A Novel Poly[2,6-(4-dialkylmethylenecyclopentadithiophene)] with "in-Plane" Alkyl Substituents

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Introduction

Concerns over global warming and increasing energy demands have generated much interest in renewable energy sources in recent years. The conversion of solar energy, along with other alternative technologies, has the potential to replace fossil fuels in the generation of electrical energy. For mobile applications, the traditional heavy-weight silicon-based, high cost solar cell modules developed since the early 1950s[1−3] have had to be replaced by cheaper lightweight solar energy technologies. Hence, organic photovoltaic devices with active layers composed of phase-separated mixtures of semiconducting donors and acceptors (so-called "bulk-heterojunction" solar cells) emerged as an interesting opportunity to bring down weight and production costs. When combined with flexible substrate materials, devices with characteristics not comparable to those of their inorganic counterparts may be obtained.

To optimize the device performance, it is crucial to control the energy levels of the donor and acceptor components and the phase-separated morphology of the active layers.[4−7] Therefore, it is of highest interest to find the synergy between a suitable solubility of the organic materials necessary for low-cost "wet"-processing into thin layers and an ordered structure of the organic semiconductor in the solid-state necessary for the sufficient transport of charge carriers.[4] We have focused our interest in cyclopentadithiophene-based (4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene, CPDT) donor polymers containing the heteroaromatic, electron-rich analogue of fluorene as the repeat unit in the polymers' backbone. In addition to the already known dialkylated CPDT monomers and polymers with the side chains orthogonal (out-of-plane) to the plane of the conjugated backbone,[8,9] we have now synthesized CPDT-type polymers bearing the alkyl side chains in-plane via an olefinic dialkylmethylene group in 4-position.

This work focuses on the synthesis of such dialkylated, planarized cyclopentadithiophene-type monomers and polymers, which have not been reported up to date. The resulting polymers are expected to show strong solid-state interaction of the polymer chains by $\pi-$stacking which benefits both from the symmetrical structure and the planar geometry of the repeat unit.

Results and Discussion

The starting molecule for our synthesis, cyclopentadithiophene (4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene, CPDT, **1**), was synthesized following procedures well-known from the literature.[10] In a first reaction step toward the envisaged polymers, CPDT **1** was deprotonated and reacted with CS_2 resulting in a ketene dithiolate anion, followed by an in situ alkylation with methyl iodine to yield the dimethylated thioacetal **2** (Scheme 1).[11] In the next reaction step **2** was treated with 2 equiv of an alkyl Grignard reagent in THF at −5 °C for 4 h to give the 4-dialkylmethylene-CPDT derivative **3.** Using this method, monomers with both hexyl (**3a**) and decyl side chains (**3b**) were synthesized.

The resulting monomers could be oxidatively polymerized to the polymers **4a/b** using $FeCl_3$ as oxidizing agent as extensively described for poly(alkylthiophene)s.[12] Hereby, a mixture of $FeCl_3$ and monomer **3**, respectively, was stirred in chloroform for 48 h in a light stream of argon.[8,13,14] After dedoping treatment with hydrazine hydrate a dark blue polymer was isolated by precipitation into methanol. The crude product was purified by Soxhlet extraction with methanol and acetone and reprecipitation from chloroform into methanol. The resulting polymer was fully soluble in chloroform. GPC analysis using polystyrene standards determined reasonably high mean average molecular weights M_n (Table 1) of 4200 for polymer **4a** and 5700 for polymer **4b**. The polymer structure was confirmed by ^{1}H NMR spectroscopy.

An alternate route toward polymer **4** followed a standard Yamamoto-type aryl−aryl coupling protocol (Scheme 2). First, compound **3a** was brominated with a mixture of benzyltrimethylammonium tribromide and zinc chloride, yielding the dibromo monomer **5.** The $Ni(COD)_2$-catalyzed polycondensation was carried out utilizing a microwave-assisted heating protocol. This method is known to give polymers in reasonable yields and high molecular weights.[15] However, for monomer **5** polymer **4c** was achieved only in low yields (14%) indicating that the dibromo derivative **5** is not well-suited for Yamamoto-type aryl−aryl couplings. The polymer **4c** obtained via Yamamoto-type coupling was purified by Soxhlet extraction of the precipitate with methanol, acetone, and chloroform, respectively, while an insoluble part remained as a dark colored powder. GPC measurements of the chloroform-soluble fraction against polystyrene standards showed a mean average molecular weight M_n of only 1600 g/mol.

