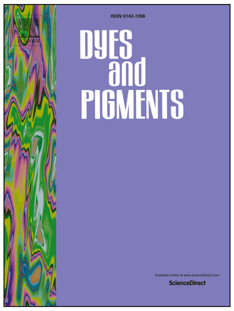


Facile synthesis of a narrow-bandgap strong-donor-*alt*-strong-acceptor copolymer of poly(5,6-difluorobenzo-[*c*][1,2,5]-thiadiazole-*alt*-5*H*-dithieno[3,2-*b*:2′,3'-*d*]pyran) *via* direct C-H arylation polymerization

Amsalu Efrem, Kai Wang, Mingfeng Wang

PII: S0143-7208(17)30764-7

DOI: 10.1016/j.dyepig.2017.05.040

Reference: DYPI 6002

To appear in: *Dyes and Pigments*

Received Date: 8 April 2017

Revised Date: 20 May 2017

Accepted Date: 20 May 2017

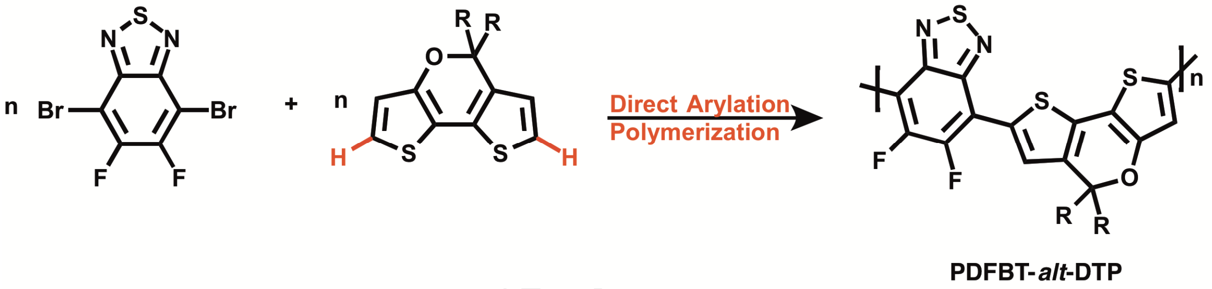
Please cite this article as: Efrem A, Wang K, Wang M, Facile synthesis of a narrow-bandgap strong-donor-*alt*-strong-acceptor copolymer of poly(5,6-difluorobenzo-[*c*][1,2,5]-thiadiazole-*alt*-5*H*-dithieno[3,2-*b*:2′,3'-*d*]pyran) *via* direct C-H arylation polymerization, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.05.040.

Graphical abstract

Facile Synthesis of a Narrow-Bandgap Strong-Donor-*alt*-Strong-Acceptor Copolymer of Poly(5,6-Difluorobenzo-[*c*][1,2,5]-thiadiazole-*alt*-5*H*-Dithieno[3,2-*b*:2',3'-*d*]pyran) *via* Direct C-H Arylation Polymerization

Amsalu Efrem, [a] Kai Wang, [a] Mingfeng Wang,*, [a]

[a] *School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459*



Facile Synthesis of a Narrow-Bandgap Strong-Donor-*alt*-Strong-Acceptor Copolymer of Poly(5,6-Difluorobenzo-[*c*][1,2,5]-thiadiazole-*alt*-5*H*-Dithieno[3,2-*b*:2',3'-*d*]pyran) *via* Direct C-H Arylation Polymerization

Amsalu Efrem, [a] Kai Wang, [a] Mingfeng Wang*[,a]

[a] *School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459*

ABSTRACT

A narrow bandgap D-A conjugated polymer based on 5*H*-dithieno[3,2-*b*:2',3'-*d*]pyran alternating with 5,6-difluoro-2,1,3-benzothiadiazole (denoted as **PDFBT-*alt*-DTP**) was synthesized *via* direct C-H arylation polymerization (DAP) as an atomically efficient protocol. The optimal reaction condition for the DAP gave the target polymers with moderate number-average molecular weights (M_n) using optimized catalytic condition of $Pd_2(dba)_3/(o\text{-}MeOPh)_3P/PivOH/K_2CO_3$ in *o*-xylene. UV-vis-NIR absorption spectra of the obtained polymers show the presence of aggregation and interchain interaction in thin films. ^{1}H-NMR spectroscopic analysis indicates good C-H selectivity corresponding to an alternating strong-donor-*alt*-strong-acceptor conjugated backbone. The hole mobility of the resulting polymers in a magnitude of 10^{-4} $cm^2V^{-1}s^{-1}$ was reached in bottom-gate top-contact field-effect transistors fabricated and tested under ambient conditions.

Keywords: benzothiadiazole, conjugated polymer, direct arylation polymerization, organic electronics.

1. Introduction

Conjugated organic semiconductors have interesting properties like solution processability which could enable cheap and flexible organic electronics devices such as organic field-effect transistors (OFETs)[1-6], organic photovoltaics (OPVs)[7-12], and organic light emitting diodes (OLEDs) to be readily obtained.[13, 14] Conventionally, π-conjugated polymers are synthesized by transition metal-catalyzed polycondensation reactions such as Suzuki–Miyaura and Migita–Kosugi–Stille couplings.[15-18] However, the great versatility and choice, these protocols require the preparation of high-purity organometallic reagents such as arylene diboronic acid and distannyl arylenes using flammable (*n*-BuLi) and toxic organothin precursors. Meanwhile, the polycondensations also produce a stoichiometric amount of toxic byproducts such as trialkyltin compound, which would become key issues in the future commercialization of conjugated polymers. Recently, direct C–H arylation polymerization (DAP) has attracted tremendous attention to synthesize π-conjugated polymers. DAP involves the coupling of an aryl halide monomer directly with another arene monomer without preactivation of the C-H bonds.[19-21]Therefore, it is an economically efficient and environmentally benign approach compared to the traditional coupling methods such as Stille and Suzuki couplings.[22-26]

Copolymerization of alternating electron donor and acceptor moieties has been proved to be a successful strategy to tailor the optoelectronic properties of conjugated copolymers.[27-31] Nowadays, a large library of donor and acceptor moieties are available for the synthesis of D-A conjugated polymers for organic electronics applications. For instance, some of the largely studied donor moieties include carbazole (Cz), benzodithiophene (BDT), dithienosilole (DTS), dithienogermole (DTG), and cyclopentadithiophene (CPDT) units (Scheme 1). A structurally similar donor moiety, 5*H*-dithieno[3,2-*b*:2′,3′-*d*]pyran (DTP) has an electron-donating oxygen atom in the pyran ring, which makes DTP a stronger electron donor moiety than the aforementioned moieties in Scheme 1. In addition to this, the inclusion of fused-ring structures in the conjugated backbone could enhance planarity and thus extended the conjugation length.[32-37] Therefore, copolymerizing DTP with a strong acceptor moiety like DFBT could give a low bandgap D-A conjugated polymer which possesses UV-vis absorption spectra extended to NIR region.

