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# Synthesis of Poly(4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-*alt*-2,1,3-benzothiadiazole) (PCPDTBT) in a Direct Arylation Scheme

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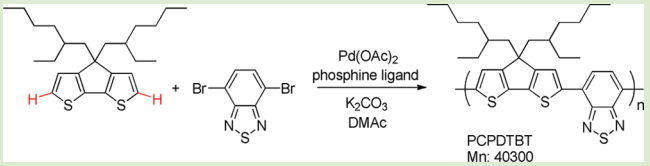
Supporting Information

**ABSTRACT:** Poly(4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene-*alt*-2,1,3-benzothiadiazole) (PCPDTBT), a potentially interesting low bandgap donor copolymer for bulk heterojunction-type organic solar cells with a power conversion efficiency >5.5%, can be now synthesized in a direct arylation scheme starting from 4,4-dialkyl-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene (CPDT) and 4,7-dibromo-2,1,3-benzothiadiazole (4,7-dibromo-BT) as monomers. The direct arylation procedure leads to PCPDTBT with an $M_n$ of up to 40 000 and circumvents the use of costly diboronic acid/ester or distannyl monomers.




High potential for future industrial applications as a photoactive component of bulk heterojunction-type organic solar cells (BHJ OSCs) resulted in rapidly increasing interest in low bandgap conjugated polymers, especially so-called alternating donor−acceptor copolymers that are composed of alternating electron-rich ("donor") and electron-deficient ("acceptor") aromatic building blocks.[1] The classical synthetic routes toward such copolymers are palladium-catalyzed AA/BB-type (hetero)aryl-(hetero)aryl cross couplings of dihaloarylene monomers and suitably functionalized bifunctional aromatic counterparts, mostly arylene diboronic acids/diboronic esters (Suzuki-type coupling) or distannyl arylenes (Stille-type coupling). Such transition metal-catalyzed cross couplings are today recognized as the most powerful tool for aryl−aryl bond formation. Applied to polymer synthesis the synthetic schemes involve the use of difunctional boron- or tin-functionalized aromatic anion equivalents, often as the most costly component. Moreover, aromatic stannyl derivatives and the resulting stannyl-containing byproduct after aryl−aryl coupling are toxic and environmentally risky compounds. Therefore, so-called direct arylation schemes that utilize unsubstituted arylene monomers in combination with the corresponding dihaloarylene components came into the focus of interest. Such direct arylations have been used in the synthesis of small molecules/oligomers, already with a focus on organic electronics applications.[2] Only a few examples have been published in the field of polymer synthesis. An early example reports a direct arylation approach toward poly(3-alkylthiophene)s.[3] Pioneering work in high molecular weight polyarylene synthesis by direct arylation have been published by Kanbara and co-workers for poly(fluorene-*alt*-tetrafluorobenzene)[4] or poly(fluorene-*alt*-dithiophene) derivatives[5] and by Leclerc and co-workers for poly(thienopyrroledione-*alt*-dithiophene).[6] High mean average molecular weights of 30 000−56 000 of these copolymers have been reported that can compete well with the corresponding values for structurally identical polymers prepared in Suzuki- or Stille-type cross coupling schemes. Another very attractive low bandgap-type target polymer for organic electronics applications is poly(4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-*alt*-2,1,3-benzothiadiazole) (PCPDTBT). Depending on the kind of the solubilizing alkyls in 4,4-position of the cyclopentadithiophene (CPDT) unit they can show a very high organic field-effect transistor (OFET) hole mobility of >5 $cm^2/(V\ s)$ or noticeably high power conversion efficiencies (PCE) of 3−5.5% in BHJ OSCs with PCPDTBT/PCBM or PCPDTBT/CdSe blends as the photoactive component.[7−9] The PCPDTBT copolymers for these device studies have been prepared both in Suzuki- or Stille-type cross coupling schemes.[10,11] Here, we would now like to present an alternate direct arylation route toward high molecular weight PCPDTBT using nonactivated 4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene and 4,7-dibromo-2,1,3-benzothiadiazole as coupling monomers. The target PCPDTBT is accessible in good yields (up to 80%) with mean average molecular weights $M_n$ of up to 40 000.

