



Positive side of disorder: Statistical fluorene-carbazole-TTBTBTT terpolymers show improved optoelectronic and photovoltaic properties compared to the regioregular structures

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ABSTRACT

We report a systematic study of a family of statistical fluorene-carbazole-TTBTBTT terpolymers with a variable fluorene-to-carbazole ratio. It has been shown that changing the molecular composition of the polymers affects significantly their characteristics such as absorption spectrum, extinction coefficients, position of the frontier energy levels and charge carrier mobility. Power conversion efficiencies of 6.4–7.0% were obtained for the best-performing carbazole-rich and fluorene-rich terpolymers. Most importantly, we showed that optoelectronic properties (particularly, the extinction coefficients defining the light harvesting ability) and photovoltaic performances of conventional regioregular copolymers in the blends with [70]PCBM can be significantly improved simply by introducing a “rational disorder” in the polymer chains using statistical copolymerization of certain building blocks taken in appropriate ratios.

1. Introduction

The first plastic organic solar cells designed at the beginning of 2000s were based on conjugated homopolymers such as MEH-PPV, MDMO-PPV and P3HT [1,2]. However, unsatisfactory optoelectronic properties of these electron donor materials stimulated the development of different types of “push-pull” copolymers comprising alternating electron rich and electron deficient units. Conjugated fluorene-thiophene-benzothiadiazole copolymer abbreviated as F8TBT was one of the first successful materials competing with the conventional homopolymers [3,4]. It was recognized at that time that alternating thiophene-benzothiadiazole-thiophene (TBT) system has a big potential to be applied in the design of novel promising materials for organic photovoltaics. Subsequent research resulted in the design and exploration of novel combinations of the TBT building block with the alkylated fluorene and silafluorene units which provided power conversion efficiencies of 4.5–5.5% in organic solar cells [5,6].

The design of the carbazole-TBT copolymer called PCDTBT led to a breakthrough in the field since it was one of the first push-pull type of materials outperforming clearly P3HT which served as a “running horse” of organic photovoltaics for many years [7]. The solar cells

based on PCDTBT demonstrated reasonably high light power conversion efficiencies (6–7%) in combination with excellent photochemical and thermal stability under the real device operation conditions [8]. The lifetime of the bulk heterojunction solar cells based on the PCDTBT/[70]PCBM blends was estimated to be in the range of 6–8 years which is an impressive result for organic photovoltaics [9].

In spite of a considerable success in the design of the aforementioned TBT-based conjugated copolymers, their photovoltaic performances got stuck at the level of 5–7% due to their unbalanced optoelectronic properties. For instance, PCDTBT has a band gap of 1.9 eV which limits the efficiency of the photon harvesting using this material and results in modest short circuit current densities of 10–12 mA/cm² [8]. It is also known that LUMO(D)-LUMO(A) energy offset for the optimized donor (D) / acceptor (A) systems has to be in the range of 0.25–0.30 eV. However, the LUMO energy level of PCDTBT lies ca. 0.55 eV above the LUMO level of PCBM which results in a considerable energy loss at the donor/acceptor interface. Therefore, there is a clear need for developing an alternative polymer design strategy which could deliver new materials with improved optoelectronic properties (in particular, lower band gaps) and good operation stability comparable to that of PCDTBT.

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We have addressed this challenge recently and proposed replacing the conventional TBT unit with an extended TBTBT or TTBTBT building blocks in the design of novel polymer-based materials [10,11]. The first synthesized carbazole-TTBTBT copolymer demonstrated low band gap of 1.65 eV, a deep lying HOMO energy level (−5.49 eV) and a decent photovoltaic performance (6.4%). Very recently we have investigated a family of copolymers comprising fluorene, carbazole and TTBTBT units which delivered solar cell power conversion efficiencies of 6.7% with a potential for a further increase up to 10–11% [12]. It should be emphasized that novel family of the TTBTBT-based copolymers demonstrated good operation stability in devices under a continuous photothermal aging within 6000 h, resembling closely the behavior of the benchmark material PCDTBT [10]. Moreover, some of the synthesized polymers could be easily processed using large-area compatible techniques such as doctor blading and slot die coating providing 6.5% and 6.0% efficiencies for devices based in rigid and flexible substrates, respectively [13]. The obtained results imply that the designed materials have a potential to be used in the development of high-efficiency plastic solar cells.

