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A comparison of the photovoltaic response of head-to-head and head-to-tail coupled poly{(benzo-2,1,3-thiadiazol-4,7-diyl)-(dihexyl[2,2']dithiophene-5,5'-diyl}

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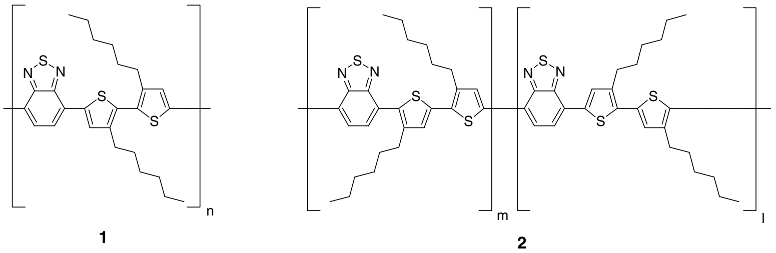
Summary

The synthesis of two copolymers of benzothiadiazole and dihexyldithiophene were obtained by employing oxidative ferric chloride polymerisation and Stille cross coupling polymerisation. Weight average molecular weights of respectively 15200 g mol^{-1} and 3200 g mol^{-1} were obtained. The polymers have an optical band gap of ~2 eV. Photovoltaic devices were prepared using the pure polymer materials and mixtures of the polymers and a soluble fullerene derivative. Efficiencies of 0.024% were obtained. Head-to-head and head-to-tail coupling was not found to influence the maximum photovoltaic performance that could be obtained.

Introduction

Recent developments within the field of polymer photovoltaics [1-3] have demonstrated photovoltaic conversion efficiencies of 3.8% [4] and shown the possibility of reaching the benchmark of 5% efficiency. [5] Common to most conjugated polymer systems employed for polymer photovoltaics is a poor match of the absorption spectrum of the material to the solar spectrum. A lowering of the bandgap to values found for inorganic semiconductors like silicon is of interest and is expected to open for the possibility for an increase in efficiency. [6,7]



1

2

Scheme 1. Copolymers of benzothiadiazole and head-to-head coupled dihexyldithiophene (**1**) and head-to-tail coupled dihexyldithiophene (**2**).

In this paper we present the simple synthesis of a copolymer of benzothiadiazole and dihexyldithiophene by two different polymerisation mechanisms and demonstrate a band gap of ~2 eV for both methods of preparation.

Experimental

Methods. Commercially available compounds were purchased from Aldrich. 3,4'-Dihexyl[2,2']dithiophene was obtained as described in ref. [8], 4,7-dibromo-benzo-2,1,3-thiadiazole was prepared as described in ref. [9] Two alkyl group signals are missing in the ^{13}C NMR for compound **5**. This is ascribed to accidental isochrony.

Poly{(benzo-2,1,3-thiadiazol-4,7-diyl)-(3,3'-dihexyl[2,2']dithiophene-5,5'-diyl} (1). To a mixture of $FeCl_3$ (801.2mg, 1.13 mmol) in $CHCl_3$ (120mL) di-(3-hexyl-thiophene)-benzothiadiazole (1.01g, 2.15 mmol) in $CHCl_3$ was added drop wise. The reaction was left stirring for 25 hours. After 25 hours of reflux the reaction was cooled, washed with aq. H_2SO_4, aq. Na_2SO_3, separated, dried ($MgSO_4$), filtered and evaporated to a smaller fraction, which was poured into MeOH. The suspension was filtered to give poly-(di-(3-hexyl-thiophene)-benzothiadiazole) as a red solid. Yield: 150mg (15%). ^{1}H NMR (250MHz, $CDCl_3$, 300K, TMS): δ= 0.91-0.84 (m, 6H), 1.49-1.26 (m, 12H), 1.72-1.66 (m, 4H), 2.74-2.68 (m, 4H), 7.89 (s, 2H), 8.11 (s, 2H). SEC (500Å + 10000Å + 1000000Å) $M_w = 15244$; $M_p = 13605$; $M_w/M_n = 2.87$; DP = 11.