Recently, Dou et al. have reported the synthesis of a new low bandgap (1.38 eV) D-A conjugated polymer poly(5,6-difluoro-2,1,3-benzothiadiazole-*alt*-dithienopyran (denoted as **PDFBT-*alt*-DTP**) via Stille polymerization of 5*H*-dithieno[3,2-*b*:2',3'-*d*]pyran (**DTP**) as an electron donor and 5,6-difluorobenzo[c][1,2,5]thiadiazole (**DFBT**) as an electron acceptor moiety. **PDFBT-*alt*-DTP** as an electron donor mixed with PCBM as an electron acceptor in the bulk heterojunction (BHJ) configuration exhibited a high power conversion efficiency (PCE) of 8%.[38] Nevertheless, the traditional C-C coupling technique of Migita–Kosugi–Stille couplings requires a tedious preactivation of C-H bonds to obtain reactive precursors (boronic acid or trialkyltin) using toxic (stannyl agents) and flammable (*n*-BuLi) agents, associated with the stoichiometric amount of toxic stannyl byproducts.[15-18] As a consequence, an environment-friendly, scalable reaction which retains high yield for mass production of these type of high performance conjugated polymers is required for the future large-scale production and commercialization of organic electronic devices (OFETs, OPVs).

Recently, we have employed direct arylation polymerization (DAP) to synthesize a series of linear D–A conjugated polymers as well as 2D/3D conjugated polymer networks and investigated the factors including catalysts, solvents, ligands, bases, additives, the concentration of reactants, and phase transfer agents on the polymerization. Our synthetic optimization of the DAP reactions has led to a variety of high-quality polymers with minimal structural defects.[24, 25, 39-52] In contrast to Suzuki or Stille coupling, DAP avoids the tedious preactivation of C-H bonds in arenes as monomers using highly flammable (e.g. *n*-butyl lithium) and/or highly toxic stannyl agents that are often involved in Stille coupling, thus enabling facile synthesis of π-conjugated polymers in fewer synthetic steps, i.e. in a more atomically efficient way.[23-25, 39-42, 53-59]

In this article, we present the DAP synthesis of a narrow-bandgap D-A conjugated polymers, poly(5,6-difluoro-2,1,3-benzothiadiazole-*alt*-dithienopyran) (denoted as **PDFBT-*alt*-DTP**) with solubilizing alkyl chain attached on the donor moiety. Its synthetic optimization towards high molecular weight has been carried out via changing the reaction time, temperature, and concentration of monomers. The structure-property relationship of the polymers was characterized using nuclear magnetic resonance (NMR) spectroscopy, size-exclusion chromatography (SEC), thermogravimetric analysis (TGA), UV-vis-NIR spectroscopy, and cyclic voltammetry. The charge carrier properties of the synthesized polymers were characterized in OFET devices, which are fabricated in the air without any encapsulation and protective atmosphere.

2. Experimental Section

2.1. *Materials and Instrumentation.*

All chemicals and solvents were obtained from commercial sources and used without further purification unless otherwise stated. 4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-4-one were commercially obtained from SunaTech Inc. and 4,7-dibromo-5,6-

difluorobenzo[*c*][1,2,5]thiadiazole (**DBrDFBT**) were obtained from Derthon optoelectronics materials. Compound **2**, **3**, & **4** were synthesized according to reported procedures.[38]

^{1}H NMR spectra were recorded on a Bruker AV 300 spectrometer with TMS as the internal reference. Molecular weights of the polymers were obtained from a Gel permeation chromatography (GPC) using $CHCl_3$ as eluent at 80 ^oC after calibration with standard polystyrene. UV–vis absorption spectra were recorded on a Cary 5000 spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Diamond TGA/DTA, at a heating rate of 10 ^oC min^{-1} from 25 to 800 ^oC under a nitrogen atmosphere. Cyclic voltammetry (CV) measurements were conducted on a three-electrode electrochemistry workstation (Model CHI006D) in 0.1 M anhydrous acetonitrile solution of tetrabutylammonium hexafluoro phosphate (Bu_4NPF_6) at 25 ^oC under a nitrogen atmosphere with ferrocene as an internal standard. A glassy carbon disk coated with a thin layer of the polymer film was used as working electrode, a silver wire as a pseudo-reference electrode and a platinum wire as counter electrode. Tapping-mode AFM images of pristine polymer films on OTS-modified Si/SiO_2 substrates at room temperature and annealed at 120 ^oC were taken by using asylum research MFP-3D AFM.

Bottom-gate/top-contact OFETs were fabricated using heavily doped Si wafer as the bottom gate electrode with 300 nm of the SiO_2 layer as the gate dielectric. Gold source and drain electrodes (60 nm) were patterned by the vacuum thermal evaporation. The substrate was cleaned in acetone, isopropanol, and dried on the hot plate at 110 °C then it was further cleaned with piranha solution (H_2SO_4: H_2O_2, 3:1 v/v), washed with deionized water and dried at 100 °C. After that, the substrate was immersed in the octadecyltrichlorosilane (ODTS) solution in toluene solvent overnight, rinsed with toluene to remove excess ODTS, and dried on the hot plate at 110 °C. The polymers dissolved in dichlorobenzene at a concentration of 5 mg mL^{-1} by stirring for 1 day at 60 ^oC. The polymer films were spin-cast at 2000 rpm and annealed at 100 °C for 15 min. Finally, the gold electrode (60 nm) was thermally evaporated in vacuum through a shadow mask with two different dimension length (L) of 200 μm and channel width (W) of 4.0 mm. The field effect mobilities were extracted from the saturation regime using the equation: $\mu_{sat} = (2\ I_{ds}\ L)/\ (W\ C_i\ (V_g - V_{th})^2)$, where I_{ds} denotes the saturation drain current, C_i is the capacitance ($C_i = 10.8 \times 10^{-9}$ F cm^{-2}) of SiO_2 dielectric, V_d is the gate bias, and V_{th} is the threshold voltage.

2.2. *General synthesis procedure for PDFBT-**alt**-DTP polymer via direct arylation polymerization (DAP)*

A mixture of 5-(3,7-dimethyloctyl)-5-(3-methyloctyl)-5*H*-dithieno[3,2-*b*:2',3'-*d*]pyran (Compound **4)** (1 equiv.) and 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (**DBrDFBT**) (1 equiv.), palladium source, ligand, base, PivOH, and o-xylene was added in a reaction vial containing a magnetic stirring bar under nitrogen atmosphere. The vial sealed with an aluminum cap with PTFE/silicone septum and then heated in a preheated oil bath at 100 ^oC except for Entry 1, **E1-DTP** heated at 140 ^oC. After being cooled to room temperature, the reaction mixture was diluted with $CHCl_3$ and added dropwise to methanol (150 mL), precipitates were collected by filtration and then subjected to Soxhlet extraction with methanol, acetone, hexane, and chloroform sequentially each for 24 h. The chloroform and/or chlorobenzene fraction was concentrated and precipitated into methanol. The precipitates were collected by filtration and dried under vacuum before further characterization.

Entry 1: $Pd_2(dba)_3$ (5 mol%), (*o*-MeOPh)$_3$P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and the monomers (0.1 M in *o*-xylene) at 140 °C. Yield: 48% from $CHCl_3$ fraction.

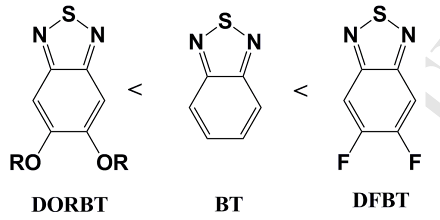
Entry 2: $Pd_2(dba)_3$ (5 mol%), (*o*-MeOPh)$_3$P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and the monomers (0.2 M in *o*-xylene) at 100 °C. Yield: 88% from $CHCl_3$ fraction.

Entry 3: $Pd(OAc)_2$ (5 mol%), (*o*-MeOPh)$_3$P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and the monomers (0.2 M in *o*-xylene) at 100 °C. Yield: 80% from $CHCl_3$ fraction.

