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The Eco-Friendly Direct (Hetero)-Arylation Polymerization: Scope and Limitation

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Abstract

Polymer semiconductors have recently attracted considerable attention owing to their (i) excellent optical properties, (ii) processability, (iii) inherent tunability of the energetics, and (iv) synthetic versatility. Consequently, researchers show great interest in developing eco-friendly polymerization methods to reduce the synthetic cost of such macromolecular materials, including the so-called direct (hetero)-arylation polymerization (DHAP). In addition to reducing the number of synthetic steps, required in conventional cross-coupling polymerizations, DHAP avoid the use of lithiated and/or stannylated intermediates that are highly toxic and/or dangerous. In this contribution, we reviewed a number of conjugated polymers prepared by DHAP for applications in organic electronics, and more precisely for organic photovoltaics and field-effect transistors. Moreover, emphasis is given to the polymerization reaction conditions (i.e., the nature of the catalysts, ligands and solvents) and their impact on the materials properties. Even though some optimizations still remain, regarding the current trends, it is obvious that DHAP will play a larger role in the design and synthesis of polymer semiconductors.

Keywords: Direct (hetero)-arylation polymerization, polymer semiconductor, organic photovoltaics, organic field-effect transistors

1. Introduction

Transition-metal-catalyzed C-C coupling reactions have been and continue to be one of the most principal reactions in organic chemistry, widely applied to the synthesis of natural products, pharmaceutical intermediates or even organic functional materials. Until recently traditional cross-coupling reactions, namely, Suzuki-Miyaura, Stille, Negishi, Sonogashira and Kumada, have been the primary means of forming Carbon-Carbon (C-C) bonds.¹⁻³ However, these methods typically involve halogenated and organometallic reagents, thus generating stoichiometric amounts of undesirable and toxic by-products. Moreover, additional synthetic steps, including group-protection and/or activation of aromatic rings, are required to prepare these intermediates. It is noteworthy that such synthetic and environmental problems have plagued researchers for a long time.⁴ Furthermore, within the current

context of an increasing demand for atomic economy reactions and green chemistry,⁵ researchers have more recently focused their efforts on the exploration of new cross-coupling methods.

Considering that the Carbon-Hydrogen (C-H) bond is one of the most common chemical bonds among organic compounds, the formation of a C-C bond by coupling an aromatic hydrogen activated compound directly with an halogenated aromatic reagent would provide a powerful tool that fulfils the atomic economy requirement since the only by-product generated within the media is an hydrogen halide (H-X).⁶ This synthetic method, called direct (hetero)-arylation (DHA), has shown over the last few years great potential to synthesize compounds without organometallic reagents (such as Grignard reagents, organozinc or organotin).⁷ Additionally, this method is not only a good way to resolve problems inherent within traditional cross-coupling reactions but also a particularly appealing strategy for generating C-C bonds as well as C-X bonds.⁸ Many researchers have been eyeing this emerging field in recent decades. In 2002, Lemaire *et al.*¹ summarized results gained in the field of aryl-aryl bond formation using various kinds of reactions and technologies. To some extent they drew a relatively complete picture of the current efforts in this area. More recently Leclerc and fellow researchers⁸ systematically and comprehensively summed up present studies about direct (hetero)-arylation polymerization (DHAP). They discussed general and adaptable reaction conditions for the synthesis of

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defect-free as well as high-molecular-weight conjugated polymers; a discussion which constructed a broad prospect about the field.

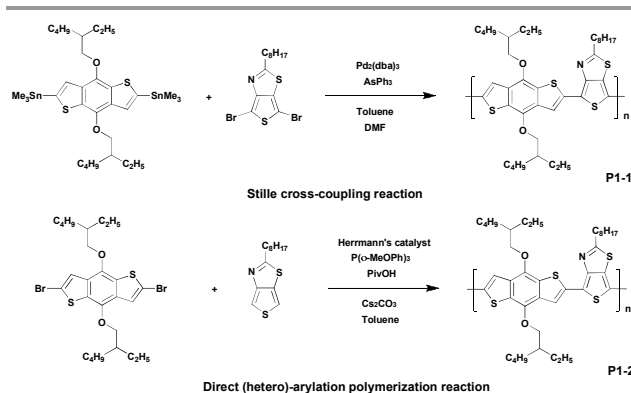
Thus, DHA represents an efficient strategy for the preparation of a large number of aromatic blocks or monomers. Particularly, it offers a highly valuable and economical synthetic method for large-scale productions, and commercially viable preparations of various compounds for organic electronics⁴ including application such as organic photovoltaics (OPV),⁹⁻¹³ organic field-effect transistors (OFET)¹⁴⁻¹⁹ and/or organic light-emitting diodes (OLED),^{20,21} for instance, polymer solar cells (PSCs) and polymer photovoltaic materials have benefitted from significant and remarkable advances over the last decades.²² New photovoltaic materials (donors and acceptors) and device structures are reported with each passing day, and peak power conversion efficiency (PCE) is regularly being increased.²³⁻²⁶

As a C-H activation method, DHAP can simplify and shorten the synthetic process, minimize the presence of difficult-to-remove by-products, and at the same time afford new compounds that can be achieved with relatively less cost.²⁷ Consequently, this method will undoubtedly contribute in removing technological and practical barriers. In this context, the aim of this review is to summarize selected examples of conjugated polymers prepared by DHAP and to discuss the added value, the scope and limitation inherent in this method with a particular focus on the structure-property relationships.

2. Comparison with Traditional Cross-coupling Reactions

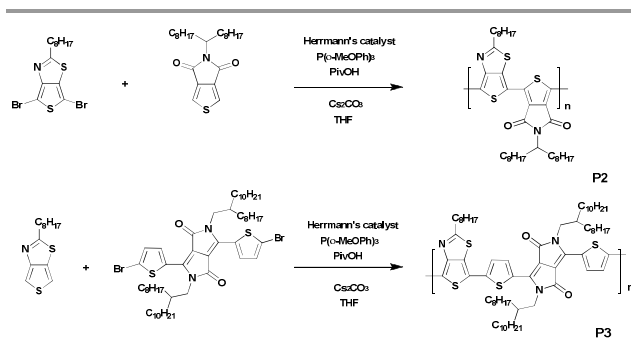
Recently, DHAP has emerged to provide efficient access to new conjugated macromolecular materials. Since then, a significant amount of effort goes into developing, refining, and popularizing this new method. Indeed, among its advantages recent literature has reported DHAP as a cheap and atom-economical tool when compared to conventional organometallic cross-coupling reactions.²⁸⁻³¹

Allard *et al.*³² described for the first time the preparation of thieno[3,4-d]thiazole-based (TTz) alternating copolymers synthesized by Stille, Suzuki or DHAP (Scheme 1). First, polymer **P1-1** was synthesized via conventional Stille cross-coupling between 2-octylthieno[3,4-d]thiazole and 2,6-dibromo-4,8-di(ethylhexyl-oxy)benzo[1,2b:4,5b']dithiophene (BDT) and compared to its analogous **P1-2** synthesized via DHAP. Both polymers showed comparable molecular weight (M_n) of ca 32 kDa,³³ demonstrating that direct arylation is a possible method to obtain M_n as high as those achieved by conventional coupling reactions.



