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Synthesis of statistical carbazole–fluorene–thiophene–benzothiadiazole copolymers and their investigation in organic solar cells

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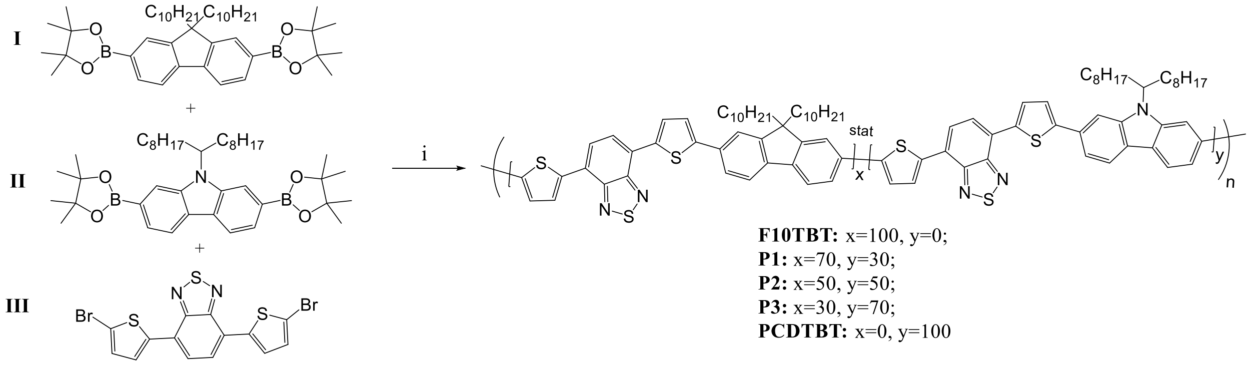
Contents

General procedure for synthesis of conjugated polymers

Monomers **I** (x mmol), **II** (1-x mmol) and **III** (1 mmol) taken in precise stoichiometric amounts were introduced into a 150 ml round-bottom three necked flask equiped with a thermometer and reversed condenser. Toluene (75 ml), 2M aqueous solution of K_2CO_3 (6 ml), aliquat 336 (1 drop, ca. 80 mg) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were added in the listed here sequence. The reaction mixture was deaerated, immersed into an oil bath and heated at reflux for 3-6 h. The molecular weight characteristics of the formed product were controlled every 30 min. The reaction was stopped when the average molecular weight M_w reached *ca*. 100000 g mol^{-1} or product started to form a precipitate on the walls of the flask. To terminate the reaction, we introduced 0.1 mmol of phenylboronic acid, heated the mixture at reflux for additional 1 h and then introduced 2 mmol of bromobenzene and continued the heating for additional 2 h. Afterwards, the reaction mixture was cooled down to room temperature, the polymer was extracted with 500 ml of toluene, the resulting solution was washed 3 times with deionized water (250 ml), dried and concentrated in 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 to the cellulose thimble and processed using Soxhlet extraction with hexanes (12 h), acetone (12 h), dichloromethane (12 h), chloroform (8 h) and chlorobenzene (12 h). The chlorobenzene extract was concentrated in vacuum and precipitated in methanol. The obtained solid was collected by filtration and dried in vacuum. The resulting crude polymer was further purified from the residual Pd catalyst as described (K. T. Nielsen, K. Bechgaard and F. C. Krebs, *Macromolecules*, 2005, **38**, 658 and K.T. Nielsen, K. Bechgaard and F.C. Krebs, *Synthesis*, 2006, **10**, 1639). The total yield of the purified polymers varied between 80 and 90% depending on the initial molecular weight and number of the applied dissolving/precipitation cycles. All prepared polymer samples were transferred immediately inside argon glove box where they were stored in the absence of direct light.



Scheme S1

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. Starting monomers **I-III** (Scheme S1) were synthesized according to the standard procedures described in the literature (see, for example, S. J. Park, J. M. Cho, W.-B. Byun, J.-C. Lee, W. S. Shin, I.-N. Kang, S.-J. Moon and S. K. Lee, *J. Polym. Sci A: Polym. Chem.*, 2011, **49**, 4416).

AFM images were obtained using a NTEGRA PRIMA instrument (NT-MDT, Russia). Absorption spectra (for solutions of polymers in DCB and thin films) and PL spectra were obtained using an Avantes AvaSpec-2048 optical fiber spectrometer.

Molecular weight characteristics of conjugated polymers were obtained using a Shimadzu LC20 instrument equipped with a Phenomenex Luna Phenogel 5u column (0.78×30 cm, 5-500 kDa). The measurements were performed using freshly distilled THF or toluene as eluents (flow rate 0.5 ml min^{-1}). The column was calibrated using a series of commercial polystyrene standards obtained from Fluka (THF as eluent) or using custom-made F8BT standards with PDI<1.5 (toluene used as eluent). Molecular weights of the F8BT standards were cross-checked additionally using a Waters Alliance GPCV 2000 instrument equipped with multi-angle scattering detector HELEOS II (Wyatt). Each polymer sample was analyzed in several (3-5) concentrations to discriminate effects of aggregation on the molecular weight characteristics of the material. All polymers showed very weak (or no) aggregation when they were analyzed in toluene at low concentrations.

