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/cm^2 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.

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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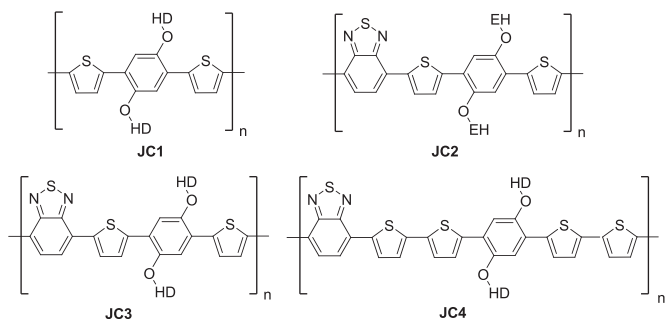E-mail address: mijq@risoe.dtu.dk (M. Jørgensen).

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-dihydroxy-benzene (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%. ^{1}H NMR (CDCl$_3$, 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. ^{1}H NMR (CDCl$_3$, 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).^{13}C NMR (CDCl$_3$, 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-hexyldecanyloxy*)*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%. ^{1}H NMR (CDCl$_3$, 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. ^{1}H NMR (CDCl$_3$, 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% ^{1}H NMR (CDCl$_3$, 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-bromothio-phene*) (**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% . ^{1}H NMR (CDCl$_3$, 250 MHz) δ: 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). ^{13}C NMR (CDCl$_3$, 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-Di-bromo-benzo[*c*][1,2,5]thiadiazole (19.99 g, 68 mmol), 2-(trimethyl-stannyl)thiophene (61.4 g, 165 mmol) and PdCl$_2$(PPh$_3$)$_2$ (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%. ^{1}H NMR (CDCl$_3$, 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*]*thiadia-zole* (**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 chloro-form were added and the organic phase was dried over MgSO$_4$, filtered and the solvent evaporated in vacuum. It was recrystal-lized from heptane, filtered and the solvent evaporated in vacuum at low heat to give the product. Yield: 2.65 g, 4.2 mmol, 64%. ^{1}H

NMR (CDCl$_3$, 250 MHz), δ: 0.45 (s, 18H), 7.30 (d, 2H), 7.88 (s, 2H), 8.19 (d, 2H).

4,7-Bis(5-tributylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (7b): Prepared as described for (**7a**). Instead of trimethyltin chloride, tributyltin chloride was used. Purification was done by column chromatography on alumina, pretreated with triethylamine and using toluene/EtOAc (1:10) as eluent to give the product as red oil. Yield: 5.1 g, 6.0 mmol, 91%. ^{1}H NMR (CDCl$_3$, 250 MHz), δ:0.95 (t, 18H), 1.20 (m, 12H), 1.40 (m, 12H), 1.65 (t, 12H), 7.30 (d, 2H), 7.90 (s, 2H), 8.20 (d, 2H). ^{13}C NMR (CDCl$_3$, 500 MHZ) δ: -6.73, 125.84.

Poly{2,2′-(2,5-bis(2-hexyldecyloxy)-1,4-phenylene)dithiophene} (**JC1**): Anhydrous ferric chloride (0.23 g, 1.42 mmol) was mixed with chloroform (10 mL) and compound **4b** (354 mg, 0.71 mmol) in chloroform (5 mL) was added under stirring. The mixture was stirred over night. The mixture was poured into methanol (100 mL), by which the polymer precipitated. The crude polymer was purified by Soxhlet extraction and reprecipitation as describe below for the general Stille cross-coupling polymerization. Yield: 188 mg 0.38 mmol, 53%.