Scheme 1. Preparation of **P1-1** via Stille coupling and **P1-2** via DHAP

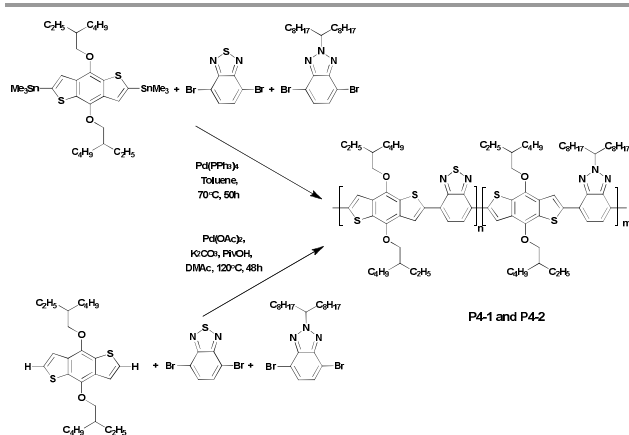
In parallel, polymer **P2** and polymer **P3** were both synthesized by DHAP (Scheme 2). For **P2**, 5-(2-ethylhexyl)thieno[3,4-c]pyrrole-4,6-dione (TPD) was coupled with 4,6-dibromo-2-octylthieno[3,4-d]thiazole. A low molecular weight of 8 kDa was determined and correlated to the strong rigidity of the polymer backbone resulting from the interaction between the thiophene ring of the TTz unit and the ketone borne by the TPD unit, resulting in the reduction of the solubility of this material.³⁴ However, it turns out that DHAP is probably the only available method to afford this polymer. Indeed, all attempts performed in conventional conditions failed. Polymer **P3** has also been synthesized under the same conditions used for **P2** by polymerizing the 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione and 2-octylthieno[3,4-d]thiazole monomers. In this case, a molecular weight of ca 17 kDa was measured. It is noteworthy that **P3** could also be prepared by Suzuki coupling since diketopyrrolopyrrole (DPP) units bearing pinacol borane groups have already been reported.³⁵ However, the synthesis cost of **P3** by Suzuki coupling is quite high, which leads to DHAP as a method of choice.



Scheme 2. Synthesis of **P2** and **P3** by DHAP

In 2015, Marzano *et al.*³⁶ reported a new random copolymer prepared via both Stille polymerization (**P4-1**) and DHAP (**P4-2**), and which contained two different acceptor units, namely the benzo[c][1,2,5]thiadiazole and the benzo[d][1,2,3]triazole along with one donor moiety, namely the benzo[1,2-b;4,5-b']dithiophene (Scheme 3). The DHAP

afforded the polymer **P4-2** in lower yields (70% vs 85% for **P4-1**) but with longer chains ($M_n = 10.3$ kDa for **P4-2** vs $M_n = 20$ kDa for **P4-1**). All polymers synthesized were tested in bulk heterojunction (BHJ) solar cells with [6,6]-Phenyl C71 butyric acid methyl ester (PC₇₁BM). The device based on **P4-1** showed a modest power conversion PCE of 2.5%. However, after adding 2% (v/v) of 1-chloronaphthalene (**CN**), which was reported to improve the PCEs,³⁷ the device performance was significantly risen to 4.8%. Meanwhile, without additive **P4-2** exhibited comparable PCE of *ca* 1.9%. Upon **CN** processing the PCE of **P4-2** was bearily improved to 2.8%, indicating that the polymer **P4-2** is almost insensitive to this treatment probably due to the structural defects of DHAP polymers.³⁸



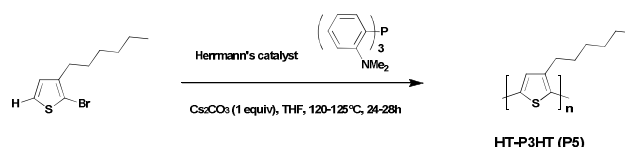
Scheme 3. Preparation of **P4-1** via Stille coupling and **P4-2** via DHAP

3. Homopolymers Synthesized by DHAP

Polythiophenes are considered to be part of the most promising material family in both conductive polymers and photovoltaic materials. However, without substituents, the later are neither soluble nor feasible. To solve this solubility issue, alkyl-substitution turns out to be the most effective shortcut. For instance, poly(3-alkylthiophene) (**P3AT**) appears to be the most common polythiophene bearing alkyl-substituted side chains, and the famous poly(3-hexylthiophene) (**P3HT**) can be cited as a key example.³⁹⁻⁴¹ For the most part, the polymerization typically occurs in the 2-position and 5-position of thiophene. If 2-position is chosen as the “head” (simply as “H”) of the polythiophene units and 5-position as the “tail” (simply as “T”), the proportion of the units with “head-to-tail” (HT-HT) structures in the Poly(3-alkylthiophene) is called the regioregularity.⁴² Due to the small steric hindrance among the repeated units, such a process is more likely to achieve better planarity and stronger interchain interaction. Thus, compared with irregular polythiophene, head-to-tail regioregular (RR) P3ATs have not only elevated effective conjugated chain length, but also higher charge mobility.⁴³

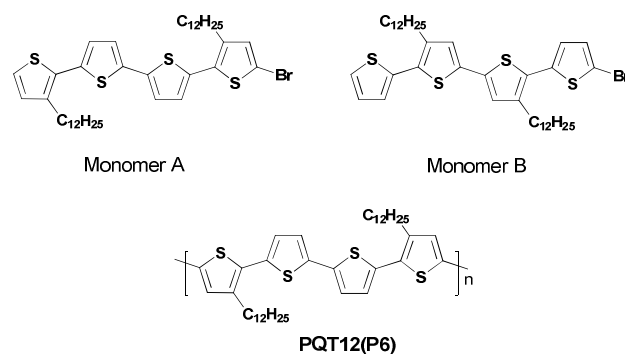
In 2010, Ozawa *et al.*⁴⁴ have reported the palladium-catalyzed direct arylation polymerization of 2-halo-3-hexylthiophene affording RR-P3HT (Scheme 4). The use of

Herrmann’s catalyst and tris(2-dimethylaminophenyl)phosphine as the ligand lead to the preparation of **P5** characterized by high molecular weight ($M_n = 30.6$ kDa) and a promising regioregularity of *ca* 98% in almost quantitative yield (99%). Interestingly, the regioregularity improved significantly with increasing molecular weight, probably because of the cross-coupling reaction between C-H and C-Br that dominates the polymerization at the later stage. From these experimental data higher regioregularity leads higher charge mobility and conductivity, therefore improving the PCEs when the polymer is used in BHJ solar cells.



