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## Direct Arylation Polycondensation for Synthesis of Optoelectronic Materials

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Running Head

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### **ABSTRACT**

Direct arylation polycondensation has been investigated to develop efficient methods for the preparation of conjugated polymer materials for optoelectronic applications. The reaction conditions have been examined to achieve a high molecular weight and minimal structural defects in the recurring structure. Under the optimal conditions, the direct arylation method has several advantages over the conventional method, for example, having few synthetic steps and yielding a high-molecular-weight and high-purity polymer. The obtained high-quality polymer materials show superior performance to those obtained using a conventional method when used in optoelectronic devices such as organic photovoltaics and field effect transistors. Recent developments in C-H/C-H coupling polycondensation are also described.

## **INTRODUCTION**

Conjugated polymers are expected to serve as the main materials in optoelectronic devices such as organic photovoltaics (OPVs),<sup>1</sup> light emitting diodes (OLEDs),<sup>2</sup> and field effect transistors (OFETs).<sup>3-5</sup> High-performance polymers have been developed by logical molecular designs,<sup>6,7</sup> and the development of conjugated polymer materials will allow practical application of organic optoelectronic devices. For the wide practical application, the mass production of conjugated polymer materials is required while also satisfying demands concerning cost and environmental issues.<sup>8,9</sup> As a practical method for the production of conjugated polymer materials, polycondensation using C-H direct arylation<sup>10-12</sup> is a promising candidate because this method does not require the use of organometallic monomers, which are essential in polycondensation using the conventional cross-coupling reactions. The elimination of organometallic monomers reduces the number of synthetic steps for monomer preparation and undesirable metal-containing waste after polymerization. By having fewer synthetic steps, the process is less expensive, and the reduction in the waste reduces the environmental burden, as well as increasing the purity of the product.<sup>8,9</sup> To take advantage of this in material production, direct arylation polycondensation must fulfill the following three requirements.<sup>13</sup>

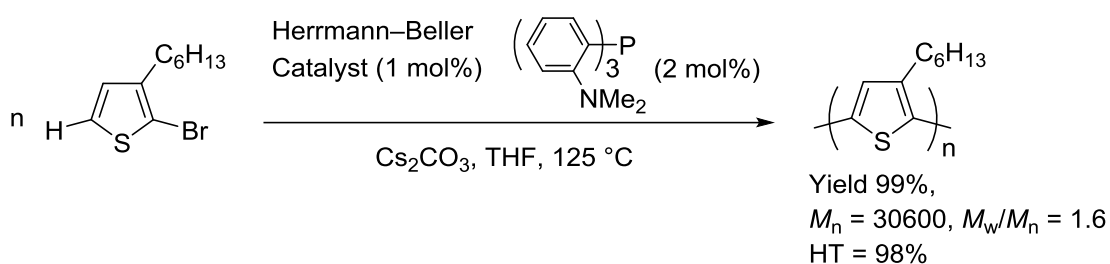
1. High molecular weight: A synthetic method should afford a high-molecular-weight polymer, which generally show better performances regarding carrier mobility and photoelectric conversion.<sup>14-17</sup> To achieve a high molecular weight, the conversion of the coupling reaction must be high.
2. High selectivity: Selectivity in bond formation must be almost perfect because structural defects in polymers cannot be removed, even in a purification step. The structural defects act as carrier trapping sites, lowering device performance.<sup>18,19</sup>
3. High purity: Impurities from metal catalysts or by-products should be easily removed from the polymer materials because impurities lower the initial performance of the polymer and long-term stability.<sup>20,21</sup> A reduced amount of catalyst and easily separable by-products are required for obtaining highly pure materials through simple purification processes. Incorporation of decomposed phosphine ligands at chain ends<sup>22</sup> should be avoided because the terminal defect may act as impurity, which cannot be removed in purification steps.