General procedure for Stille cross-coupling polymerization: One equivalent each of the acceptor monomer (**6**) and the appropriate donor monomer (**2a, 2b, 4a** or **4b**) were dissolved in degassed toluene. Trio-o-tolylphosphine (0.4 mol%) and tris-(dibenzylidene acetone) dipalladium(0) (0.05 mol%) were added and the solution was brought to reflux where it was stirred for at least 24 h. The solvent was evaporated under vacuum and the product was dissolved in a minimum amount of boiling chloroform. The polymer was precipitated in about 10 volumes of methanol. The suspension was filtered to give the polymer which was purified by Soxhlet extraction, first with methanol, then with hexane and finally with chloroform. The chloroform fraction was evaporated under vacuum to a minimum volume, still keeping the polymer in solution. The polymer was then precipitated by pouring it into 10 volumes methanol. The suspension was filtered and dried in vacuum oven to give the purified polymer.

*Poly{4-(5-(2,5-bis(2-ethylhexyloxy)-4-(thiophen-2-yl)phenyl) thiophen-2-yl)benzo[c][1,2,5]thiadiazole} (**JC2**):* From **2a** (246.2 mg, 0.50 mmol) and **7a** (313. 02 mg, 0.50 mmol) as described above.- Yield: 170 mg (30%).

*Poly{4-(5-(2,5-bis(2-hexyldecyloxy)-4-(thiophen-2-yl)phenyl) thiophen-2-yl)benzo[c][1,2,5]thiadiazole} (**JC3**):* From **2b** (513.5 mg, 0.704 mmol) and **7a** (440.1 mg, 0.704 mmol) as described above. Yield: 215 mg (23%).

*Poly{4-(5′-(2,5-bis(2-hexyldecyloxy)-4-(thiophen-2-yl)phenyl)-2,2′-bithiophen-5-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole} (**JC4**):* From **2b** (632.0 mg, 0.708 mmol) and **7a** (443.0 mg, 0.708 mmol) as described above. Yield: 242 mg, 23%. From **2b** (g, mmol) and **7b** (g, mmol) as described above. Yield: 180 mg, (26%).

2.2. Device preparation

The photovoltaic cells were fabricated on glass substrates coated with a patterned indium tin oxide (ITO) layer to give an active area of 2 or 0.5 cm^2. The substrates were first ultrasonically cleaned in water and 2-propanol then poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was spin coated on top, cleaned with water and dried at 150 °C. The substrates were transferred to a glove box where they were heated at 150 °C for 5 min. A solution of polymer:PCBM in dichlorobenzene, with a concentration of 50 mg/mL, were spin coated on the PEDOT:PSS layer and allowed to dry and the contacts cleaned with dichlorobenzene. They were transferred to a vacuum chamber, where the aluminum electrode was applied by thermal evaporation at a pressure below 6×10^{-6} mBar. The system was brought to atmospheric pressure and the solar cells analyzed immediately after.

3. Results and discussion

3.1. Synthesis

The dithienyl-dialkoxy donors **4a** and **4b** were prepared as outlined in Scheme 1. 1,4-dihydroxybenzene was alkylated with either 2-ethylhexyl bromide as described by Egbe et al. [18] or 2-hexyldecyl bromide in the presence of sodium hydroxide in DMSO to yield the dialkoxybenzenes **1a** and **1b**. These compounds were then subjected to bromination giving the 2,5-dibromo-1,4-dialkoxy-benzenes (**2a** and **2b**). Thiophene groups were introduced by Stille coupling with 2-tributyltin-thiophene to give **3**. Finally, the donor monomer **4** was obtained by bromination with N-bromosuccinimide (NBS). Compound **3** has previously been prepared via Suzuki coupling of 3 with thiophene-2-boronic acid, followed by bromination to the monomer **4** [19].

