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Design of highly soluble PCDTBTBT-type conjugated polymers for organic solar cells

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Materials and instrumentation

All solvents and reagents were purchased from Sigma-Aldrich or Acros Organics and used as received or purified according to standard procedures. Absorption spectra (for solutions of polymers in 1,2-DCB) were obtained using Avantes AvaSpec-2048 optical fiber spectrometer.

^{1}H and ^{13}C NMR spectra were collected on a Bruker AVANCE 600 at 600 MHz (^{1}H) in deuterated chloroform solution. Mass spectra were obtained using electrospray/APCI combined ionization technique and GC-MS LCMS-2020 instrument.

Cyclic voltammetry measurements

The cyclic voltammetry measurements were performed for thin films (150–250 nm thick) of polymers **P3** and **P4** deposited on a glassy carbon disc electrode (working electrode, d = 5 mm, BAS Inc.) by drop casting from 1.2-dichlorobenzene, chlorobenzene, chloroform or their mixtures. The measurements were performed in a three-electrode electrochemical cell using 0.1 M solution of Bu_4NPF_6 in acetonitrile as a supporting electrolyte, platinum wire as a counter electrode and a silver wire immersed in 0.01 M solution of $AgNO_3$ in 0.1 M TBAP (CH_3CN) as a reference Ag/Ag^+ electrode (BAS Inc.). Ferrocene was used as an internal reference. The electrolyte solution was purged with argon before the measurements. The voltammograms were recorded using an ELINS P-30SM instrument at room temperaturewith a potential sweep rate of 50 mV s^{-1}.

Fabrication of photovoltaic devices

The conjugated polymers **P3**, **P4** (7 mg) and [60]PCBM (7–28 mg) were dissolved together in 1 mL of 1,2-dichlorobenzene while stirring at room temperature for 48 h. Afterwards, 1,8-diiodooctane(DIO) was added to the blend solution to achieve 0.12 to 6.0% volume concentration. The prepared solution was filtered through a PTFE 0.45 μm syringe filter and subjected to spin-coating at 700–2100 rpm for 150 s on the top of the annealed PEDOT:PSS (Clevios HTL) films deposited on the patterned ITO electrodes. The obtained films were transferred immediately inside the glove box and thermally annealed in an argon atmosphere at 95˚C for 10 min. The top electrode comprising Ca (20 nm) and Ag (100 nm) was deposited by thermal evaporation at the pressure below 4×10^{-6} mbar in a vacuum chamber integrated inside the MBraum glove box. The size of the active area in photovoltaic cells was ~ 0.5 cm^2 as it was defied by a shadow mask.

Synthesis of 4a

A round-bottom two necked flask equipped with a reversed condenser was filled with argon. 4,7-Dibromo-2,1,3-benzothiadiazole (1.4 g; 4.8 mmol), tributyl[4-(2-ethylhexyl)thiophen-2-yl]stannane (2.32 g; 4.8 mmol), tetrakis(triphenylphosphine)palladium(0) (10 mg), and toluene (25 mL) were introduced in the sequence listed here. The reaction mixture was deaerated using repeated cycles of freezing in liquid nitrogen, evacuation, filling with argon, and heating up to a room temperature. Then the mixture of reagents was heated at reflux and formation of the desired monosubstitution product (4-bromo-7-[4-(2-ethylhexyl)thiophen-2-yl]-2,1,3-benzothiadiazole, **3a**) was controlled by HPLC. When the content of the monosubstitution product in the mixture exceeded 50%, 2.5-bis(trimethylstannyl)thiophene (0.98 g, 2.4 mmol) was added. The reaction mixture was heated at reflux for 24 h, then cooled down and poured into deionized water (150 mL) and extracted by dichloromethane. The combined organic phase was washed with deionized water and dried over anhydrous $MgSO_4$. The crude product obtained after removal of the solvent was further purified by column chromatography (silica gel, 40–60 mm, 60Å). The title compound was eluted with toluene–hexane 4:6 v/v mixture. The yield of the dark red solid **4a** was 40%.^{1}H NMR ($CDCl_3$, 600 MHz) 8.22 (s, 2H); 7.99 (s, 2H); 7.97 (d, *J*=7.6 Hz, 2H); 7.88 (d, *J*=7.6 Hz, 2H); 7.06 (s, 2H); 2.66 (d, *J*=6.9 Hz, 4H); 1.62-1.67 (m, 2H); 1.28-1.38 (m, 16H); 0.88-0.92 (m, 12H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) 152.69; 143.18; 140.57; 138.77; 129.71; 128.42; 127.97; 126.53; 125.77; 125.49; 122.77; 40.35; 34.71; 32.53; 28.93; 25.67; 23.12; 14.21; 10.90. ESI, m/z =741,4 ($[M-H]^-$).