Poly{(benzo-2,1,3-thiadiazol-4,7-diyl)-(3,4'-dihexyl[2,2']dithiophene-5,5'-diyl} (2). Compound **4** (4.005g, 6.066 mmol) and 4,7-dibromo-benzo-2,1,3-thiadiazole (1.783 g, 6.066 mmol) were mixed in DMF (75 mL) and degassed with argon. $Pd(PPh_3)_2Cl_2$ (80.0mg, 0.11 mmol) was added and the reaction was heated to 150°C. After 2 hours a dark tarry mass separated (prepolymer, SEC: $M_w = 1824$; $M_p = 1564$; $M_w/M_n = 1.19$). The mixture was cooled and THF (150mL) was added followed by reflux overnight. The mixture was cooled and the THF evaporated. MeOH (400mL) was added. The mixture was filtered and the solid washed with MeOH (3 x 100mL) and dried. Yield: 2.6g (92%). The product was found to contain 583 ppm palladium nanoparticles that were removed. ^{1}H NMR (250MHz, $CDCl_3$, 300K, TMS): δ= 0.91-0.79 (m, 6H), 1.78-1.22 (m, 16H), 2.73-2.61 (m, 2H), 2.96-2.80 (m, 2H), 7.17-6.94 (m, 0.5H), 7.52-7.46 (m, 0.5H), 7.74-7.67 (m, 1H), 7.94-7.84 (m, 1H), 8.07-7.97 (m, 1H). SEC (100Å + 1000Å) $M_w = 3205$; $M_p = 1971$; $M_w/M_n = 1.43$; DP = 5.

5-Tributylstannyl-3-hexylthiophene (3). To a solution of 3-hexylthiophene (33.6g, 0.2 mol) in dry THF (300mL) cooled to –78°C under argon, LDA in THF/ ethylbenzene/heptane (2M, 100mL, 0.2 mol) was added drop wise. At the end of the addition the mixture was allowed to reach 0°C in 3h. The mixture was then cooled back down to –78°C and tributylstannylchloride (63.6 g, 0.2 mol) was added in one portion. The mixture was then allowed to reach room temperature. Hexane (300 mL) was added to the reaction mixture was washed with water, dried ($MgSO_4$), filtered, evaporated and destilled to give 3-hexyl-5-tributylstannylthiophene. Yield: 95.36g (52%), bp = 136-138°C/5mBar. ^{1}H NMR (250MHz, $CDCl_3$, 300K, TMS): δ= 0.94-0.89 (m, 12H), 1.16-1.03 (m, 6H), 1.43-1.29 (m, 12H), 1.68-1.53 (m, 8H), 2.97 (t, 2H, J= 7.75Hz), 6.98 (s, 1H), 7.20 (s, 1H); ^{13}C NMR (63MHz, $CDCl_3$, 300K, TMS): δ= 11.28, 14.19, 14.60, 23.25, 27.83, 29.69, 29.75, 30.58, 31.35, 32.37, 126.12, 136.25, 137.18, 144.59; Anal. Calcd for $C_{22}H_{42}SSn$: C, 57.78; H, 9.26. Found: C, 55.70; H, 9.28.

