Supporting Information

All-Conjugated Donor-Acceptor Block Copolymers
featuring a Pentafulvenyl-Polyisocyanide-Acceptor

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Artem A. Bakulin, Elizabeth von Hauff, Frank Pammer

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Experimental Section and Supplementary Analytical Data

1. Materials and Instrumentation

All reactions and manipulations of sensitive compounds were carried out under an atmosphere of pre-purified argon using either Schlenk techniques or an inert-atmosphere glovebox (MBraun Labmaster, Sylatech GB 1500-E). Toluene, Et2O, THF, DMF and dichloromethane were purified using a solvent purification system (MBraun; alumina / copper columns for hydrocarbon solvents). Hexane and benzene were dried by distillation from CaH2 under argon atmosphere prior to use. 5-(4-isocyanobenzylidene)-1,2,3,4-phenylcyclopentadiene,1 and 2-bromo-3-dodecyl-5-iodothiophene,2 5-bromo-2-chloro-4-(trihexylsilyloxymethyl)-thiazole,3 and Ni(o-anisyi)(dppe)Br4 were prepared according to published procedures. PFN-P1 (Poly[(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)]) were purchased from 1-MATERIAL and Chlorobenzene (Anhydr ous, 99.8%) was purchased from Sigma-Aldrich. Other reagents were commercially available (Aldrich, Acros, Alfa Aesar) and were either used as obtained or purified by standard procedures.5 1H-, 13C- and 31P-NMR spectra were recorded at 293 K on a Bruker Avance DRX 400 (400 MHz) spectrometer or a Bruker Avance 500 AMX (500 MHz). Solution 1H and 13C NMR spectra were referenced internally to the solvent residual signals.6 UV-visible absorption spectra and photoluminescence spectra were acquired on a Perkin Elmer Lambda 19 UV-vis/NIR spectrometer and a Perkin Elmer LS 55 fluorescence spectrometer, respectively. Thermal gravimetry measurements were carried out on a TGA/SDTA 851e by Mettler Toledo, with an Al2O3 70μL sample holder 25-800°C, 10°C/min 50ml/min N2, Software STAre Version 9.30.

Powder X-ray diffraction: Wide Angle X-Rays scattering: PXRD-measurements were taken on a PANalytical X’Pert MPD Pro using copper radiation (Ka1 = 1.5405980 Å), equipped with an X’Celerator-detector.

Electron Microscopy: Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Energy-dispersive X-ray spectroscopy (EDX) were performed with support from Prof. Dr. Paul Walther7 and coworkers at the electron microscopy department of the University of Ulm. SEM micrographs were recorded either on a Helios Nanolab 600 (Thermo Fisher Scientific) or on an Hitachi S-5200 Fe-SEM. Images were recorded in analysis mode of the secondary electron signal. TEM was measured on a Jeol 1400 TEM (Jeol, Tokio, Japan) with voltage of 120 kV. Images were recorded with a Veleta CCD Kamera (Olympus, Münster, Germany) and digitized with the iTEM Software 5.2 (Olympus). EDX spectroscopy was performed on a Quanta 3D FEG (Thermo Fisher Scientific) equipped with...
an Apollo XV SDD EDX Detector (EDAX-AMETK). The data was analyzed and processed with the Genesis 6.5 Software-Pacage (EDAX AMETEK). SEM- and EDX-samples were drop-cast on glass-slides (Menzelgäser) and metallized with 150 Hz of platinum or carbon before measurements. TEM samples were drop-cast on copper grids (Plano GmbH) and were measured without prior treatment.

**Transient Absorption Spectroscopy (TAS).** For TAS, a 1 kHz Ti:sapphire regenerative amplifier (Spectra-Physics Solstic, Newport Corporation) provided seed pulses (800 nm, ~ 100 fs) for the pump and probe. The pump was generated by an optical parametric amplifier (TOPAS, Light Conversion) coupled to a frequency mixer (NIRUVis, Light Conversion), whereas the broad-band NIR probe (~ 850 – 1350 nm) was generated in an yttrium aluminum garnet crystal inside the commercially available TAS setup (HELIOS, Ultrafast Systems). The pump and probe were focused onto a 0.5 mm 2 spot on the sample, which was placed in an N₂-purged cuvette for measurements. The pump was modulated at 500 Hz, and the delay between the pump and probe was controlled with a mechanical stage in the probe beam path. All analyses were conducted in MATLAB and Origin. The measurements were performed by time-correlated single photon counting (TCSPC). Kinetics were studied at 660 nm after an excitation at 467 nm. The kinetics of ultrafast TA measurements (Figure D-F) are performed with a 500 nm pump beam having an intensity of 20 μJ/cm² and near 1200 nm infrared probe beam.