Cyclic voltammetry measurements

The cyclic voltammetry measurements were performed for thin films (150-250 nm thick) of polymers P1-P5 deposited on 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 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 internal reference. The electrolyte solution was purged with argon before the measurements. The voltammograms were recorded using an ELINS P-30SM instrument at room temperature with a potential sweep rate of 50 mV s^{-1}.

Characterization of organic solar cells

The current-voltage (I-V) characteristics of the devices were obtained in dark and under the simulated 100 mW cm^{-2} AM1.5 solar irradiation provided by a KHS Steuernagel solar simulator integrated in MBraun glove box. The intensity of the illumination was checked every time before the measurements using a calibrated silicon diode with known spectral response. The I-V curves were recorded in inert atmosphere using a Kethley 2400 source-measurement unit. The active areas of all devices were measured with a good accuracy just after the J-V measurements to estimate the short circuit current densities. The obtained J_{SC} values were reconfirmed by integrating the EQE spectra against standard AM1.5 spectrum. The EQE spectra were measured in normal air atmosphere without applying any special encapsulation or protection to the photovoltaic devices using specially designed setup, LOMO instruments, Russia.

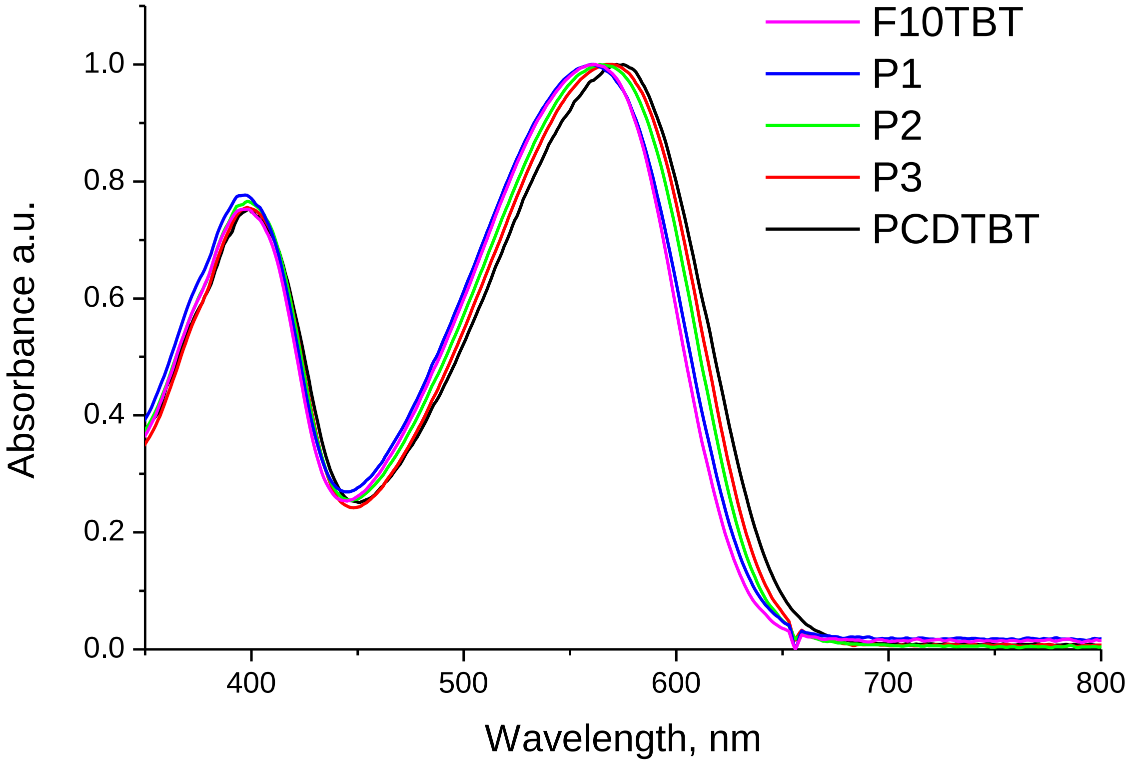


Figure S1 Absorption spectra of polymers F10TBT, PCDTBT and P1-P3 in 1,2-dichlorobenzene.