As mentioned before, polymer **4** is expected to form π-stacked solid-state aggregates due to the in-plane arrangement of the alkyl side chains. The indeed observed distinct red shift of the absorption maximum of the solid-state UV−vis spectrum of **4b** (Figure 1) compared to the solution spectrum (dilute solution in chloroform) suggests a significant face-to-face interchain stacking of the polymer chains in the solid state. A dilute chloroform solution of **4b** (R: *n*-decyl) shows a long-wavelength UV−vis maximum at 621 nm. The solid-state absorption maximum is red-shifted to 699 nm indicating the formation of electronically interacting, π-stacked aggregates. This observation is supported by the presence of a vibronic sideband (shoulder at 645 nm) in the solid-state UV−vis spectrum, a total quenching of the fluorescence emission and a decreased solubility of **4b** when stored in solution for several days (ongoing aggregate formation).

For comparison, Figure 2 shows the absorption spectra of poly(dialkyl-CPDT) **6** bearing out-of-plane alkyl substituents.[9] **6** shows a solution absorption maximum peaking at 566 nm (dilute chloroform solution, Figure 2). The solid-state UV−vis spectrum of **6** does not exhibit any red shift of the absorption maximum.

The comparison of the absorption spectra of **4** and **6** (Figures 1 and 2) illustrates the dominating role of out-of-plane vs in-

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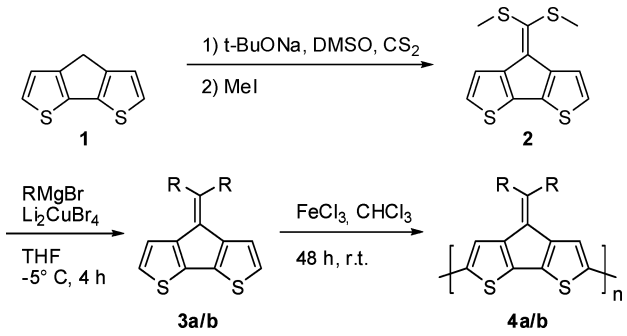
Scheme 1. Synthetic Scheme toward Poly[2,6-(4-dialkylmethylene-cyclopentadithiophene)] Polymers 4a (R = Hexyl) and 4b (R = Decyl)



Scheme 2. Synthesis of Polymer 4c via a Yamamoto-Type Aryl−Aryl Coupling (R = Hexyl)

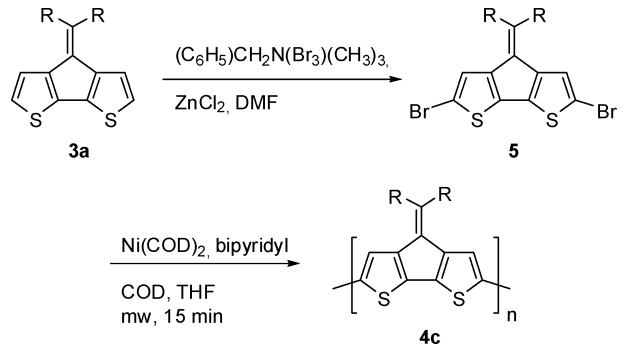


Table 1. Data for Poly(dialkylmethylene-CPDT)s 4a−c and, for Comparison, Poly(didecyl-CPDT) 6 (Structure Given as Inset of Figure 2)[a]

polymer	coupling agent	yield [%]	M_n/M_w	abs max λ_{max} chloroform solution/film [nm]
4a	$FeCl_3$	32	4200/9700	593/n.m.
4b	$FeCl_3$	44	5700/10400	621/699
4c	$Ni(COD)_2$	14	1600/3300	570/n.m.
6	$NiCl_2$/Zn	40	9000/16300	566/567

[a] **4a,c**: R = hexyl. **4b**: R = decyl.

