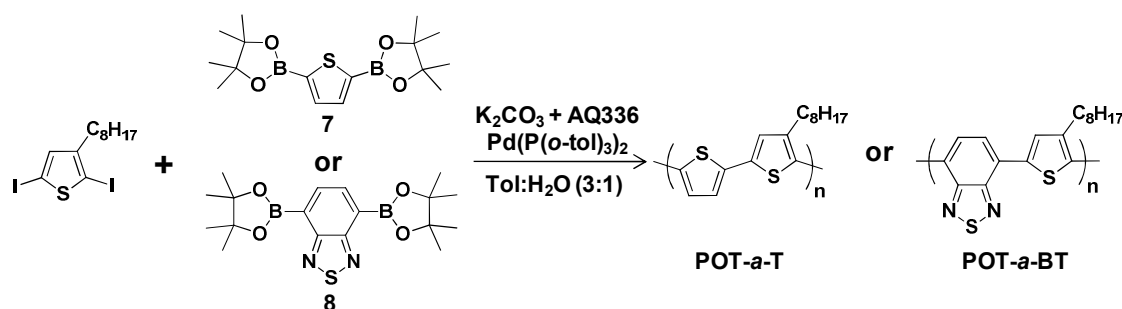
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Scheme S1. Synthesis of benzothiadiazole A₂-monomer

Synthesis of 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (8).

Following the procedure of Müllen and coworkers,¹ to a dry 1-neck, 25 mL round-bottom flask equipped with a magnetic stir bar and septum, and flushed with argon, was added 4,7-dibromobenzo[c][1,2,5]thiadiazole² (1.0 g, 3.4 mmol), bis(pinacolato)diboron (2.0 g, 7.9 mmol), anhydrous potassium acetate (2.0 g, 20 mmol) and [1,1'-bis(diphenylphosphine)ferrocene]dichloropalladium-DCM adduct (0.25 g, 0.3 mmol). The flask was evacuated and backfilled with argon (3x). The contents were dissolved upon stirring with anhydrous 1,4-dioxane (10 mL) (degassed with argon). The mixture was stirred and heated to 80 °C for 24 hours. The mixture was cooled to room temperature and water was added to quench the reaction, followed by extraction of the crude product into ethyl acetate. The organic fractions were combined, dried over anhydrous MgSO₄, filtered and concentrated to obtain a dark red / brown solid. The product was purified by column chromatography on silica-gel, eluting with hexanes then ethyl acetate:hexanes (5:95). Removal of the solvent gave **8** as a light yellow solid (0.98 g, 74%). ¹H NMR (300 MHz, Methylene Chloride-d₂) δ 8.10 (s, 2H), 1.40 (s, 28H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 25.27, 84.86, 138.10, 157.52.



Scheme S2. Suzuki coupling to alkylated polymers

Synthesis of 2,5-diiodo-3-octylthiophene. A 50 mL, 1-neck round bottom flask equipped with a magnetic stir bar and inlet adapter was flushed with nitrogen. 3-Octylthiophene (2.0 g, 10.2 mmol) and CHCl_3 : CH_3COOH (10 mL each) were added to the flask. The mixture was stirred under nitrogen and wrapped with aluminum foil. N-iodosuccinimide (5.7 g, 25.5 mmol) was added and the reaction was stirred at room temperature for 12 hours, quenched with aqueous sodium hydroxide (10 wt%) and aqueous sodium thiosulfate (10 wt%) with vigorous stirring. The product was extracted into Et_2O (2 x 100 mL) and washed with water (3 x 100 mL). The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated to obtain a crude orange oil. The product was purified further by column chromatography on silica gel, eluting with hexanes. Removal of the solvent gave 2,5-diiodo-3-octylthiophene as a yellow oil (3.83 g, 84%). ^1H NMR (700 MHz, CDCl_3) δ 6.89 (s, 1H), 2.51 (t, $J = 7.8$ Hz, 2H), 1.53 (p, $J = 7.7$ Hz, 2H), 1.36 – 1.22 (m, 10H), 0.89 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (176 MHz, CDCl_3) δ 14.28, 22.82, 29.28, 29.35, 29.50, 30.09, 32.02, 32.08, 75.93, 77.13, 137.93, 149.67.