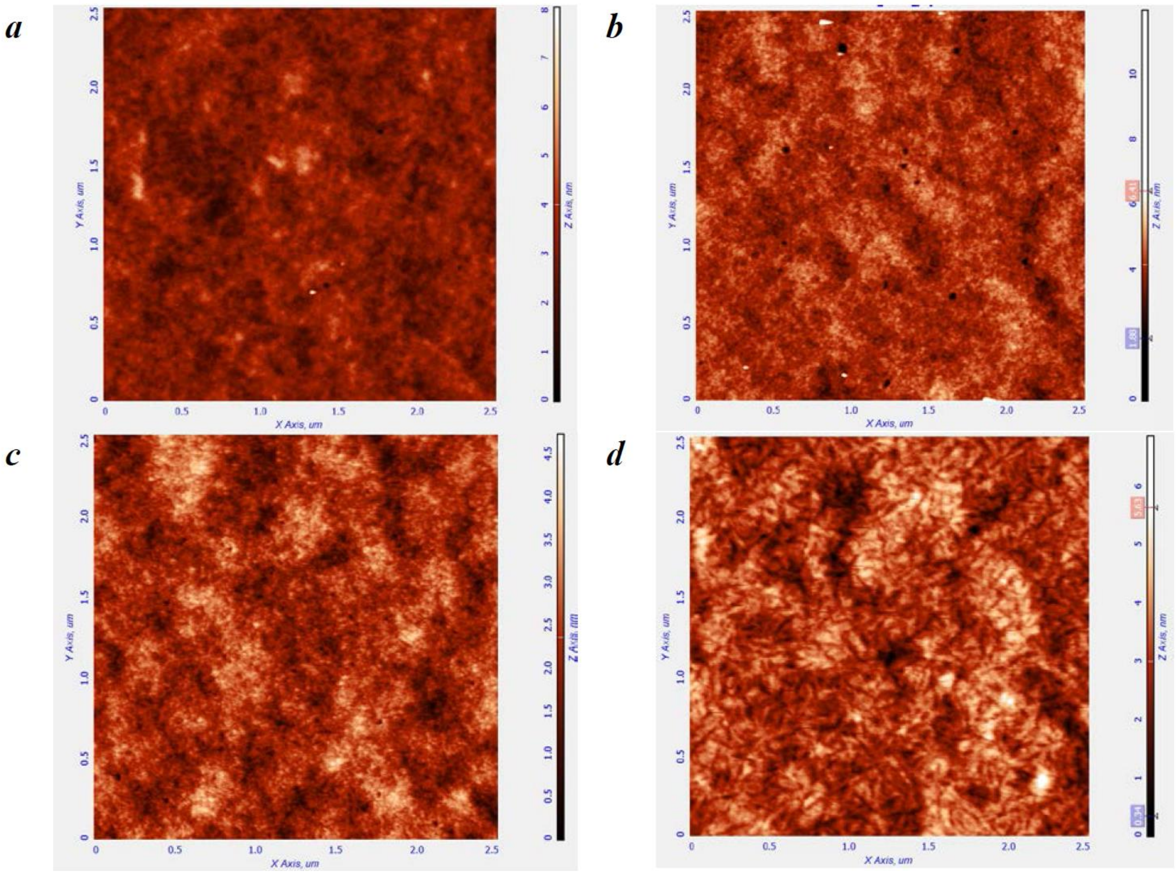


Figure S2 AFM images of thin films of F10TBT (a), P1 (b), P3 (c) and PCDTBT (d) composites with [70]PCBM.

Table S1 Parameters of photovoltaic cells based on F10TBT, PCDTBT and P1-P3.

Polymer	**Acceptor**	**Conditions**	**V_{OC}, mV**	**J_{SC}, mA/cm^2**	**FF, %**	**η, %**
F10TBT	[60]PCBM	7 : 28;[1] 800 rpm,[2] 95 °C/10 min[3]	898	6.7	51	3.1
	[70]PCBM	7 : 21; 1000 rpm, 95 °C/10 min	878	9.7	53	4.5
P1	[60]PCBM	6 : 12; 600 rpm, 95 °C/10 min	821	7.4	44	2.7
	[70]PCBM	6 : 12; 800 rpm, 95 °C/10 min	869	9.8	46	4.0
P2	[60]PCBM	6 : 12; 900 rpm, 95 °C/10 min	901	8.0	51	3.7
	[70]PCBM	6 : 12; 900 rpm, 95 °C/10 min	845	10.7	47	4.3
		6 : 12; 0.3% DIH[4], 800 rpm, 95 °C/10 min	838	10.4	57	5.0
		6 : 12; 0.6% DIH[4], 900 rpm, 95 °C/10 min	828	10.7	61	5.4
		6 : 12; 1.2% DIH[4], 900 rpm, 95 °C/10 min	852	8.6	63	4.6
P3	[60]PCBM	5 : 10; 800 rpm, 95 °C/10 min	851	8.3	50	3.6
	[70]PCBM	6 : 18; 1100 rpm, 95 °C/10 min	838	11.6	55	5.4
PCDTBT	[60]PCBM	7 : 28; 900 rpm, 90 °C/60 min	831	9.7	57	4.6
	[70]PCBM	6 : 12; 800 rpm, 65 °C/50 min	807	12.3	61	6.1

[1] Hereinafter, the concentrations of the polymer and fullerene derivative are given in mg cm^{-3}; [2] the optimal spin-coater frequency for active layer deposition is given; [3] the optimal active layer annealing regime is provided; [4] addition of 0.6 vol% of 1,6-diiodohexane as processing additive improved the photovoltaic performance of the system.