The polycondensation of the two monomers was carried out under different conditions, by varying the amount of palladium catalyst and/or phosphine ligands, solvents, and reaction time (Scheme 1, Table 1).

Table 1 summarizes the results of our direct arylation experiments. The crude products after aryl−aryl coupling have been solvent-extracted to remove low molecular weight byproducts (with methanol, ethyl acetate, and hexane). The following soluble dichloromethane (DCM) and chloroform fractions have been used in the calculation of molecular weights and yields (Table 2). First, we have focused on $Pd(OAc)_2$/$PCy_3{\cdot}HBF_4$ as a catalytic system since it was reported as a very

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**Scheme 1. Polycondensation of 4,4-Di(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT) and 4,7-Dibromo-2,1,3-benzothiadiazole to PCPDTBT**

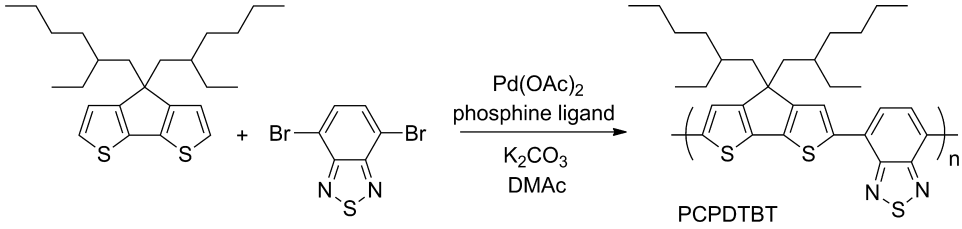


**Table 1. Polycondensation of 4,4-Di(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT) and 4,7-Dibromo-2,1,3-benzothiadiazole to PCPDTBT[a]**

| entry | catalyst (mol %) | phosphine ligand (mol %) | solvent | time (h) | $M_n$[b] | $M_w/M_n$[b] | yield (%)[c] |
|---|---|---|---|---|---|---|---|
| P1 | 4 | 8 | DMAc | 72 | 24600 | 3.91 | 80 |
| P2 | 4 | 8 | toluene | 72 | 2400 | 1.56 | 12 |
| P3 | 2 | 4 | DMAc | 72 | 22000 | 3.26 | 68 |
| P4 | 4 | none | DMAc | 72 | 36800 | 3.28 | 42 |
| P5 | 4 | 8 | DMAc | 24 | 19700 | 2.78 | 61 |
| P6 | 4 | none | DMAc | 24 | 40300 | 3.48 | 70 |

[a]Reactions were carried out at 110 °C using $Pd(OAc)_2$ as the catalyst, $PCy_3{\cdot}HBF_4$ as the ligand, and $K_2CO_3$ (1.5 equiv) in DMAc (10 mL). [b]Estimated by gel permeation chromatography (GPC) with polystyrene calibration. [c]Yield is based on the amount of high molecular weight DCM and chloroform fractions.

**Table 2. Distribution of Polymer**

| | amount of fraction (mg) | | |
|---|---|---|---|
| entry | hexane | DCM | chloroform |
| P1 | 9.9 | 248.8 | 482.6 |
| P2 | 105.9 | 102.4 | |
| P3 | 59.5 | 336.6 | 290.4 |
| P4 | n.d.[a] | 194.6 | 192.4 |

[a]Not determined.