The dithienyl acceptor monomer was prepared as shown in Scheme 2 by a Stille coupling of 2,4-dibromo-benzothiadiazole (**5**) with 2-tributylstannylthiophene as described by Hou et al. to give **6** [20]. Lithiation with *n*-butyl lithium followed by reaction with trimethyl tin chloride gave the acceptor monomer **7a** or with tributyl tin chloride to give **7b**.
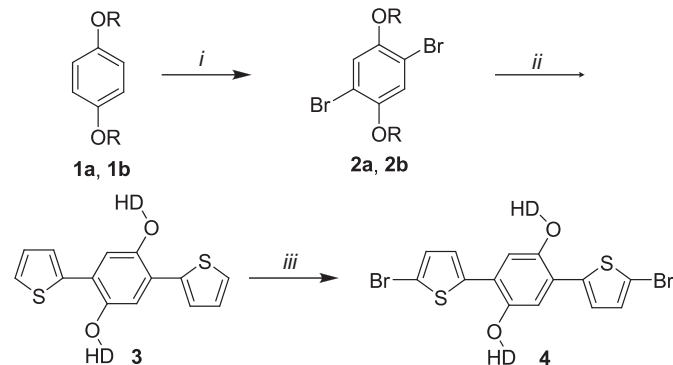
Scheme 1. Synthesis of the donor monomer 4. 1a: 54.5%, 1b: 40.5%. (*i*) Br$_2$ (2a: 84%, 2b: 92.6%), (*ii*) 2-(Tributyltin)-thiophene, Pd(PPh$_3$)$_4$, (3: 75.1%), (*iii*) NBS, (4: 60.2%). HD: 2-hexyldecanyl. R: 2-ethylhexyl or 2-hexyldecanyl.
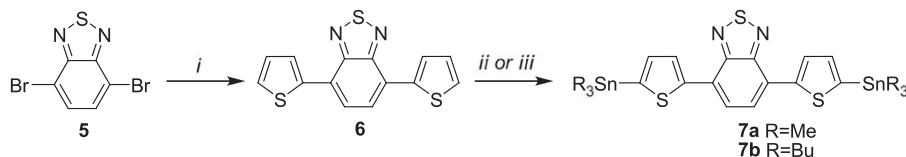
Scheme 2. Synthesis of the acceptor monomer 7a (R=methyl) and 7b (R=butyl). (*i*) 2-(tributylstannyl)thiophene, PdCl$_2$(PPh$_3$)$_2$, (89%), (*ii*) THF, LDA, trimethyltin chloride, (7a: 63.6%), (*iii*) THF, LDA, tributyltin chloride, (7b: 63.6%).
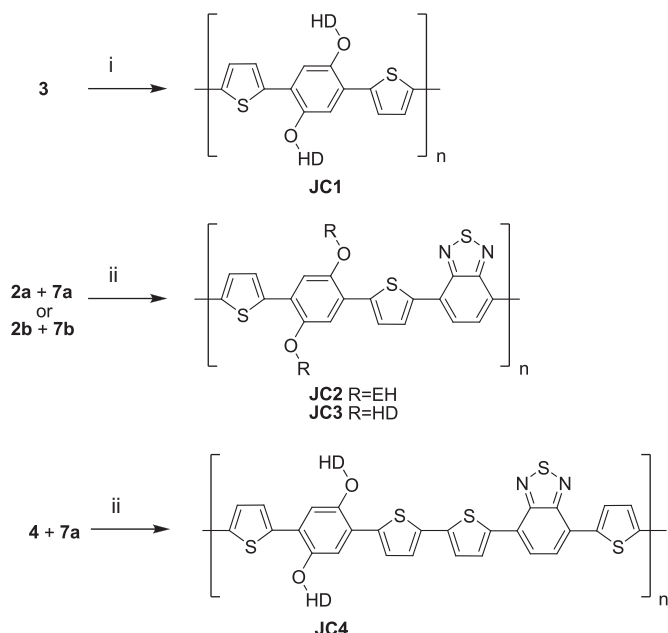
Scheme 3. Synthesis of four polymers JC1, JC2, JC3 and JC4. (i) FeCl₃ in CHCl₃ (ii) toluene, tri-o-tolylphosphine, tris-(dibenzylidene acetone) dipalladium(0).