In addition to satisfying these demands, the synthetic method must be broadly applicable for the preparation of state-of-art polymer materials. Because several review papers on direct arylation polycondensation have been published in recent years,<sup>23-25</sup> this focus review describes the recent results of the author and the author's collaborators.

## **INITIAL DEVELOPMENT OF DIRECT ARYLATION POLYCONDENSATION**

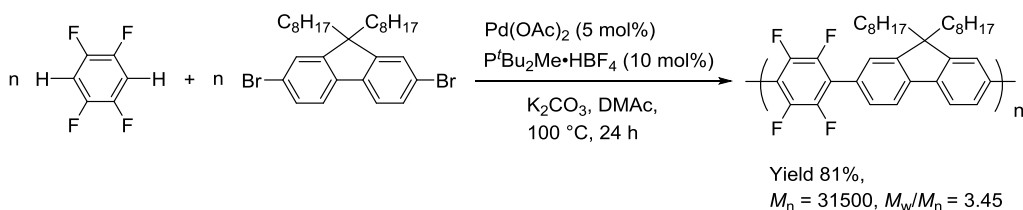
Direct arylation polycondensation of alkylthiophenes was reported in 1999.<sup>26</sup> Although the idea was

quite innovative, polymerization results did not satisfy the demands mentioned above; the molecular weight and selectivity of the bond formation (head-to-tail content) were somewhat lower than those of conventional methods. In 2010, Takita and Ozawa reported the successful synthesis of poly(3-hexylthiophene) (P3HT) via Pd-catalyzed direct arylation (Scheme 1).<sup>27</sup> This method afforded high-molecular-weight P3HT and a high head-to-tail content, as well as a good yield. Mori reported synthesis of P3HT from the same monomer with Knochel-Hauser base through formation of the Grignard reagent, which affords high head-to-tail content, control molecular weight, and narrow molecular weight distribution.<sup>28,29</sup>



Scheme 1. The first successful direct arylation polycondensation for the preparation of P3HT.

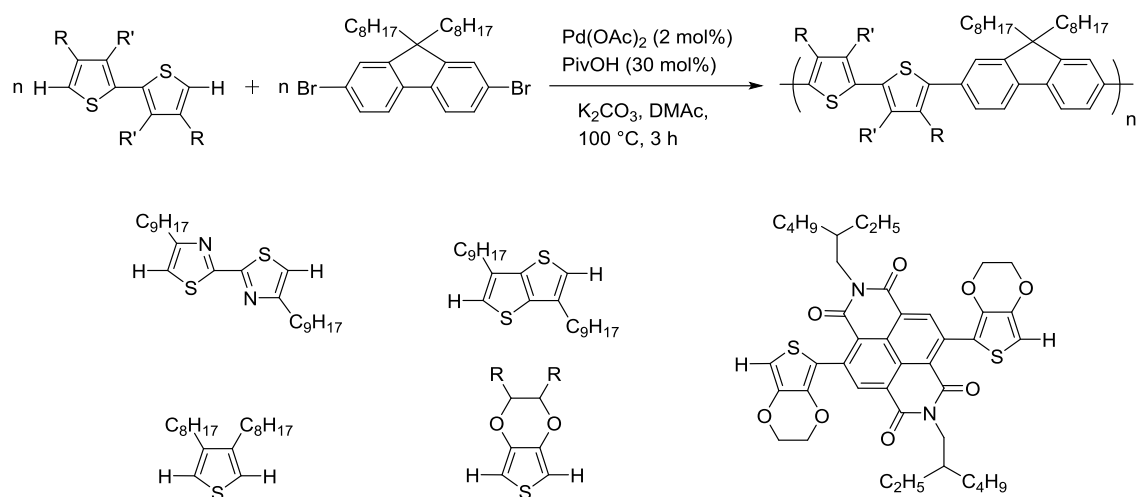
Shortly after the Ozawa and Mori's report, we reported the direct arylation polycondensation of tetrafluorobenzene with a dibromofluorene derivative (Scheme 2).<sup>30</sup> The reaction with  $\text{Pd}(\text{OAc})_2$  and  $\text{P}^t\text{Bu}_2\text{Me}\cdot\text{HBF}_4$  afforded the corresponding polymer with a high molecular weight in a good yield. The molecular weight and the yield were higher than those of the polymer prepared by polycondensation using the conventional Suzuki–Miyaura coupling reaction ( $M_n = 16500$ , 74% yield).<sup>31</sup> In addition, the high purity of the obtained polymer was confirmed by elemental analysis. The high purity is presumably due to the easily separable by-products ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{KBr}$ ) in the direct arylation polycondensation. In addition, the pure polymer acted as a hole-blocking material in OLEDs.<sup>32</sup> These initial examples show the high potential of direct arylation polycondensation for the preparation of optoelectronic materials.<sup>33</sup>



