Supporting Information

Photoswitchable Poly(3-hexylthiophene)

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**General Information:** THF was destilled from benzophenone and potassium prior to use. Starting materials were purchased from Acros, Aldrich, Fluka, Merck und Riedel De Haen. For column chromatography Kieselgel 60 (0.04-0.06 mm, Macherey and Nagel) was used.

**Instrumentation:** \textsuperscript{1}H-\textsuperscript{13}C-NMR measurements were carried out on a BRUKER Cryomagnet BZH 250/52 instrument with a field of 5.87 Tesla and a current of 54.80 A. Mass spectroscopic data were obtained from a FINNIGAN MAT 8500. FTIR - data were achieved by a BIO RAD DigiLab Division FTS 40/13130 and a Bruker FTIR-Tensor-37 spectrometer. For photophysical and photochemical studies a HITACHI Model U 3000 Spectrophotometer (UV/Vis) and a SHIMADZU RF-5301 PC (fluorescence spectroscopy) were used. CV measurements were carried out using a three electrode assembly microcell from E&G Princeton Applied research and a Potentiostat/Galvanostat Model 263A. MALDI-TOF data were obtained from a Bruker Reflex III with „high mass detector“ and GPC data were achieved by means of a Polymer-SEC equipped with a tunable UV detector set at 254 nm (model 486) and a refractive index (model 410) detector from WATERS. THF was used as eluent at a flow rate of 0.5 ml/min and polystyrene standards were used for calibration. \textit{o}-Dichlorobenzene was used as internal standard. SDV-Gel (PSS, length 5cm, diameter 0.8cm, particle size 5 µm, pore size 100 Å) was used as a precolumn, followed by two analytical columns filled with mixed-C PL-Gel (PL, length 30cm, diameter 0.8 cm, particle size 5µm).

The thermal properties were studied using a Mettler Toledo SDTA 851\textsuperscript{e} (TGA) and a Perkin Elmer Diamond DSC under N\textsubscript{2} atmosphere. For photochemical reactions a white light emitting light source (Oriel Xe 150 W) equipped with optical filters was employed. For UV irradiation a Schott filter UG 11 and for irradiation with visible light Schott filters GG 475 (yellow glass) and OG 550 (orange glass) were used.
Switching cycles: P3HT-BTF-P3HT 4 was dissolved at a concentration of $c=3.0 \times 10^{-6}$ (wt%) in toluene. In order to initialize the BTF unit in the closed isomer state the cuvette with the solution was irradiated for 5 seconds with light at 334 nm that was provided from a mercury lamp (200 W, Oriel) and passed a suitable band pass filter (Schott UG 11). Subsequently the cuvette was placed into a UV-VIS spectrometer (Perkin Elmer Lambda 750) and the absorption was measured. These irradiation/spectroscopy sequences were repeated 7 times which corresponds to about 35 s of accumulated UV exposure time. Next the BTF unit was converted back to the open isomer by irradiation of the cuvette for 20 s with light in the visible spectral range around 620 nm. The light was provided by the same lamp and passed a long pass filter (Schott OG550). Again the irradiation/spectroscopy sequences were repeated 7 times, corresponding to about 140 s of accumulated exposure time with light in the visible spectral range.
A) Synthesis, H-NMR and MALDI TOF MS

Synthesis of Poly(3-hexylthiophene) monobromide (2)

A Schlenk flask was heated under vacuum, backfilled with argon, and charged with 6158 mg (18.884 mmol) 2,5-Dibrom-3-hexylthiophene 1. After purging with argon, 20 mL dry THF and 22.1 mL tBuMgCl (solution in THF, 17.68 mmol, c = 0.8 molL⁻¹) were added in succession by syringe. After stirring for 2h at room temperature the mixture was diluted with 80 mL dry THF and cooled to 0 °C. A separate Schlenk flask was heated under vacuum, backfilled with argon, and charged with 930 mg (1.717 mmol) Ni(dppp)Cl₂. After purging with argon, 5 mL dry THF were added. The suspension was added to the reaction mixture at 0°C by syringe as fast as possible. The mixture was allowed to warm to room temperature, and after 10 min the polymerization was quenched by the addition of 5 mL 5 N hydrochloric acid. After evaporation of the solvent under reduced pressure, the residue was suspended in methanol, filtered into a soxhlet thimble, extracted with methanol overnight and redissolved in THF. The solution was concentrated and methanol was added. This mixture was stirred overnight and the supernatant methanol layer was decanted (three times). Residual methanol was evaporated under reduced pressure and the remaining reddish slurry product was freeze-dried with benzene. SEC (THF, polystyrene standard): $M_n$: 1500, $M_w/M_n$: 1.1. MALDI-TOF: $M_n$: 1500, $M_w/M_n$: 1.1.