2. Synthetic Procedures

2.1. Synthesis of Poly(3DT-block-IC2) (BP11, BP21, BP31)

**BP11:** Inside a glovebox under argon atmosphere 2-brom-5-iodo-3-dodecylthiophen (1, 72.0 mg, 157 μmol, 1.0 Eq.) was dissolved in 1.3 mL of dry THF and a solution of PrMgCl*Et₂O (27.0 mg, 153 μmol, 1.0 Eq.) in 1.3 mL dry THF was added. The reaction mixture was stirred for 30 min at ambient temperature, and subsequently 0.76 mL (2 mol-%) of a solution of Ni(o-anisyl)(dppe)Br (4.13 mmol/L in THF) were quickly injected. The reaction mixture was stirred for another 2 h, after which a sample was taken for analyses by GPC, and a solution of isocyanide 3 b (76.0 mg, 157 mmol, 1.0 Eq.) in 1.3 mL of dry THF was added. Subsequently, the reaction mixture was quenched by pouring it into methanol, and the precipitate was washed on a glass fiber filter with MeOH, Acetone, and n-hexane, followed by extraction with dichloromethane. The DCM-fraction was concentrated diluted with benzene, and freeze-dried to furnish 72.1 mg of BP11.

**BP21/BP31:** Thiophene 1 (103 mg, 225 μmol) was metalated and polymerized with 2 mol-% of Ni(o-anisyl)(dppe)Br as described above, and a GPC-sample was taken. The reaction mixture was then divided by weight into two equal parts, and 0.50 and 0.33 equivalents of isocyanide 3 were added, respectively. The polymers were isolated by precipitation into methanol and purified by washing on a Soxhlet-apparatus with MeOH, acetone, and n-hexane, followed by extraction with Chloroform, and freeze-drying from benzene. The procedure yielded 27.5 mg of BP21 and 26.0 mg of BP31.

2.2. Synthesis of Poly(TzTHX-block-IC2) (BP4)

Inside a glovebox under argon atmosphere a 5-Bromo-2-Chloro-4-((trihexylsilyloxy)-methylene)-thiazole (2, 73 mg, 143 μmol, 1.0 Eq.) was dissolved in 1.0 mL of dry THF and a solution of PrMgCl*Et₂O (25.0 mg, 143 μmol, 1.0 Eq.) in 0.8 mL THF was added, and the reaction mixture was stirred for 30 min at ambient temperature. Subsequently, 0.46 mL (2 mol-%) of a solution of Ni(o-anisyl)(dppe)Br (6.20 mmol/L in THF) were quickly injected, and the mixture was stirred for another 4 h. A sample of the homopolymer was then taken, a solution of the isocyanide 3 (70.0 mg, 143 μmol, 1.0 Eq.) in 1.1 mL THF was injected, and the mixture was stirred for 19 h. Subsequently, the reaction was quenched by addition of methanol, and the precipitating polymer was filtered off. The crude polymer was purified by sequential
washing with methanol and acetone on a Soxhlet apparatus, followed by extraction with \( n \)-hexane. The \( n \)-hexane-fraction was then further fractionated by preparative GPC to furnish 30 mg of the main fraction of BP4. Unless stated otherwise, all analytical studies have been performed with this purified fraction.

Table S1. Properties of new block-copolymers, and reference data for corresponding homo polymers.

<table>
<thead>
<tr>
<th>BCP</th>
<th>Feed ratio n/m</th>
<th>PT / PTz-Block Mn [kg/mol]</th>
<th>PDI</th>
<th>Block-Copolymers Mn [kg/mol]</th>
<th>PDI</th>
<th>PT-block Mn [kg/mol]</th>
<th>PIC2-block Mn [kg/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP11</td>
<td>1/1</td>
<td>15.7</td>
<td>2.05</td>
<td>22.9</td>
<td>1.06</td>
<td>63</td>
<td>15</td>
</tr>
<tr>
<td>BP21</td>
<td>2/1</td>
<td>20.8</td>
<td>1.02</td>
<td>24.5</td>
<td>1.03</td>
<td>83</td>
<td>8</td>
</tr>
<tr>
<td>BP31</td>
<td>3/1</td>
<td>20.8</td>
<td>1.02</td>
<td>21.4</td>
<td>1.03</td>
<td>83</td>
<td>1</td>
</tr>
<tr>
<td>BP4[a]</td>
<td>1/1</td>
<td>33.6</td>
<td>1.13</td>
<td>38.4</td>
<td>1.04</td>
<td>85</td>
<td>10</td>
</tr>
</tbody>
</table>

Table S1 continued.