Scheme 2. Direct arylation polycondensation of tetrafluorobenzene.

## DIRECT ARYLATION POLYCONDENSATION OF BITHIPHENES

We have investigated the direct arylation polycondensation of thiophene, bithiophene, and their analogs because a thiophene unit is the most promising unit for excellent semiconducting materials. Initial assessment of the catalytic system revealed that a Pd precatalyst ( $\text{Pd}(\text{OAc})_2$ ) with no phosphine ligand is the most effective catalyst for the direct arylation polycondensation of alkylated bithiophenes (Scheme 3). The highly active catalytic system allows the preparation of the corresponding polymer with a high molecular weight ( $M_n = 31800$ ) in 3 h.<sup>34</sup> In addition to bithiophene derivatives, this reaction system is available for the polycondensation of bithiazole, thienothiophene, monothiophene derivatives, and naphthalenediimide-based monomers (Scheme 3).<sup>35–43</sup> This simple catalytic system has been used for the preparation of a variety of conjugated polymers by other groups,<sup>44–47</sup> presumably because of its high reactivity and ease of use. It is important to note that this highly reactive system sometimes induces side reactions causing structural defects; a direct arylation reaction can occur at undesired C-H bonds.<sup>34,35,45</sup> Appropriate choice of monomers and the optimization of reaction conditions are essential to avoid side reactions.<sup>43,48</sup>