Scheme 4. Synthesis of regioregular polymer P3HT by DHAP

Then in 2015 the DHAP method, which could selectively synthesize unprotected thiophene units under an appropriated catalytic system, was first reported by Bura *et al.*⁴⁵ The use of Herrmann–Beller catalyst and P(o-NMe₂Ph)₃ in the solvent of dioxane with the existence of acidic additive was quite useful to achieve well-defined thiophene-thiophene couplings. High molecular weight of poly(3,3′′-didodecyl-2,2′:5′,2′′:5′,2′′′-quaterthiophene) (**PQT12**) (**P6**) (43 kDa) was achieved by synthesizing 5-bromo-3,3′′-didodecyl 2,2′:5′,2′′:5′,2′′′-quaterthiophene (monomer A) and 5-bromo-3,4′′-didodecyl-2,2′:5′,2′′:5′,2′′′-quaterthiophene (monomer B) (Scheme 5). Experiments pointed out that adding steric hindrance protection around the β-positions of the brominated thiophene unit is of great importance to improve the selectivity of the cross-couplings at the α-positions. Plus, these experiments also proved that the DHAP could be a practicable synthetic tool to obtain various polythiophene derivatives applied in both organic electronics and in the fabrication of photovoltaic devices.

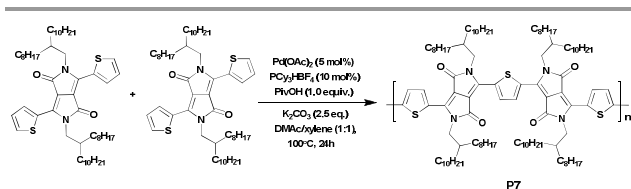


Scheme 5. Synthesis of polythiophene **P6** by DHAP

To date, polythiophene is one of only a few homopolymers that can synthesized via DHAP. Beyond this a wide variety of homopolymers, based on different monomers prepared by DHAP, have been attempted and studied for years. **DPP**, which

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is naturally regarded as an acceptor-type building block, is a suitable option. In 2013, Guo *et al.*⁴⁶ prepared the dithienyldiketopyrrolopyrrole (DTDPP)-based homopolymer **P7**, which is traditionally synthesized by nickel-mediated Yamamoto-type polycondensation,⁴⁷ via the concise, and highly efficient new method, DHAP (Scheme 6). With optimized reaction conditions of 5 mol% of Pd(OAc)₂, 10 mol% of PCy₃·HBF₄ (Cy = cyclohexyl), 2.5 equivalents of K₂CO₃ and 1.0 equivalent of pivalic acid in the mixed solvent of N,N-dimethylacetamide (DMAc)/xylene (1:1), unsymmetrical DTDPP-DTDPP copolymer **P7** with different alkyl substituents on each DPP unit⁴⁸ was obtained as a black solid in a moderate yield of 43% with M_n of 30.2 kDa and the polymer dispersity index (PDI) of 3.56. The optical and electrochemical properties were characterized as well. The UV-vis-NIR absorption spectrum of **P7** in film on quartz plate was tested and the absorption band edge (λ_{onset}) was 1014 nm, which showed strong and broad NIR absorption bands. In addition, **P7** exhibited remarkable optical low bandgap (E_g^{opt}) down to 1.22 eV, which estimated from the absorption band edge in film (λ_{onset}), probably was due to the common features of ideal planarity and good π-conjugation. Such structural features may make it a promising feature in OPV materials.

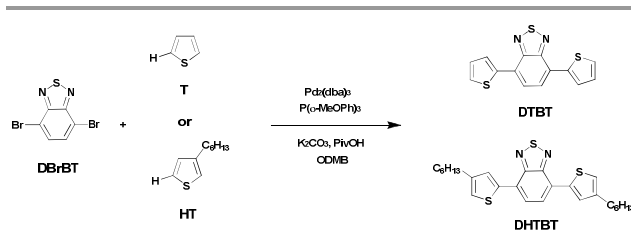
Scheme 6. Synthesis of homopolymer **P7** via DHAP

4. D-A Conjugated Polymers Synthesized by DHAP

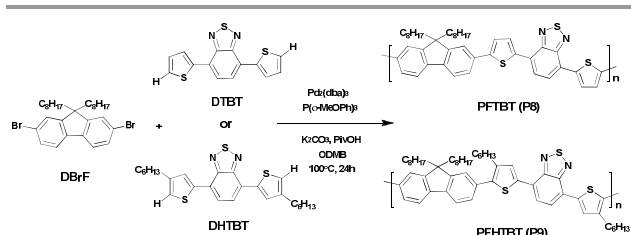
4.1 Polymers Containing Benzothiadiazole (BT)

Benzothiadiazole (BT) is an altogether applicable acceptor unit exceptionally suited for photovoltaic materials owing to its appropriate electron-withdrawing ability. Retaining a relative low highest occupied molecular orbital (HOMO) energy level in the copolymers, which is advantageous for the chemical stability of the copolymers as well as for attaining a high open-circuit voltage (V_{OC}) in the final organic photovoltaics, makes it stand out among the numerous acceptor groups (such as thienothiadiazole, thienopyrazine, etc.).^{49–51} Consequently BT has become an extremely important building block employed in efficient photovoltaic materials. And the utilization of a BT unit in push-pull conjugated polymers has shown high PCE of up to 9.1% in dye-sensitized solar cells.⁵²

Wang *et al.*⁵³ recently reported the synthesis of small molecules containing bare thiophene and alkyl-substituted thiophene and 4,7-dibromo-2,1,3-benzothiadiazole (DBrBT) (Scheme 7). In optimized conditions, Pd₂(dba)₃-catalyzed DHAP produced the corresponding small molecules, i.e., thiophene-flanked benzothiadiazole derivative (DTBT) and 4,7-bis(4-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (DHTBT), with a comparable yield to that of the reference Stille or Suzuki coupling reactions.