Here we report a systematic study of a series of the fluorene-carbazole-TTBTBT terpolymers in order to reveal fundamental correlations between the molecular composition of the materials, their optical and electronic characteristics and also the photovoltaic performance in devices.

2. Experimental section

2.1. 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. AFM images were obtained using NTEGRA PRIMA instrument (NT-MDT, Russia). Absorption spectra (for solutions of polymers in DCB and thin films) and PL spectra were obtained using Avantes AvaSpec-2048 optical fiber spectrometers. Molecular weight characteristics of conjugated polymers were obtained using 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). 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 "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.

2.2. Synthesis of conjugated polymers

All polymers were synthesized using Suzuki-Miyamura polycondensation reaction as it is shown in Fig. 1.

Monomers **A** (y mmol), **B** (x mmol; $x+y=1.0$ mmol) and **C** (1443.8 mg, 1.0 mmol) taken in precise stoichiometric amounts were introduced into a 150 mL round-bottom three-necked flask equipped with a thermometer and reflux condenser. Toluene (75 mL), 2 M 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 degassed, immersed into an oil bath and heated at reflux for 3–6 h. The molecular weight characteristics of the formed product were monitored every 30 min using gel permeation chromatography (GPC). The reaction was stopped when the weight average molecular weight M_w reached ca. 150,000 g/mol 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 into a 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 using a chelating reagent similar to the one described previously by Krebs et al. [14,15]. 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 stored inside argon glove box where they were stored in the absence of direct light.

2.3. Cyclic voltammetry measurements

The cyclic voltammetry measurements were performed for thin films (150–250 nm thick) of polymers **P1**, **P2** and **P3a-f** deposited on glassy carbon disc electrode (working electrode, $d=5$ mm, BAS Inc.) by drop casting from a mixture of 1,2-dichlorobenzene, chlorobenzene, and chloroform (1:1:3 v/v). The measurements were performed in a three-electrode electrochemical cell using 0.1 M solution of Bu_4NPF_6 (TBAP) in acetonitrile as supporting electrolyte, platinum wire as a counter electrode and a silver wire immersed in a 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 were performed. The voltammograms were recorded using an ELINS P-30SM instrument at room temperature with a potential sweep rate of 50 mV/s.

2.4. Optical measurements and modelling

Transmission and reflection measurements of blend layers on float glass substrates were carried out on an UV-Vis spectrometer (Perkin Elmer Lambda 950) in combination with an integrating sphere at the Fraunhofer ISE in Freiburg, Germany. The commercially available modelling software "SCOUT" (W. Theiss Hard and Software for optical Spectroscopy; www.mtheiss.com) was used to fit the measurement data with a dielectric function model in order to calculate the optical constants n and k . The photogenerated current densities for the different photoactive absorber layers were optically simulated with the "rigorous coupled wave analysis", RCWA, method. The simulated solar cell stack consisted of a 1 mm float glass substrate, a 230 nm thick ITO layer, a 40 nm thick PEDOT:PSS (AI 4083) layer, the photoactive layer with varied layer thickness and a 100 nm thick aluminum back electrode. The modelled n & k -values served as input parameters for the RCWA simulation.

2.5. Fabrication and characterization of organic solar cells

The conjugated polymer **P1**, **P2** or **P3a-f** (5–10 mg) and the fullerene derivative ([60]PCBM or [70]PCBM, 5–35 mg) were dissolved together in 1 mL of 1,2-dichlorobenzene while stirring at room temperature for 48 h. The 1,8-diiodooctane (DIO) processing additive was added to the blend solution to achieve an optimal volume concentration (see Table 2 below). The prepared solution was filtered through a PTFE 0.45 μ m syringe filter and subjected to spin-coating at

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