General Suzuki polycondensation procedure to alkylated polymers. A 5 mL pressure tube equipped with a magnetic stir-bar was obtained and bis(tri-*o*-tolylphosphine)palladium(0) (0.005 mmol), **8** (112 mg, 0.25 mmol), diboronate ester B_2 monomer (**6** or **7**) (0.25 mmol) and one drop of Aliquat 336 were added. The atmosphere was flushed with argon, then toluene (3 mL) and 2 M K_2CO_3 (aq) (1 mL), previously degassed with argon were added. The cap was sealed tightly, the tube wrapped with aluminum foil and the mixture was heated to 90 °C with vigorous stirring for 24 hours. The contents were cooled to room temperature and precipitated into MeOH. The solid was filtered into a Soxhlet thimble and extracted with MeOH, acetone, Hex and CHCl_3 subsequently. The CHCl_3 fraction was collected and solvent removed under reduced pressure.

Poly(octylthiophene-*alt*-thiophene) (**POT-*a*-T**) was obtained as a red-gold, lustrous solid (40 mg, 58%) (GPC) $M_n = 7,800$ g / mol, $\bar{D} = 1.6$; ^1H NMR (300 MHz, Chloroform-*d*) δ 7.20 – 6.58 (br, 3H), 3.00 – 2.44 (br, 2H), 1.92 – 1.48 (br, 2H), 1.53 – 0.97 (br, 10H), 1.05 – 0.62 (br, 3H).

Poly(octylthiophene-*alt*-benzothiadiazole) (**POT-*a*-BT**) was obtained as a purple-gold, lustrous solid (63 mg, 77%). (GPC) $M_n = 18,600$ g / mol, $\bar{D} = 1.9$; ^1H NMR (300 MHz, CDCl_3) δ 8.26 – 8.11 (br, 1H), 8.04 – 7.92 (br, 1H), 7.81 – 7.65 (br, 1H), 3.02 – 2.63 (br, 2H) 1.87 – 1.63 (br, 2H), 1.45 – 1.11 (br, 10H), 0.93 – 0.80 (br, 3H).

Solution and solid-state absorption

Solution (0.025 mg / mL in trifluoroethanol) and thin film (on cleaned glass slides) absorption of the CPZs is shown in **Figure S1**. The bathochromic shift is due to interchain electronic interactions. The glass slides were cleaned with detergent (1x), water (2x), acetone (1x) and isopropanol (1x) subsequently. The slides were dried in an oven at 150 °C for 12 hours, cooled to room temperature, treated with UV-ozone for 20 minutes and the polymers were spun-cast from trifluoroethanol (10 mg / mL) at 1500 rpm over 60 seconds.