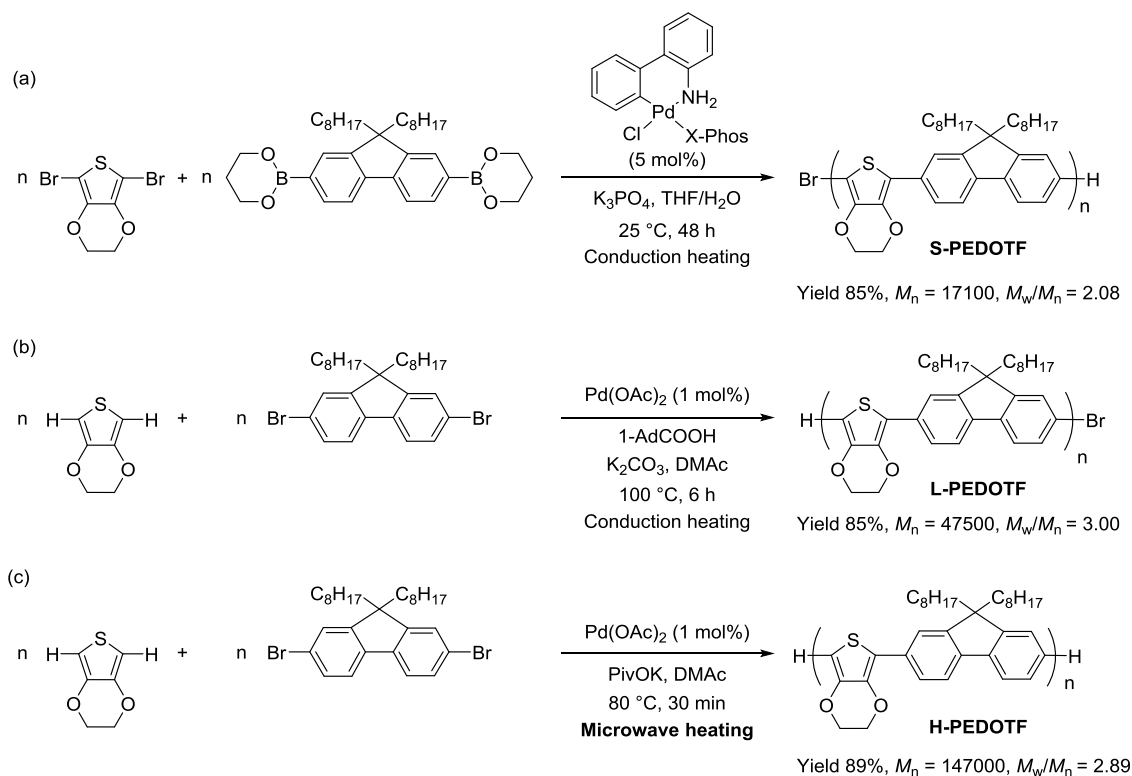


Scheme 3. Direct arylation polycondensation of various thiophene derivatives with a phosphine-free catalytic system.

## EVALUATION OF POLYMERS PREPARED BY DIRECT ARYLATION POLYCONDENSATION

For the further development of direct arylation polycondensation, the reaction conditions were investigated in a model reaction with 3,4-ethylenedioxythiophene (EDOT),<sup>49</sup> which possesses highly reactive C-H bonds for direct arylation (Scheme 4).<sup>37,50,51</sup> The target polymer can be prepared by the conventional cross-coupling method (Scheme 4a, S-PEDOTF).<sup>51</sup> Investigation of the reaction conditions for the direct arylation polycondensation of EDOT revealed that 1-adamantanecarboxylic acid (1-AdCOOH) is an effective additive that assists the C-H bond cleavage process. The reaction

with 1-AdCOOH afforded the corresponding polymer (Scheme 4b, L-PEDOTF) in the presence of only 1 mol% of the Pd precatalyst.<sup>37</sup> The molecular weight of L-PEDOTF ( $M_n = 47500$ ) is higher than that of S-PEDOTF ( $M_n = 17100$ ), which was prepared by the conventional method. In addition, direct arylation polycondensation under microwave heating gave the corresponding polymer with an extraordinarily high molecular weight (Scheme 4c, H-PEDOTF).<sup>50</sup> Possibly, the uniform heating under microwave irradiation promoted efficient coupling. These results show that optimized direct arylation polycondensation has the potential to achieve higher molecular weights than conventional methods. One reason for the high molecular weight of L- and H-PEDOTF is the high tolerance of the C-H bonds to the reaction conditions. The lack of degradation of the reactive point is advantageous, especially compared to the monomers used in the conventional method. For example, the C-Br moiety in the brominated EDOT in Scheme 4a is known to be unstable<sup>52</sup> and the boronate ester moiety can be decomposed via protodeboronation.<sup>53</sup>



Scheme 4. Three methods for the synthesis of EDOT-based polymers (PEDOTF).

<Table 1>

The purity and semiconducting properties of PEDOTFs were investigated to confirm the advantages of the direct arylation method (Table 1). The results of the elemental analysis of H-PEDOTF are well-matched to the values calculated from the formula of the repeating unit. Bromine was not

