

Low band gap polymers based on 1,4-dialkoxybenzene, thiophene, bithiophene donors and the benzothiadiazole acceptor

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ABSTRACT

Four new copolymers of 1,4-dialkoxybenzene, thiophene, bithiophene and benzothiadiazole have been prepared and investigated for optical properties and in photovoltaic devices. The structures were chosen to show the effect of successively introducing an acceptor moiety, longer alkoxy side chains and finally, substituting thiophene for bithiophene. The absorption spectra and IPCE showed that these are low band gap polymers that can harvest light in the visible spectrum (400 to 700 nm) and that photoelectrons are generated in the whole range. The photovoltaic devices produced short circuit current densities (J_{sc}) of 2.6 to 4.6 mA/cm² under AM1.5 G illumination. The open circuit voltage (V_{oc}) was 0.56 to 0.64 V and the efficiencies (η) of 0.8% to 2.2% depending on the structure.

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1. Introduction

Research on polymer based solar cells has attracted interest due to the promise of high volume production at low cost [1–8]. Most of the efforts have been directed towards improving the power conversion efficiency for small laboratory devices [9–11]. Equally important but less explored areas of research are the stability/degradation [8] and processing issues [12–14].

Presently, a major effort in polymer photovoltaic research is the development of new types of polymers based on donor and acceptor groups to improve absorption of light at longer wavelengths. This strategy has proven successful as shown by Leclerc et al. and later improved by Park et al. to give devices with an efficiency of 6.5% and internal quantum efficiency near 100% [15]. This is well above the limit reached for the more established and researched poly-3-hexylthiophene (P3HT) polymer [16]. Many types of these low band gap polymers with alternating donor and acceptor groups have already been prepared by several groups and shown to exhibit a strong charge transfer (CT) absorption band in addition to the usual π - π^* bands common to all conjugated polymers [17]. Both the donor and acceptor groups can be varied and a great number of polymers are therefore possible. The donor and acceptor properties together with the overlap between the groups make it possible to tune the absorption spectrum and the band gap defining the photovoltaic properties. The most important result is that the better coverage of the solar spectrum may increase the short circuit current

density (J_{sc}) through an increase in the number of absorbed photons and hence the efficiency (η_e). On the other hand, the lower band gap may also work in the other direction to decrease the open circuit voltage (V_{oc}).

A number of other factors such as the degree of conjugation along the main chain as well as the overlap between neighboring polymer molecules in the solid phase and many others influence on how well a given polymer performs in a solar cell device. The optimal choices does not yet seem open to rational design and therefore at present this is resolved through a trial and error process.

Here we present the synthesis of four new polymers (see Chart 1) based on thiophene substituted dialkoxybenzene donor systems and the benzothiadiazole acceptor together with their application in photovoltaic devices. This donor structure has to our knowledge not been explored previously in the context of solar cells, but has advantages in the simple synthesis of the two alkoxy groups to ensure solubility and processability.

The **JC1** polymer has alternating electron rich dialkoxybenzene and bithiophene units and is therefore purely a donor type polymer, similar to e.g. P3HT. **JC2** and **JC3** are both comprised of dialkoxybenzene donor and benzothiadiazole acceptor groups connected by thiophene units. They differ in the alkyl side chains being either 2-ethylhexyl (EH) or 2-hexyldecyl (HD) groups. The HD alkyl groups are double the size of the EH groups and serve as better solubilizing groups. **JC4** is similar to **JC3**, but with bithiophene groups instead of the single thiophene units. These four polymers allowed investigation of the effect of introducing the acceptor moiety (**JC1** → **JC2**), the variation in alkyl side chains (**JC2** → **JC3**) and the number of thiophene groups (**JC3** → **JC4**). Finally, the **JC1** could also be compared to P3HT.

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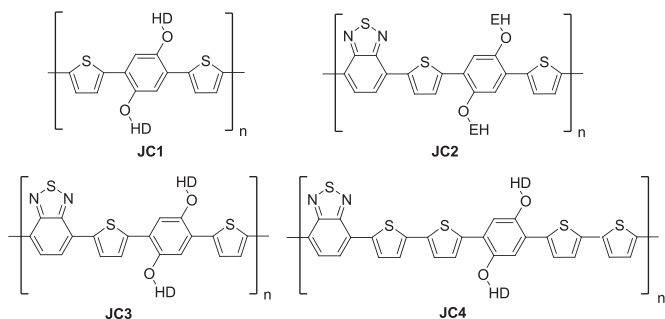


Chart 1. The four different polymers prepared and tested in photovoltaic devices, EH=2-ethylhexyl, HD=2-hexyldecanyl.