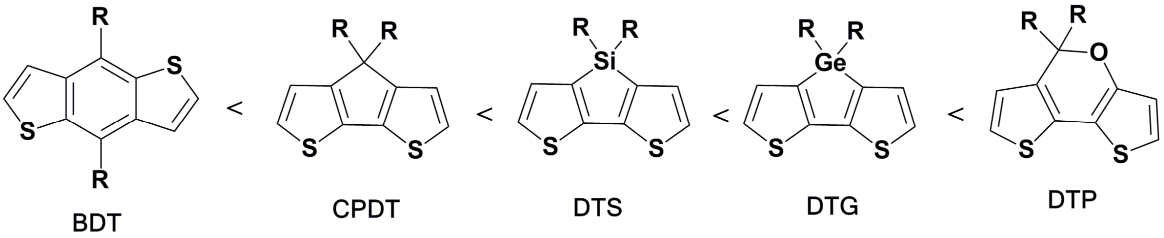
Entry 4: Herrmann's catalyst (5 mol%), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (4 equiv.), PivOH (50 mol%), and the monomers (0.2 M in *o*-xylene) at 100 °C. no polymerization.

Entry 5: $Pd_2(dba)_3$ (5 mol%), (*o*-MeOPh)$_3$P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and the monomers (0.3 M in *o*-xylene) at 100 °C. Yield: 83% from $CHCl_3$ fraction.

Entry 6: $Pd_2(dba)_3$ (5 mol%), (*o*-MeOPh)$_3$P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and the monomers (0.5 M in *o*-xylene) at 100 °C. Yield: 15% from $CHCl_3$ fraction.

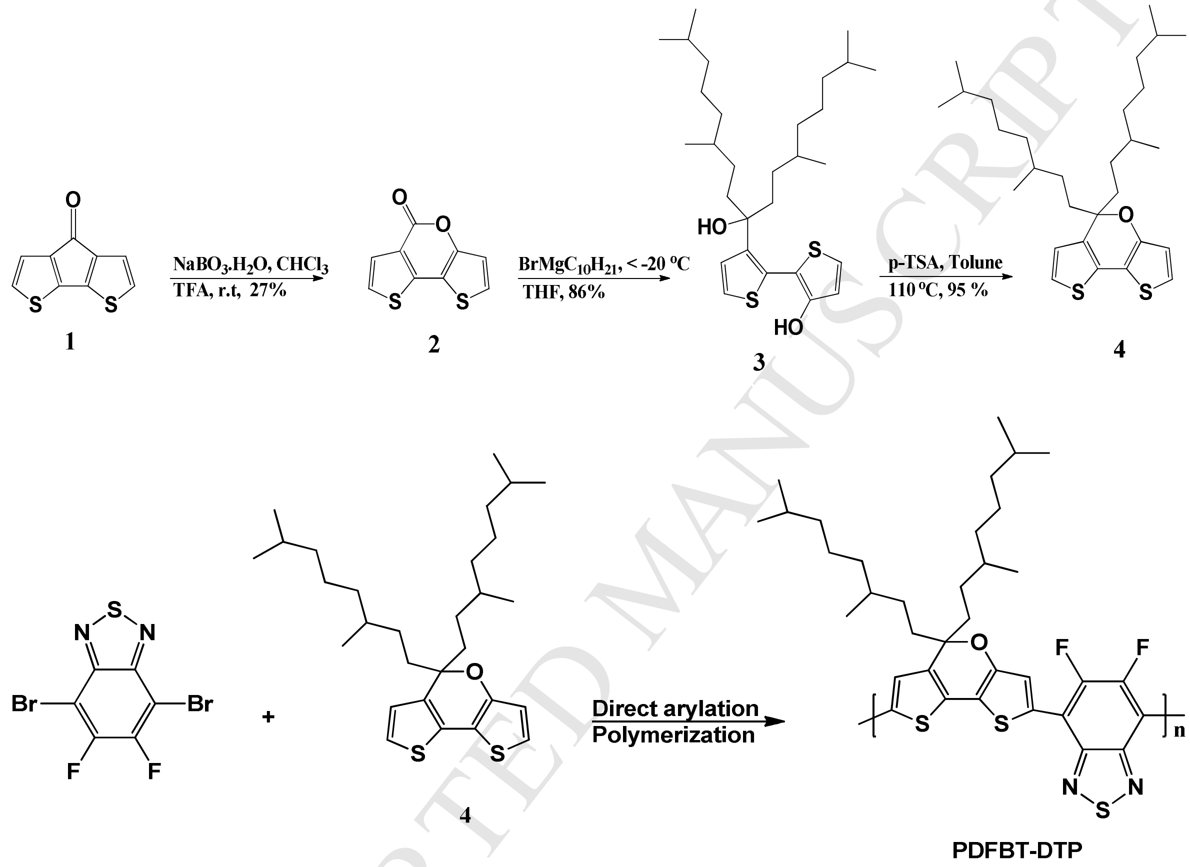


Increasing order of electron accepting strength



Increasing order of electron donating strength

Scheme 1. Chemical structures of electron donor units (BDT, CPDT, DTS, DTG, and DTP) and electron acceptor units (BT, DORBT, DFBT). (R = alkyl chains); arranged in increasing order of electron donating and electron accepting strength.[60-62]



Scheme 2. Synthetic route to **PDFBT- *alt*-DTP** polymer *via* DAP.

3. Results and discussion

3.1. *Synthesis and structural characterization*

The synthetic route to the donor moiety 5-(3,7-dimethyloctyl)-5-(3-methyloctyl)-5*H*-dithieno[3,2-*b*:2',3'-*d*]pyran (Compound **4**, **DTP**) and its copolymerization with 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (**DBrDFBT**) are shown in Scheme 2. The synthesis of Compound **2** to **4** were conducted according to reported procedure.[38]

The optimization of the DAP reaction was carried out by changing conditions, such as palladium-catalyst, concentration of monomers, and reaction temperature (see Table 1) and the progress of reaction was monitored by the color change from dark red to dark cyan (which is the characteristics color of the **PDFBT-*alt*-DTP** polymer as reported in the literature).[38] First, Compound **4** and DBrDFBT (0.1 M) were reacted in the presence of $Pd_2(dba)_3$ as the catalyst, (o-MeOPh)$_3$P as the ligand, PivOH as the additive, K_2CO_3 as the base in *o*-xylene at 140 ^oC for 24 h (**E1-DTP**), which gives **PDFBT-*alt*-DTP** polymer in a relatively low yield of 48% (M_n of 6.8 kDa) from the chloroform fraction. The effort to further increase the yield and molecular weight was carried out by increasing the monomer concentration to 0.2 M and decreasing the reaction temperature to 100 ^oC (**E2-DTP**) to give **PDFBT-*alt*-DTP** polymer with an increased yield of 88% from chloroform fraction with comparable molecular weight (M_n of 6.9 kDa) with **E1-DTP**. Further increase in concentration to 0.3 M (**E5-DTP**) provides a yield of 83% and M_n of 6.6 kDa comparable to that of entry **E1**- & **E2-DTP**. Further increase of the monomer (**E6-DTP**) concentration to 0.5 M did not result in significant improvement of M_n (7.1 kDa from chloroform fraction, Entry **E6-DTP**, Table 1). However, in Entry **E6-DTP** the yield in chloroform fraction has decreased dramatically to 15% with the presence of an insoluble residue which was later completely dissolved in chlorobenzene (M_n of 11.4 kDa) with rather broad PDI (11.2), possibly attributed to side reactions, such as crosslinking or β-branching occurred in Compound **4**.

Table 1. DAP optimization entries for the synthesis of the **PDFBT-*alt*-DTP** polymers.