$^1$H-NMR (250 MHz, CDCl₃): $\delta$/ppm = 0.90 (21H, m, CH₃), 1.33 (40H, m, (CH₂)₃), 1.67 (14H, m, CH₂), 2.76-2.53 (16H, m, α-CH₂), 6.82 (1H, s, CThienylH, P3HT), 6.90 (1H, s, CThienylH, P3HT), 6.97 (4H, m, CThienylH, P3HT).

$^{13}$C-NMR (250 MHz, CDCl₃): $\delta$/ppm: 14.05, 22.58, 29.20, 30.45, 31.64 (CH₃, CH₂), 126.56-128.54, 139.72-139.82 (CThienyl).

FTIR (ATR) ν/cm⁻¹: 3063 (m, sp²C-H) 2951 (m, νas, CH₃), 2923 (m, νs, CH₂), 2851 (m, νs, CH₂), 1516 (m, νC=C), 1458 (m, δs, CH₃), 826, 721, 663 (s, γ(CH)Aryl).

UVVis (CHCl₃) $\lambda_{max}$/nm: 423 (toluene).
Suzuki coupling of P3HT monobromide 2 and BTF bisborolane 3

1,2-Bis[2-methyl-5’-(4’’-(poly-3-hexythiophenyl)phenyl)thiophen-3’-yl]hexafluorocyclopentene P3HT-BTF-P3HT (4)

362 mg (0.29 mmol) P3HT monobromide 2 and 100 mg (0.129 mmol) 1,2-bis[2’-methyl-5’-(4’’-(4,4,5,5-tetramethyl-2,3-dioxaboronyl)phenyl)thiophene-3’-yl]hexafluorocyclopentene 3 were dissolved in 10 mL THF and 10 mL aqueous sodium carbonate solution (20%) was added. After degassing for one hour, 130 mg (0.11 mmol) [Tetrakistriphenylphosphin palladium (0)] was added and the mixture was refluxed for 18 h. The progress of the reaction was followed up by TLC (silicagel/chloroform). A single spot of the photochromic product indicated that the educt 3 was completely used up. After cooling to room temperature the reaction mixture was extracted with diethylether and the combined organic phases were washed with saturated sodium hydrogen carbonate solution (3 x 100 mL), and with water (2 x 100 mL), respectively. After evaporation of the solvents the residue was dried in vacuo (10^{-3} mbar, 60°C). The solid was redissolved in chloroform and filtered through an 8 cm silicagel plug to remove residual palladium catalyst. The chloroform solution was concentrated under reduced pressure and precipitated into methanol. After removing the supernatant orange coloured solution the residue was washed with methanol, dried in vacuo and purified by column chromatography (silicagel; 0.04-0.06 mm, cyclohexane/chloroform gradually increasing from 20:1 to 15:1) to remove unreacted P3HT. The product was then eluted from the column with chloroform. A crude product (0.08 mmol; 63% related to BTF-Borolane 3) was obtained and washed three times with 100 mL of a 10:1 mixture methanol/aqueous ammonium hydroxide (25%) at 60°C until the solution remained colourless. After drying the product in vacuo it was treated two times with methanol, two times with ethanol and three times alternately with warm acetone and aqueous ammonium hydroxide (25%), washed with acetone and ethanol, and finally dried in vacuo. Yield: 200 mg (0.07 mmol) reddish polymer (54%). The purification process was followed up by preparative GPC. Product before preparative GPC (THF, polystyrene standard): $M_n$: 3600, $M_w/M_n$: 1.2; MALDI-TOF: $M_n$: 3000, $M_w/M_n$: 1.1. Product after preparative SEC (THF, polystyrene standard): $M_n$: 5800, $M_w/M_n$: 1.03. MALDI-TOF: $M_n$: 3620, $M_w/M_n$: 1.01.
Elemental analysis calculated for: \( \text{H(C}_{10}\text{H}_{16}\text{S})_{7}(\text{C}_{27}\text{H}_{18}\text{F}_{6}\text{S}_{2})(\text{C}_{10}\text{H}_{16}\text{S})_{7}\text{H}, \)
\((1\text{H}_{166,30}(518,56))(166,30)_{7}\): C, 70.42%, H, 7.57%, S, 18.01%; found: C, 69.88% H, 7.93%, S, 17.99%.