2. Experimental section

2.1. Synthesis

1,4-bis(2-ethylhexyloxy)benzene (1a) [18]: A suspension of potassium hydroxide (100 g, 1782 mmol) in dried DMSO (400 mL) was stirred and degassed for 10 min. 1,4-dihydroxybenzene (22.04 g, 200 mmol) and 2-ethylhexylbromide (97 g, 500 mmol) were added. The mixture was stirred at room temperature for 3 days. After about 30 min the mixture changed color and became dark. It was poured into ice water and the organic phase was collected. The water phase was washed twice with hexane (2 × 400 mL). The organic phases were collected transferred to ether (1.5 L), by extraction. It was washed once with water, 600 ml, to remove traces of DMSO. It was dried over magnesium sulphate filtered and the solvent was evaporated to give the product as a light yellow oil. Yield: 36.463 g, 109 mmol, 54.5%. ¹H NMR (CDCl₃, 250 MHz), δ: 0.90–1.00 (m, 12H), 1.28–1.61 (m, 16H), 1.74–1.90 (m, 2H), 3.83 (d, 4H) 6.87 (s, 4H).

1,4-Dibromo-2,5-bis(2-ethylhexyloxy)benzene (2a)[19]: Compound **1a** (20 g, 59.8 mmol) was dissolved in 10 times the volume of chloroform. The bromine (19.59 g, 123 mmol) was dropwise added to the mixture under stirring at room temperature. The mixture was poured into ice water. The two phases were separated and the aqueous phase was extracted twice with ether. The organic phases were collected and dried over magnesium sulphate and the solvent evaporated in vacuum, to give yellow/red oil. This was dissolved in ether and stirred over night with sodium carbonate, to remove traces of hydrogen bromide. It was filtered and the solvent evaporated to give the product as a yellow oil. Yield: 24.61 g, 50.0 mmol, 84% yield. ¹H NMR (CDCl₃, 250 MHz) δ: 0.90–1.00 (m, 12H), 1.28–1.61 (m, 16H), 1.74–1.90 (m, 2H), 3.84 (d, 4H), 7.09 (s, 2H). ¹³C NMR (CDCl₃, 250 MHz) δ: 11.14, 14.03, 23.00, 23.91, 29.05, 30.48, 39.49, 72.60, 111.12, 118.27, 150.25.

1,4-Bis(2-hexyldecyloxy)benzene (1b): A suspension of sodium hydroxide (50 g, 1.25 mol) in dried DMSO (400 ml) was stirred and degassed for 10 min. 1,4-dihydroxybenzene (12.75 g, 115.8 mmol) and 2-hexyldecanyl bromide (53.5 g, 175 mmol) were added. The mixture was stirred at room temperature over night. After about 30 min the mixture changed color and became dark. It was poured into ice water and the organic phase was collected. The water phase was washed twice with hexane (2 × 200 mL). The organic phases were collected transferred to ether, by extraction. It was washed once with water, 300 mL, to remove traces of DMSO. It was dried over magnesium sulphate, filtered and the solvent was evaporated under vacuum and dissolved in hexane: Purified by column chromatography on silica gel using hexane/EtOAc (1:4) as eluent to give the product as a colorless oil. Yield: 19.77 g, 35.4 mmol, 40.5%. ¹H NMR (CDCl₃, 250 MHz), δ: 0.80–0.95 (m, 12H), 1.2–1.4 (m, 48H), 1.74–1.80 (m, 2H), 3.77 (d, 4H) 6.82 (s, 4H).

1,4-Dibromo-2,5-bis(2-hexyldecanyl)benzene (2b): Compound **1b** (19.77 g, 35.35 mmol) was dissolved in 10 times the volume of chloroform. Then bromine (12.16 g, 76.13 mmol) was added dropwise to the mixture under stirring at room temperature. The mixture was poured into ice water and the two phases were separated. The aqueous phase was extracted twice with ether. The organic phases were collected and dried over magnesium sulphate and the solvent evaporated in vacuum, to give yellow/red oil. This was dissolved in ether and stirred over night with sodium carbonate, to remove traces of hydrogen bromide. It was filtered and the solvent evaporated under vacuum. Purified by column chromatography on silica gel using hexane as eluent to give the product as a colorless oil. Yield: 23.43 g, 32.7 mmol, 92.6% yield. ¹H NMR (CDCl₃, 250 MHz), δ: 0.80–0.95 (m, 12H), 1.2–1.4 (m, 48H), 1.74–1.80 (m, 2H), 3.77 (d, 4H) 6.82 (s, 2H).