Entry no.	**Catalyst**	**$C_{monomer}$ (M)**	**Temperature (^oC)**	**Yield (%)**	**[d]M_n (kDa)**	**M_w/M_n**
E1-DTP	$Pd_2(dba)_3$	0.1	140	48	6.8	3.2
E2-DTP	$Pd_2(dba)_3$	0.2	100	88	6.9	8.5
E3-DTP	$Pd(OAc)_2$	0.2	100	80	5.7	3.2
E4-DTP	Hermann	-	100	[c]-	-	-
E5-DTP	$Pd_2(dba)_3$	0.3	100	83	6.6	4.5
E6-DTP	$Pd_2(dba)_3$	0.5	100	[a]15	7.1	6.4
			100	[b]72	11.4	11.2

[a]Yield of the polymer from chloroform fraction. [b]Yield of the polymer from chlorobenzene fraction. [c]No precipitate in methanol. [d]Measured by GPC with polystyrene as standard and $CHCl_3$ as eluent at 80 °C. For all entries; PiVOH additive, $P(o\text{-}MeOPh)_3$ ligand, and K_2CO_3 base were used for a reaction time of 24 h.

$Pd(OAc)_2$ and Herrmann's catalyst were employed to gain more information about the effect of a catalyst on the DAP reaction between Compound **4** and **DBrDFBT**. Thus, in **E3-DTP**, $Pd(OAc)_2$ gave a polymer with a lower molecular weight (M_n of 5.7 kDa), whereas Herrmann's catalyst in **E4-DTP** gave no polycondensation product, where the color of the reaction mixture after 24 h was dark purple and no precipitate was obtained from methanol. Based on the aforementioned optimization results, the combination of $Pd_2(dba)_3/(o\text{-}MeOPh)_3P/PivOH/K_2CO_3/o$-xylene is found to be the best DAP reaction condition for the synthesis of high molecular weight **PDFBT-*alt*-DTP** polymer. These results indicate that the M_n of **PDFBT-*alt*-DTP** polymers obtained under the present DAP conditions remains lower compared to that (M_n = 28.5 kDa) of the same type of polymer synthesized through Stille coupling polymerization.[38] One possible factor that contributes to such low-molecular-weight polymers is the relatively low reactivity of the dibromo-DFBT monomer involved in the DAP, which was also observed by our group in the DAP of dibromo-DFBT with thienoisoindigo-based monomers.[48]

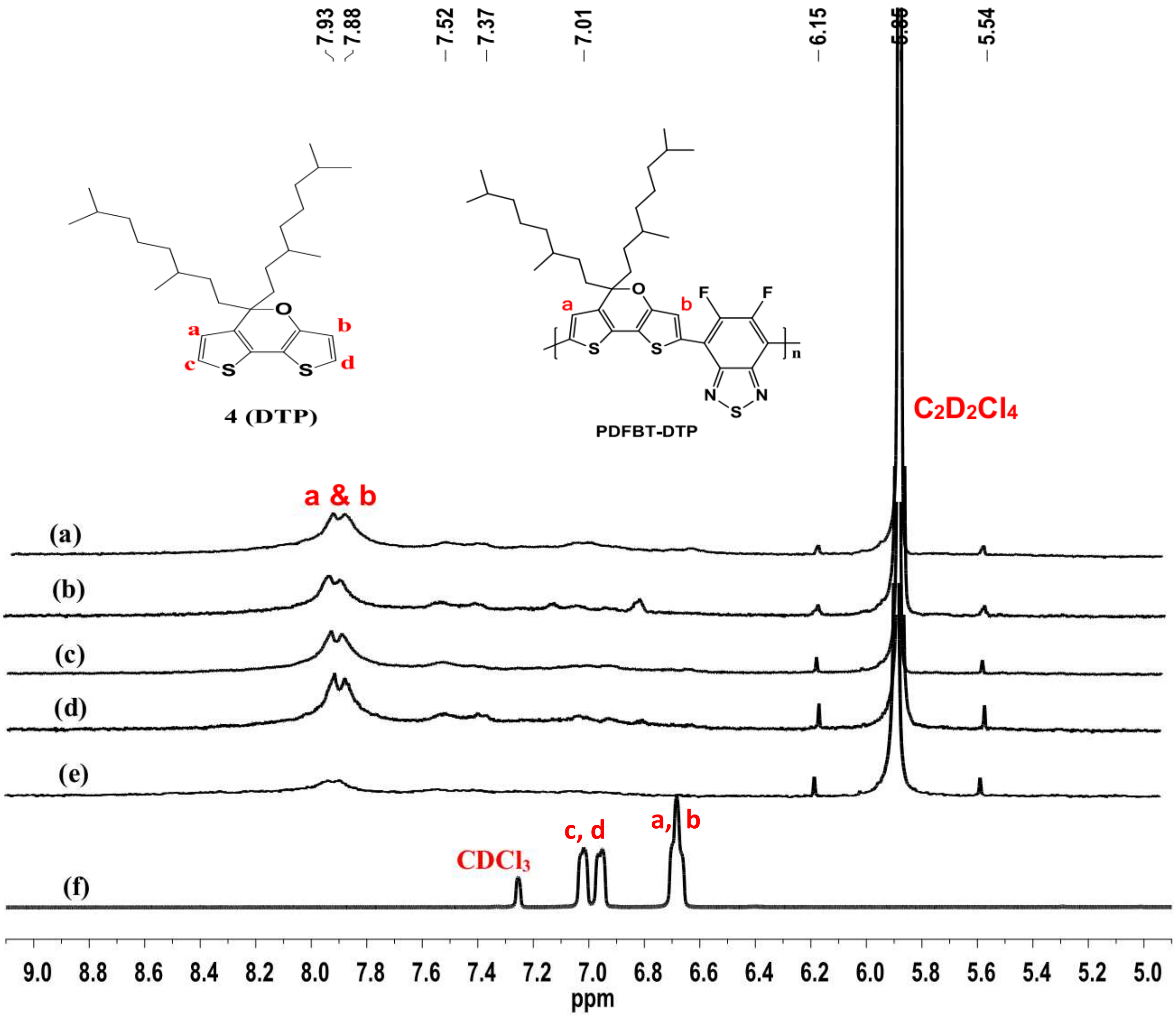


Figure 1. ^{1}H-NMR (300 MHz) spectra of the **PDFBT-*alt*-DTP** polymers synthesized *via* DAP, **E1-DTP** (A), **E2-DTP** (B), **E3-DTP** (C), **E5-DTP** (D), and **E6-DTP-CB** (E) at 100 ^{o}C in $C_2D_2Cl_4$. **DTP** monomer **(4)** (F) in $CDCl_3$ at r.t.

To characterize the chemical structure of **PDFBT-*alt*-DTP** polymers synthesized *via* DAP, high temperature (100 ^{o}C) ^{1}H-NMR spectra in $C_2D_2Cl_4$ as the solvent were collected (see

Figure 1). The extra little peaks found in the ^{1}H-NMR spectra can be related to different end groups from the monomers. For instance, as shown in Figure 1, there are tiny peaks around 7.52, 7.38 and 6.99 ppm, which could correspond to end groups from Compound **4** in the polymer. The selectivity of (α)C-H over (β)C-H protons in Compound **4** is good as indicated by the presence of (β)C-H protons around 7.93 and 7.88 ppm in the ^{1}H-NMR spectra of all entries of the DAP polymers. As described by Dou et al.,[38] it was difficult to get highly pure stannylated monomer of Compound **4** in the synthesis of **PDFBT-*alt*-DTP** by Stille polymerization and thus affected the quality of **PDFBT-*alt*-DTP** polymer and it's device performance unless it was end-caped with bromobenzene. Therefore, employing direct arylation polymerization for the synthesis **PDFBT-*alt*-DTP** polymer might avoid stannylation-related problems.

