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Conjugated Triblock Copolymers Containing Both Electron-Donor and Electron-Acceptor Blocks

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ABSTRACT: We report a straightforward two-step synthesis toward conjugated DAD-type triblock copolymers with both electron-donor (D) and electron-acceptor (A) blocks. Cyano-substituted poly(phenylenevinylene) (CN−PPV) prepolymers with two bromide end groups hereby act as the central electron-acceptor building block and are generated under Yamamoto conditions. The dibromo prepolymers are finally coupled with monobromo-terminated regioregular poly(3-hexylthiophene) (P3HT), which is selected as the electron-donor block (D). The molecular weight of the different blocks, especially the acceptor block, can be controlled by adjusting the polymerization time and the substitution pattern (degree of alkyl substitution) of the monomers. Elemental analysis, NMR, DSC, and optical spectroscopy prove that the DAD conjugated triblock copolymers. Atomic force microscopy (AFM) images of one triblock copolymer (P3HT1−HCNPPV−P3HT1) exhibit the formation of regular nanosized mesostructures in thin films. The resulting conjugated triblock copolymer shows a distinctly different morphology as compared to a corresponding polymer blend. A covalent connection of donor (P3HT) and acceptor (CN−PPV) blocks is a favorable way to control the scale length of nanostructure formation.

Introduction

The self-assembling ability of block copolymers to form supramolecular structures has draw particular attention due to their potential applications in materials science, nanochemistry and biochemistry. Among block copolymers, di- (AB-type) or triblock (ABA-type) rod−coil copolymers are well-known to self-assemble into defined nanostructures. Thereby, the rod blocks align along their long axes into nanoscaled domains, and the block copolymers often form liquid crystalline mesophases.[1−3] When a conjugated polymer block serves as such a rod block, the resulting block copolymers promise interesting applications, especially in electronic and nanodevices.[4−7] Several kinds of rod−coil block copolymer materials containing one semiconducting block have been synthesized.[8−14] It was found that the manipulation of the supramolecular structure of the conjugated rod segment is crucial to control the electronic and optoelectronic properties. However, conjugated block copolymers with two or more π-conjugated functional blocks define a further attractive target. Such block copolymers will allow novel applications (e.g., in organic solar cells) which are not accessible for block copolymers with only a single kind of functional block.[15,16] For "traditional" rod−coil di- or triblock copolymers, flexible coil blocks such as polystyrene or poly(ethylene oxide) are commonly used, which only support the self-assembly into nanostructures. This feature limits the optoelectronic response of this type of block copolymers. Therefore, there is the challenge to design block copolymers with two (or more) electronically active blocks toward novel multifunctional semiconducting materials.[17] In our previous reports, we have first described the synthesis of conjugated di- and triblock copolymers containing two kinds of conjugated blocks segments of rather different electronic properties starting from end-functionalized polyfluorene (PF) precursors. PANI−PF−PANI triblock copolymers synthesized in this way, for instance, exhibited a spontaneous formation of nanosized mesostructures in thin films or layers.[17c] However, up to now, there is no report about conjugated block copolymers with both electron-donor (D) and electron-acceptor (A) functional blocks within the backbone. Such donor−acceptor block copolymers are also expected to phase-separate into nanostructured materials with domains rich in the electron-donor or the electron-acceptor block. These nanostructured materials will exhibit a different morphology as compared to the corresponding polymer blends or homopolymers.

In this paper, we will describe a straightforward two-step synthesis toward conjugated DAD-type triblock copolymers with both electron-donor (D) and electron-acceptor (A) blocks. For this, monobromo-terminated, regioregular poly(3-hexylthiophene) (P3HT) was selected as the electron-donor block (D) for its solubility in organic solvents and its high solid state order.[18] A dibromo-prepolymer is generated as the central electron-acceptor block (A) under Yamamoto conditions starting from suitable dibromo building blocks and finally coupled with the monobromo-P3HT macromonomer as end-capper. In our synthetic Scheme 1, three different cyano-substituted oligo- or poly(phenylenevinylene)s (CN−PPV) are used as the acceptor blocks. The molecular weight of the blocks, especially the acceptor blocks, can be controlled by adjusting the polymerization time and the substitution pattern (degree of alkyl substitution) of the dibromo monomers, which allows us to modulate the scale length of nanostructure formation in the resulting triblock copolymers.