<table>
<thead>
<tr>
<th>BCP</th>
<th>Feed ratio n/m</th>
<th>m我们也 [b]</th>
<th>T also [b] (°C)</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
<th>( \lambda_{\text{inset}} ) [nm]</th>
<th>( E_{\text{opt}} )</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP11</td>
<td>1/1</td>
<td>28</td>
<td>335</td>
<td>380</td>
<td>550</td>
<td>605 (sh), 373</td>
<td>649</td>
</tr>
<tr>
<td>BP21</td>
<td>2/1</td>
<td>21</td>
<td>328</td>
<td>406</td>
<td>533</td>
<td>605, 558, 523</td>
<td>650</td>
</tr>
<tr>
<td>BP31</td>
<td>3/1</td>
<td>17</td>
<td>284</td>
<td>441</td>
<td>539</td>
<td>610, 561, 525</td>
<td>653</td>
</tr>
<tr>
<td>BP4[a]</td>
<td>1/1</td>
<td>29</td>
<td>336</td>
<td>483</td>
<td>545</td>
<td>545 (sh), 502</td>
<td>578</td>
</tr>
<tr>
<td>P3DT[b]</td>
<td>1/1</td>
<td>445</td>
<td>545</td>
<td>483</td>
<td>545</td>
<td>607, 558, 525</td>
<td>655</td>
</tr>
<tr>
<td>PTzTHX[c]</td>
<td>14</td>
<td>408</td>
<td>486</td>
<td>545</td>
<td>509</td>
<td>575</td>
<td>2.16</td>
</tr>
<tr>
<td>PIC2[d]</td>
<td>43</td>
<td>365</td>
<td>368</td>
<td>520</td>
<td>381</td>
<td>560</td>
<td>2.21</td>
</tr>
</tbody>
</table>

[a] After purification by preparative GPC. [b] \( m_\text{res} \) = Residual masses at 800°C. T\(_D\) = decomposition temperature. Data for PIC2[d] and PTzTHX[c] adopted from literature, data for P3DT newly recorded by the authors. [c] Recorded in DCM-solution. [d] Absorption data adopted from Ref.\(^3\). [e] Recorded in THF. [f] Prepared analogously to the macroinitiators for BP11-BP31, Mn = 24.5 kg/mol, PDI = 1.10.

Table S2. Block copolymer composition determined by EDX-spectroscopy, end-group analysis via NMR, and from GPC-data.

<table>
<thead>
<tr>
<th></th>
<th>N [mol%]</th>
<th>S [mol%]</th>
<th>S/N ratio</th>
<th>S/N ratio</th>
<th>S/N ratio</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>EDX</td>
<td>EDX</td>
<td>EDX</td>
<td>NMR</td>
<td>GPC</td>
</tr>
<tr>
<td>BP11</td>
<td>2.97 (±0.01)</td>
<td>1.41 (±0.01)</td>
<td>0.5:1</td>
<td>0.85:1</td>
<td>4.2:1</td>
</tr>
<tr>
<td>BP21</td>
<td>2.75 (±0.01)</td>
<td>5.36 (±0.01)</td>
<td>2.1</td>
<td>1.26:1</td>
<td>10:1</td>
</tr>
<tr>
<td>BP31</td>
<td>1.70 (±0.16)</td>
<td>7.70 (±0.31)</td>
<td>4.5:1</td>
<td>6.6:1</td>
<td>83:1</td>
</tr>
<tr>
<td>BP4</td>
<td>3.19</td>
<td>2.71</td>
<td>5.7:1</td>
<td>2.2:2</td>
<td>8.5:1</td>
</tr>
</tbody>
</table>

[a] Average of three different measurements on aggregated material. Sampled metallized with platinum before measurement.
3. Supplementary Analytical Data

Figure S1. GPC-Elution traces of a) P(3DT-b-IC2) (feed 1:1) and b) P(3DT-b-IC2) (feed 2:1 and 3:1), and GPC traces of the corresponding P3DT-homo blocks. Elution at 1mL/min, 35°C in THF.

Figure S2. GPC-Elution traces of BP4. 35°C in THF, elution at 1 mL/min.

Figure S3. $^1$H NMR spectrum of P(3DT-b-IC2) (feed 1:1). $^{13}$C-satellite signals of CHCl$_3$ also visible. Recorded in CDCl$_3$(*)
Figure S4. $^1$H NMR spectrum of $P$(TzTHX-b-IC2) (BP4).
# $^{13}$C-satellite signals of CHCl$_3$. Recorded in CDCl$_3$ (*).