The four different polymers were then prepared according to Scheme 3. Homo polymerization of monomer **3** with anhydrous ferric chloride in chloroform gave the simple polymer **JC1** with alternating thiophene and 1,4-dialkoxybenzene moieties. A very similar polymer with octyl groups instead of the hexyldecanyl groups of **JC1** has previously been reported by Pelter et al [21]. We also tried to prepare a similar polymer from an octyl substituted analog to **4**, but found the resulting material to be very insoluble. Generally it is found that the alkyl side chains should have roughly the same number of atoms other than hydrogen as in the main chain to obtain solubility in normal organic solvents. It should be noted that alkoxy groups prefer an "in-plane" arrangement between the alkyl group and the benzene ring as opposed to simple alkylarenes [22]. The monomers **2a** and **2b** together with the acceptors **7a** and **7b** were then used to prepare donor–acceptor type polymers **JC2** and **JC3** by a Stille type coupling, differing only in the alkyl side chains. Finally, a donor–acceptor polymer **JC4** with bithiophene units separating the dialkoxybenzene and benzothiadiazole groups were prepared from monomer **4** and the acceptor monomer **7a**.

3.2. Characterization of the polymers

The four polymers were characterized by size exclusion chromatography (SEC) and shown to be of small to medium molecular weight (5200 to 16000 MW) which is not unusual for polymers prepared through the Stille type coupling method. Absorption spectra of the polymers were obtained both in chloroform solution and of films cast on glass slides (see Fig. 1a and b). In the case of the polymer **JC1** with no acceptor groups one absorption peak with a maximum at 476 nm in solution was observed. This is comparable to the spectrum of P3HT and indicates a good conjugation between the thiophene and benzene moieties. In the absorption spectrum of the film the maximum is red shifted by a small amount to ca. 479 nm and vibronic structures are clearly visible. This behavior resembles that of P3HT and may indicate some inter chain interactions and ordering in the film [23]. Introduction of the benzothiadiazole acceptor group into the polymers **JC2**, **JC3** and **JC4** changes the absorption
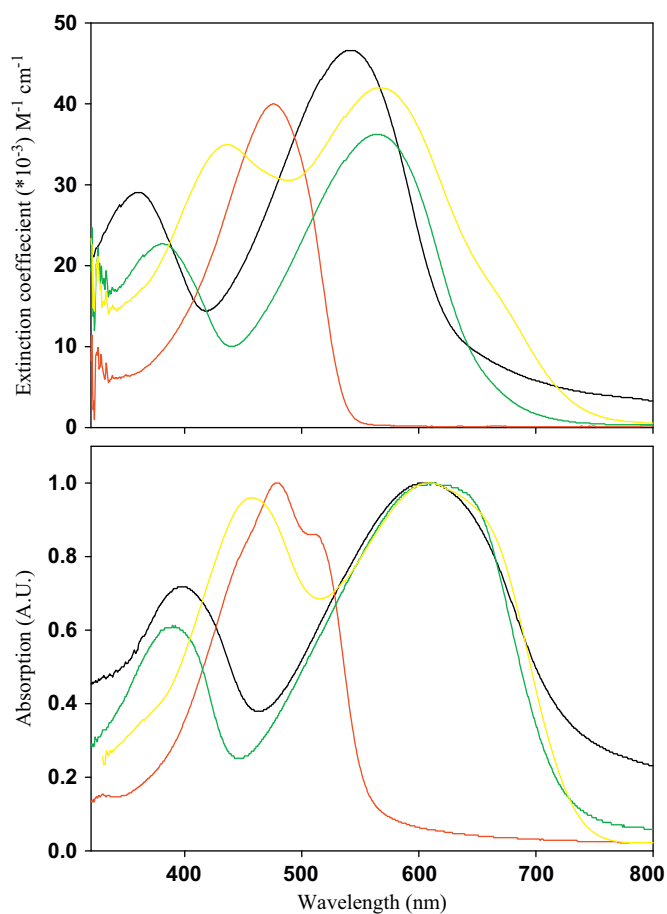