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Experimental Section

General Data. All reactions were carried out under an argon atmosphere. Solvents were used in commercial quality (HPLC grade). The following compounds were synthesized according to the literature: 2-Bromo-3-hexylthiophene,[19] bis(4-bromophenyl)-fumaronitrile (**1**)[20] and 4-bromo-2,5-dihexyl-benzaldehyde.[21] All the other chemicals are commercially available.

Characterization. ^{1}H NMR data were obtained on a Bruker ARX 400 spectrometer; Gel permeation chromatographic analysis (GPC) utilized polystyrene (PS) columns (three columns, 5 μm gel, pore widths 10^3, 10^5, and 10^6 Å) connected with UV−vis and refractive index diction. All GPC analysis were performed on solutions of polymers in THF at 30 °C with a flow rate of 1 mL/min (concentration of the polymer: ca. 1.5 gL^{-1}). The calibration was based on polystyrene standards with narrow molecular weight distribution; Elemental analyses were done on a Vario EL II (CHNS) instrument. The DSC analysis was determined using a Perkin-Elmer DSC7 instrument at 10 K min^{-1} under argon from 0 to 260 °C. The TGA analysis was carried out using a Mettler TG50 at 10 K min^{-1} under argon from 35 to 600 °C. UV−vis absorption spectra were recorded on a Jasco V550 spectrophotometer; fluorescence spectra on a Varian Cary Eclispse instrument.

Monomer Synthesis. Synthesis of Monomer 2. 4-Bromobenzaldehyde (1.46 g, 8.4 mmol) and 1,4-phenylenediacetonitrile (0.60 g, 3.8 mmol) were dissolved in ethanol (100 mL). A solution of NaOH (100 mg) in ethanol (60 mL) was added dropwise to the mixture under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. The product precipitates, was filtered off and washed with water to give **2** as a yellow powder. After recrystallization from acetone, 1.66 g of **2** were obtained with a yield of 90%. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.80 (d, 4H), 7.77 (s, 4H), 7.39 (d, 4H), 7.54 (s, 2H). FAB-MS: *m*/*z* 489 [M + H]. Anal. Calcd for ($C_{24}H_{14}Br_2N_2$): C, 58.81; H, 2.88; N, 5.71. Found: C, 58.82; H, 2.75; N, 5.81.

Synthesis of Monomer 3. 4-Bromo-2,5-dihexylbenzaldehyde (1.50 g, 4.2 mmol) and 1,4-phenylendiacetonitrile (0.30 g, 1.9 mmol) were dissolved in ethanol (50 mL). A solution of NaOH (50 mg) in ethanol (30 mL) was added dropwise to the mixture under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. The product precipitates, was filtered off and washed with water to give 1.50 g of **3** as a white powder (yield 95%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.81 (s, 2H), 7.77 (s, 6H), 7.46 (s, 2H), 2.78 (t, 4H), 2.65 (t, 4H), 1.68 (m, 4H), 1.59 (m, 4H), 1.47−1.28 (m, 24H), 0.86−0.93 (m, 12H). ^{13}C (CDCl$_3$, 400 MHz): δ 141.59, 140.75, 140.33, 135.14, 133.67, 131.49, 129.79, 127.23, 126.88, 117.16, 113.16, 35.74, 32.91, 31.64, 30.97, 29.75, 29.04, 22.56, 14.04. FAB-MS: *m*/*z* 826 [M + H]. Anal. Calcd for ($C_{48}H_{62}Br_2N_2$): C, 69.73; H, 7.56; N, 3.39. Found: C, 69.73; H, 7.75; N, 3.51.

Polymer Synthesis. Monobromo-terminated, regioregular head-to-tail poly(3-hexylthiophene) (Br−P3HT) was synthesized according to a literature procedure.[21] Two different Br−P3HTs were obtained by varying the reaction time (31 min (Br−P3HT1); 28 min (P3HT2)).