detected by the elemental analysis, even though the fluorene terminal units may, in principle, possess a Br moiety. No Br termini would be due to the small number of the terminal units as well as minor debromination reactions in the later stage of polymerization. In contrast, the analytical results show that L- and S-PEDOTF contain some impurities and Br termini. Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements reveal that direct arylation polycondensation achieved lower Pd residue in the polymers than the conventional method, which is due to the low loading of Pd (1 mol%) in the direct arylation method. It should be noted that high-molecular-weight and high-purity H-PEDOTF was obtained through simple purification steps, only requiring washing with several solvents and reprecipitation. Soxhlet extraction and high-performance liquid chromatography (HPLC) purification were not required. H-PEDOTF showed better semiconducting properties in OPVs and OFETs than the other samples (Table 1).<sup>51</sup> Bulk heterojunction (BHJ) solar cells with H-PEDOTF and PC<sub>70</sub>BM reached 4% power conversion efficiency (PCE), although that with S-PEDOTF was only 0.48%. Because the PCE correlates with the hole mobility of the polymers in OFETs, the better performance of H-PEDOTF in the OPV is probably caused by high hole mobility of the polymer. Because H-PEDOT has a higher molecular weight and purity than the other samples, the dominant factor for the improvement is unknown. Therefore, the effects on terminal structure, the residual amount of Pd, and the molecular weight were investigated for the model polymers. Thus, PEDOTF samples with different terminal structures (Br or H), the amount of residual Pd, and the molecular weights were tabulated for comparison (Table 2).<sup>54</sup> P1 is the same sample as L-PEDOTF. P2 has almost no Br termini because of the treatment of the C-Br moiety at the end of polymerization. The amount of Pd residue was reduced to 3 ppm in P3 by washing the polymer with an aqueous solution of sodium *N,N*-diethyldithiocarbamate. P4 has a similar purity to P3 but a higher molecular weight. Regarding both the PCE and hole mobility, P1 has lower values than those of P2–P4, indicating that the terminal structure is the most dominant factor in this case. The Br terminals may act as hole-trapping sites.<sup>55</sup> In contrast, the Pd residue and molecular weight had a negligible effect on the initial performance of the OPVs and OFETs. The stability tests of the OPV devices showed that Pd residue and the molecular weight of the polymer affect the lifetime of the device; the device containing P4 has the longest lifetime among P2–P4, although the initial performances are almost same.<sup>54</sup>

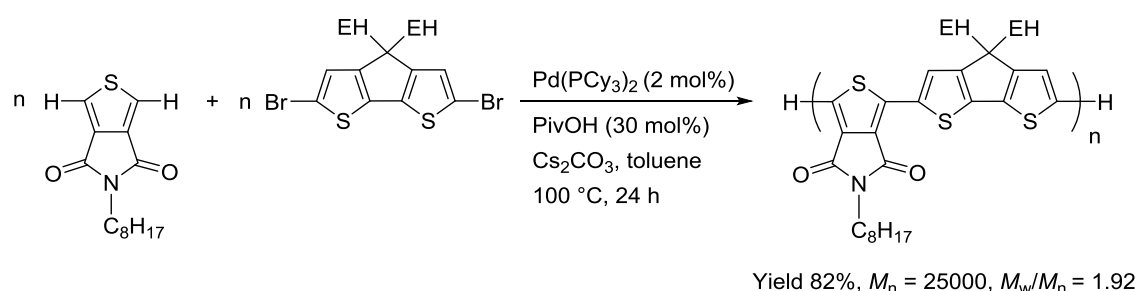
<Table 2>

## **SYNTHESIS OF DONOR-ACCEPTOR POLYMER**

Direct arylation polycondensation for the synthesis of donor-acceptor (D-A) polymers was investigated after the establishment of the model reactions because donor-acceptor polymers often show high performance in OPVs; the donor-acceptor structure possesses a narrow HOMO/LUMO