3.2. *Thermal Properties*

The thermal stability of **PDFBT-*alt*-DTP** polymer was investigated using thermogravimetric analysis (TGA) with a heating rate of 10 °C min^{-1} under N_2 atmosphere. The decomposition temperature (T_d, corresponding to 5% weight loss) is located at 335 ^{o}C for the **PDFBT-*alt*-DTP** polymer with the highest M_n obtained by DAP **(E2-DTP)** (see Figure S1), demonstrating its sufficient high thermal stability for the application in organic electronic devices.

3.3. *Optical properties*

The UV-VIS-NIR absorption spectra for **PDFBT-*alt*-DTP** polymers were acquired from solutions in chloroform and in chlorobenzene (for **E6-DTP** of chlorobenzene fraction) and spin-cast thin films prepared from chlorobenzene solution, respectively. The spectra are shown in Figure 2 and the relevant data are summarized in Table 2. Broad absorption bands across the visible region were observed for both solution and thin films. The absorption maxima for **PDFBT*alt*-DTP** polymers in solution (see Figure 2a) shows a red shift and an intense shoulder peak as the molecular weight increased. **E2-DTP** has λ_{max} ($\lambda_{shoulder}$) of 711 (776) nm which is red-shifted ca.10-15 (14) nm as compared to the polymers from the other entries. **E6-DTP** from CB fraction, despite its higher average molecular weight than other batches (e.g. **E1**-**5**), shows a blue shift of ca. 60 nm in $\lambda_{max.abs}$, which might be due to the presence of crosslinking or β-branching in the polymer backbone.

The thin film of **PDFBT-*alt*-DTP** polymers prepared by spin casting at 1500 rpm on a quartz substrate from their respective chlorobenzene solutions showed red-shifted absorbance (ca.10 nm for **E2-DTP**) as compared with its absorption spectra in chloroform. A shoulder peak at 780 nm with much increased intensity was observed in the thin-film spectra of **E2-DTP** as compared with its solution state, which indicates strong intermolecular interaction in solid thin films. However, the intensity of the peak at 780 nm relative to that at 719 nm has weaker intensity in **E2-DTP** polymer compared to the similar polymer synthesized by Stille polymerization,[38] which is probably due to the lower M_n of the polymer synthesized via DAP. Estimation from the onset absorption wavelength of their thin film spectra gave an optical bandgap (E_g^{opt}) of 1.41 eV for the **E2-DTP** polymer, which is almost equal to that of the same type of polymer synthesized by Stille polymerization as previously reported (see Table 2).[38] Such a small bandgap is attributed to the intramolecular charge transfer between the strongly electron-donating DTP unit and strongly electron-withdrawing DFBT unit.[28-31, 63]

Table 2. Optical data of **PDFBT-*alt*-DTP** polymers.

Entry no.	**In $CHCl_3$**		**Film**		
	$\lambda_{max.abs}(\lambda_{shoulder.abs})$ (nm)	**$\lambda_{onset.abs}$ (nm)**	**$\lambda_{max.abs}(\lambda_{shoulder.abs})$ (nm)**	**$\lambda_{onset.abs}$ (nm)**	**E_g^{opt} (eV)**
E1-DTP	694 (767)	860	704 (770)	868	1.43
E2-DTP	711 (776)	874	719 (780)	878	1.41
E3-DTP	694 (767)	860	712 (776)	868	1.43
E5-DTP	698 (767)	860	712 (780)	876	1.42
E6-DTP (1) [c]	698 (767)	860	712 (780)	885	1.40
E6-DTP (2) [d]	638 (767) [e]	860 [e]	664 (786)	873	1.42

[a]Film at room temperature. [b]E_g^{opt}(eV)=1240/λ_{onset}[nm]. [c]**E6-DTP** (1) is $CHCl_3$ fraction and [d]**E6-DTP** (2) is chlorobenzene fraction. [e]From chlorobenzene solution.

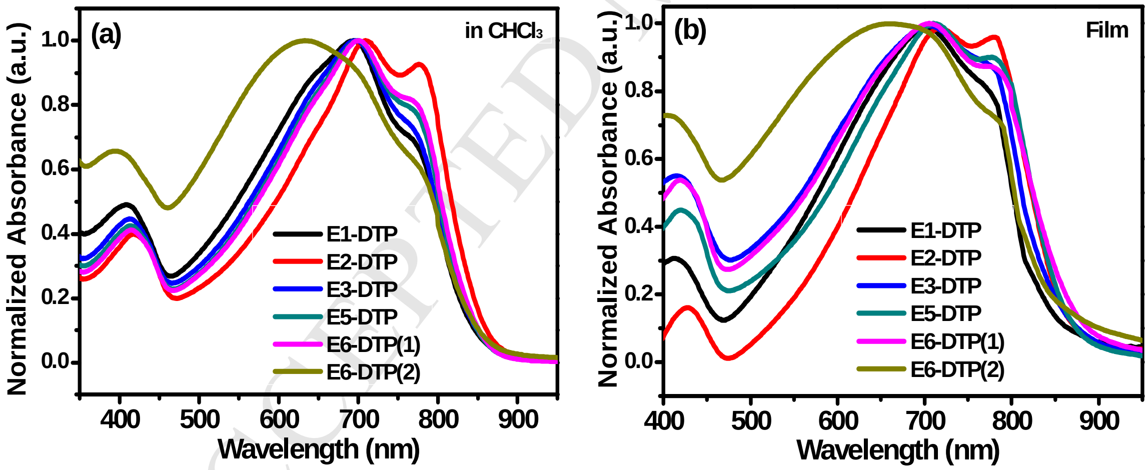


Figure 2. UV-vis-NIR absorption spectra of **PDFBT-*alt*-DTP** polymers (a) in $CHCl_3$, except **E6-DTP (2)** in chlorobenzene; and (b) in the thin film prepared by spin casting from their chlorobenzene solutions. **E6-DTP (1)** is $CHCl_3$ fraction and **E6-DTP (2)** is chlorobenzene fraction.

3.4. *Electrochemical properties*

The electrochemical properties of **PDFBT-*alt*-DTP** polymers were investigated by cyclic voltammetry (CV) using ferrocene (Fc/Fc^+) as the standard (see Figure 3 and S2). It shows that the electrochemical oxidation and reduction process of **PDFBT-*alt*-DTP** polymers is reversible. Table 3 summarizes the HOMO/ LUMO energy levels and the bandgap of **PDFBT-*alt*-DTP** polymers. The oxidation was observed with an onset potential (E_{ox}) at 0.83 to 1.05 V vs. Ag/Ag^+ and the onset reduction potentials (E_{red}) were observed at -0.77 to -0.96 V vs. Ag/Ag^+. Thus, the $HOMO^{ele}/LUMO^{ele}$ energy levels were calculated by the following equation: $HOMO^{ele} = -(4.8 - E_{1/2,Fc/Fc+} + E_{ox})$ eV and $LUMO^{ele} = -(4.8 - E_{1/2,Fc/Fc+} + E_{red})$ eV, where $E_{1/2,Fc/Fc+} = 0.5$ V. Therefore, $HOMO^{ele}$ of ca.-5.2 eV and $LUMO^{ele}$ of ca.-3.4 to -3.5 eV were calculated for all polymers from their corresponding E_{ox} and E_{red}, respectively. The $LUMO^{opt}$ calculated using $LUMO^{opt} = HOMO^{ele} - E_g^{opt}$ is -3.77 eV for **E2-DTP**. The electrochemical bandgap (E_g^{ele}) of **PDFBT-*alt*-DTP** polymers is in the range of 1.71 to 1.97 eV which is slightly larger than that of the optical bandgap (E_g^{opt}) (1.40 to 1.43 eV). The discrepancy of E_g values lies within the range of experimental errors.[64] The HOMO level (5.18 eV) of **E2-DTP** polymer with a higher M_n is comparable with the HOMO level (5.2 eV) of Stille polymer as reported by Dou et al.[38] In addition to this, the electrochemical bandgap (1.76 eV) of the **E2-DTP** polymer is slightly higher than that of Stille polymer (1.62 eV). This difference could be explained based on M_n, where the Stille polymer has higher M_n of 28 kDa, thus presumably a higher average conjugation length than that of **E2-DTP** polymer (M_n = 6.9 kDa).