Br−P3HT1: $\bar{M}_n$ = 25 600, $\bar{M}_w/\bar{M}_n$ = 1.30. Anal. Calcd for H($C_{10}H_{14}S$)$_{65}$Br: C, 71.8; H, 8.37; S, 19.1; Br, 0.73. Found: C, 71.98; H, 8.35; S, 17.35; Br, 0.85.

Br−P3HT2: $\bar{M}_n$ = 16 800, $\bar{M}_w/\bar{M}_n$ = 1.25. Anal. Calcd for ($C_{10}H_{14}S$)$_{45}$Br: C, 71.5; H, 8.34; S, 19.1; Br, 1.05. Found: C, 72.12; H, 8.15; S, 17.24; Br, 1.57.

P3HT1—BCNPPV—P3HT1. Ni(COD)$_2$ (0.24 g, 0.8 mmol), 2,2′-bipyridyl (0.12 g, 0.75 mmol), and bis(4-bromophenyl)-fumaronitrile (97 mg, 0.25 mmol) were put into a flask. Then, THF (4 mL) and COD (0.20 mL) were added, and the mixture was heated to 80 °C for 8 h. Next bromo-terminated poly(3-hexylthiophene) (0.10 g, Br−P3HT1) in 4 mL of THF was added into the flask. The mixture was stirred and allowed to react in the dark for 48 h at 80 °C. The resulting solution was concentrated and poured into methanol. The precipitate was collected by filtration and fractionated by Soxhlet extraction with acetone, hexane, dichloromethane, and chloroform. The highest molecular weight chloroform fraction was used for further characterization (80 mg, yield 75%). $\bar{M}_n$ = 51 100, $\bar{M}_w/\bar{M}_n$ = 1.44; ($C_{10}H_{14}S$)$_x$($C_{16}H_8N_2$)$_y$($C_{10}H_{14}S$)$_x$. Anal. Calcd for x = 65, y = 5: C, 72.9; H, 8.19; S, 18.31; N, 0.62. Found: C, 72.97; H, 8.45; S, 14.95; N, 0.60.

P3HT1—CNPPV—P3HT1. Ni(COD)$_2$ (0.24 g, 0.8 mmol), 2,2′-bipyridyl (0.12 g, 0.75 mmol), and monomer **2** (0.123 g, 0.25 mmol) were given into a flask. Then, THF (4 mL) and COD (0.20 mL) were added, and the mixture was heated to 80 °C for 8 h. Next, bromo-terminated poly(3-hexylthiophene) (0.10 g, Br−P3HT1) in 4 mL of THF was added to the reaction mixture. The mixture was allowed to react in the dark for 24 h at 80 °C. The resulting solution was concentrated and poured into methanol. The precipitate was collected by filtration and fractionated by Soxhlet extraction with acetone, hexane, dichloromethane, and chloroform. The highest molecular weight chloroform fraction was used for further characterization (80 mg, yield 78%). $\bar{M}_n$ = 53 200, $\bar{M}_w/\bar{M}_n$ = 1.40

($C_{10}H_{14}S$)$_x$($C_{24}H_{14}N_2$)$_y$($C_{10}H_{14}S$)$_x$. Anal. Calcd for x = 65, y = 2: C, 72.71; H, 8.31; S, 18.70; N, 0.29. Anal. Found: C, 72.07; H, 8.24; S, 16.41; N, 0.16.

P3HT—HCNPPV—P3HT. Ni(COD)$_2$ (0.36 g, 1.2 mmol), 2,2′-bipyridyl (0.24 g, 1.50 mmol), and monomer **3** (0.413 g, 0.50 mmol) were placed into a flask. Then THF (5 mL) and COD (0.30 mL) were added, and the mixture was heated to 80 °C for 14 h. Next, bromo-terminated poly(3-hexylthiophene) (0.20 g, Br−P3HT1 or Br−P3HT2) in 5 mL of THF was added to the mixture. The mixture was stirred and allowed to react in the dark for 48 h at 80 °C. The resulting solution was concentrated and poured into methanol. The precipitate was collected and fractionated by Soxhlet extraction with acetone, hexane, dichloromethane, and chloroform. The highest molecular weight chloroform fraction was used for further characterization.