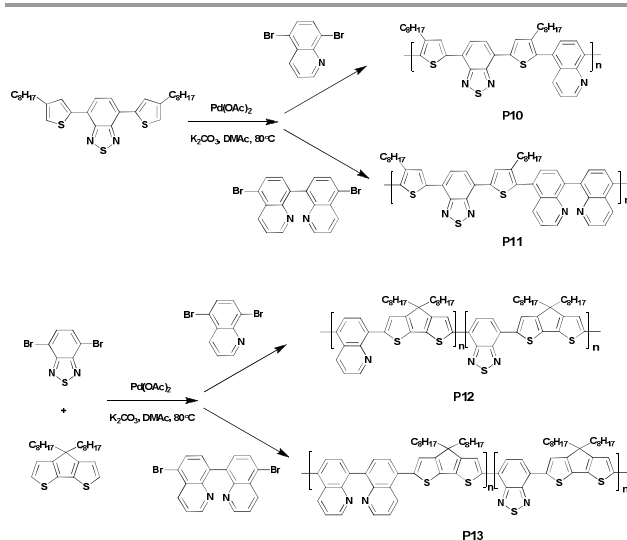
Scheme 7. Synthesis of the small molecules **DTBT** and **DHTBT**

DTBT and **DHTBT** were then used respectively to synthesize conjugated polymers **PFTBT** (**P8**) and **PFHTBT** (**P9**) with 9,9-dioctyl-2,7-dibromofluorene (DBrF) still via DHAP in high yield, i.e., 82% and 91% respectively. In addition, **P8** was characterized by a M_n of 13.8 kDa while **P9** by a slightly higher M_n of 17.6 kDa. Due to the presence of hexyl side chains on the thiophene units the solubility of **P9** was remarkably improved compared to **P8**. According to the high-temperature NMR, this method of DHAP catalyzed with Pd₂(dba)₃ allows the synthesis of almost defect-free polymers with good C-H selectivity. Furthermore, it is worth noting that **P9** exhibits a hypsochromic-shifted absorption spectrum compared with **P8** of ca 35 nm, attributed to the steric hindrance of the hexyl groups on the thiophene rings. Indeed, it is supposed that the π-conjugation along the backbone in **P9** could be impeded by the increasing dihedral angles between the thiophene and fluorene unit.⁵⁴

Scheme 8. Synthesis of **P8** and **P9** by DHAP using the same condition

In 2016, Tomar *et al.*⁵⁵ reported four donor-acceptor type polymers based on benzothiadiazole and thiophene-benzothiadiazole-thiophene (TBTT) synthesized by DHAP (Scheme 9). Under the optimizing conditions of Pd(OAc)₂, Pivalic acid, DMAc at 80°C and nitrogen atmosphere, alternate polymers **P10** and **P11** were achieved by reacting thiophene-benzothiadiazole-thiophene with quinoline and biquinoline, respectively; random polymer **P12** was achieved by reacting benzothiadiazole, cyclopentadithiophene (CPDT) and quinoline; and **P13** was obtained using biquinoline instead of quinoline. All polymers exhibited good solubility in ordinary organic solvents and the number-average molecular weights of 3.6 kDa, 5.03 kDa, 5.3 kDa and 7.6 kDa were obtained by the measurements of gel permeation chromatography against polystyrene standards. The UV/Vis absorption spectra of the four polymers were then investigated, which revealed that **P10** (494 nm) and **P12** (664 nm) showed higher value of absorbance maxima compared to **P11** (481 nm) and **P13** (649 nm) on account of more efficient electron delocalization

caused by the more planar structure.^{56,57} In addition, the deep-lying HOMO energy levels of **P10**, **P11**, **P12** and **P13**, which were -5.82 eV, -5.75 eV, -5.19 eV, -5.03 eV, respectively, showed improved oxidative stability for this variety of polymers. Furthermore, OFET characteristics were also studied. **P12** and **P13** could be observed exhibiting hole-type transport of $11 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, whereas **P10** and **P11** did not show any OFET characteristics due to the existence of the dominant contact resistance in **P10** and **P11** systems.



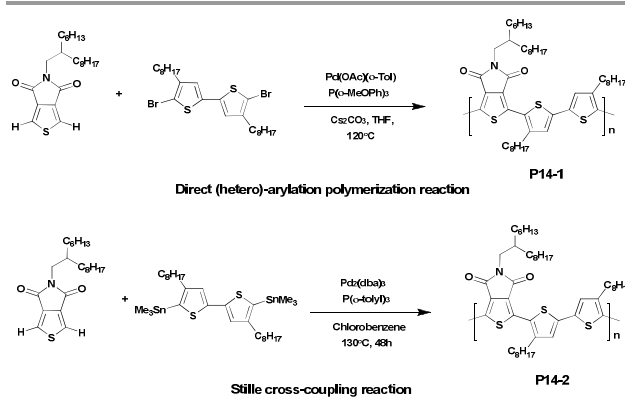
Scheme 9. Synthesis of **P10**-**P13** by DHAP

4.2 Polymers Containing Thieno[3,4-c]Pyrrole-4,6-Dione (TPD)

TPD unit is a good electron-withdrawing co-monomer which has great potential for photovoltaic applications. Indeed, recent studies reported some high efficient TPD-based PSCs have exhibiting PCE up to 8.5% when fabricated and tested under inert atmosphere.⁵⁸⁻⁶¹ Its relatively planar structure could prove beneficial for electron delocalization when incorporated into conjugated polymers promoting intra-molecular/intermolecular interactions. In addition, its strong electron-withdrawing effect could lead to low HOMO and lowest unoccupied molecular orbital (LUMO) energy levels.²² For these reasons the TPD based materials were shown to be good electron donors when synthesizing donor-acceptor conjugated polymers, developing specific interactions between the imide group and the fullerene derivatives.⁶² Moreover, the imide group in TPD moiety could also be used as a directional activating group so that C-H activation could typically occur in the 2-position and 5-position of thiophene.⁶³

In 2012, Leclerc *et al.*⁶⁴ synthesized a TPD-bithiophene based polymer via DHAP in high yield (96%). In optimal conditions, using the tris(3-methoxyphenyl)phosphine as the ligand and Pd(OAc)(*o*-Tol) as the catalyst, high molecular weights of *ca* 60 kDa were achieved. In parallel, the Stille polymerization was carried out using the Pd₂(dba)₃ as the catalyst and the tris(3-methoxyphenyl)phosphine as the ligand. The resulting polymer (**P14-2**) showed lower yield (71%) and