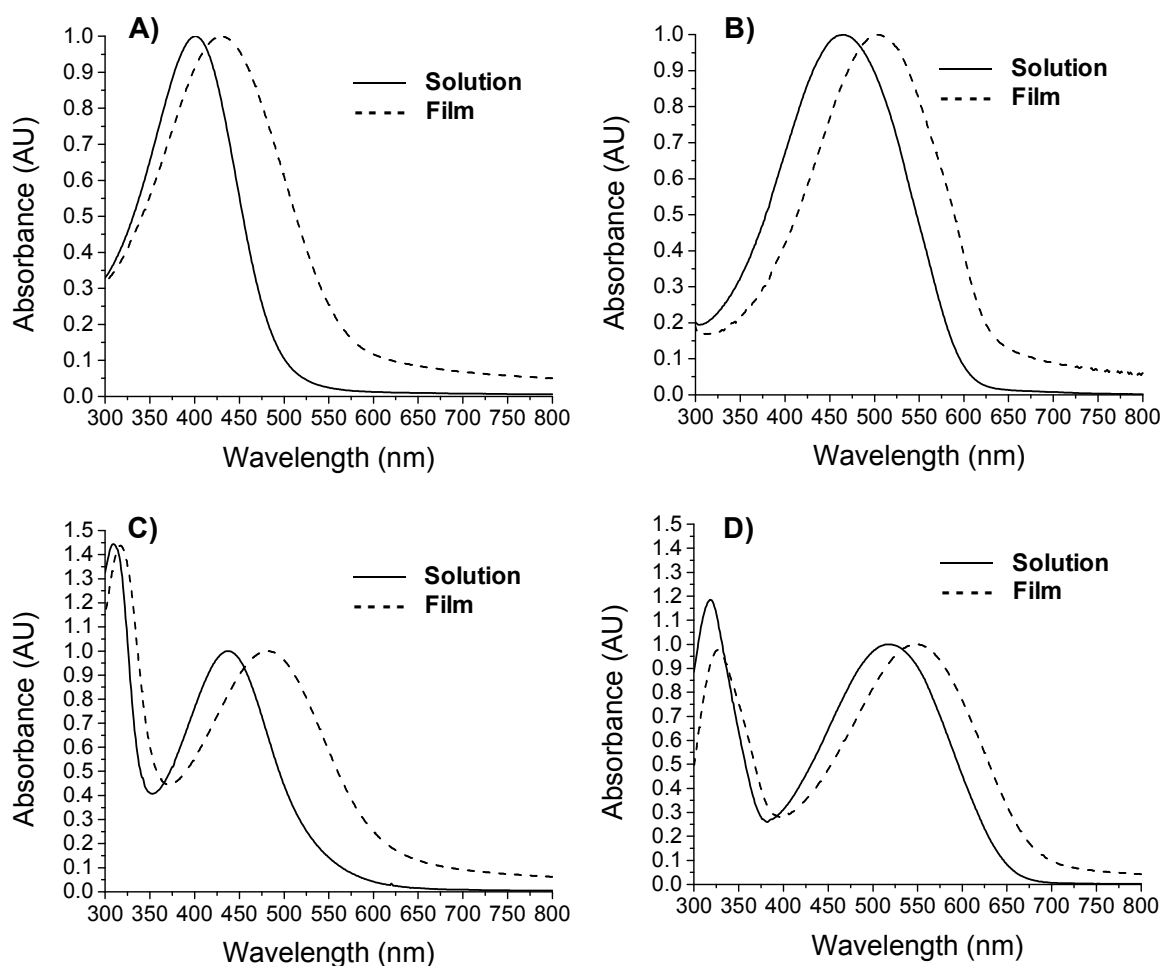


Figure S1. Solution and film absorption of CPZs. (A) PTSB-1; (B) PTSB-2; (C) PTBTSB-1; (D) PTBTSB-2

As evidence that maximum conjugation length was reached for the short chain CPZs, thin film absorption of three different number average molecular weight (M_n) polymers (PTSB-1 and

PTBTBSB-1) was done, showing no significant change in absorption (**Figure S2**). Molecular weights were determined using aqueous gel permeation chromatography, relative to poly(ethylene oxide) standards.