\(^{1}\text{H-NMR}(250\text{ MHz, CDCl}_{3}):\delta/\text{ppm} = 0.89 (42\text{H, m, CH}_{3}), 1.38 (84\text{H, m, (CH}_{2})_{3}), 1.68 (28\text{H, m, CH}_{2}), 1.98 (6\text{H, s, CH}_{3}), 2.68 (28\text{H, m, }\alpha\text{-CH}_{2}), 6.90 (2\text{H, s, C}_{\text{Thienyl}}, \text{P3HT}), 6.97 (12\text{H, m, C}_{\text{Thienyl}}, \text{P3HT}), 7.35 (2\text{H, s, C}_{\text{Thienyl}}, \text{BTF}), 7.48 (4\text{H, m, C}_{\text{Phenyl}}), 7.60 (4\text{H, m, C}_{\text{Phenyl}}).

\(^{13}\text{C-NMR}(250\text{ MHz, CDCl}_{3}):\delta/\text{ppm}: 14.04, 14.84, 22.43, 26.83, 28.81, 30.31, 31.42 (\text{CH}_{3}, \text{CH}_{2}), 125.52, 126.40, 129.47, 130.41 (\text{C}_{\text{Phenyl}}), 119.92, 133.49, 141.76-143.58 (\text{C}_{\text{Thienyl}}).

\text{FTIR (ATR) }\nu/\text{cm}^{-1}: 3063 (m, sp^2\text{C-H}) 2954 (m, \nu_{as}, \text{CH}_{3}), 2924 (m, \nu_{s}, \text{CH}_{2}), 2854 (m, \nu_{s}, \text{CH}_{2}), 1554, 1512 (m, \nu_{C=C}), 1458 (m, \delta_{s}, \text{CH}_{3}), 821, 725, 663 (s, \gamma(\text{CH})\text{Aryl}).

\text{UV-Vis (CHCl}_{3}) \lambda_{\text{max}}/\text{nm}: 427 (open form); 612 (closed form).

**GPC analysis of P3HT-Br 2 and the final product P3HT-BTF-P3HT 4**

![Figure S1. GPC curves of P3HT-Br 2, the raw product P3HT-BTF-P3HT 4 and the purified product P3HT-BTF-P3HT 4. The MALDI spectrum in S2 is taken from the P3HT-BTF-P3HT sample after preparative GPC. The purified fraction had a PDI of 1.03 and a Mn of 5800g/mol in SEC (MALDI: PDI= 1.01, Mn= 3620g/mol).](image)
**MALDI-TOF Analysis of monobrominated P3HT-(H/Br) (2)**

*Figure S2.* MALDI-TOF of P3HT 2: Populations of brominated (very strong intensity) and non-brominated product (very weak intensity) were detected. For example, in the P3HT-(H/Br) series, the molecular weight of 1577 Da corresponds to 9-mer with H/Br end groups and in the P3HT-(H/H) series, 1497 Da represents a 9-mer with H/H end groups. The ratio of intensities of non-brominated P3HT-(H/H) and P3HT-(H/Br) 2 give a P3HT-(H/Br) 2 percentage of 95%; The difference between two neighbouring peaks in the both series corresponds to the mass of a single 3-hexylthiophene monomer unit (166.3 Da).

*Figure S3.* MALDI-TOF spectrum of P3HT-BTF-P3HT 4. The difference between the adjacent peaks of P3HT-BTF-P3HT 4 is 166.3 Da (= single 3HT unit). A single series with uniform H-H end groups is present. The peak molecular weight 3514 corresponds to 18 3HT repeating units carrying one single BTF photoschalter moiety and two H end groups; calculated as $1 + (166.3)18 + 518.6(BTF) + 1 = 3514$. 
$^1$H NMR Spectra of monobrominated P3HT (2) and P3HT-BTF-P3HT (4)

Figure S4. Aromatic region of the $^1$H-NMR spectra of P3HT-Br 2 and P3HT-BTF-P3HT 4.

Figure S5. Aliphatic region of the $^1$H-NMR spectra of P3HT-Br 2 and P3HT-BTF-P3HT 4.
B) Thermal characterization of P3HT (2) and P3HT-BTF-P3HT (4)

![Graph showing mass % vs. temperature for P3HT 2 and P3HT-BTF-P3HT 4.]