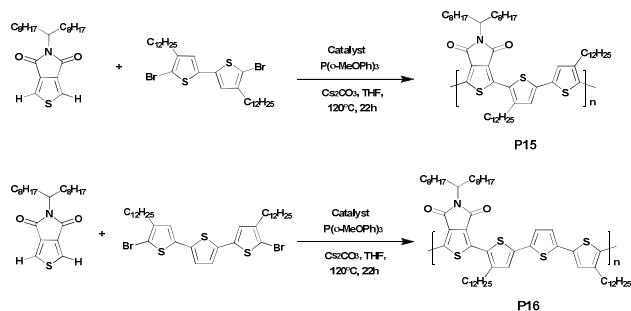
molecular weight (*M_n* of 9 kDa). The UV/Vis absorption spectra of two analogues were then investigated and revealed that both **P14-1** and **P14-2** exhibit comparable features in chloroform solutions and in the solid-state. However, compared to **P14-2** the absorption maximum of **P14-1** is slightly red shifted, of *ca* 18 nm in film, probably because of the different molecular weights and morphology/packing in the solid state. Additionally, X-Ray and thermal analyses were performed to study the structural regularity of these polymers, showed that both the enthalpies of crystallization and melting are higher for **P14-1** than for **P14-2**.



Scheme 10. Preparation of **P14-1** via DHAP and **P14-2** via Stille coupling

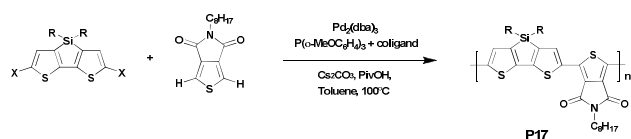
In 2012, two TPD based polymers, namely **P15** and **P16**, containing a bithiophene or a terthiophene as electron-rich moieties, respectively, were prepared by Jo *et al.*⁶⁵ via a direct heteroarylation procedure in the presence of trans-di(μ -acetato)bis[*o*-(dio-tolyl-phosphino)benzyl]dipalladium(II) and tris(*o*-methoxyphenyl)phosphine (Scheme 11). The bithiophene-containing polymer **P15** achieved in 94% yield was characterized by a *M_n* of 50 kDa while **P16** barely reached a *M_n* of 41 kDa with a similar yield (92%). Furthermore, it is worth noting that these polymers exhibit HOMO energy levels of *ca* -5.66 eV. From this, BHJ solar cells based on photoactive films made of a blend of **P15** or **P16** with [6,6]-phenyl C71-butyric acid methyl ester (PC₇₀BM) were fabricated. Upon optimization, PCEs of 1.90% and 6.10% were obtained from the **P15** and **P16** based devices respectively. These differences are probably induced by the terthiophene unit favouring a better conjugation along the backbone, a higher electron mobility and better π - π stacking.⁶⁶ Indeed, it is noteworthy that the absorption spectrum of **P16** exhibits a vibronic shoulder at 600 nm, indicating that polymers chains are already aggregated in solution. Moreover, this peculiar aggregation shows that integrating the polymers into field-effect transistors led to better charge carrier mobility ($1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **P16** vs $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **P15**).

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Scheme 11. Synthesis of **P15** and **P16** by DHAP

Despite its multiple advantages, including simplified steps and no need for preprocessing the organometallic monomers, DHAP still suffers from two main limitations: the first one concerns the homocouplings reaction leading to structural defects of the polymer chains,⁶⁷⁻⁷⁰ and the second deals with the lack of selectivity when different C-H bonds are present causing branching as well as cross-linking and generally leading to insoluble materials.⁷¹⁻⁷³

However, in 2016, Ozawa *et al.*⁷⁴ studied these two questions by exploring an original strategy (Scheme 12). When preparing **P17**, composed of a dithienopyrrole unit as the donor and **TPD** unit as the acceptor, they found that using a blend of ligands in palladium catalyzed direct arylation polymerizations may avoid side reactions effectively and favor high yield. Thus, the combined use of tris(2-methoxyphenyl)phosphine and tetramethylethylenediamine in the presence of $\text{Pd}_2(\text{dba})_3$ led to high yield, reduced defect formation and no insoluble materials.

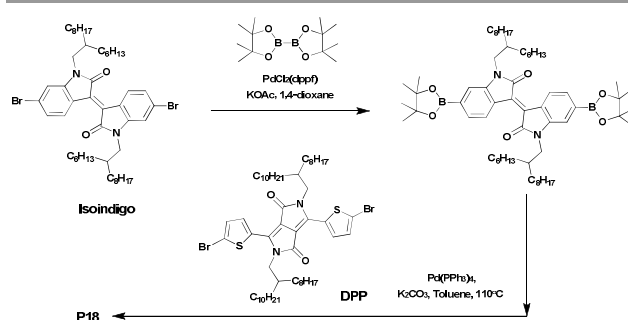
Scheme 12. Preparation of **P17** via DHAP

4.3 Polymers Containing Isoindigo

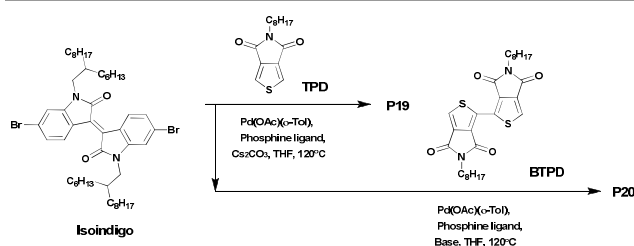
Isoindigo is an ideal building block for synthesizing D-A conjugated polymers. Indeed, the later displays many advantages such as a strong electron-withdrawing character, outstanding stability, a highly fused structure, outstanding absorption property, and so on.⁷⁵⁻⁷⁷ As a result, polymers of isoindigo generally show low bandgaps, strong π - π interactions and high charge carrier mobility, suggesting a potential compatibility in building D-A polymers for efficient organic photovoltaic materials.⁷⁸⁻⁸¹ High performance BHJ solar cells based on isoindigo polymers have already been fabricated with PCE up to 7%,⁸²⁻⁸⁴ and field-effect transistors with mobility as high as $3.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁸⁵⁻⁸⁷

Moreover, while generally used as p-type material, only few studies have been devoted to afford n-type isoindigo-based materials. In 2013, Grenier *et al.*⁸⁸ combined three different electron-withdrawing co-monomers with low steric hindrance, namely the **TPD**, the 5,5'-dioctyl-1,1'-4H-bithieno[3,4-

c]pyrrole-4,4',6,6'-(5H,5'H)-tetrone (**BTPD**) or the **DPP** with the isoindigo to prepare n-type copolymers characterized by good charge mobility, low bandgaps and low energy levels. At first, the three copolymers were synthesized via Suzuki-Miyaura cross-coupling reaction. However, only **P18** could be isolated with an acceptable yield of *ca* 70% and a M_n of 44 kDa (Scheme 13).