P3HT1−HCNPPV−P3HT1 (200 mg, yield 72%): $\bar{M}_n$ = 52 800, $\bar{M}_w/\bar{M}_n$ = 1.45. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.90−7.40 (b, HCNPPV block), 7.10−6.80 (b, P3HT block, 1.9 times of HCNPPV block, corresponding to n = 65 and m = 7), 3.00−2.55 (b, alkyl groups), 1.80−0.60 (b, alkyl groups). ^{13}C (CDCl$_3$, 400 MHz): δ 153.72, 153.29, 152.78, 150.16, 141.30, 129.99, 127.53, 127.02, 126.11, 122.58, 121.06, 121.01, 119.79, 115.46, 114.65, 68.55, 55.76, 55.33, 40.20, 29.66, 29.24, 25.67, 23.65; ($C_{10}H_{14}S$)$_x$-($C_{48}H_{62}N_2$)$_y$($C_{10}H_{14}S$)$_x$. Anal. Calcd for x = 65, y = 11: C, 75.89; H, 8.66; S, 14.39; N, 1.07. Found: C, 75.21; H, 8.32; S, 14.91; N, 1.17; Br, <0.1.

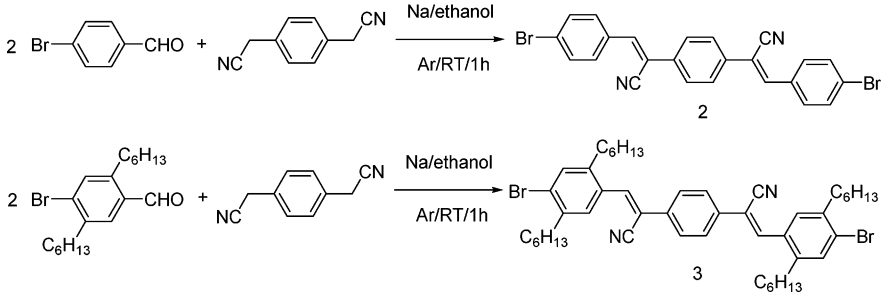
P3HT2−HCNPPV−P3HT2: (190 mg, yield 77%) $\bar{M}_n$ = 40 200, $\bar{M}_w/\bar{M}_n$ = 1.53. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.90−7.40 (b, HCNPPV block), 7.10−6.80 (b, P3HT block, 3.2 times of HCNPPV block, corresponding to n = 45 and m = 3), 3.00−2.55 (b, alkyl groups), 1.80−0.60 (b, alkyl groups). ^{13}C (CDCl$_3$, 400 MHz): δ 153.74, 153.31, 152.79, 150.12, 140.19, 140.06, 130.00, 127.53, 127.27 127.03, 126.12, 122.86, 121.06, 121.01, 119.79, 115.47, 114.66, 68.56, 55.76, 55.33, 40.19, 29.65, 29.24, 25.67, 23.66;

($C_{10}H_{14}S$)$_x$($C_{48}H_{62}N_2$)$_y$($C_{10}H_{14}S$)$_x$: Anal. Calcd for x = 45, y = 5: C, 74.87; H, 8.59; S, 15.76; N, 0.77. Found: C, 72.05; H, 8.93; S, 16.22; N, 0.72; Br, <0.1.