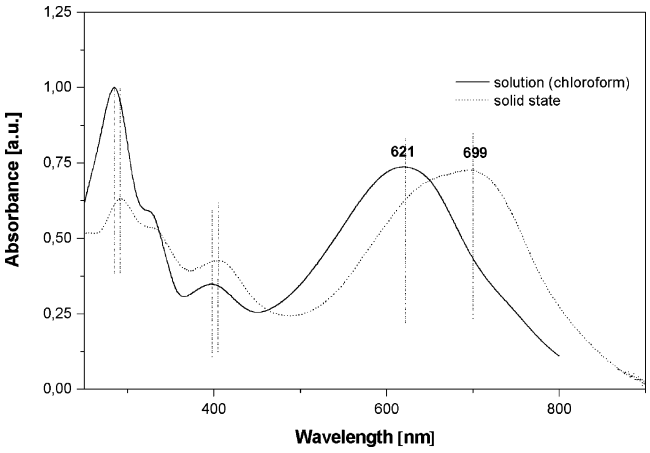


Figure 1. UV−vis spectra of poly(didecylmethylene-CPDT) **4b** in solution (chloroform) and in the solid state.

plane alkyl substituents for an efficient π-stacking in the solid state. Only the presence of in-plane substituents allows for a π-stacked face-to-face packing of the conjugated polythiophene backbones.

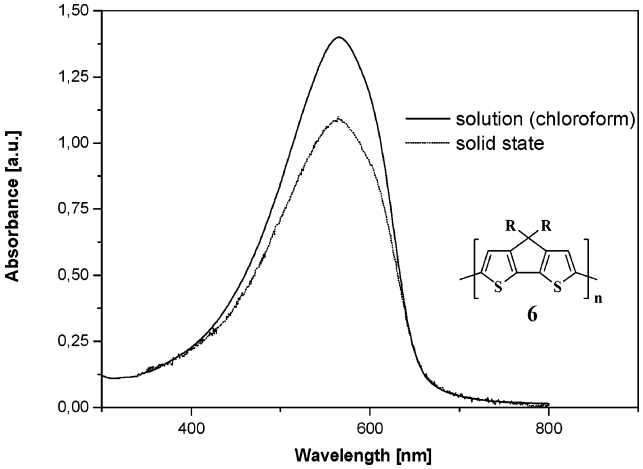


Figure 2. UV−vis spectra of poly(dialkyl-CPDT) **6** in dilute solution (chloroform) and in the solid state.[9]

Conclusion

Two novel 4-dialkylmethylene-CPDT monomers have been synthesized and oxidatively coupled using $FeCl_3$. Comparison of the UV−vis absorption spectra of poly(cyclopentadithiophene)s with either in-plane or out-of-plane alkyl chains revealed a strong preference for intermolecular π-stacking for the polymers composed of planarized building blocks. This result defines an important design rule for semiconducting polymers with optimized solid-state π-stacking: "in-plane" alkyl chains are superior over an out-of-plane arrangement of the solubilizing substituents.

Experimental Section

Materials and Characterization. Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. The solvents were used as commercial p.a. quality. The reactions were carried out under argon with the use of standard and Schlenk techniques. The vials for the microwave assisted reactions were filled in a glovebox. ^1H and ^{13}C NMR data were obtained on a Bruker ARX 400-spectrometer. The UV−vis and fluorescence spectra were recorded on a Jasco V-550 spectrophotometer and a Varian-Cary Eclipse photoluminescence spectrometer, respectively. Gel permeation chromatographic analysis (GPC) utilized PS-columns (three columns, 5 μm gel, pore widths 10^3, 10^5 and 10^6 Å) connected with UV/vis and RI detection. All GPC analyses were performed on solutions of the polymers in THF at 30 °C (concentration of the polymer: approximately 1.5 g/L). The calibration was based on polystyrene standards with narrow molecular weight distribution. Microwave-assisted syntheses were performed using a CEM Discover microwave system.

4-[Bis(methylsulfanyl)methylene]-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene (2). Sodium *tert*-butoxide (1.13 g, 11.8 mmol, 2.1 equiv) was added in small portions to a solution of cyclopentadithiophene **1** (1 g, 5.6 mmol) in dry DMSO at r.t. under argon. Carbon disulfide (472 mg, 6.2 mmol, 1.1 equiv) was added via a syringe and the reaction mixture stirred for 10 min. Methyl iodide (0.74 mL, 11.8 mmol, 2.1 equiv) was also added via a syringe and the reaction mixture was stirred for additional 4 h. The reaction mixture was poured into ice−water, and an aqueous solution of ammonia was added to bind the remaining methyl iodide. The resulting precipitate was extracted with *tert*-butyl ethyl ether and washed with water. The combined organic layers were dried over Na_2SO_4 and the solvent removed in vacuo. The crude product was purified by column chromatography (silica, hexane) to afford the product as a dark red oil (yield: 1.28 g, 81%). ^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.81 (d, 1H, J = 5.1 Hz), 7.07 (d, 1H, J = 5.1 Hz), 2.54 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 143.6, 141.3, 138.0, 133.6, 125.0, 123.3, 17.9. mass: m/z (%) = 282 (M^+,