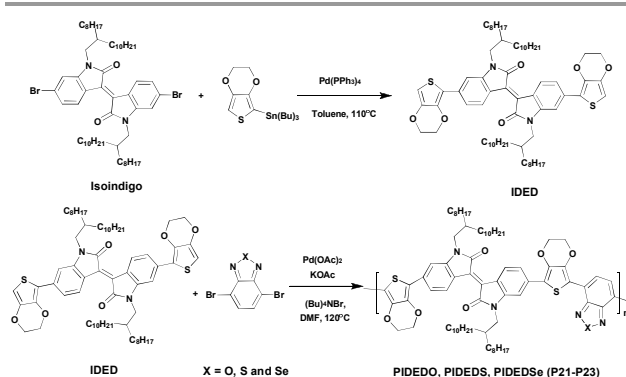
Scheme 13. Synthesis of **P18** by Suzuki-Miyaura coupling

From these observations, the synthesis of the two other copolymers was carried out by DHAP (Scheme 14). After optimization, **P19** and **P20** were isolated in 77% and 87% yield, respectively, and exhibit M_n of 24 kDa and 20 kDa, respectively. From the respective cyclic voltammograms (CV) and UV-abs, the energy levels of the copolymers **P19** and **P20** were found to be relatively stabilized with LUMO levels around -4.2 eV, i.e., close to that of PC_{61}BM .⁸⁹ Moreover, while these two polymers show no electrochemical reversibility in the oxidation process, the polymer **P18** shows reversibility in its oxidation as well as reduction. In addition, the later is characterized by a higher LUMO energy level of -4.0 eV and a HOMO energy level of -5.3 eV. As a result, **P19** and **P20** could be ideal candidates as n-type polymers and can possibly be used in all-polymer solar cells. In parallel, thin film transistor properties were investigated. **P19**, **P20** and **P18** exhibit electron mobility of *ca* $2.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $2.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, suggesting that using a **BTPD** unit instead of a **TPD** unit contributes to increase the electron mobility due to the centrosymmetric structure of the **BTPD** unit. Indeed, because of improved packing properties, copolymers containing isoindigo and centrosymmetric co-monomers may have higher charge transport properties.⁹⁰ Finally, these results show almost comparable electron mobility of that characterizing the PC_{61}BM in thin film ($\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^{91,92} meaning that they can have promising features and great potential as n-type materials in organic photovoltaics.



Scheme 14. Synthesis of P19 and P20 via DHAP

Then, Elsayy *et al.*⁹³ recently reported the synthesis and characterization of a series of D-A-D-A' copolymers incorporating different strong acceptors, i.e., the isoindigo (A) unit and the 4,7-dibromo[c][1,2,5]-(oxa, thia, or seleno)diazole (A') with the 3,4-ethylenedioxythiophene as donor (D) via DHAP (Scheme 15). In this study, the effects of different heteroatoms namely the oxygen, sulfur and selenium borne by the benzimidazole unit on the photovoltaic properties were investigated. At first, the authors prepared the 6,6'-Bis(2,3-dihydrothieno[3,4-b][1,4]-dioxin-5-yl)-1,1'-bis-(2-octyldodecyl)-[3,3'-biindolylidene]-2,2'-dione (IDED) polymer by conventional Stille coupling reaction with a high yield of ca 80%. Then the preparation of three polymers, namely P1EDDO (P21), P1IDES (P22) and P1EDSe (P23) were carried out under CH-arylation activation in high yields (>80%). Molecular weights ranging from 15.2 kDa and 17.3 kDa were estimated by gel permeation chromatography. Thin-film UV/Vis spectra exhibit red-shifted absorption profiles demonstrating more π - π stacking and ordering in solid state. In addition, moving from O to Se results in a bathochromic shift with a difference of ca 68 nm (λ_{max}) between P21 and P23.



Scheme 15. Preparation of P21-P23 by DHAP

Next, the photovoltaic performances of three polymers as donor materials were assessed through the preparation of PC₆₁BM based BHJ. The device performances are summarized in Table 1. Compared with the P21-based device, the PCE of the two other devices were significantly higher, due to the well-improved short-circuit current density (J_{sc}) parameters. This enhancement can be attributed to the higher electron densities and an appropriate morphology of the films.⁹⁴ Moreover, comparison of thiophene and selenophene based

devices revealed a superior charge balance of the P22:PC₆₁BM blend resulting in its higher J_{sc} .

Table 1. Photovoltaic performances of P21, P22 and P23

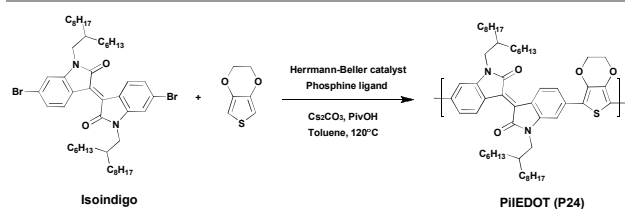
| Active Layer | J_{sc} (mA/cm ²) | Voc (V) | FF (%) | PCE (%) |
|--------------|---------------------------------------|---------|--------|---------|
| P21 | 2.27 | 0.58 | 46.0 | 0.61 |
| P22 | 8.10 | 0.56 | 35.0 | 1.60 |
| P23 | 7.13 | 0.56 | 34.0 | 1.36 |

The charge transport properties of each materials were estimated using OFETs and hole mobilities of 1.9×10^{-4} , 4.0×10^{-4} and 3.5×10^{-4} cm² V⁻¹ s⁻¹ were measured for P21, P22 and P23, respectively. From Table 2, the blend of P22:PC₆₁BM exhibits the highest electron mobility and good charge balance due to an appropriate film morphology.