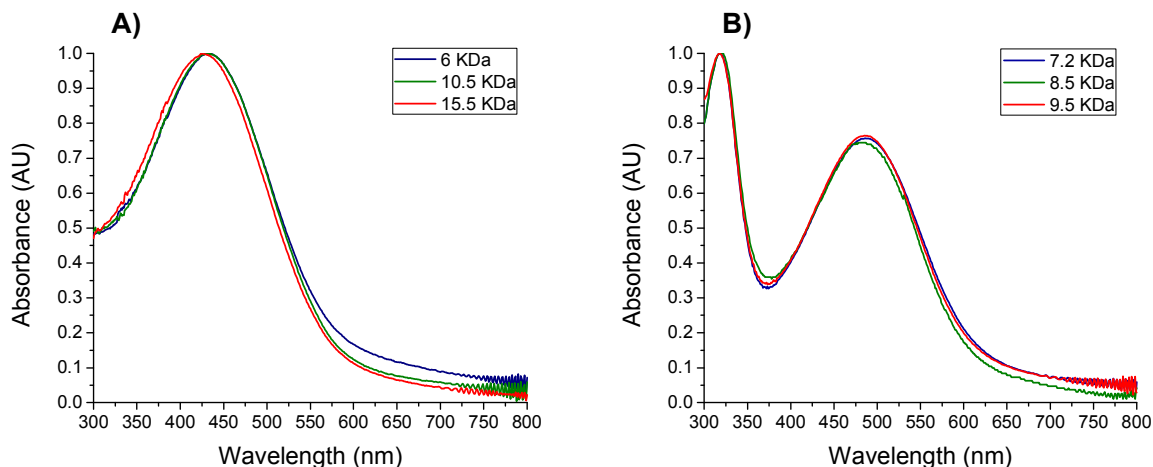


Figure S2. Thin film absorption of CPZs with three different number average molecular weights. (A) PTSB-1; (B) PTBTBSB-1

Ultraviolet photoelectron spectroscopy of CPZs

Sample Preparation and measurement for UPS. Silicon wafers (n-doped with arsenic) were cut ($\sim 7 \times 7$ mm) and cleaned with detergent, water, acetone and isopropanol. The substrates were dried in an oven at 150 °C for 12 hours, cooled to room temperature, treated with UV-ozone for 20 minutes, transferred to a nitrogen filled glove-box, and placed in a vacuum deposition chamber (2×10^{-6} mbar). A ~ 50 nm thick layer of silver or gold was deposited. Immediately after deposition the substrates were removed and the polymers spun from a 0.6 mg / mL solution of trifluoroethanol at 2000 rpm for 60 seconds. The samples were brought into the UPS analysis chamber, under ultrahigh vacuum (1×10^{-9} mbar). The ionization potentials were determined through two steps: first the intersection of a line tangent to the low kinetic energy onset of the spectrum with the abscissa axis was ascertained and subtracted from 21.2 eV (the UV-source energy), followed by the addition of the intersection of high kinetic energy onset with the abscissa axis. All measurements were done at a -3 V sample bias, allowing for facile collection of low kinetic energy electrons. The resolution of the UPS instrument was 0.1 eV as determined from the width of the Fermi level of silver. All samples were <10 nm thick as determined by the surface profiler (KLA Tencor, model Alpha-Step IQ).

Presence of two peak absorption of donor-acceptor polymers

The presence of two absorption peaks seen for donor-acceptor polymers has been explained by Salzner and Kose to occur due to the presence of an intermediate band comprised of localized states, as depicted in **Figure S3**.³ The variable peak intensities seen for **PTBTSB-1** and **PTBTSB-2** (**Figure 2**) arise from a change in the probability for light absorption to the intermediate band relative to the conduction band, which our data suggests is affected by the donor and acceptor pairing.

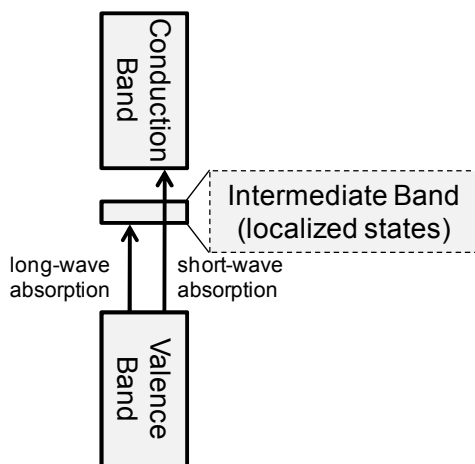


Figure S3. Depiction of energy bands giving rise to two peak absorption for donor-acceptor polymers