Table 3. Electrochemical properties of **PDFBT-*alt*-DTP** polymers.

Entry no.	E_{ox} (V)	E_{red} (V)	$^{a}HOMO^{ele}$ (eV)	$^{a}LUMO^{ele}$ (eV)	$^{b}LUMO^{opt}$ (eV)	$^{c}E_g^{ele}$ (eV)
E1-DTP	0.94	-0.77	-5.2	-3.5	-3.8	1.7
E2-DTP	0.88	-0.88	-5.2	-3.4	-3.8	1.8
E3-DTP	0.85	-0.91	-5.2	-3.4	-3.7	1.8
E5-DTP	0.83	-0.93	-5.1	-3.4	-3.7	1.7
E6-DTP (1) [d]	1.01	-0.96	-5.3	-3.3	-3.9	2.0
E6-DTP (2) [e]	1.05	-0.87	-5.4	-3.4	-3.9	2.0

[a] $HOMO^{ele} = -(4.8 - E_{1/2,\ Fc,Fc+} + E_{ox,onset})$; $LUMO^{ele} = -(4.8 - E_{1/2,\ Fc,Fc+} + E_{red,onset})$. [b] $LUMO^{opt} = E_g^{opt} + HOMO^{ele}$. [c] $E_g^{ele} = LUMO^{ele} - HOMO^{ele}$. [d] **E6-DTP** (1) is $CHCl_3$ fraction and [e] **E6-DTP** (2) is chlorobenzene fraction.

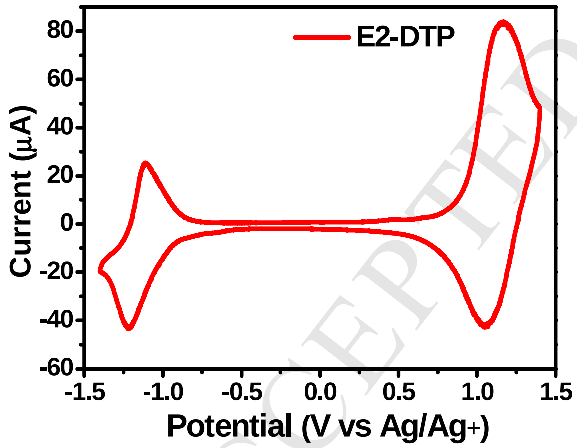


Figure 3. Cyclic voltammetry curve of **E2-DTP** polymer from $CHCl_3$ fraction.

3.5. *Field-effect transistor performance*

The charge-transport properties of **PDFBT-*alt*-DTP** polymers were studied by fabricating bottom-gate, top-contact OTFT devices on OTS-18 modified Si/SiO_2 substrate. The fabrication and measurement were done in the air without any protective atmosphere. The device performances for selected polymer (**E2-DTP)** are summarized in Table 4 and their transfer and output curves are shown in Figure 4 and S3, respectively. The hole mobility (μ_h) of the as-prepared OFET devices of **E2-DTP** polymer, which is derived from the slope of transfer curve is 1.0×10^{-4} $cm^2V^{-1}s^{-1}$. After thermal annealing at 100 °C, a slightly increased μ_h to 1.7×10^{-4} $cm^2V^{-1}s^{-1}$ was obtained. The morphological studies of **E2-DTP** polymer thin films investigated by AFM (see Figure S4) from its spin cast thin film on OTS-18 treated Si/SiO_2 substrate at room temperature displayed less number of aggregates. However, after annealing at 100 ^{o}C, the number of fine spherical aggregates has increased, which may affect the π-π stacking among the polymer chains. Consequently, a slight improvement in the hole mobility of the **E2-DTP** polymer has observed.

Table 4. Performance of OFET devices for **PDFBT-*alt*-DTP** polymer (**E2-DTP**) semiconductor on an OTS-18-treatd substrate fabricated and measured under ambient conditions.

Entry no.	**M_n (kDa)**	**Annealing Temp. (^{o}C)**	**μ_h ($cm^2V^{-1}s^{-1}$)**	**V_{th} (V)**	**On/off Ratio**
E2-DTP	6.9	R.T.	1.0×10^{-4}	7.6	10^3-10^4
		100	1.7×10^{-4}	6.3	10^3-10^4

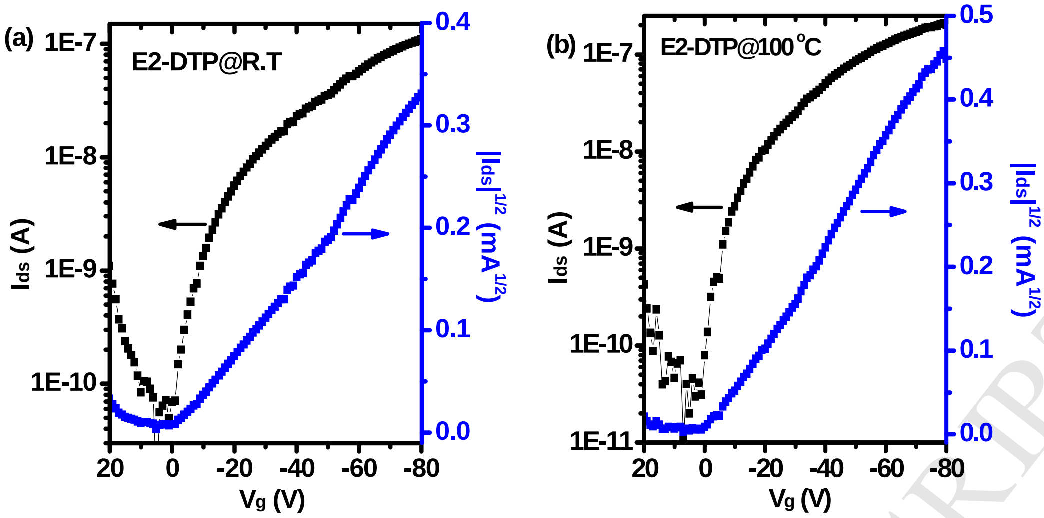


Figure 4. Transfer curves of **E2-DTP** polymer (a) at r.t and (b) after annealing at 100 °C.