Table 2. Carrier mobilities of the three polymers blended with PC₆₁BM

| Active Layer | μ_{e} (cm ² V ⁻¹ s ⁻¹) | μ_{h} (cm ² V ⁻¹ s ⁻¹) |
|-------------------------|---|---|
| P21:PC ₆₁ BM | 1.85×10^{-6} | 5.41×10^{-4} |
| P22:PC ₆₁ BM | 2.31×10^{-4} | 4.46×10^{-4} |
| P23:PC ₆₁ BM | 7.45×10^{-5} | 2.25×10^{-4} |

Although high yields and high molecular weights of isoindigo-based copolymers are reachable via DHAP, a biggest challenge still remains, that being the reproducibility. In this context, Leclerc *et al.*⁶ reported for the first time continuous flow methods applied to DHAP. This inexpensive technology uses a reactor with fixed and constant reaction conditions.^{95,96} From this set up a new D-A polymer containing a strong electron-donating unit, namely the 3,4-ethylenedioxythiophene (EDOT), and the isoindigo (ii) as acceptor (A), was synthesized and characterized by M_n ranging from 34 to 42 kDa (Scheme 16). In addition, OFET and BHJ solar cells were fabricated to estimate the charge carrier mobility and organic photovoltaic performance, respectively. Comparison of P1EDOT (P24) synthesized in conventional flask, reveals similar hole mobility of ca 2×10^{-3} cm² V⁻¹ s⁻¹ and comparable PCE of ca 1.74% and 1.80%, respectively, when blended with PC₇₁BM. Although, the V_{oc} and fill factor (FF) are nearly identical, the main limitation, impacting the PCEs, comes from the low J_{sc} recorded in both case (5.0 mA/cm²). However, it is noteworthy that both polymers exhibit comparable molecular weights. Consequently, these promising results confirmed the great potential of the continuous flow methods.



Scheme 16. Polymerization of P24 by DHAP

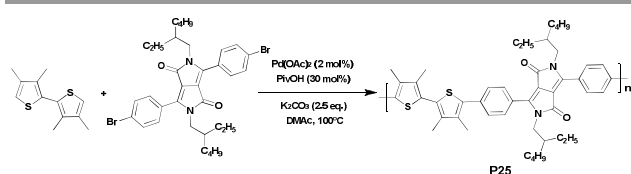
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4.4 Polymers Containing Diketopyrrolopyrrole (DPP)

Due to the strong electron-withdrawing nature, intermolecular hydrogen bonding, planar backbone and strong π - π stacking interactions, the **DPP** moiety has been widely used for the preparation of active macromolecules.⁹⁷⁻⁹⁹ For instance, high performance **DPP**-based polymers with PCEs up to 8% were reported.¹⁰⁰⁻¹⁰²

Recently, Kuwabara *et al.*¹⁰³ discussed the optimization of reaction conditions for the synthesis of height diketopyrrolopyrrole-based conjugated polymers via DHAP (Scheme 17). In this study, Kuwabara *et al.* report on the importance of reaction time to afford high-molecular-weight polymers in DHAP while avoiding overreactions in unexpected C-H bonds. Thus, polymer **P25** (copolymerized by 2,5-di-(2-ethylhexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4-dione and 3,3',4,4'-tetramethylbithiophene) was synthesized with a reaction time of 6h, was isolated in good yield, and characterized by high molecular weight (M_n of 18.1 kDa). Moreover, since the polymer has wide absorption in the visible region, as well as low-lying HOMO energy level, it was investigated as potential donor in BHJ solar cells.^{89,104} When blended with PC₆₁BM, a V_{oc} of 1.01 V, a J_{sc} of 2.93 mA/cm², a FF of 0.30 and a resulting PCE of 0.89% were achieved for **P25**. The device exhibited high V_{oc} attributed to the low-lying HOMO energy level and an optimized morphology. The low J_{sc} and FF may be due to the twisted structure of the polymer which is unsuitable for carrier transport.^{105,106} Even though the PCE value of the device is much lower than those typically recorded with P3AT-based devices,¹⁰⁷⁻¹⁰⁹ the results of this study point out that DHAP can be used commendably to synthesize polymers for PSCs.¹¹⁰

Scheme 17. Synthesis of **P25** by DHAP

Guo *et al.*⁴⁶ conducted a series of studies on **DTDPP**-based polymers synthesized via DHAP in 2013 (Scheme 18). The **DTDPP**-based copolymers exhibited outstanding photoelectronic properties, such as low bandgap and high hole mobilities, making them key prospects applied in optoelectronic materials.¹¹¹ Under the optimized reaction conditions of 5 mol% of Pd(OAc)₂, 10 mol% of PCy₃·HBF₄ (Cy = cyclohexyl), 2.5 equivalents of K₂CO₃ and 1.0 equivalents of pivalic acid in the mixed solvent of DMAc/xylene (1:1), both electron-donating units (**P28**, **P29**, **P30** and **P31**) and electron-withdrawing units (**P26** and **P27**) were successfully achieved with high yields of up to 94% and comparable molecular weights of up to 45 kDa (summarized in Table 3).

Table 3. Molecular weights, PDI and yields of **P26-P31**

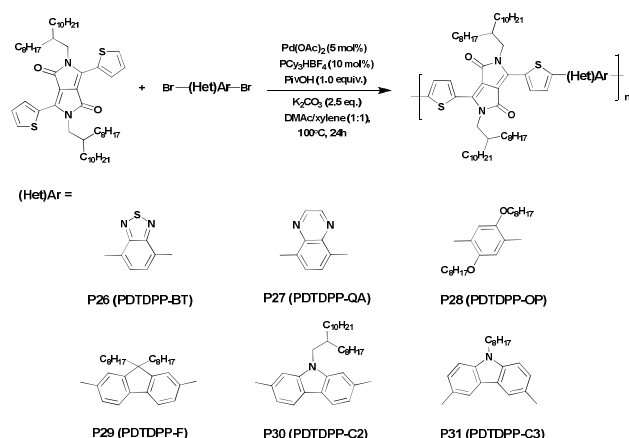
| Polymer | M_n (kDa) | PDI | Yield (%) |
|------------|-------------|------|-----------|
| P26 | 23.5 | 4.13 | 90 |
| P27 | 23.5 | 4.36 | 92 |
| P28 | 36.7 | 3.46 | 94 |
| P29 | 27.7 | 1.72 | 35 |
| P30 | 45.0 | 3.23 | 90 |
| P31 | 10.2 | 1.73 | 91 |

What's more, the optical and electrochemical properties of the polymers were characterized and summarized in Table 4.