4,7-Bis(3-hexylthiophene-5-yl)benzo-2,1,3-thiadiazole (4). To a solution of 4,7-dibromo-2,1,3-benzothiadiazole (23.36g, 0.08 mol) and 5-tributylstannyl-3-hexylthiophene (**3**) (91.45g, 0.20 mol) in THF (300mL), $Pd(PPh_3)_2Cl_2$ (3.14g, 4.49 mmol) was added. The reaction was refluxed. After 2 hours futher 5-tributylstannyl-3-hexylthiophene (**3**) (91.45g, 0.20 mol) and $Pd(PPh_3)_2Cl_2$ (3.14g, 4.49 mmol) were added. Further $Pd(PPh_3)_2Cl_2$ (0.5 g, 0.7mmol) was added after 3 and 24 hours. After 2 days the reaction was cooled, evaporated and purified by flash chromatography ($CHCl_3$). Recrystalisation from EtOH gave the product as orange crystals. Yield: 8.2g (22%), mp = 60.6-61.6°C. ^{1}H NMR (250MHz, $CDCl_3$, 300K, TMS): δ = 0.90 (6H, t, *J*= 6.75Hz), 1.45-1.26 (12H, m), 1.74-1.65 (4H, m), 2.70 (4H, t, *J*= 7.5Hz), 7.04 (2H, d, *J*= 0.75Hz), 7.83 (2H, s), 7.98 (2H, d, *J*= 1.25Hz); ^{13}C NMR (63MHz, $CDCl_3$, 293K, TMS): δ= 14.79, 23.33, 29.75, 31.18, 31.36, 32.41, 122.22, 126.23, 126.75, 129.71, 139.72, 145.07, 153.36. Anal. Calcd. for $C_{26}H_{32}N_2S_3$: C, 66.62; H, 6.88; N, 5.98. Found: C, 66.70; H, 6.70; N, 5.89.

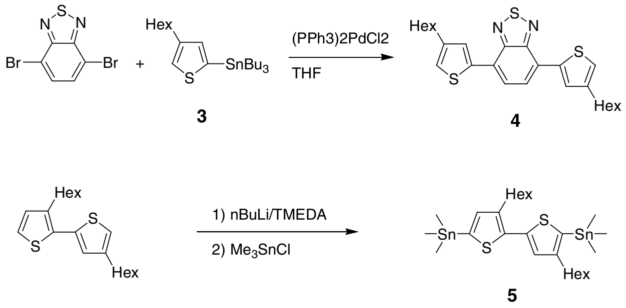
5,5'-Bis(trimethylstannyl)-3,4'-dihexyl[2,2']dithiophene (5). Dihexylbithiophene (3.34g, 10 mmol) was mixed with hexane (30mL) and TMEDA (3g, 25 mmol) and cooled to –78°C. nBuLi (16mL, 1.6M, 25 mmol) was added and the cooling bath was removed and the mixture was left overnight at RT. The following day a thick paste had formed. The mixture was cooled to –78ºC and Me_3SnCl (25 mL, 1M, 25 mmol) was added and the mixture was allowed to reach RT. After stirring at RT for 1h hexane (500mL) was added and the mixture was washed thoroughly with water and brine. Drying and evaporation gave the pure product. Yield: 6.3g (95%) ^{1}H NMR (250MHz, $CDCl_3$, 300K, TMS): δ= 0.42 (m, 9H), 0.45 (m, 9H), 0.95 (m, 6H), 1.34 (m, 12H), 1.68 (m, 4H), 2.65 (t, 2H, J=7Hz), 2.83 (t, 2H, J=7Hz), 7.04 (s, 1H), 7.14 (s, 1H); ^{13}C NMR (63MHz, $CDCl_3$, 300K, TMS): δ= -8.25, -7.84, 14.12, 22.65, 29.16, 29.31, 29.38, 30.82, 31.68, 31.82, 32.04, 32.88, 127.90, 131.72, 135.63, 137.01, 138.26, 140.14, 141.74, 151.11; Anal. Calcd for $C_{26}H_{46}S_2Sn_2$: C, 47.30; H, 7.02. Found: C, 47.29; H, 6.89.

Size exclusion chromatography (SEC). SEC was performed in chloroform using either of two preparative Knauer systems employing a pre-column and two gel columns in succession with respectively pore diameters of 100Å and 1000Å or 500Å, 10000Å and 1000000Å. All gel columns had dimensions of 25mmØ x 600mm. Polystyrene standards were used for molecular weight determination.