Fig. 1. Absorption spectra of the polymers in chloroform solution (top) and absorption spectra of films spin coated on glass (bottom, normalized); **JC1** (red), **JC2** (black), **JC3** (green) and **JC4** (yellow) spin coated on glass slides. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

spectra dramatically. The π–π* transition band is blue shifted and a new stronger band around 550 nm appears. This band is presumably due to a charge transfer transition between the thiophene/benzene donor and the benzothiadiazole acceptor groups similar to that observed for other polymers of this type. The solution spectra of **JC2** and **JC3** are somewhat similar, each having two maxima at 349/381 and 542/563 nm. These maxima are red shifted in the spectra of the films of the two polymers to ca. 392/394 and ca. 613/608 nm. In the case of **JC4** the most significant change is seen in the position of the π–π* transition that is moved to 439 nm in solution and to ca. 458 nm in the film. Compared to **JC2** and **JC3** these shifts are related to the exchange of the thiophene for the bithiophene donor unit. The effect is to close the rather pronounced gap between the two absorption bands, but at the same time absorption in the ultraviolet region up to ca. 350 nm is lost. The CT transition band for all three donor–acceptor polymers are broadened in the film spectra lowering the optical band gap to ca. 1.7 eV (Table 1).

Absorption spectra were also obtained of the finished devices using a spectrometer/light source equipped with an optical fiber. The light from the lamp passed through the device and was reflected by the aluminum back electrode through the film and into the optical fiber connected to the spectrometer. These conditions are similar to those experienced by the device under normal operation and include the double passage of light and interference and are therefore a better measure of the light that can actually be harvested (Fig. 2). The absorption features are

Table 1
Molecular weight and optical data for the four polymers.

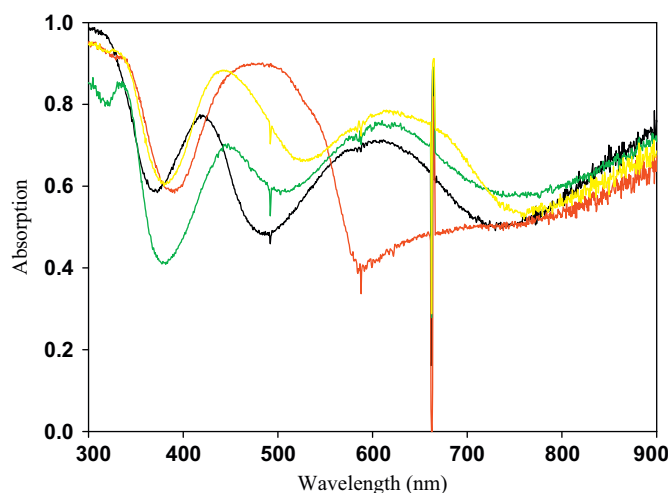| Polymer	Mw (kDa), PD	λ_{max} (nm) (ε) solution (CHCl$_3$)	λ_{max} (nm) film	Band gap (eV)
JC1	11.7, 2.4	476 (40.000)	479	2.22
JC2	5.2, 3.2	349 (29.000), 542 (47.000)	392, 607	1.70
JC3	16.2, 2.2	381 (23.000), 563 (36.000)	394, 613	1.71
JC4	10.9, 2.3	439 (35.000), 566 (42.000)	458, 608	1.69

Fig. 2. Absorption spectra of the finished photovoltaic devices. **JC1** (red), **JC2** (black), **JC3** (green) and **JC4** (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Grazing incidence wide angle X-ray scattering data as recorded for the thin film of polymer **JC1** with colors representing intensity on a log scale. The detector area covers up to a scattering vector modulus $q \sim 3.5$ Å^{-1} ($q = 4\pi \sin(\theta)/\lambda$), 2θ is the scattering angle, λ is the X-ray wavelength). The indices refer to the first 3 orders of the proposed lamellar stacking diffraction peaks.