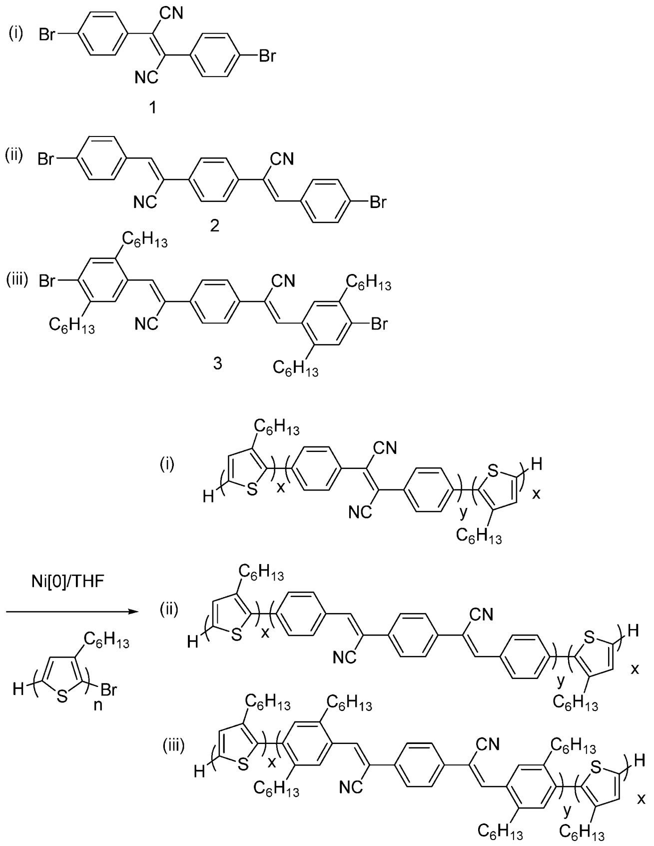
Results and Discussion

Our synthetic approach toward donor(P3HT)−acceptor-(cyanophenylenevinylene)−donor(P3HT) triblock copolymers includes two steps. First, bromo-terminated poly(3-hexylthiophene) (Br−P3HT) building blocks (as end-cappers) were prepared in a protocol described by McCullough et al.[22] By variation of the reaction time, Br−P3HT1 and Br−P3HT2 with slightly different molecular weights have been obtained. The GPC analyses of the two resulting donor macromonomers display number-average molecular weights $\bar{M}_n$ of 16800 and 25600, respectively, which corresponds to a degree of polymerization of 45 and 65 repeating units, respectively. Similar values have been reported in the literature.[22]

Scheme 1. Synthesis of Monomers 2 and 3



Scheme 2. Synthesis of the Donor/Acceptor/Donor Triblock Copolymers



In the second step, the final triblock copolymers were synthesized under Yamamoto conditions in the reaction of preformed dibromo building blocks as central acceptor segment with the monobromo Br−P3HTs as end-cappers, as shown in Scheme 2. The dibromo-terminated acceptor blocks itself are formed in a preceding Yamamoto-type coupling step of the corresponding dibromo monomers. Hereby, dibromo monomer **1** [bis(4-bromophenyl)fumaronitrile] was already reported.[20] The dibromo monomers **2** and **3** were synthesized by Knoevenagel condensation with yields of >90% according to Scheme 1. The number of the repeat units within the preformed α,*ω*-dibromo acceptor block was estimated by elemental analysis using the known degree of polymerization of the two P3HT-donor blocks. For the acceptor monomers without solubilizing side chains (monomer **1** and **2**), it was impossible to synthesize the corresponding acceptor homopolymers of reasonably high molecular weight. Therefore, for monomers **1** and **2**, low solubility of the acceptor block limits the finally obtained number of acceptor repeat units of the triblock copolymers. So, for monomers **1** and **2**, low values *y* of 6 and 2, respectively, have been estimated. For monomer **3** with 4 solubilizing hexyl side chains, the number of acceptor repeat units is distinctly increased. Depending on the reaction time (prepolymerization time) before adding the monobromo end-capper Br−P3HT, the number of the repeat units was estimated to be ca. 5 for 7 h prepolymerization time and ca. 11 for an extended time period of 14 h. In the ^{1}H NMR spectrum of P3HT1−HCNPPV−P3HT1 containing about 20 wt % of the CN−PPV block (chloroform fraction) three new and broad peaks at $\delta = 7.9-7.4$ are recorded which are not discovered for poly(3-hexylthiophene). These signals are in good agreement with the ^{1}H NMR signals of a HCNPPV homopolymer. The homopolymer used for comparison was synthesized under Yamamoto condition without the Br−P3HT end-capper. After extraction of the raw homopolymer with dichloromethane (dichloromethane fraction, yield 9.3%), a $\bar{M}_n$ of 7800 was estimated. However, a large amount of the residue was not soluble either in dichloromethane or chloroform. This solubility behavior also indicates that homopolymers as byproducts are already removed during extraction of the as-prepared block copolymers with dichloromethane. Low molecular weight oligomer fractions of the Br−P3HT end-capper and the final block copolymer have been generally removed by Soxhlet extractions with hexane and dichloromethane. Our conclusion concerning the formation of block copolymers is also supported by a GPC analysis of the P3HT-HCNPPV−P3HT block copolymer. In this experiment, the detection of the GPC profile of P3HT-HCNPPV−P3HT was carried out both at 350 and 450 nm, respectively, corresponding to the long wavelength absorption maxima of the homopolymers HCNPPV and P3HT in dilute solution. The GPC profiles display similar $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_p$ values at both detection wavelengths. This means that the resulting material is not a mixture (blend) containing homopolymer and block copolymer. For comparison, Br−P3HT1 was also homocoupled without the acceptor building block to give $(P3HT1)_2$. The chloroform fraction of this polythiophene displays a $\bar{M}_n$ of 45000, nearly the doubled $\bar{M}_n$ in relation to Br−P3HT1 and a $\bar{M}_n$ lowered by 8000 in comparison to P3HT1−HCNPPV−PT3H1. This difference of 8000 can be attributed to the molecular weight of the acceptor block in the triblock copolymer, in good agreement with the element analysis data.