Photophysical and photovoltaic methods. UV-vis spectra were obtained from chloroform solution. There was no significant red-shift when comparing solution spectra and solid film spectra. Photovoltaic devices were prepared by spincoating a 2.7µm microfiltered solution of the polymer (20mg) and PCBM (20mg) in chloroform:chlorobenzene/2:1 (1.5mL). The substrates were PEDOT:PSS coated ITO on glass slides. The typical film absorbance was 0.7-0.9 absorbance units. The films were then transferred to a vacuum chamber and pumped to a pressure < 5·10-6 mBar. The aluminium electrode (~150 nm) was applied by thermal evaporation. The active area of the devices were 3 cm^2. Devices were subsequently mounted using epoxy glue and measurements performed in the ambient atmosphere. The wavelength dependence of the photovoltaic response was performed using a set-up described earlier with additional lenses that improve the bandwidth and reduced the intensity a little. [10] IV-curves were recorded using a Keithley 2400 sourcemeter. Simulated sunlight was obtained by using a SolarKonstant 575 from Steuernagel Lichttechnik GmBH. The luminous intensity was set to 1000 W m^{-2} using a precision pyranometer from Eppley Laboratories. The spectral distribution was made as close to the AM1.5 standard as possible using a Neoceram UV-stop filter. The spectrum was monitored using an AvaSpec 2048 optical spectrum analyser from Avantes.

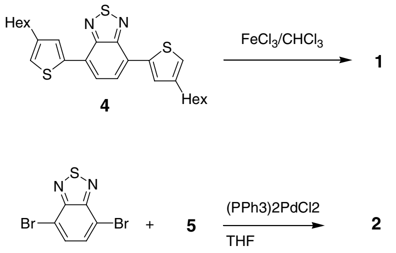
Results and discussion

Synthesis. The general synthetic procedures leading to conjugated polymers does not allow for directional synthesis where the two termini of the polymer chain have a different chemical nature. An excellent example is the polyalkylthiophenes that have been prepared in both regioregular and regiorandom forms. Ferric chloride oxidation generally gives regiorandom polymer materials whereas palladium catalysis has also been demonstrated to give regiorandom products. [11]



Scheme 2. Synthesis of the monomers **4** and **5**.

The regioregular polymers are most often obtained by a directional approach and have been employed with success for the polythiophenes by Negishi [11], Kumada [12] or Stille [13] polycondensation reactions. It should be mentioned that the physical properties of conjugated polymer materials prepared by palladium catalysis can be hampered by even tiny amounts of residual catalyst in the form of metallic palladium nanoparticles. [14] Our interest in this paper was to compare the photovoltaic response for head-to-head and head-to-tail coupled copolymers of dihexyldithiophene and benzothiadiazole.



Scheme 3. Synthesis of the polymers **1** and **2**.

The synthesis of the monomers were straight forward and involved in the case of the monomer for the head-to-head coupled polymer the regioselective lithiation of 3-hexylthiophene using LDA followed by reaction with tributylstannylchloride to give **3**. The subsequent reaction of **3** with 4,7-dibromo-benzo-2,1,3-thiadiazole gave **4** that was the monomer for the oxidative polymerisation using ferric chloride. The monomer for the head-to-tail coupled polymer involved dilithiation of 3,4'-dihexyl-[2,2']dithiophene with nBuLi in THF followed by reaction with trimethyl-stannylchloride to give **5** as an oil that was found to be somewhat unstable. It was generally used directly but could be kept for a few weeks in the dark under argon at room temperature. The synthesis is outlined in scheme 2.

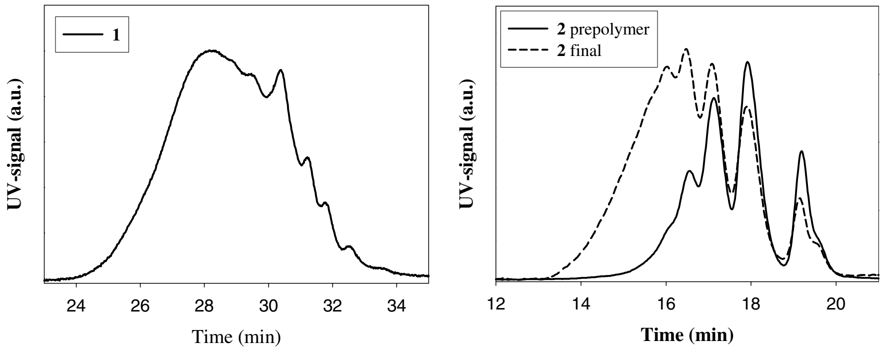


Figure 1. SEC traces of the polymers. Polymer **1** was analyzed on a gel column system column system comprising a succession of a 500Å, 10000Å and 1000000Å in pore diameter. Polymer **2** was analyzed column on a gel column system comprising a succession of a 100Å and 1000Å in pore diameter.