Fig. 4. IPCE for the photovoltaic devices based on the polymers **JC3** (red) and **JC4** (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

similar to those obtained in the standard film spectra (Fig. 1b), but modulated by interference and the absorption due to the other layers of ITO and PEDOT. A new distinct minimum below 400 nm is observed corresponding to a decrease in the absorption of the $\pi-\pi^*$ band, especially for the donor–acceptor polymers **JC2**, **JC3** and **JC4**, whereas it has been broadened considerably for the **JC1** polymer.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) patterns were obtained from thin films of the polymers, spin coated from chloroform solution on a Si substrate, using the custom designed GIWAXS setup described in Ref. [24]. By orienting the substrate surface at or just below the critical angle for total reflection with respect to the incoming X-ray beam ($\sim 0.2°$), scattering from the deposited film is maximized with respect to scattering from the substrate. In the wide angle scattering range ($> 5°$), the X-ray scattering is sensitive to crystalline structure. The polymers **JC2**, **JC3**, and **JC4** yielded no diffraction signal at all, presumably forming completely amorphous films, whereas a strong diffraction pattern was obtained from the **JC1** polymer film (Fig. 3), resembling the patterns typically obtained for spin-coated poly(3-alkylthiophenes) [25]. Adopting a similar structural model, i.e. with the aromatic planes oriented perpendicular to the substrate surface, we obtain a lamellar spacing of 13.8(1) Å from an average of the 100, 200 and 300 peak positions. This is a remarkably short distance, considering the relatively long and branched side chains as compared to e.g. poly(3-hexylthiophene) that packs with a lamellar spacing of 16.7 Å [25b]. According to Kline et al. [26] however, the lower side-chain attachment density, as compared to poly(alkylthiophenes), allows a much higher degree of
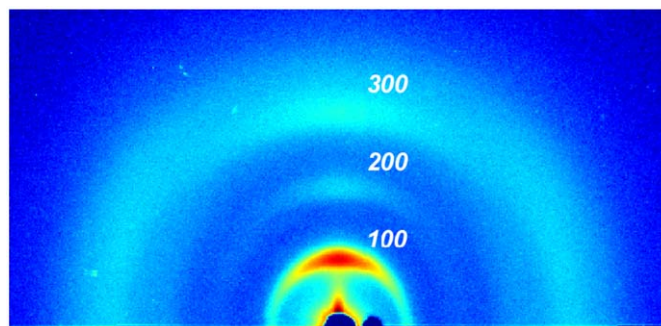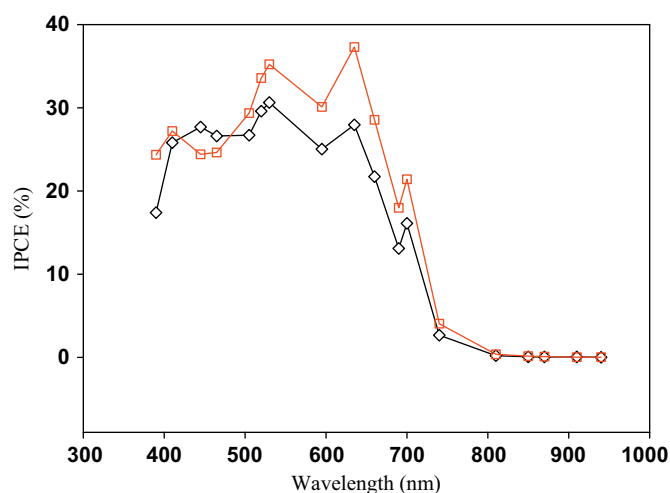
side-chain interdigitation, leading to shorter interlamellar distances. For the assumed structural and textural model, we would expect to find the diffraction features corresponding to the packing of the aromatic planes (commonly referred to as the π-stack) somewhere in the substrate plane (horizontal in Fig. 3). Although there is slightly increased in-plane intensity at a scattering vector corresponding to a d-spacing of ~ 4.3 Å, this is severely masked by the strong scattering halo, presumably originating from disordered side chains.

The incident photon to electron efficiency (IPCE) was measured for a photovoltaic device based on polymers **JC3** and **JC4**, using a LED lamp with 18 different wavelength diodes as described earlier (see Fig. 4) [27]. The outline of the IPCE is roughly equivalent to the absorption curve shown in Fig. 2. A modest level of ca. 25–35% was found in the 400 to 700 nm range proving that both absorption bands of this polymer contribute efficiently to the charge carrier generation. The low quantum yield can possibly be attributed to a non optimal device geometry and carrier recombination.