Synthesis of 5a

Compound **4a** (0.24 g, 0.32 mmol) was dissolved in 20 mL of 1,2-dichlorobenzene and *N*-bromosuccinimide (0.114 g, 0.64 mmol) was added in small portions. The mixture was stirred at room temperature for 60 min, and then the solvent was evaporated and the product was washed with ethanol. The **5a** monomer (0.26 g, yield 90%) was obtained after drying under vacuum overnight.^{1}H NMR ($CDCl_3$, 600 MHz): 8.23 (s, 2H); 7.95 (d, *J*=7.6 Hz, 2H); 7.79-7.81 (m, 4H); 2.62 (d, *J*=7.2 Hz, 4H); 1.73-1.77 (m, 2H); 1.33-1.46 (m, 16H); 0.95-1.00 (m, 12H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) 152.52; 152.38; 142.27; 140.59; 138.56; 128.82; 128.78; 125.75; 125.55; 125.47; 124.89; 112.61; 40.17; 34.04; 32.71; 29.03; 25.96; 23.39; 14.39; 11.08. ESI, m/z =898.1 ($[M-H]^-$).

Synthesis of 4b

Compound **4b** was prepared using tributyl[3-(2-ethylhexyl)thiophen-2-yl]stannane (16.5 g, 34 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (10 g, 34 mmol), 2.5-bis(trimethylstannyl)thiophene (6.95 g, 17 mmol) and following the procedure given for compound **4a**. The yield of **4b** was 35%.^{1}H NMR ($CDCl_3$, 600 MHz) 8.18 (s, 2H); 7.92 (d, *J*=7.4 Hz, 2H); 7.57 (d, *J*=7.4 Hz, 2H); 7.34 (d, *J*=5.1 Hz, 2H); 6.98 (d, *J*=5.1 Hz, 2H); 2.55 (d, *J*=7.2 Hz, 4H); 1.40-1.46 (m, 2H); 0.92-1.13 (m, 16H); 0.66 (t, *J*=6.7 Hz, 6H); 0.59 (t, *J*=7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) 154.76; 152.29; 140.89; 140.60; 132.90; 130.58; 129.86; 128.77; 127.26; 126.48; 125.64; 125.34; 40.54; 33.44; 32.55; 28.68; 25.78; 22.94; 14.09; 10.81. ESI, m/z =741.7 ($[M-H]^-$).

Synthesis of 5b

This compound was synthesized from compound **4b** (0.60 g, 0.81 mmol) and *N*-bromosuccinimide (0.288 g, 1.62 mmol) in 93% (0.68g) yield following the procedure given above for **5a**.^{1}H NMR ($CDCl_3$, 600 MHz) 8.21 (s, 2H); 7.94 (d, *J*=7.5 Hz, 2H); 7.58 (d, *J*=7.5 Hz, 2H); 7.01 (s, 2H); 2.56-2.62 (m, 4H); 1.48-1.53 (m, 2H); 0.98-1.21 (m, 16H); 0.74 (t, *J*=6.8 Hz, 6H); 0.67 (t, *J*=7.3 Hz, 6H).^{13}C NMR ($CDCl_3$, 126MHz): δ (ppm) 154.40; 152.17; 141.57;

140.57; 134.49; 132.44; 130.47; 128.97; 126.75; 125.88; 125.16; 112.85; 40.43; 33.52; 32.49; 28.66; 25.72; 22.96; 14.12; 10.80. ESI, m/z =898.1 ([M-H]$^-$).