The DSC curve of P3HT1−HCNPPV−P3HT1 exhibits a sharp endothermic peak at 217 °C (heating cycle) and an exothermic peak at 187 °C (cooling cycle), corresponding to the melting temperature (T_m) and crystallization temperature (T_c) of the P3HT donor blocks. However, the T_m and T_c of the P3HT-HCNPPV−P3HT1 are 20 and 21 °C lower if compared to the homopolymer $(P3HT1)_2$. This means that the incorporation of the acceptor block leads to a lower melting and crystallization temperature. Both P3HT1−HCNPPV−P3HT1 and $(P3HT1)_2$ show weak endothermic step transitions which can be attributed to the glass transition (T_g). The T_g of P3HT-HCNPPV−P3HT1 was found at 35.5 °C, 6.3 K lower as observed for $(P3HT1)_2$.

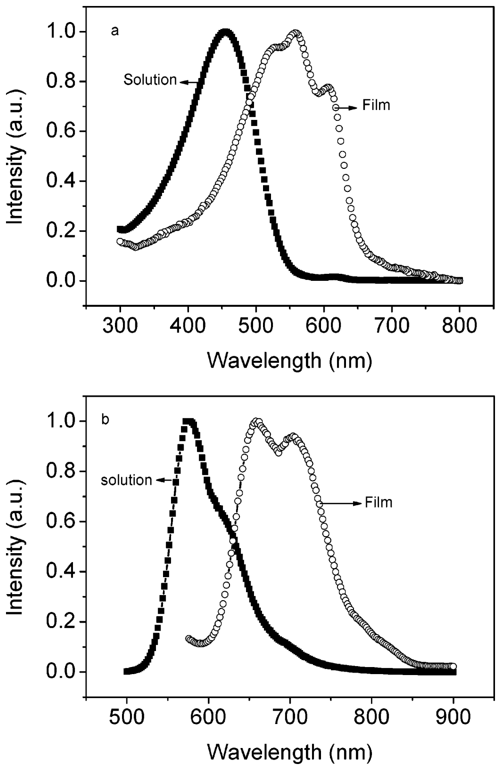


Figure 1. (a) UV−vis absorption spectra of P3HT1−HCNPPV−P3HT1 in dilute solution (0.2 mg/mL in toluene) and in a thin film (spin-coated from a 5 mg/mL solution in toluene); (b) photoluminescence spectra of P3HT1−HCNPPV−P3HT1 in dilute solution (0.2 mg/mL in toluene) and in a thin film (spin-coated from a 5 mg/mL solution in toluene).