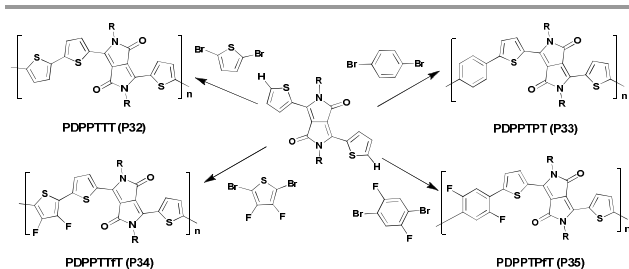
Table 4. Optical, electrochemical properties of **P26-P31**

| Polymer | UV-vis absorption spectra | | Cyclic voltammetry | | |
|------------|---------------------------|------------------|--------------------|-----------|-----------------|
| | λ_{onset} (nm) | E_g^{opt} (eV) | HOMO (eV) | LUMO (eV) | E_g^{CV} (eV) |
| P26 | 1015 | 1.22 | -5.29 | -3.70 | 1.59 |
| P27 | 1010 | 1.23 | -5.17 | -3.64 | 1.53 |
| P28 | 932 | 1.33 | -5.11 | -3.68 | 1.43 |
| P29 | 885 | 1.40 | -5.38 | -3.56 | 1.82 |
| P30 | 923 | 1.34 | -5.10 | -3.62 | 1.48 |
| P31 | 909 | 1.36 | -5.00 | -3.64 | 1.36 |

Compared with the analogues synthesized through Suzuki or Stille coupling reported previously,¹¹²⁻¹¹⁵ polymers based on DHAP showed a difference of about 10 to 40 nm in the absorption maxima, which may be interpreted as the diverse M_n , branching structures from side reactions and morphology in the solid state. In comparison with the three polymers **P28**, **P29** and **P30**, **P26** and **P27** exhibited broader absorption bands (up to 1000 nm) and bathochromic shifted absorption maxima. These phenomena imply that a donor-acceptor-donor-acceptor (D-A-D-A) sequence involving a **DTDPP** (regarded as an inherent D-A-D unit) and an acceptor unit offers advantages for red shift of the absorption.¹¹³ In addition, **P26** and **P27** exhibited remarkable optical bandgaps (E_g^{opt}) down to 1.22 eV, which were estimated from the absorption band edge in film (λ_{onset}). Additionally, the bandgaps (E_g^{CV}) estimated by CV were somewhat larger than E_g^{opt} , which can be attributed to the excitation binding energy of polymers between the polymer film and the electrode.^{115,116} So DHAP can not only offer an approach to select low-bandgap and NIR absorbing polymers, but also accelerate the discovery of high-performance organic photovoltaics.

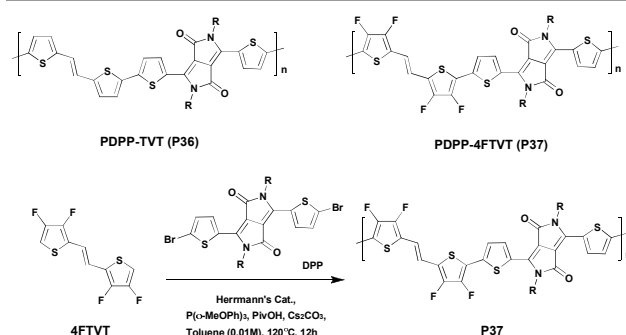
Scheme 18. Synthesis of **P26-P31** by DHAP

In 2015, Homyak *et al.*¹¹⁷ used a synthetic method of DHAP to prepare four **DPP**-based polymers (Scheme 19). High molecular weights (M_n) polymers ranging from 10 to 30 kDa were achieved, the polymers were applied in OPV as well as OFET devices. While **PDPPTTT** (**P32**) and **PDPPTPT** (**P33**) achieved an average PCE of 3.8%-3.9%, their fluorinated analogues (**PDPPTTfT** (**P34**) and **PDPPTPft** (**P35**)) show much lower efficiencies mainly due to an inappropriate energy gap between the LUMO energy levels of the polymers and the fullerene derivative. However, although OFET devices revealed that all materials showed high hole mobilities within the same order of magnitude ($ca\ 10^{-2}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), values obtained for the fluorinated derivatives **P34** and **P35** materials are 2-3 times higher than that of **P32** and **P33** materials.

Scheme 19. Synthesis of **P32-P35** by DHAP

To further improve the charge transport properties, the use of oligothiophene derivatives appears to be an effective option.¹¹⁸ However, the later often display low reactivity when involved in direct arylation,¹¹⁹ and the multiple C-H bonds borne by the aromatic rings may lead to undesired cross-linked defects.^{72,120,121} Consequently, to solve these problems fluorine-atoms were introduced in β -positions of thiophene rings (position 3 and 4) and a new **DPP**-based high-mobility conjugated polymer containing (E)-1,2-bis(3,4-difluorothiophen-2-yl)ethene (**4FTVT**) was synthesized via DHAP in high yield (93%) by Gao *et al.*¹²² (Scheme 20). In optimal conditions using the Herrmann's catalyst, a polymer with M_n of 60 kDa was achieved.

HOMO and LUMO energy levels of **PDPP-4FTVT** (**P37**) were estimated from the CV and UV-abs. The incorporation of fluorine-atom resulted in a significant stabilization of both the HOMO and LUMO energy levels (-5.36 eV and -3.50 eV vs 5.17 eV and -3.35 eV for the reference material **PDPP-TVT** (**P36**)). From bottom-gate and top-contact OFETs **P37** shows an ambipolar characteristics and a hole mobility (μ_h) of $ca\ 3.40\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ vs an electron mobility (μ_e) of $ca\ 5.86\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. It is noteworthy that these values are comparable to those reached by analogous polymers synthesized by Stille cross coupling reaction.¹²³⁻¹²⁷

Scheme 20. Polymerization of **P36** and **P37** by DHAP

5. Summary and Outlook

This review summarizes and gathers data on several donor-acceptor conjugated polymers synthesized via direct(hetero)-arylation polymerization with applications in organic electronics. The use of DHAP as a route toward the formation of the specific C-C bond has been a great challenge in organic chemistry over the past twenty years, but the results reported herein clearly demonstrate the way has been paved. According to the recent literature DHAP offers a powerful approach for the synthesis of efficient active materials, and a strong substitute for conventional cross-coupling reactions. However, there are still shortcomings that cannot be ignored. For some monomers the reactions are actually controllable with difficulties generating branched, cross-linked polymer and or by-products due to activation of more than one C-H bond. Additionally, the effects of the steric hindrance of the monomers may have an impact on the polymerization and should also be taken into consideration. Furthermore, it is worth noting that reaction conditions require specific optimization for each monomer. There are actually, up to date, no universal catalytic systems. Under palladium catalysis many parameters including the nature of the additive(s), solvent, ligand(s), reaction temperature and time have a great impact on the conversion. Therefore, the optimum reaction conditions of this non-stationary catalytic system should be achieved by repeated experiments and data analysis. Many questions still remain unanswered and much work needs to be further conducted. Nevertheless, comparisons of materials obtained by DHAP with their analogues prepared via conventional cross-coupling reaction clearly show that DHAP is a method of choice. Indeed, efficient materials prepared by

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DHAP for polymer solar cells and OFETs have already been reported and that is hopefully just the beginning.

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