4. Conclusion

In summary, direct arylation polymerization (DAP) has been used in the synthesis of low bandgap 5*H*-dithieno[3,2-*b*:2',3'-*d*]pyran (**DTP**) based polymer, **PDFBT-*alt*-DTP**. A series of DAP optimizations have led to an optimal catalytic condition, i.e. $Pd_2(dba)_3$/(*o*-MeOPh)$_3$P/PivOH/K_2CO_3/*o*-xylene (0.2 M), which resulted in the target polymers with M_n up to 6.9 kDa. The obtained **PDFBT-*alt*-DTP** polymers show a strong shoulder peak in the red edge of their optical absorption spectra, which corresponds to the presence of strong π-π interaction in solid films. Charge transport behavior of **PDFBT-*alt*-DTP** polymers shows a hole mobility of 1.7×10^{-4} cm^2 V^{-1} s^{-1}, evaluated in bottom-gate top-contact OFET devices fabricated and measured under ambient conditions. These results indicate that further optimization of DAP reaction conditions such as catalyst type, reaction time and temperature, ligand type could lead to the higher molecular weight of the **PDFBT-*alt*-DTP** polymer and consequently higher charge carrier mobility in its OFET device. Therefore, this work further demonstrates the potential of DAP for the facile and efficient synthesis of a variety of high-performance semiconducting polymers for optoelectronic applications.

Acknowledgments

M.W. is grateful to the funding support by a start-up grant (M4080992.120) of Nanyang Assistant Professorship from Nanyang Technological University, and AcRF Tier 1 (M4011061.120, RG49/12) from the Ministry of Education, Singapore. A. E. gratefully acknowledges the Ph.D. research scholarship from Nanyang Technological University.

References

[1] Wang C, Dong H, Hu W, Liu Y, Zhu D. Semiconducting π-conjugated systems in field-effect transistors: a material odyssey of organic electronics. Chem Rev. 2011;112(4):2208-67.

[2] Deng Y, Chen Y, Zhang X, Tian H, Bao C, Yan D, et al. Donor–acceptor conjugated polymers with dithienocarbazoles as donor units: effect of structure on semiconducting properties. Macromolecules. 2012;45(21):8621-7.

[3] Mei J, Diao Y, Appleton AL, Fang L, Bao Z. Integrated materials design of organic semiconductors for field-effect transistors. J Am Chem Soc. 2013;135(18):6724-46.

[4] Facchetti A. Organic semiconductors: Made to order. Nat Mater. 2013;12(7):598-600.

[5] Tsao HN, Müllen K. Improving polymer transistor performance via morphology control. Chem Soc Rev. 2010;39(7):2372-86.

[6] Takeda Y, Andrew TL, Lobez JM, Mork AJ, Swager TM. An Air-Stable Low-Bandgap n-Type Organic Polymer Semiconductor Exhibiting Selective Solubility in Perfluorinated Solvents. Angew Chem Int Ed. 2012;51(36):9042-6.

[7] Koster L, Shaheen SE, Hummelen JC. Pathways to a new efficiency regime for organic solar cells. Adv Energy Mater. 2012;2(10):1246-53.

[8] Li J, Grimsdale AC. Carbazole-based polymers for organic photovoltaic devices. Chem Soc Rev. 2010;39(7):2399-410.

[9] Chen H-Y, Hou J, Zhang S, Liang Y, Yang G, Yang Y, et al. Polymer solar cells with enhanced open-circuit voltage and efficiency. Nat Photon. 2009;3(11):649-53.

[10] Huo L, Zhang S, Guo X, Xu F, Li Y, Hou J. Replacing alkoxy groups with alkylthienyl groups: a feasible approach to improve the properties of photovoltaic polymers. Angew Chem. 2011;123(41):9871-6.

[11] He Z, Zhong C, Su S, Xu M, Wu H, Cao Y. Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure. Nat Photon. 2012;6(9):591-5.

[12] You J, Dou L, Yoshimura K, Kato T, Ohya K, Moriarty T, et al. A polymer tandem solar cell with 10.6% power conversion efficiency. Nat Commun. 2013;4:1446.

[13] Grimsdale AC, Leok Chan K, Martin RE, Jokisz PG, Holmes AB. Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices. Chem Rev. 2009;109(3):897-1091.

[14] Huang F, Wu H, Cao Y. Water/alcohol soluble conjugated polymers as highly efficient electron transporting/injection layer in optoelectronic devices. Chem Soc Rev. 2010;39(7):2500-21.

[15] Carsten B, He F, Son HJ, Xu T, Yu L. Stille polycondensation for synthesis of functional materials. Chem Rev. 2011;111(3):1493-528.

[16] Okamoto K, Luscombe CK. Controlled polymerizations for the synthesis of semiconducting conjugated polymers. Polym Chem. 2011;2(11):2424-34.

[17] Sakamoto J, Rehahn M, Wegner G, Schlüter AD. Suzuki polycondensation: polyarylenes à la carte. Macromol Rapid Commun. 2009;30(9-10):653-87.

[18] Amatore C, Jutand A, Le Duc G. The Triple Role of Fluoride Ions in Palladium-Catalyzed Suzuki–Miyaura Reactions: Unprecedented Transmetalation from [ArPdFL2] Complexes. Angew Chem. 2012;124(6):1408-11.

[19] Ball LT, Lloyd-Jones GC, Russell CA. Gold-catalyzed direct arylation. Science. 2012;337(6102):1644-8.

[20] Alberico D, Scott ME, Lautens M. Aryl-aryl bond formation by transition-metal-catalyzed direct arylation. Chem Rev. 2007;107(1):174-238.

[21] Wencel-Delord J, Glorius F. CH bond activation enables the rapid construction and late-stage diversification of functional molecules. Nat Chem. 2013;5(5):369-75.

[22] Khlyabich PP, Burkhart B, Rudenko AE, Thompson BC. Optimization and simplification of polymer–fullerene solar cells through polymer and active layer design. Polymer. 2013;54(20):5267-98.

[23] Okamoto K, Zhang J, Housekeeper JB, Marder SR, Luscombe CK. C–H arylation reaction: atom efficient and greener syntheses of π-conjugated small molecules and macromolecules for organic electronic materials. Macromolecules. 2013;46(20):8059-78.

[24] Mercier LG, Leclerc M. Direct (hetero) arylation: a new tool for polymer chemists. Acc Chem Res. 2013;46(7):1597-605.

[25] Wang K, Wang M. Direct arylation polymerization: a green, streamlining synthetic approach to π-conjugated polymers. Curr Org Chem. 2013;17(9):999-1012.

[26] Rudenko AE, Thompson BC. Optimization of direct arylation polymerization (DArP) through the identification and control of defects in polymer structure. J Polym Sci, Part A: Polym Chem. 2015;53(2):135-47.

[27] Frechet J, Thompson B. Polymer-fullerene composite solar cells. Angew Chem Int Ed. 2008;47:58-77.

[28] Cheng Y-J, Yang S-H, Hsu C-S. Synthesis of conjugated polymers for organic solar cell applications. Chem Rev. 2009;109(11):5868-923.

[29] Boudreault P-LT, Najari A, Leclerc M. Processable low-bandgap polymers for photovoltaic applications. Chem Mater. 2010;23(3):456-69.

[30] Beaujuge PM, Fréchet JM. Molecular design and ordering effects in π-functional materials for transistor and solar cell applications. J Am Chem Soc. 2011;133(50):20009-29.

[31] Li Y. Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption. Acc Chem Res. 2012;45(5):723-33.

[32] Usta H, Lu G, Facchetti A, Marks TJ. Dithienosilole-and dibenzosilole-thiophene copolymers as semiconductors for organic thin-film transistors. J Am Chem Soc. 2006;128(28):9034-5.

