Supporting Information

Synthesis of Poly[(4,4'-(dihexyl)dithieno(3,2-b;2',3'-d)silole] and Copolymerization with 3-Hexylthiophene: New Semiconducting Materials with Extended Optical Absorption

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Characterization methods

^{1}H NMR spectra were recorded at room temperature in $CDCl_3$ (30 mg.mL^{-1}) and referenced to TMS (tetramethylsilane) at 0 ppm. All chemical shifts and coupling constants are reported in ppm and Hz, respectively.

Average molecular weights and molecular weight distributions of the polythiophenes were measured using size exclusion chromatography (SEC) on a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1mL.min^{-1}), a Marathon autosampler (loop volume = 200 µL, solution conc. = 1mg.mL^{-1}), a PL-DRI refractive index detector and three columns: a PL gel 10 µm guard column and two PL gel Mixed-B 10µm columns (linear columns for separation of MWPS ranging from 500 to 10^6 daltons). The eluent used was $CHCl_3$ at a flow rate of 1 mL.min^{-1} at 45°C. Polystyrene standards were used to calibrate the SEC.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-Tof) mass spectra were recorded using a spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J.m^{-2} delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in reflection mode at a resolution of about

10000. All samples were analyzed using (DCTB) trans-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile that matrix was prepared as 40 mg.mL^{-1} solution in $CHCl_3$. The matrix solution (1 µL) was applied to a stainless steel target and air dried. Polymer samples were dissolved in CH_2Cl_2 to obtain 1 mg.mL^{-1} solutions. 1µL aliquots of those solutions were applied onto the target area already bearing the matrix crystals, and air dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 500 to 10000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time.

Atomic Force Microscopy (AFM) measurements were performed in ambient conditions with a Multimode microscope equipped with a Nanoscope V controller (Veeco Bruker) operating in tapping mode. Si cantilevers with a resonance frequency in the 200-500 kHz range were used. The images were displayed and analyzed with the Bruker software NanoScope Analysis. The images were recorded using a 1024*1024 points resolution and a flatten was applied on the images.

Thermogravimetric analyses were carried out on a TA Instruments Q500 with a heating rate of 10 °C.min^{-1} under a flow of nitrogen, using Pt crucibles and 10 mg of sample for each analysis.

UV-Visible in film were performed on a Perkin Elmer LAMBDA 650S.

The GC-MS analyses were performed using a Waters GCT Premier instrument based on a time-of-flight analyzer. The gas chromatograph was equipped with a Restek Rtx-5Sil MS column (30 m length, 0.25 mm ID and 0.25 µm DF). Typical GC conditions were: injector temperature, 250 °C; splitless mode; Helium carrier gas flow rate, 1 mL/min; interface temperature: 250 °C. The temperature program was as follow: initial temperature, 55 °C; 1 °C/min ramp; final temperature, 150 °C; 5 °C/min ramp; final temperature, 250 °C (hold 5 min). Electron Ionization (EI) source conditions were: source temperature, 200 °C; electron energy, 70 eV; trap current, 200 μa; emission current, 400 μa. All ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass-analyzed with a 1 s integration time. Data were acquired in continuum mode. The GCT Premier instrument is a high sensitive instrument and, for instance, in EI positive ionization mode, 1 pg of hexachlorobenzene gives S/N > 10/1 whilst acquiring full spectra over a mass range up to *m/z* 800. Accurate mass measurements were performed using perfluorotributylamine as internal calibrant.