For the other copolymers containing monomer **1** and **2**, similar trends have been observed. T_g, T_m, and T_c for P3HT1-BCNPPV−P3HT1 are 38.9, 233, and 200 °C, respectively. These values are closer to $(P3HT1)_2$, reflecting the presence of very short acceptor blocks. A thermogravimetric analysis (TGA) of P3HT1−HCNPPV−P3HT1 displays an initial weight loss (5%) at 290 °C, with the main decomposition occurring at 467 °C (50%). P3HT1-BCNPPV−P3HT1 behaves similar to P3HT1−HCNPPV−P3HT1, with an initial weight loss (5%) at 275 °C and the main decomposition occurring at 474 °C (50%). For $(P3HT1)_2$ without the acceptor block, a higher thermal stability is observed with an initial 5% weight loss at 410 °C and the main decomposition occurring at 485 °C (50%). The introduction of the cyanophenylenevinylene acceptor blocks into the block copolymers decreases the thermal stability.

Figure 1a shows the UV−vis spectra of P3HT1−HCNPPV−P3HT1 in dilute solution and as thin film. The UV−vis spectra of the triblock copolymer are almost similar to those of P3HT1 or $(P3HT1)_2$ due to the dominant contribution of the polythiophene blocks (80 wt %). The weak absorption maximum of the HCNPPV acceptor block at 350−370 nm is overlapped by the P3HT1 absorption and only visible as a red-shift shoulder in the solid-state spectrum. Compared to the UV−vis spectrum in solution, the absorption spectrum of a thin film is significantly red-shifted. The absorption at $\lambda_{max} \sim 610$ nm results from a crystallization of the P3HT chains under transition into a coplanar intrachain comformation.[23] This conclusion is also supported by the already described DSC results.

The photoluminescence spectra of P3HT1−HCNPPV−P3HT1 is also very similar to P3HT1 or $(P3HT1)_2$ (Figure 1b). No emission of the HCNPPV acceptor blocks at 410−430 nm (for a PL spectrum of the HCNPPV homopolymer, see Figure 2) was observed both in solution and in a thin film. This indicates an efficient excitation energy transfer from the HCNPPV acceptor block to the P3HT1 donor block. Figure 2 also illustrates the good overlap between the absorption spectrum of the donor P3HT1 and the photoluminescence spectrum of the acceptor HCNPPV in solution as well as in the thin film. This overlap should allow for an efficient excitation energy transfer in the block copolymers from the acceptor to the donor block. The electrochemical properties of the P3HT1−HCNPPV−P3HT1 triblock copolymers are dominated by the P3HT blocks. No significant oxidation and reduction waves of the higher band gap acceptor blocks have been recorded in CV experiments.

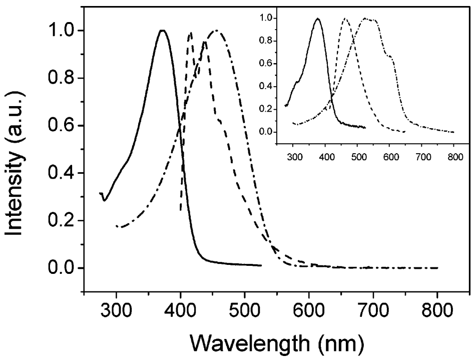


Figure 2. (a) UV−vis spectrum (solid line) and photoluminescence spectra of homopolymer HCNPPV (dashed line) and the UV−vis spectrum of $(P3HT1)_2$ (dash dot line) in solution; (b) inset showing the UV−vis (solid line) and photoluminescence spectra of homopolymer HCNPPV (dashed line) and UV−vis spectrum of $(P3HT1)_2$ (dash dot line) in a thin film.