The polymerisation of **4** using ferric chloride in chloroform proceeded smoothly to give the regioregular polymer **1** with a moderate weight average molecular weight in the range of 15000 g mol^{-1}. The polymerisation using Stille cross coupling to give the head-to-tail coupled polymer **2** was best achieved by starting the polymerisation in DMF. This gave a prepolymer that separates as a slimy solid. Addition of THF at this point dissolved the prepolymer and allowed for continuation of the polymerisation reaction (scheme 3). The results from SEC analysis of the polymer products are shown in figure 1. Spin coating of **1** and **2** gave good films and it was decided to prepare photovoltaic devices in spite of the difference in molecular weight.

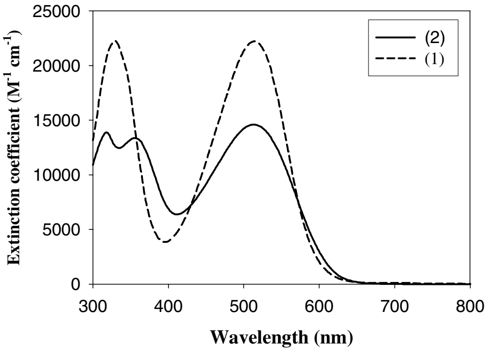


Figure 2. UV-vis spectra of the polymers **1** and **2** in chloroform solution.

Photophysical and photovoltaic measurements. The UV-vis spectra of the two polymers are similar in solution as shown in figure 2. The extinction coefficients at the maximum wavelength of absorption are 22300 M^{-1} cm^{-1} and 22200 M^{-1} cm^{-1} (λ_{max} = 330 nm and 514 nm) for **1** and 14000 M^{-1} cm^{-1}, 13000 M^{-1} cm^{-1} and 15000 M^{-1} cm^{-1} for **2** (λ_{max} = 318 nm, 356 nm and 514 nm). From the UV-vis spectra the bandgap is estimated to be 2 eV. The UV-vis spectra in solution and in the solid were very similar. The similarity of the UV-vis properties for the head-to-head and head-to-tail coupled polymers is in contrast to for instance the polyalkylthiophenes where a pronounced effect of the regioregularity is seen lowering the bandgap from 2.1 eV to

1.7 eV in the solid. [11] The photovoltaic devices based on the homopolymers gave as expected very low conversion efficiencies in the ppm range and fill factors, FF, close to 25%. It is noticeable that polymer **1** has an efficiency that is four times better than **2**. The open circuit voltage (V_{oc}) and the short circuit current (I_{sc}) are larger for **1** then for **2** (see table 1).

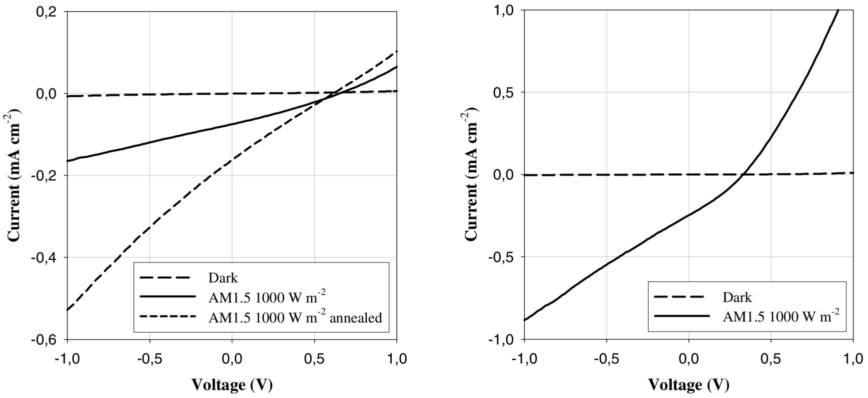


Figure 3. IV-curves for the polymers **1** (left) and **2** (right).