100), 252 (10), 220 (43), 203 (31), 176 (17), 132 (7), 110 (12), 69 (6), 45 (11). Anal. Found (calcd): C, 50.97 (51.02); H, 3.82 (3.57); S, 45.12 (45.41).

4-(Dihexylmethylene)-4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene (3a). To a stirred solution of 4-[bis(methylsulfanyl)methylene]-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**2**) (400 mg, 1.4 mmol) in THF (10 mL) at −5 °C under nitrogen lithium tetrachlorocuprate (0.35 mL, 2.5 mol %, 0.1 M in THF) was added, followed by a dropwise addition of hexylmagnesium bromide (3.1 mL, 3.1 mmol, 1 M in Et_2O), keeping the temperature below 0 °C. The reaction was stirred for a further 4 h at −5 °C and then quenched by the addition of a concentrated aqueous solution of sodium hydroxide (10 mL). The mixture was stirred for 10 min and then filtered through Celite and extracted with ethyl acetate until the organic solution was clear. The combined organic phases were washed with a concentrated aqueous solution of sodium hydroxide, saturated sodium bisulfite, and brine. The organic layer was dried over sodium sulfate and the solvent removed in vacuo. The crude product was purified by column chromatography (silica, hexane) to afford the product as a yellow oil (yield: 266 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.13 (d, 2H, J = 5.0 Hz), 7.07 (d, 2H, J = 5.0 Hz), 2.58 (m, 4H), 1.56 (m, 4H), 1.39 (m, 4H), 1.27 (m, 8H), 0.84 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 149.9, 143.6, 136.8, 127.9, 123.7, 123.1, 35.8, 34.1, 31.8, 29.9, 29.7, 29.1, 22.6, 22.3, 14.1. Mass: m/z (%) = 358 (100), 274 (8), 217 (17), 203 (17), 189 (12), 43 (16). Anal. Found (calcd): C, 73.21 (73.68); H, 7.99 (8.43); S, 17.69 (17.88).

4-(Didecylmethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (3b). To a stirred solution of lithium tetrachlorocuprate (1.8 mL, 2.5 mol %, 0.1 M in THF) in THF (10 mL) at −5 °C under nitrogen 4-[bis(methylsulfanyl)methylene)]-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene (**2**) (2.0 g, 7.1 mmol) in THF (20 mL) was added, followed by a dropwise addition of decylmagnesium bromide (20.0 mL, 20.0 mmol, 1 M in Et_2O), keeping the temperature below 0 °C. The reaction was stirred for a further 9 h at −5 °C and then quenched by the addition of a concentrated aqueous solution of sodium hydroxide (10 mL). The mixture was stirred for 10 min and then filtered through Celite and extracted with ethyl acetate until the organic solution was clear. The combined organic phases were washed with a concentrated aqueous solution of sodium hydroxide, saturated sodium bisulfite, and brine. The organic layer was dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica, hexane) to afford the product as a yellow oil (yield: 2.07 g, 62%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ [ppm] = 7.14 (d, 2H, J = 5.0 Hz), 7.07 (d, 2H, J = 4.9 Hz), 2.59 (m, 4H), 1.56 (m, 4H), 1.39 (m, 4H), 1.22 (m, 12H), 0.83 (t, 6H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ [ppm] = 151.0, 143.8, 136.8, 127.8, 124.3, 123.5, 36.0, 32.1, 30.5, 29.9, 29.8, 29.8, 29.6, 29.4, 23.0, 14.5. Mass: m/z (%) = 470 (M^+, 100), 329 (6), 216 (27), 202 (21), 189 (12), 184 (9), 176 (7), 43 (15). Anal. Found (calcd): C, 76.92 (76.53); H, 9.43 (9.85); S, 14.01 (13.62).