Figures 3a and b present AFM morphology images of spin-coated thin films of P3HT1−HCNPPV−P3HT1 as-prepared and after annealing, respectively. Films of P3HT1−HCNPPV−P3HT1 triblock copolymers form nanosized spherical aggregates with a diameter of 60−90 nm. Annealing of these thin films (6 h, 120 °C) leads to an increased surface roughness, which indicates an ongoing aggregation and nanostructure formation of P3HT1−HCNPPV−P3HT1 during the thermal treatment. In the case of the homopolymer Br−P3HT1, nanosized aggregates are also formed (as shown in Figure 3c), but with a little larger diameter (70−120 nm) and an increased dispersity if compared to the P3HT1−HCNPPV−P3HT1 triblock copolymer. This finding indicates that the nanostructure formation is mainly driven by the crystallization of the P3HT segments. In contrast, a 2:1 blend of Br−P3HT1 and HCNPPV as spin-coated films (as-prepared and annealed, respectively) forms irregular nanostructures, as shown in Figure 3d with much lager acceptor and donor domains. Such a morphology may be disadvantageous for the design of efficient bulk heterojunction solar cell devices when considering the short exciton diffusion of length <20 nm in organic semiconductors. These results document one main advantage of our block copolymer approach. The covalent connection of P3HT donor and HCNPPV acceptor blocks limits the scale length of nanostructure formation and may allow the optimization of bulk heterojunction solar cell devices.[24] Further investigations toward a detailed understanding of the nanostructure formation and their influence on the optoelectronic properties are in progress.

In conclusion, we could present a straightforward synthetic strategy toward semiconducting triblock copolymers with both electron-donor and electron-acceptor blocks. Our simple two-step procedure allows for a control of the molecular weight of the different blocks by adjusting the solubility of the monomers

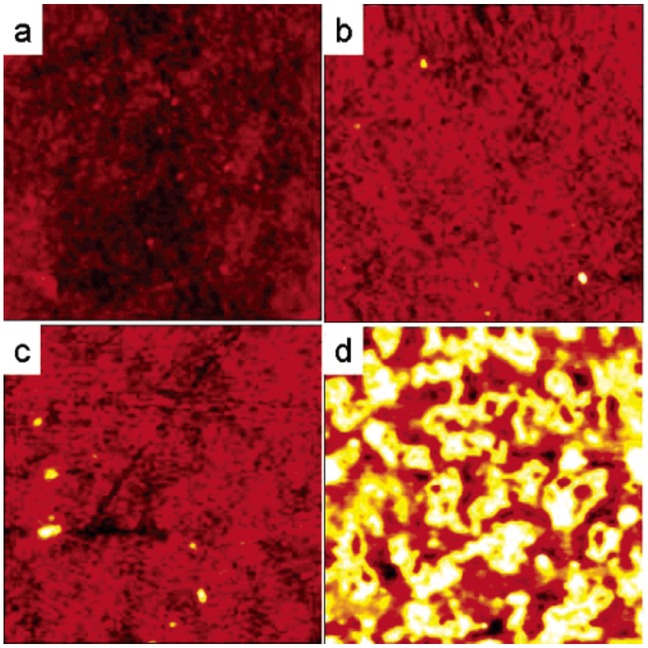


Figure 3. Contact-mode atomic force microscopy (AFM) images (5 × 5 μm) of thin films spin-coated onto SiO_2 from chloroform (concentrated 2 mg/mL): (a) P3HT1−HCNPPV−P3HT1 (as-prepared), (b) P3HT1−HCNPPV−P3HT1 (annealed for 6 h at 120 °C), (c) Br−P3HT1 (annealed for 6 h at 120 °C), and (d) a blend of Br−P3HT1 and HCNPPV with a molar ratio of 2:1(annealed for 6 h at 120 °C). *Z* range, 10 nm.

and the polymerization time. The resulting conjugated DAD-type triblock copolymers exhibit a high structural order in the solid state, as proved by DSC and optical spectroscopy. The triblock copolymers form well-characterized, nanosized mesostructures. Our conjugated block copolymer approach seems to be a favorable strategy toward defined nanomaterials, especially for an use in bulk heterojunction solar cell devices. Our next step will be the fine-tuning of the HOMO and LUMO levels of donor and acceptor blocks in order to favor charge separation at the internal interface over the energy transfer processes which are still occurring in our donor−acceptor system. One main focus, hereby, is the reduction of the HOMO−LUMO energy gap of the acceptor component.

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