When a mixture of the soluble fullerene derivative PCBM [15] was mixed with the conjugated polymer material in a 1:1 w/w ratio the efficiency was increased by more than an order of magnitude in both cases and the efficiencies became similar (0.024%).

Table 1. Photovoltaic performance and dark resistance, R_d, of the devices (1000 W m^{-2}, AM1.5)

Compound	V_{oc} (V)	I_{sc} (μA cm^{-2})	FF (%)	R_d (kΩ)	η (%)
1	0.68	-7.4	25	74	0.0013
1+PCBM	0.65	-75	28	58	0.0140
1+PCBM (annealed)	0.61	-162	24	n.d.	0.0240
2	0.57	-2.4	25	57	0.0003
2+PCBM	0.33	-247	30	58	0.0240

Polymer **1** exhibited the phenomenon of annealing upon initial illumination whereas polymer **2** did not exhibit this. During illumination the sample quickly heats up to an equilibrium temperature of ~70°C. We ascribe the increase in efficiency in **1** by a factor of two to be due to annealing of the polymer material. This is supported by DSC measurements. They showed that **1** exhibits a glass transition in the 60 – 80 °C range. There were no thermal transitions for polymer **2**. The IV-curves are shown in figure 3 where it is evident that annealing in the case of **1** lowers V_{oc} but increases I_{sc}. The lifetimes of the devices were generally short and the short circuit decreased to less than 10% in 24 hours. The addition of PCBM increased the lifetime but the practical applications of these devices are limited to fundamental measurements on freshly prepared or annealed samples (see figure 4). The lifetime behavior of devices based on **1** and **2** were similar.

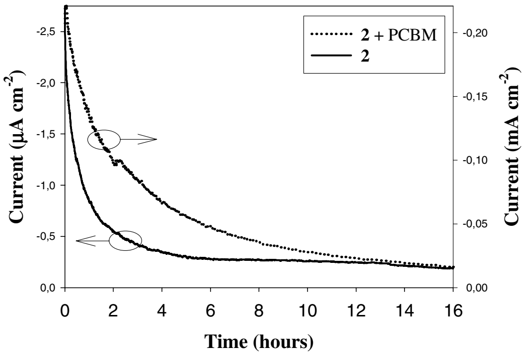


Figure 4. Lifetime curves for photovoltaic devices based on **2** monitored as I_{sc}.

The photovoltaic response as a function of the incident wavelength was finally monitored and the result is shown in figure 5 for devices based on **2** where the device absorption is shown along with I_{sc} as a function of the incident wavelength.

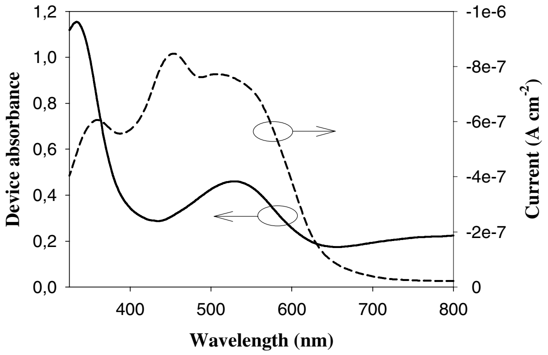


Figure 5. The device absorption (solid curve) and the photocurrent (grey curve). The broad weak band at 800 nm stems from the PEDOT:PSS layer. A plot of I_{sc} is also shown.