Synthesis of P3 and P4

Monomers **6** (657.6 mg, 1.0 mmol) and **5a-b** (898 mg, 1.0 mmol) were introduced into a 50 mL round-bottom three necked flask equipped with a thermometer and a reversed condenser. Toluene (25 mL), 2 M aqueous solution of K_2CO_3 (2mL), aliquat 336 (1 drop, ca. 80 mg) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were added in the sequence listed here. The reaction mixture was deaerated, immersed into an oil bath and heated at reflux for 3–6 hours.The molecular weight characteristics of the formed products were controlled every 30 min. The reaction was stopped when the weight average molecular weight M_w did not show further increase within 3–4 h. Then the reaction mixture was cooled down to a room temperature, the polymer was extracted with 300 mL of toluene, the resulting solution was washed 3 times with deionized water (250 mL), dried and concentrated in a vacuum (rotary evaporator) to 40 mL. Addition of 150 mL of methanol precipitated the crude polymer. Subsequent purification was achieved using several additional dissolving/precipitation cycles. Finally, the precipitated polymer flakes were filtered through the cellulose thimble and processed using Soxhlet extraction with hexanes (12 h), acetone (12 h), and chloroform (8 h). The chloroform extract was concentrated in a vacuum and precipitated in methanol. The obtained solid was collected by filtration and dried in a vacuum. The total yields of the purified polymers **P3** and **P4** were 76% and 60%, respectively.

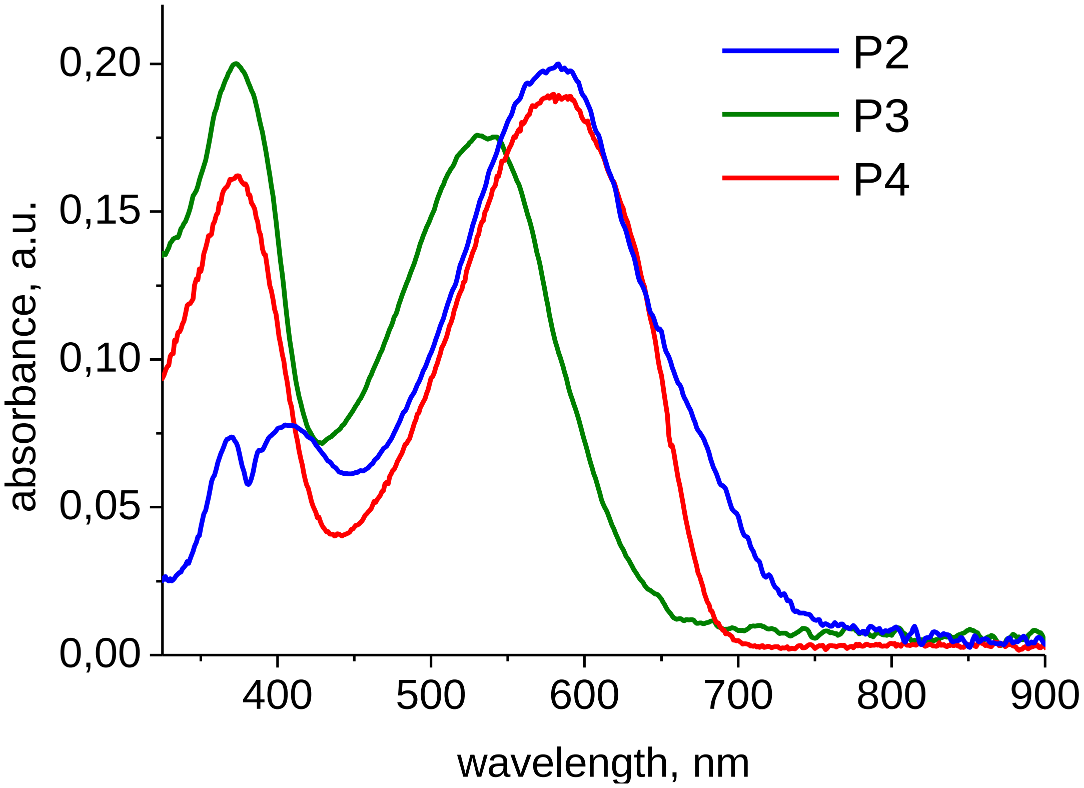

Figure S1 Absorption spectra of polymers **P2**−**P4** in thin films.