2,2'-(2,5-Bis(2-hexyldecanyl)-1,4-phenylene)dithiophene (3): 2-(tributyltin)-thiophene (5.71 g, 15.31 mmol) and compound **2b** (4.77 g, 6.66 mmol) was dissolved in dry toluene (60 ml). Tetrakis triphenylphosphine palladium(0) (1.0 g) catalyst was added and the solution was stirred at reflux over night. The solvent was evaporated under vacuum and the product purified by column chromatography on silica gel using hexane/EtOAc (1:9) as eluent. The product was further purified by distillation of the excess of 2-(tributyltin)-thiophene. This gave the product as a light green oil. Yield: 3.65 g, 5.0 mmol, 75.1% ¹H NMR (CDCl₃, 250 MHz) δ: 0.80–0.95 (m, 12H), 1.2–1.6 (m, 48H), 1.80–1.95 (m, 2H), 3.95 (d, 4H) 7.10 (m, 2H), 7.25 (s, 2H), 7.33 (dd, 2H), 7.53 (dd, 2H).

5,5'-(2,5-Bis(2-hexyldecyloxy)-1,4-phenylene)bis(2-bromothiophene) (4): Compound **3** (0.96 g, 1.33 mmol) was dissolved in THF (15 ml). A solution of N-bromosuccinimide (0.48 g, 2.69 mmol) in THF (10 mL) was added to the solution in small portions and then stirred under argon at room temperature for 2 h. Water and ether was added and the phases separated. The organic phase was washed with water and dried over magnesium sulphate, filtered and the solvent evaporated under vacuum. Purified by column chromatography on silica gel using hexane/EtOAc (1:50) as eluent to give the product as a greenish oil. Yield: 700 mg 0.8 mmol, 60.2%. ¹H NMR (CDCl₃, 250 MHz) δ: 0.80–0.95 (m, 12H), 1.2–1.4 (m, 48H), 1.80–1.95 (m, 2H), 3.95 (d, 4H), 7.03 (d, 2H), 7.15 (s, 2H), 7.25 (d, 2H). ¹³C NMR (CDCl₃, 250 MHz) δ: 14.05, 26.64, 26.78, 26.80, 29.29, 29.53, 29.62, 29.96, 31.33, 31.81, 31.88, 37.99, 73.03, 111.10, 118.27, 150.23.

4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (6) [20]: 4,7-Dibromo-benzo[c][1,2,5]thiadiazole (19.99 g, 68 mmol), 2-(trimethylstannyl)thiophene (61.4 g, 165 mmol) and PdCl₂(PPh₃)₂ (0.97 g, 1.382 mmol) were dissolved in THF and brought to reflux under argon with stirring and left over night. The solvent was evaporated in vacuum, which gave a bright red colored solid that was recrystallized from ethanol, filtered and dried in vacuum. Because of some impurities (water, ethanol and grease) the product was washed with hexane, filtered and the rest of the solvent was evaporated in vacuum to give the product as a red solid. Yield: 18.23 g, 60.7 mmol, 89%. ¹H NMR (CDCl₃, 250 MHz), δ: 7.22 (dd, 2H), 7.46 (dd, 2H), 7.87 (s, 2H), 8.13 (dd, 2H).

4,7-Bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (7a): Compound **6** (2 g, 6.66 mmol) was dissolved in dry THF (120 mL) and cooled to –78 °C. LDA (60 ml, 33.3 mmol) was added over 15 min. The color changed from orange to dark purple. It was stirred for an hour at –78 °C. Trimethyltin chloride (7.2 g, 36.1 mmol) in 14 mL dry THF was added over 15 min which changed the color to orange. It was allowed to slowly reach room temperature where it was stirred over night. Water and chloroform were added and the organic phase was dried over MgSO₄, filtered and the solvent evaporated in vacuum. It was recrystallized from heptane, filtered and the solvent evaporated in vacuum at low heat to give the product. Yield: 2.65 g, 4.2 mmol, 64%. ¹H

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