The photovoltaic response is symbatic with the absorption spectrum as expected. The decrease in the photocurrent below 350 nm is ascribed to the absorbance of the glass. The maximum for conversion of incident photons to electrons in the external circuit (incident photon to current efficiency, IPCE) is 0.6% at 450 nm. Polymer materials similar to **1** have been reported [16,17] while no photovoltaic data were given. Also copolymers of dithienylbenzothiadiazole with pyrrole [6,7] and dialkylfluorenes [18,19] have been employed in photovoltaics where efficiencies of respectively 1% and 2.4% were documented. Common to the literature results were a smaller bandgap with values down to 1.6 eV and the possibility for the incorporation of a much larger weight fraction of PCBM (a polymer:PCBM ratio of 1:3 and 1:4 w/w respectively). A large weight fraction of PCBM has been shown to be important for the efficient conduction of electrons. [20] In our case a 1:1 ratio was employed since the formation of good homogenous films could not be obtained with a higher ratio. Provided that good films could be obtained with a 1:3 or 1:4 w/w ratio of **1** or **2** and PCBM higher efficiencies would be expected.

Conclusions

We have presented the synthesis of two conjugated polymer materials based on copolymers of benzothiadiazole and dihexyldithiophene. The materials were characterised using NMR and SEC. The photovoltaic response of the materials were investigated and compared. We found the efficiency of homopolymer devices based on the head-to-head coupled material to be higher than for the head-to-tail material. The efficiency of devices based on mixtures of the polymer materials and the soluble fullerene derivative PCBM were however similar and too low to be of practical importance. The lifetimes of the devices were short but sufficient for physical measurements.

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References

1. Brabec CJ, Sariciftci NS, Hummelen JC (2001) Adv. Func. Mater. 11:15.
2. Spanggaard H, Krebs FC (2004) Sol. En. Mater. Sol. Cells 83:125.
3. Hoppe H, Sariciftci NS (2004) J. Mater. Res. 19:1924.
4. Waldauf C, Schilinsky P, Hauch J, Brabec CJ (2004) Thin Solid Films 451-452:503.
5. Brabec CJ (2004) Sol. En. Mater. Sol. Cells 83:273.
6. Dhanabalan A, van Duren JKJ, van Hal PA, van Dongen JLJ, Janssen RAJ (2001) Adv. Funct. Mater. 11:255
7. Brabec CJ, Winder C, Sariciftci NS, Hummelen JC, Dhanabalan A, van Hal PA, Janssen RAJ (2002) Adv. Funct. Mater. 12:709.
8. Kirschbaum T, Briehn CA, Bäuerle P (2000) J. Chem. Soc. Perkin. I 1211; Krebs FC, Spanggaard H (2005) Sol. En. Mat. Sol. Cells, In Press.
9. Pilgram K, Zupan M, Skiles R (1970) J. Hetercycl. Chem. 7:629.
10. Krebs FC, Jørgensen M (2003) Rev. Sci. Instr. 74:3438.
11. Chen TA, Wu X, Rieke RD (1995) J. Am. Chem. Soc. 117:233.
12. McCullough RD, Lowe RD, Jayaraman M, Anderson DL (1993) J. Org. Chem. 58:904.
13. Iraqi A, Barker GW (1998) J. Mater. Chem. 8:25.
14. Krebs FC, Nyberg RB, Jørgensen M (2004) Chem. Mater. 16:1313; Nielsen KT, Bechgaard K, Krebs FC (2005) Macromolecules 38: 658-659.
15. Hummelen JC, Knight BW, LePeq F, Wudl F, Yao J, Wilkins CL (1995) J. Org. Chem. 60:532.
16. Jayakannan M, van Hal PA, Janssen RAJ (2002) J. Pol. Sci. Part A 40:251.
17. Jayakannan M, van Hal PA, Janssen RAJ (2002) J. Pol. Sci. Part A 40:2360.
18. Svensson M, Zhang F, Veenstra SC, Verhees VJH, Hummelen JC, Kroon JM, Inganäs O, Andersson MR (2003) Adv. Mater. 15:988-991.
19. Inganäs O, Svensson M, Zhang F, Gadisa A, Persson NK, Wang X, Andersson MR (2004) Appl. Phys. A 79:31-35.
20. Geens W, Martens T, Poortmans J, Aernouts T, Manca J, Lutsen L, Heremans P, Borghs S, Mertens R, Vanderzande D (2004) Thin Solid Films 451-452:498-502.