gap enabling wide light absorption and high hole mobility because of the strong interchain interactions.<sup>1</sup> For the synthesis of D-A polymers, a new reaction system was needed because the conditions mentioned above are not applicable to the C-H bonds in the acceptor monomers, although donor monomers, such as EDOT, can be readily polymerized. The investigation of the reaction conditions for acceptor C-H monomers revealed that the addition of PCy<sub>3</sub> ligands and the selection of low polar solvent, toluene, are effective for the smooth polycondensation of an acceptor monomers<sup>56</sup> such as thienopyrroledione derivatives.<sup>57,58</sup> In addition, a Pd(0) precatalyst (Pd(PCy<sub>3</sub>)<sub>2</sub>) has been found to be a suitable precatalyst, avoiding side reactions such as the homo-coupling reaction, by mechanistic studies of direct arylation.<sup>42,59</sup> On the basis of these insights, the polycondensation of thienopyrroledione and dibromocyclopentadithiophene derivatives was conducted with Pd(PCy<sub>3</sub>)<sub>2</sub> as the catalyst and toluene as the solvent (Scheme 5).<sup>60</sup> The reaction afforded the corresponding D-A polymer with a molecular weight of 25000 in 82% yield, higher than previously reported values for the Migita–Kosugi–Stille coupling polycondensation.<sup>61</sup> NMR and mass spectrometry (MS) analyses show that the polymer has no structural defects and no Br termini, which might be a result of a minor debromination reaction during the polycondensation reaction. Elemental analysis indicates the high purity of the polymer. This D-A polymer served as the p-type semiconducting materials in BHJ solar cells with PC<sub>70</sub>BM. The maximum PCE of the solar cell was 6.8% after optimization of the device structure. The PCEs of the devices were comparable to those of the polymer obtained from the Migita–Kosugi–Stille coupling polycondensation,<sup>61</sup> thus confirming that the direct arylation polycondensation yields high-performance semiconducting materials.

The in-depth studies of other groups have also enabled the synthesis of high-performance polymers without structural defects.<sup>62–64</sup> Further development of this method will enable the synthesis of state-of-art materials, leading to practical applications.

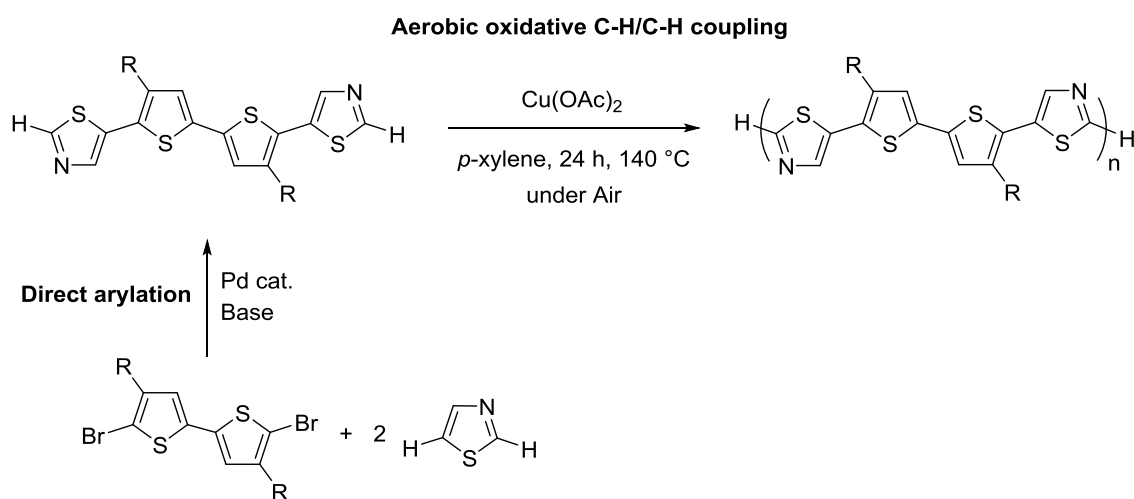


Scheme 5. Synthesis of D-A polymer by direct arylation polycondensation.