Poly{2,6-[(4-(didecylmethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene)]} (4b). In a two-neck round-bottom flask 4-(didecylmethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**3b**) (750 mg, 1.6 mmol) was mixed with dry chlorobenzene (50 mL). To this solution was added anhydrous $FeCl_3$ (1.04 g, 6.4 mmol) in dry chlorobenzene, and the mixture was stirred for 48 h at room temperature under a gentile stream of argon. The (oxidized) polymer was precipitated into methanol and the crude product was dedoped by refluxing it in chloroform/hydrazine hydrate for 24 h. Soxhlet extraction methanol, acetone, and further precipitation into methanol gave the blue colored polymer **4b** (yield: 329 mg, 44%). ^{1}H NMR (400 MHz, toluene-d_8, 353 K): δ [ppm] = 7.06 (br, s, 2H); 1.79−0.87 (br, m, 42H). UV/vis: λ_{max} [nm] 621 (chloroform), 699 (film). Anal. Found (calcd): C, 76.43 (76.86); H, 9.33 (9.46); S, 13.44 (13.68). GPC [g/mol]: M_n, 5900; M_w, 10400.

Poly{2,6-[(4-(dihexylmethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene)]} (4a) was prepared as described for polymer **4b** (yield: 32%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K): δ [ppm] = 7.13 (br, s, 2H), 2.49 (m, 4H), 1.65 (br, m, 4H), 1.49 (br, m, 4H), 1.32 (br, m, 8H), 0.80 (br, m, 6H). UV/vis: λ_{max} [nm] 593 (chloroform). Anal. Found (calcd): C, 73.33 (74.10); H, 6.91 (7.91); S, 16.84 (17.98). GPC [g/mol]: M_n, 4200; M_w, 9700.

2,6-Dibromo-4-(dihexylmethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (5). To a mixture of benzyltrimethylammonium tribromide (2.06 g, 5.3 mmol) and zinc chloride (0.75 g, 5.5 mmol) a solution of 4-(dihexylmethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene (**3a**) (0.9 g, 2.5 mmol) in DMF (40 mL) was added via a syringe and the mixture stirred at room temperature for 2.5 h. Afterward water (20 mL) and an aqueous solution of $NaHSO_3$ (20 mL) were added dropwise. After the solvents were removed, the crude product was purified by column chromatography (silica, hexane/ethyl acetate 95/5) to give an orange solid (yield: 1.6 g, 56%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ [ppm] = 7.11 (s, 2H), 2.52 (m, 4H), 1.51 (m, 4H), 1.37 (m, 1H), 1.26 (m, 1H), 0.84 (t, 1H, J = 7.0 Hz). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ [ppm] = 152.8, 141.0, 136.4, 127.4, 126.0, 110.0, 35.7, 31.7, 29.7, 29.1, 22.5, 14.0. mass: m/z (%) = 516 (42), 498 (11), 279 (82), 217 (24). Anal. Found (calcd): C, 50.97 (51.17); H, 4.88 (5.47); S, 12.03 (12.42); Br, 32.12 (30.95).

Poly{2,6-[(4-(dihexylmethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene)]} (4c) 2,6-Dibromo-4-(dihexylmethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene **5** (55 mg, 0.1 mmol), $Ni(COD)_2$ (70.3 mg, 0.26 mmol), and 2,2′-bipyridyl (36.6 mg, 0.23 mmol) were mixed in a 10 mL microwave tube in the glovebox. Afterward THF (2 mL) and COD (25.3 mg, 0.23 mmol) were added via a syringe. The mixture was heated in a microwave reactor to a maximum temperature of 110 °C for 15 min. The precipitate was isolated and Soxhlet extracted with chloroform. The chloroform solution was concentrated and reprecipitated into methanol, yielding a blue colored solid (yield: 5 mg, 14%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353 K): δ [ppm] = 7.11 (br, s, 2H), 2.53 (m, 4H), 1.62 (br, m, 4H), 1.45 (br, m, 4H), 1.32 (br, m, 8H), 0.84 (br, m, 6H). UV/vis: λ_{max} [nm] 570 (chloroform). Anal. Found (calcd): C, 73.54 (74.10); H, 7.21 (7.91); S, 17.44 (17.98). GPC [g/mol]: M_n, 1600; M_w, 3300.

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