effective catalyst for direct arylations.[5,12] In contrast to the literature reports we did not use pivalic acid as a further additive. Polycondensation in DMAc yielded PCPDTBT with a rather high molecular weight ($M_n$: 24 600) in good yield (80%, entry P1). Switching to toluene as a solvent (toluene is often used as effective solvent in PCPDTBT synthesis after Stille) only produces low molecular weight oligomers ($M_n$: 2400) in low yield (entry P2). Next we modified the reaction parameters by utilizing a different phosphine. Berrouard et al. reported maximum molecular weights in the synthesis of 5-alkyl[3,4-*c*]thienopyrrole-4,6-dione-based copolymers with tris(2-methoxyphenyl)phosphine as a ligand and $Pd(OAc)_2$ as a catalyst.[6] Based on their results we also tested this catalyst/ligand combination for PCPDTBT synthesis both in DMAc and toluene as solvents. However, this combination failed in both solvents. Going back to the original catalyst/ligand couple we decreased the amounts of catalyst (2 mol %) and ligand (4 mol %, entry P3). The molecular weight of the obtained product was quite similar ($M_n$: 22 000), but the PCPDTBT yield was reduced (compare to entry P1). Comparing entries P1 and P3 (Table 2) demonstrates that the reduced catalyst and ligand loading increases the percentage of the hexane-soluble, lower molecular weight fraction. This indicates that 4 mol % of Pd catalyst is preferred toward high yields.

Fujinami et al. have described the phosphine-free direct arylation of 3,3′,4,4′-tetramethylbithiophene and 2,7-dibromo-9,9-dioctylfluorene to poly(9,9-dioctylfluorene-*alt*-3,3′,4,4′-tetramethylbithiophene).[5] To clarify if the direct arylation synthesis of PCPDTBT is also possible under phosphine-free conditions, we carried out a ligand-free polycondensation in DMAc using 4 mol % Pd catalyst and 1.5 equiv of $K_2CO_3$ as the base. This polycondensation (entry P4) yielded a high molecular weight PCPDTBT ($M_n$: 36 800) in a moderate yield of 42%.

Next we checked the influence of the reaction time (initially 72 h) on the polycondensation. For a shorter reaction time (24 h) in the presence or absence of phosphine ligand ($PCy_3{\cdot}HBF_4$) we achieved high molecular weight PCPDTBT ($M_n$: 19 700 and 61% yield with $PCy_3{\cdot}HBF_4$, $M_n$: 40 300 and 70% yield without ligand, entries P5 and P6). The results for the ligand-free system are quite remarkable and agree with results of Hartwig and co-workers, who described a faster direct arylation under phosphine-free conditions.[13] Comparing P6 and P4, the two ligand-free direct arylation entries, the reduced yield after 72 h reaction time is caused by the formation of an increasing amount of cross-linked byproduct most probably via trisubstitution of CPDT cores.

Figure 1 exemplarily shows the $^1$H NMR spectrum of one PCPDTBT sample (entry P4) made by direct arylation. The $^1$H NMR spectrum of the direct arylation product P4 is very similar to one of a PCPDTBT sample ($M_n$: 10 000) that was made in a Stille-type cross coupling (see the Supporting Information). Two weak low field signals in the aromatic region of the $^1$H NMR spectrum of the direct arylation product at 8.2 and 8.6 ppm indicate a small amount of 3,6-disubstituted and/or 2,3,6-trisubstituted CPDT units. The UV−vis and PL spectra of two PCPDTBTs made after Stille or in a direct arylation (entry P4) show only very minor differences (Figure 2). The long wavelength UV−vis maxima are detected at 719 (Stille-type PCPDTBT) and 712 nm (direct arylation product). The PL maxima are recorded at 788 (Stille-type PCPDTBT) or 780 nm (direct arylation product, PL excitation at 620 nm). The reasons for the weak blue shifts in the optical spectra of the direct arylation products are not clear, but they may be caused by a slightly reduced regioregularity of the coupling regarding the CPDT units (see the discussion of the $^1$H NMR spectra).