Polycondensation using C-H/C-H coupling reactions have been investigated to develop next-generation methods.<sup>65–68</sup> One example is the aerobic oxidation polycondensation of thiazole



monomers (Scheme 6).<sup>69</sup> This polymerization proceeds with a catalytic amount of  $\text{Cu}(\text{OAc})_2$  and oxygen from the air and yields a bithiazole-based conjugated polymer along with the formation of  $\text{H}_2\text{O}$ , which is a green by-product. The obtained thiophene-thiazole polymer served as a semiconducting material in OFETs. Because the monomer is synthesized by direct arylation of thiazole at the 5-position, this strategy skips the preparation of an organometallic reagent and reduces the overall number of reaction steps.



Scheme 6. Combination of direct arylation and aerobic oxidative coupling polycondensation.

**Table 1** Purity and material properties of the polymers

Polymer	$M_n^a$	Elemental analysis			ICP-AES	PCE <sup>b</sup>	$\mu_h^c$
		[%]			[ppm]	[%]	[ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ]
		C	H	Br	Pd		
<b>S-PEDOTF</b>	17100	77.48	8.42	0.08	4390	0.48	$3.2 \pm 0.2 \times 10^{-5}$
<b>L-PEDOTF</b>	47500	78.52	8.01	0.34	2300	2.55	$7.7 \pm 0.4 \times 10^{-4}$
<b>H-PEDOTF</b>	147000	79.44	8.33	0	1590	4.08	$1.2 \pm 0.1 \times 10^{-3}$
		79.50 <sup>d</sup>	8.39 <sup>d</sup>	0 <sup>d</sup>			

<sup>a</sup> Estimated by gel permeation chromatography (GPC) calibrated with polystyrene standards. <sup>b</sup> OPV configuration: ITO/PEDOT:PSS (40 nm)/polymer:PC<sub>70</sub>BM (1:4)/LiF (1 nm)/Al (80 nm). Illuminated at 100 mWcm<sup>-2</sup> AM 1.5 simulated solar light. <sup>c</sup> The average values with standard error were calculated from the results of six or more OFET samples. OFET configuration: Glass/Au gate electrode/Parylene-C insulator/polymer/Au source–drain electrodes. <sup>d</sup> The values were calculated from the formula of the constituting repeating unit.

**Table 2** Effects of terminal units, Pd residue, and molecular weight on material properties

	Br [%] <sup>a</sup>	Pd [ppm] <sup>b</sup>	$M_n^c$	PCE [%]	$\mu_h$ [ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ]
<b>P1</b>	0.34	2300	47500	$2.9 \pm 0.1$	$0.77 \pm 0.04 \times 10^{-3}$
<b>P2</b>	< 0.20 <sup>d</sup>	1400	40300	$4.66 \pm 0.04$	$1.3 \pm 0.1 \times 10^{-3}$
<b>P3</b>	< 0.20 <sup>d</sup>	3.0	38000	$4.7 \pm 0.2$	$1.3 \pm 0.2 \times 10^{-3}$
<b>P4</b>	< 0.20 <sup>d</sup>	1.7	140000	$4.6 \pm 0.2$	$1.3 \pm 0.2 \times 10^{-3}$

<sup>a</sup> Residual amount of Br determined by elemental analysis. <sup>b</sup> Residual amount of Pd determined by ICP-MS or ICP-AES. <sup>c</sup> Estimated by GPC calibrated with polystyrene standards. <sup>d</sup> Less than 0.20%

## CONFLICT OF INTEREST

The author declares no conflict of interest.

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#### Figure legends

Scheme 1. The first successful direct arylation polycondensation for the preparation of P3HT.

Scheme 2. Direct arylation polycondensation of tetrafluorobenzene.

Scheme 3. Direct arylation polycondensation of various thiophene derivatives with a phosphine-free catalytic system.

Scheme 4. Three methods for the synthesis of EDOT-based polymers (PEDOTF).

Scheme 5. Synthesis of D-A polymer by direct arylation polycondensation.

Scheme 6. Combination of direct arylation and aerobic oxidative coupling polycondensation.

Table 1 Purity and material properties of the polymers

Table 2 Effects of terminal units, Pd residue, and molecular weight on material properties



GRAPHICAL ABSTRACT