Figure S5. $^1$H NMR spectra of anisyl-capped $P$3DT.
Spectra Recorded in CDCl$_3$ (*). The polymer were prepared analogously to the macroinitiators for BP11-BP31.
Figure S6. TGA thermograms of BP11, BP21, BP31 (A) and BP4 (B). Data for rr-P3DT and PIC2, and PTzTHX included for reference. Heating rate 10°C per minute. The mass-loss of BP21 between 100 and 150°C is attributed to evaporation of trapped solvent. Comments: The relative proximity of the decomposition temperatures of P3DT and PTzTHX, to the one of PIC2, and the gradual degradation of PIC2 above 400 °C, did not allow direct observation of sequential decomposition of the individual blocks. However, the residual masses of the BCPs at 800°C correlate with the relative content of PIC2, since PIC2 leaves about 43 mass-% while P3DT and PTzTHX which leave just 17 and 14 mass-%, respectively (see also Table S1).

Figure S7. DSC thermograms of homo- and block-copolymers. Heating rate 20°C per minute. * The artefact signal at 250-270 °C also present in the background scan. PIC2 and BP11 (not depicted) do not melt prior to decomposition. The melting points observed from P3DT agree with values from literature.10
Figure S8. Fluorescence spectra of BCPs in solution vs. in the solid state. A) BP31 and BP21, B) BP4. All solution spectra recorded in DCM.

Figure S9. Aggregation of a P3DT in hot hexane monitored by UV-vis absorption

Figure S10. BP4 in n-heptane solution monitored by UV-vis absorption and fluorescence spectroscopy.
Figure S11. Temperature dependent UV-vis-data of PTzTHX in hexane solution. A) Absorption spectra. B) Fluorescence spectra. C) Comparison of fluorescence of BP4 and PTzTHX in solution.

Figure S12. A) Absorption spectra BP4 in DCM solution and of thin films, B) and emission spectrum recorded in DCM solution. Spectra for PIC2 and PTzTHX included for reference.

Figure S13. UV-vis spectra of BPCs reproduced by overlay of homo polymer spectra.
Figure S14. SAXS and WAXS refractograms of aggregated BP11 (A) and BP21 (B).

Figure S15. SAXS (black) and WAXS (red/gray) refractograms of BP31 and a reference sample of P3DT. Bulk samples retrieved after DSC measurements. Grey: experimental data, red: smoothed fit.
4. Electron Microscopy Data

Figure S16. Scanning electron micrographs of aggregated BP11.

Figure S17. Scanning Electron Micrographs of aggregated BP21.
Figure S18. Scanning Electron Micrographs of aggregated BP31 after fast cooling.

Figure S19. Transmission Electron Micrographs of aggregated BP31 after fast cooling.
Figure S20. Scanning Electron Micrographs of aggregated BP31 after slow cooling.
5. Electrical characterization and devices

5.1. Test in block-copolymer solar cells

Device fabrication: PEDOT:PSS (Clevios P, VP.AI 4083 Lösung von Heraeus) was doctor-bladed onto pre-cleaned, patterned indium tin oxide (ITO) substrates from Naranjo Substrates (15 cm²) at 50 °C upon 30–40 nm thick layers were obtained. The active layer solution of BP11 (total concentration of 15 mg mL⁻¹, stirred at 80 °C for >1 h) was deposited by doctor-blading from chloroform at 80 °C. The cells were then annealed under chloroform vapor at 40°C for 1 min. Thin layers of LiF (0.7 nm) and Al (100 nm) were then deposited by high-vacuum evaporation at pressures <5 × 10⁻⁶ mbar (Nano 36, Kurt J. Lesker Co.). The photoactive areas of the cells were 0.09 and 0.16 cm². Finalized devices were evaluated using an Oriel Instruments solar simulator (class AAA, AM 1.5G, 100 mW cm⁻²) and a Keithley 2400 source meter. The EQE was measured under monochromatic light from a 300 W Xenon lamp in combination with a monochromator (Oriel, Cornerstone 260), modulated with a mechanical chopper. The response was recorded as the voltage over 220 resistance, using a lock-in amplifier (Merlin 70104). A calibrated Si cell was used as a reference (Newport 70356_70316NS).
Table S3. Solar cells performance of BP11, BP21, and BP31.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Conditions</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [µA/cm²]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BP11</td>
<td>AC</td>
<td>0.87</td>
<td>17.4</td>
<td>0.26</td>
<td>0.004</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>SVA</td>
<td>0.89</td>
<td>24.4</td>
<td>0.25</td>
<td>0.005</td>
</tr>
<tr>
<td>3</td>
<td>BP21</td>
<td>AC</td>
<td>0.65</td>
<td>38.7</td>
<td>0.25</td>
<td>0.006</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>TA</td>
<td>0.55</td>
<td>66.2</td>
<td>0.30</td>
<td>0.011</td>
</tr>
<tr>
<td>5</td>
<td>BP31</td>
<td>AC</td>
<td>0.45</td>
<td>45.6</td>
<td>0.30</td>
<td>0.006</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>SVA</td>
<td>0.48</td>
<td>56.9</td>
<td>0.29</td>
<td>0.008</td>
</tr>
</tbody>
</table>