3.3. Photovoltaic devices

Photovoltaic devices were prepared from each of the four polymers blended with the electron acceptor PCBM in the ratio

1:1 or 1:1,5 with the geometry: Glass/ITO/PEDOT/Polymer:PCBM/Aluminum as described in the experimental section.

IV scans of the devices were carried out under AM1.5G conditions with a calibrated solar lamp and the data were used to extract the solar cell properties. Representative results are shown in Fig. 5 and Table 2. Modest short circuit current densities (J_{sc}) of 2.6 mA/cm^2 were obtained for the devices based on the polymer **JC1** without the benzothiadiazole acceptor group, while the three other donor–acceptor polymers **JC2**, **JC3** and **JC4** gave current densities from 4.1 to 4.7 A/cm^2. All devices had about the same open circuit voltage (V_{oc}) of 0.56 to 0.67 V which is low compared to the optical band gap. The effect of incorporating the acceptor groups into the polymers are also clearly illustrated in the doubling of the efficiency (η_e) from 0.4% (**JC1**) to 1% or above (**JC2**, **JC3** and **JC4**). The differences in the device parameters for the three donor–acceptor polymers are not conclusive although the highest efficiency was obtained for those based on **JC3** (2.2%) and **JC4** (1.5%). This may be ascribed to the somewhat higher fill factor of these particular devices.

3.4. Structure property relationship

The photovoltaic properties of the four polymers reflect the differences in their internal structure. As can be seen from Table 2, the short circuit current density is much smaller for **JC1**, than that of **JC2**, **JC3** and **JC4**, which are comparable. This is in accordance with the spectral properties of the polymers where **JC1** has only one strong absorption band at 479 nm, while **JC2**, **JC3** and **JC4** have an extra CT band at 610 nm and are therefore able to harvest
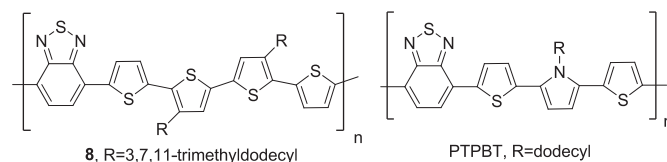
Scheme 4. Related polymers from the literature.

a much greater range of the visible spectrum. There seems to be no added benefit from the extra thiophene ring incorporated in **JC4** compared to **JC2** and **JC3**. Indeed the highest efficiency was obtained for **JC3**. This group of polymers can also be compared to similar low band gap polymers reported in the literature (see Scheme 4). A polymer (**8**) with four thiophene groups as donor groups and a benzothiadiazole unit as the acceptor group was investigated by Bundgaard and coauthors [28,29]. The photovoltaic properties of devices based on polymer **8** and PCBM gave efficiencies up to 0.90%, (V_{oc}: 0.62 V, J_{sc}: 3.61 mA/cm^2). Another relevant comparison is with the PTPTB polymer resembling **JC2** and **JC3**, with an N-alkyl pyrrole unit instead of the dialkoxy benzene group. The photovoltaic properties of devices based on PTPTB/PCBM gave efficiencies up to 1.0%, (V_{oc}: 0.72 V, J_{sc}: 3.1 mA/cm^2) [30,31].

The optical and photovoltaic properties thus seem rather insensitive to the exact chemical nature of a donor group in this position in the polymer whether it is a thiophene, a pyrrole or an 1,4-dialkoxybenzene group.