**Figure S6.** a) TGA trace of P3HT 2; b) P3HT-BTF-P3HT 4 – measured at a heating rate of 10 Kmin⁻¹. The first step in TGA at a weight loss of approx. 50%, corresponds to alkyl chain degradation, while the second one entails the complete degradation of the molecule.

![Graph showing heat flow vs. temperature for P3HT-BTF-P3HT 4.]

**Figure S7.** DSC measurement of P3HT-BTF-P3HT 4 (enlarged region): heating curve (40 Kmin⁻¹): glass transition at 12°C. The glass transition showed a strong dependence on the heating rate. Therefore the measurements were carried out at heating rates of 10, 20 and 40 Kmin⁻¹ in a range from -60 to 200°C. The first two DSC curves, measured at 10 Kmin⁻¹, exhibited no thermal transition. Upon increasing the rate on 40 Kmin⁻¹ the most intensive glass transition was observed. For such low molecular weights of P3HT, no crystalline nature can be expected.
C) Photochemical Properties of Reference Photoswitch BTF-Me (5)

Scheme S1. Reversible photoisomerization reaction of the reference photoswitch BTF-Me 5; the ring closure (photocyclization) was initiated using a 150 W Xe lamp, equipped with a Schott UG 11 filter, the ring opening (cycloreversion) was triggered with visible light by using a Schott GG 475 filter.

Figure S8. Absorption spectra of reference molecule BTF-Me 5 recorded in toluene (c = 10^{-5} M) in the open and closed form.
D) Photophysics of P3HT-BTF-P3HT (4)

**Figure S9.** Normalized emission spectrum P3HT-(H/Br) 2 (dashed-dotted line) and normalized absorption spectrum of BTF-Me 5 (solid line): The overlap of the emission spectrum of P3HT-(H/Br) 2 and the UV/Vis spectrum of the pure photoswitch reference molecule BTF-Me 5 (closed form) proves clearly that the requirement for energy transfer from the P3HT segments to the closed BTF units is fulfilled.

**Photoswitching of P3HT-BTF-P3HT (4) in film:**

**Figure S10.** UV/Vis spectra in film of open form (dotted line) and closed form (solid line) of P3HT-BTF-P3HT 4. The low molecular weight of the P3HT segments ensure that there is no spectral overlap between P3HT and the closed form of the photoswitch. The films were spincoated from a 2 wt% chloroform solution at 2000 r/min (film thickness: d = 290 nm).
E) Cyclic Voltammetry traces of P3HT-(H/Br) 2 and P3HT-BTF-P3HT (4) and BTF reference molecule BTF-Me (5)

The measurements were carried out in dry methylene chloride (H$_2$O < 0.005%) with 0.1 molL$^{-1}$ tetrabutylammonium hexafluorophosphate as electrolyte. A Ag/AgNO$_3$ electrode was employed as a reference electrode and each measurement was calibrated with ferrocene (fc). Oxidation and reduction potentials were calculated according to $E_{1/2} = ½(E_{pc} + E_{pa})$ and HOMO/LUMO levels were estimated based on the reference level of ferrocene with 4.8 eV below vacuum. HOMO and LUMO levels were calculated from the onset oxidation and reduction potentials.

![Cyclic Voltammetry traces of P3HT-(H/Br) 2 and P3HT-BTF-P3HT (4) and BTF reference molecule BTF-Me (5)](image)

**Figure S11.** Cyclovoltammetry traces (oxidation): a) P3HT-Br 2 b) P3HT-BTF-P3HT 4 – 3.9 mg substance in 5 mL methylene chloride, (nBu)$_4$PF$_6$ (0.1 M) scan rate 50 mVs$^{-1}$.

![Cyclic Voltammetry traces of BTF-Me 5 (reference BTF): a) closed form; b) open form – 3.9 mg substance in 5 mL methylenchloride, (nBu)$_4$PF$_6$ (0.1 M), scan rate 50 mVs$^{-1}$](image)

**Figure S12.** Cyclovoltammetry traces (oxidation) of BTF-Me 5 (reference BTF): a) closed form; b) open form – 3.9 mg substance in 5 mL methylenchloride, (nBu)$_4$PF$_6$ (0.1 M), scan rate 50 mVs$^{-1}$.