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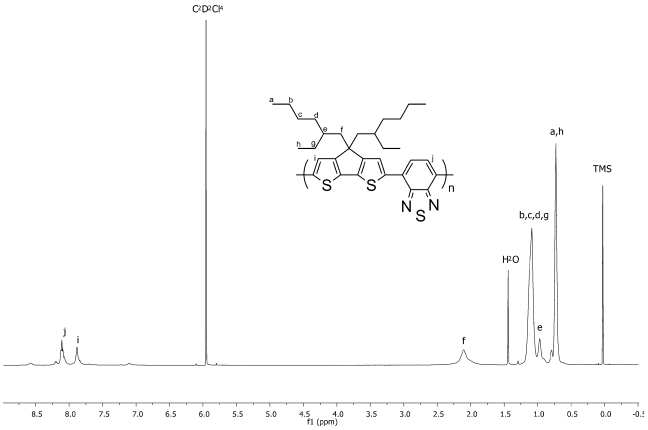


**Figure 1.** $^{1}$H NMR spectrum of PCPDTBT (entry P4, 600 MHz, in $C_2D_2Cl_4$, 80 °C).

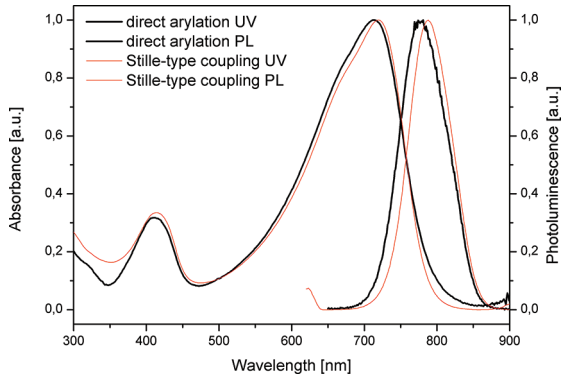


**Figure 2.** UV−vis and PL spectra of two PCPDTBTs made by direct arylation (entry P4) or Stille-type coupling (PL excitation wavelength: 620 nm).

In summary, direct arylation polycondensation is a new and efficient method for high molecular weight PCPDTBT synthesis. In contrast to conventional methods for PCPDTBT synthesis (Stille- or Suzuki-type coupling) the use of arylene dianion equivalents (diboronic acids/esters, distannyl arylenes) is no longer necessary. Furthermore, the direct arylation scheme works efficiently without additional phosphine ligands and with a relatively short reaction time (24 h).

## EXPERIMENTAL METHODS

Both condensation monomers have been prepared due to literature procedures.[14,15] The solvents have been used in commercial quality. All other reagents are commercially available and have been used without further purification. The preparation of PCPDTBT after Stille is described in the literature.[16]

A mixture of $Pd(OAc)_2$ (15.0 mg, 0.068 mmol), $K_2CO_3$ (353 mg, 2.55 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (500 mg, 1.70 mmol), and 4,4-di(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (685 mg, 1.70 mmol) was stirred in anhydrous dimethylacetamide DMAc (10 mL) for 72 h under argon atmosphere. After cooling to room temperature the reaction was quenched by addition of 10 mL of 6 M aqueous HCl, poured into chloroform, and stirred for further 30 min. After phase separation the organic layer was washed with aqueous ethylenediaminetetraacetic acid (EDTA) disodium salt, 2 M aqueous HCl, saturated aqueous $Na_2CO_3$ solution, and brine and finally dried over anhydrous magnesium sulfate. After removing the solvent the crude polymer was precipitated from $CHCl_3$ into acidified MeOH and purified by Soxhlet extraction with methanol, ethyl acetate, and hexane before collecting the higher molecular weight dichloromethane and chloroform fractions.

Entry P4: $M_n$ = 36800, $M_w/M_n$ = 3.28. $^{1}$H NMR (600 MHz, $C_2D_2Cl_4$, 80 °C): $\delta$ 0.73 (bs, 12H), 0.97 (bs, 2H), 1.09 (bs, 16H), 2.10 (bs, 4H), 7.88 (s, 2H), 8.01 (t, $J$ = 8.12 Hz, 2H). $^{13}$C {$^{1}$H} NMR (150 MHz, $C_2D_2Cl_4$, 80 °C): $\delta$ 159.86, 152.96, 140.76, 139.48, 126.64, 124.67, 122.87, 54.59, 43.86, 36.04, 34.81, 29.08, 27.95, 23.04, 14.13, 10.99.

## ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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