4. Conclusions

Four new conjugated polymers **JC1**, **JC2**, **JC3** and **JC4** composed of thiophene, 1,4-dialkoxybenzene and benzothiadiazole groups have been prepared. The main advantage of incorporating the dialkoxybenzene group into the polymer structure is its symmetrical nature that obviates region selective synthetic procedures as in the case of alkyl thiophenes. It is also of value that two solubilizing groups can be incorporated with one simple monomer unit. The chemical differences were designed to investigate the effect of substituting a thiophene group for a dialkoxybenzene group would have on the optical and photovoltaic device properties. The **JC1** polymer with alternating dialkoxybenzene and thiophene groups could be compared to the all thiophene polymer P3HT. Spectroscopy revealed similarities both in the position of the absorption band and also the appearance of vibronic fine structure in the solid phase spectra. This similarity is further underlined by the results of the X-rays scattering experiments, that revealed a crystalline structure and texture very akin to that observed for P3HT. Introduction of the benzothiadiazole acceptor into the polymers **JC2** and **JC3** resulted, as expected, in a new absorption band ascribed to a charge transfer transition, similar to other low band gap polymers reported. The increased size of the side chains in **JC3** compared to those in **JC2** improved solubility, but left the optical properties almost unchanged, except for a somewhat smaller molar extinction. Polymer **JC4** with extra thiophene units had the π–π* transition red shifted compared with **JC2** and **JC3** by ca. 60 nm in the solution spectra. A less pronounced but significant red shift was also observed in the spectra of the polymer in the solid state.

No stability studies have been performed with these new materials, but we have noted a tendency for devices to degrade fairly rapidly. The cause of this degradation has not been established and must await further investigations.

The IPCE of the devices based on **JC3** and **JC4** covered the region from 400 to 740 nm demonstrating efficient charge carrier
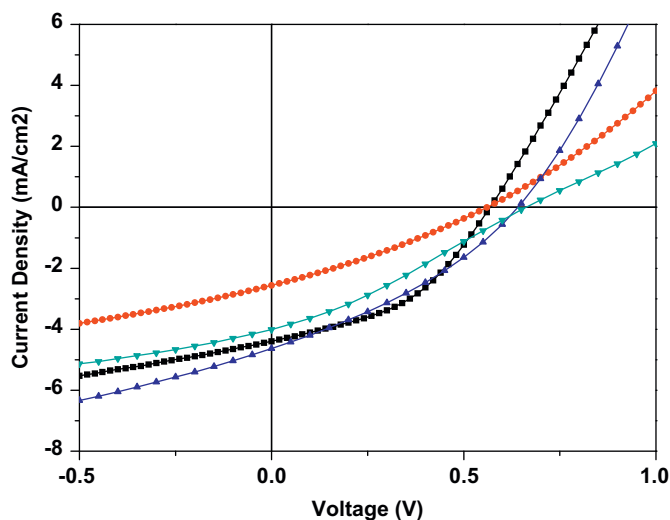

Fig. 5. Representative IV scans for the photovoltaic devices under AM1.5 conditions. **JC1** (red circles), **JC2** (blue triangles), **JC3** (green triangles) and **JC4** (black squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Photovoltaic parameters for selected devices with the structure glass/ITO/PEDOT/polymer:PCBM (1:1)/Al.

Polymer	Polymer/PCBM	Jsc (mA/cm^2)	Voc (V)	FF (%)	η (%)
JC1	1:1	2.6[a]	0.56	29	0.4
JC2	1:1	4.6[a]	0.64	33	1.0
JC3	1:1.5	4.7[b]	0.67	52	2.2
JC4	1:1	3.6[b]	0.63	49	1.5

[a] Measured at 100 mW/m^2 and with an active area of 2 cm^2.
[b] Measured at 74 mW/m^2 and with an active area of 0.5 cm^2.

generation from the entire visible spectrum although with a modest yield. IV scans of photovoltaic devices under AM1.5 G illumination showed that incorporation of the benzothiadiazole acceptor increased the short circuit current density (J_{sc}) from 2.6 to 4.7 mA/cm^2, whereas the open circuit voltage (V_{oc}) increased from 0.56 to 0.67 V. A low fill factor limited the power conversion (η) to 0.4% for a device based on the **JC1** polymer, 1% for the device based on **JC2** and 1.5% for the device based on **JC4**, while polymer **JC3** gave the most successful devices with an efficiency of 2.2%.

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