AK: as cast from CHCl₃; TA: thermal annealing at 200 °C, SVA: solvent vapor annealing with CHCl₃

5.2. Electrical characterization of PIC1 – PIC3

Preparation of single carrier devices: Hole only diodes were fabricated with the structure: ITO/PE-DOT:PSS/Polymer layer/MoO₃/Ag and electron only diodes were prepared with the structure: ITO/PFN-P1/Polymer layer/Ca/Al.

ITO patterned glass substrate was subsequently cleaned using acetone, isopropanol and MiliQ water in ultrasonic bath for 15 mins each, followed by UV-ozone treatment for another 15 mins. For the hole only diode, PEDOT: PSS was dissolved in isopropanol with volume ratio 1:1. PEDOT:PSS solution was first filtered using a 0.45µm PVDF filter and then after spin coated onto the cleaned substrate at 3500 rpm for 30 s and then thermally annealed at 120°C for 15 mins on a hot plate under ambient condition and transferred into the glove box for further processing. All the following procedures were done in nitrogen atmosphere.

For the electron only device, PFN-P1 was dissolved in methanol in the presence of a small amount of acetic acid (2 µl/ml) with a concentration of 2 mg/ml and was left stirring overnight at room temperature. The PFN-P1 solution was filtered using a 0.2µm PTFE filter and spin-coated on top of cleaned ITO substrate at 3500 rpm for 30 sec.

PIC1, PIC2, or PIC3 were dissolved in Chloroform with a concentration of 5mg/ml, and the solutions was left stirring overnight at 60°C under nitrogen atmosphere. The polymer layer was spin-coated in two steps; first at 600 rpm for 30 sec and then at 1000 rpm for 10 sec to gain a smooth film. Finally, a 10 nm of MoO₃ and 100 nm of Ag were thermally evaporated onto the polymer layer for hole only diode and a 20 nm of Ca and 100 nm of Al were thermally evaporated onto the polymer layer for electron only diode.
**Electrical characterization of single carrier diodes:** Electrical measurements were performed in the dark, inside a nitrogen filled airtight electrical holder. We performed current-voltage measurements on the single carrier diodes using a Keithley 2400 source meter controlled by a LabView program by scanning the voltage from -1V to +1 V.

The carrier mobility was extracted from the JV curves using Space Charge Limited Current (SCLC) theory. At low voltages, the current varies linearly with the applied voltage (Ohmic regime). At higher voltages, the current varies quadratically (SCLC regime). The carrier mobility $\mu$ is extracted from the JV curve at higher voltages by applying Child’s law

$$J = \frac{9}{8} \varepsilon \mu V^2 \frac{1}{d^3}$$

Where $\varepsilon$ is the dielectric constant of the polymer (assumed to be 3) and $d$ is the thickness of the polymer film.

**Figure S24.** Current density versus Voltage (JV) curves of three exemplary single carrier devices, the inset image shows corresponding log J versus log V fitted curve used for the calculation of mobility (A) Hole-only diode behavior and (B) Electron-only diode behavior.

**Table S4.** Summary of mobility measurements for PIC1, PIC2, and PIC3.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Electron mobility (cm$^2$/Vs)</th>
<th>Hole Mobility (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIC1</td>
<td>$4.0 \times 10^{-5} \pm 1.6$</td>
<td>$3.4 \times 10^{-5} \pm 2.3$</td>
</tr>
<tr>
<td>PIC2</td>
<td>$1.04 \times 10^{-2} \pm 2.5$</td>
<td>$1.13 \times 10^{-4} \pm 1.4$</td>
</tr>
<tr>
<td>PIC3</td>
<td>$4.0 \times 10^{-4} \pm 2.8$</td>
<td>$2.1 \times 10^{-5} \pm 1.56$</td>
</tr>
</tbody>
</table>
6. References


[10] V. Causin, C. Marega, and A. Marigo Crystallization and Melting Behavior of Poly(3-butylthiophene), Poly(3-octylthiophene), and Poly(3-dodecylthiophene). Macromolecules 2005, 38, 409 - 415