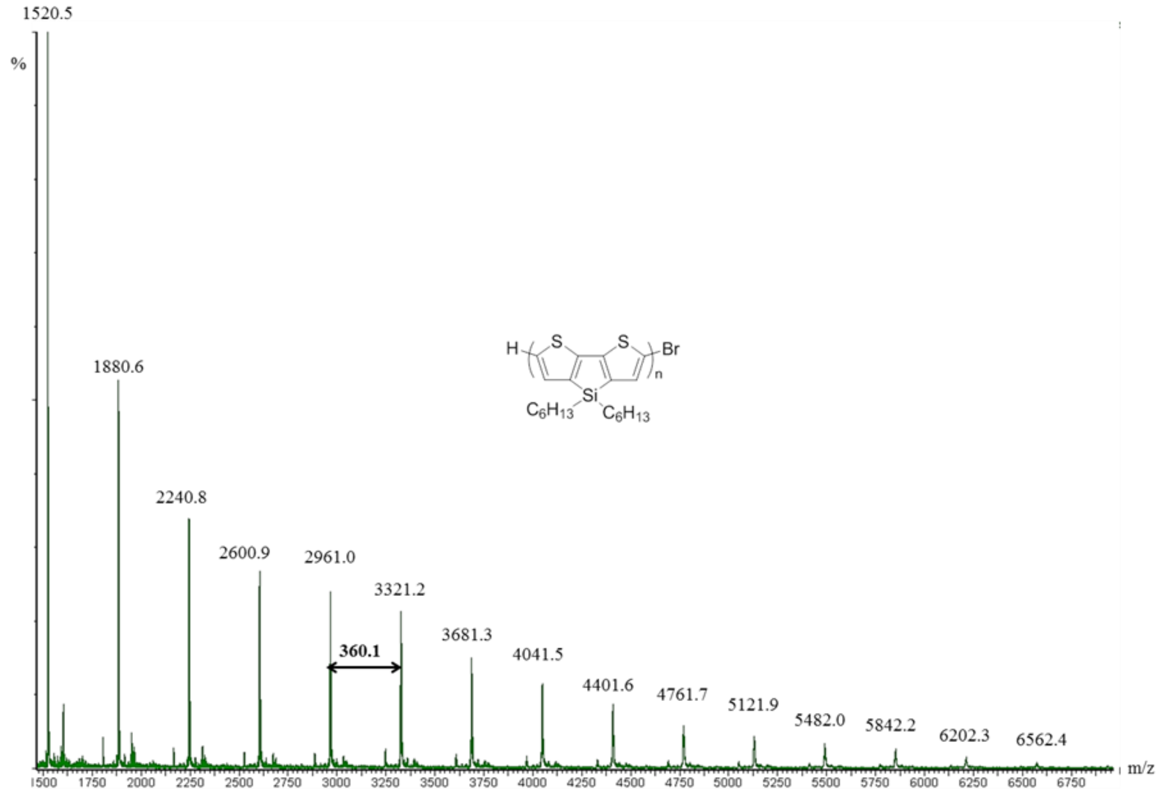

Figure S1. MALDI-Tof analyse of the homopolymer ***<u>P1b</u>***

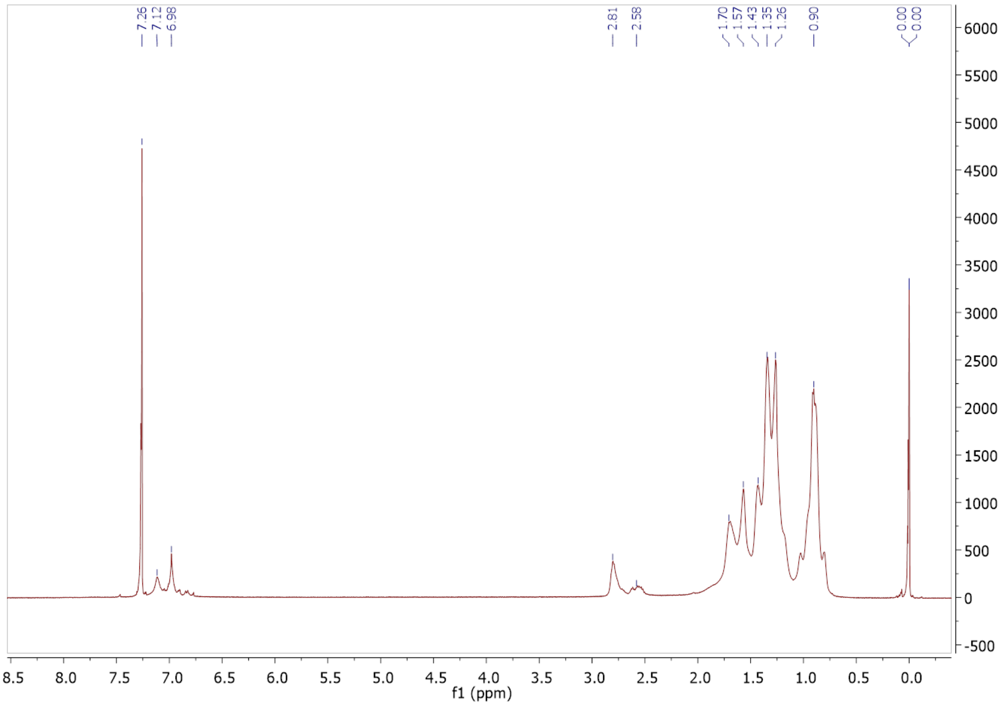

Figure S2. Proton NMR of the diblock copolymer ***P2b*** *in CDCl3 recorded on a 500MHz machine*

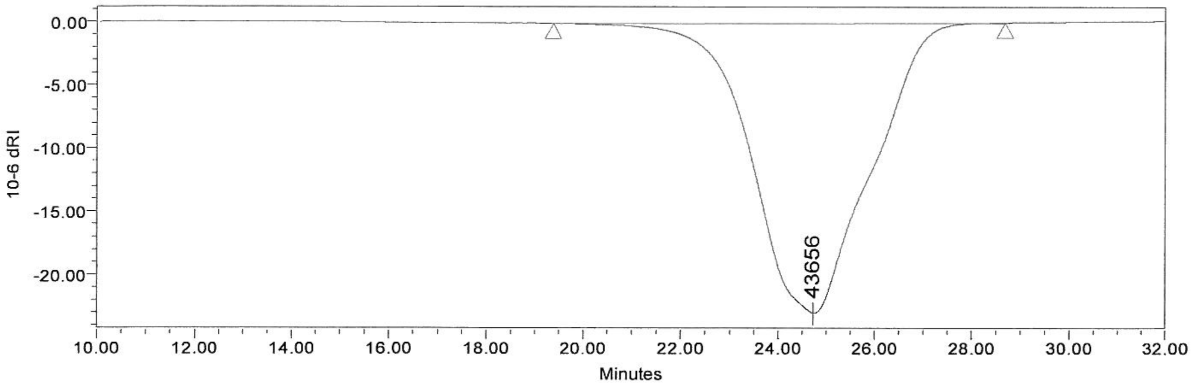

Figure S3. SEC chromatogram of the diblock copolymer ***P2b*** *in* $CHCl_3$

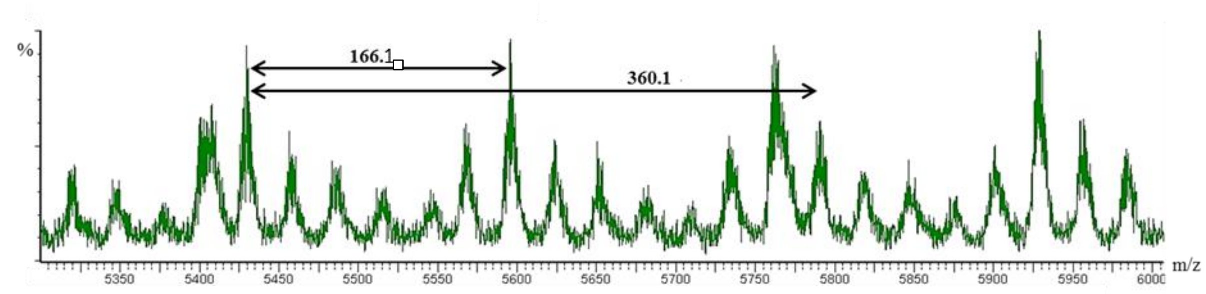

Figure S4. MALDI-ToF spectrum of the diblock copolymer ***P2a*** *-magnification between m/z 5250 and 6000*

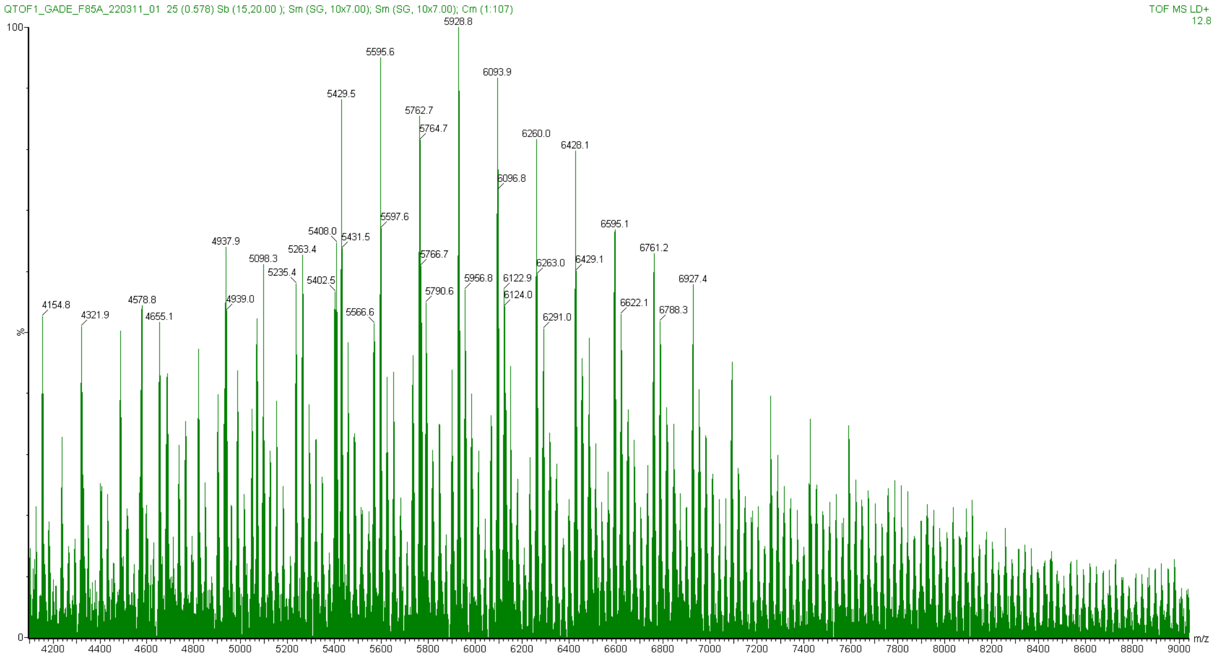

Figure S5. MALDI-ToF spectrum of the diblock copolymer ***<u>P2a</u>***