[33] Hou J, Chen H-Y, Zhang S, Li G, Yang Y. Synthesis, characterization, and photovoltaic properties of a low band gap polymer based on silole-containing polythiophenes and 2, 1, 3-benzothiadiazole. J Am Chem Soc. 2008;130(48):16144-5.

[34] Yue W, Zhao Y, Shao S, Tian H, Xie Z, Geng Y, et al. Novel NIR-absorbing conjugated polymers for efficient polymer solar cells: effect of alkyl chain length on device performance. J Mater Chem. 2009;19(15):2199-206.

[35] McCulloch I, Heeney M, Bailey C, Genevicius K, MacDonald I, Shkunov M, et al. Liquid-crystalline semiconducting polymers with high charge-carrier mobility. Nat Mater. 2006;5(4):328-33.

[36] Liang Y, Xu Z, Xia J, Tsai ST, Wu Y, Li G, et al. For the bright future—bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%. Adv Mater. 2010;22(20).

[37] Beaujuge PM, Pisula W, Tsao HN, Ellinger S, Müllen K, Reynolds JR. Tailoring Structure− Property Relationships in Dithienosilole− Benzothiadiazole Donor− Acceptor Copolymers. J Am Chem Soc. 2009;131(22):7514-5.

[38] Dou L, Chen C-C, Yoshimura K, Ohya K, Chang W-H, Gao J, et al. Synthesis of 5 H-dithieno [3, 2-b: 2′, 3′-d] pyran as an electron-rich building block for donor–acceptor type low-bandgap polymers. Macromolecules. 2013;46(9):3384-90.

[39] Bura T, Morin P-O, Leclerc M. En Route to Defect-Free Polythiophene Derivatives by Direct Heteroarylation Polymerization. Macromolecules. 2015;48(16):5614-20.

[40] Rudenko AE, Khlyabich PP, Thompson BC. Random poly (3-hexylthiophene-co-3-cyanothiophene) copolymers via direct arylation polymerization (DArP) for organic solar cells with high open-circuit voltage. ACS Macro Lett. 2014;3(4):387-92.

[41] Luzio A, Fazzi D, Nübling F, Matsidik R, Straub A, Komber H, et al. Structure–Function Relationships of High-Electron Mobility Naphthalene Diimide Copolymers Prepared Via Direct Arylation. Chem Mater. 2014;26(21):6233-40.

[42] Kuwabara J, Yasuda T, Choi SJ, Lu W, Yamazaki K, Kagaya S, et al. Direct Arylation Polycondensation: A Promising Method for the Synthesis of Highly Pure, High-Molecular-Weight Conjugated Polymers Needed for Improving the Performance of Organic Photovoltaics. Adv Funct Mater. 2014;24(21):3226-33.

[43] Efrem A, Wang K, Jia T, Wang M. Direct arylation polymerization toward a narrow bandgap donor–acceptor conjugated polymer of alternating 5, 6-difluoro-2, 1, 3-benzothiadiazole and alkyl-quarternarythiophene: From synthesis, optoelectronic properties to devices. J Polym Sci Part A: Polym Chem. 2017; DOI: 10.1002/pola.28555.

[44] Wang X, Wang M. Synthesis of donor–acceptor conjugated polymers based on benzo [1, 2-b: 4, 5-b′] dithiophene and 2, 1, 3-benzothiadiazole via direct arylation polycondensation: towards efficient C–H activation in nonpolar solvents. Polym Chem. 2014;5(19):5784-92.

[45] Wang X, Wang K, Wang M. Synthesis of conjugated polymers via an exclusive direct-arylation coupling reaction: a facile and straightforward way to synthesize thiophene-flanked benzothiadiazole derivatives and their copolymers. Polym Chem. 2015;6(10):1846-55.

[46] Shao J, Wang G, Wang K, Yang C, Wang M. Direct arylation polycondensation for efficient synthesis of narrow-bandgap alternating D–A copolymers consisting of naphthalene diimide as an acceptor. Polym Chem. 2015;6(38):6836-44.

[47] Wang K, Wang G, Wang M. Balanced Ambipolar Poly (diketopyrrolopyrrole-alt-tetrafluorobenzene) Semiconducting Polymers Synthesized via Direct Arylation Polymerization. Macromol Rapid Commun. 2015;36(24):2162-70.

[48] Huang J, Wang K, Gupta S, Wang G, Yang C, Mushrif SH, et al. Thienoisoindigo-based small molecules and narrow bandgap polymers synthesized via C–H direct arylation coupling. J Polym Sci Part A: Polym Chem. 2016;54(13):2015-31.

[49] Bohra H, Shao J, Huang S, Wang M. Facile synthesis of naphthodithiophenediimide based small molecules and polymers via direct arylation coupling. Tetrahedron Lett. 2016;57(13):1497-501.

[50] Bohra H, Tan SY, Shao J, Yang C, Efrem A, Zhao Y, et al. Narrow bandgap thienothiadiazole-based conjugated porous polymers: from facile direct arylation polymerization to tunable porosities and optoelectronic properties. Polym Chem. 2016;7(41):6413-21.

[51] Wang K, Wang M. Hyperbranched narrow-bandgap DPP homopolymers synthesized via direct arylation polycondensation. J Polym Sci Part A: Polym Chem. 2017;55(6):1040-7.

[52] Efrem A, Wang K, Amaniampong PN, Yang C, Gupta S, Bohra H, et al. Direct arylation polymerization towards narrow bandgap conjugated microporous polymers with hierarchical porosity. Polym Chem. 2016;7(30):4862-6.

[53] Lu W, Kuwabara J, Kanbara T. Polycondensation of dibromofluorene analogues with tetrafluorobenzene via direct arylation. Macromolecules. 2011;44(6):1252-5.

[54] Berrouard P, Najari A, Pron A, Gendron D, Morin PO, Pouliot JR, et al. Synthesis of 5-Alkyl [3, 4-c] thienopyrrole-4, 6-dione-Based Polymers by Direct Heteroarylation. Angew Chem Int Ed. 2012;51(9):2068-71.

[55] Facchetti A, Vaccaro L, Marrocchi A. Semiconducting polymers prepared by direct arylation polycondensation. Angew Chem Int Ed. 2012;51(15):3520-3.

[56] Pouliot J-Rm, Grenier Fo, Blaskovits JT, Beaupré S, Leclerc M. Direct (Hetero) arylation Polymerization: Simplicity for Conjugated Polymer Synthesis. Chem Rev. 2016;116(22):14225-74.

[57] Kowalski S, Allard S, Zilberberg K, Riedl T, Scherf U. Direct arylation polycondensation as simplified alternative for the synthesis of conjugated (co) polymers. Prog Polym Sci. 2013;38(12):1805-14.

[58] Wakioka M, Kitano Y, Ozawa F. A Highly Efficient Catalytic System for Polycondensation of 2, 7-Dibromo-9, 9-dioctylfluorene and 1, 2, 4, 5-Tetrafluorobenzene via Direct Arylation. Macromolecules. 2013;46(2):370-4.

[59] Wang Q, Takita R, Kikuzaki Y, Ozawa F. Palladium-catalyzed dehydrohalogenative polycondensation of 2-bromo-3-hexylthiophene: An efficient approach to head-to-tail poly (3-hexylthiophene). J Am Chem Soc. 2010;132(33):11420-1.

[60] Zhou H, Yang L, You W. Rational design of high performance conjugated polymers for organic solar cells. Macromolecules. 2012;45(2):607-32.

[61] Li Z, Zhang Y, Holt AL, Kolasa BP, Wehner JG, Hampp A, et al. Electrochromic devices and thin film transistors from a new family of ethylenedioxythiophene based conjugated polymers. New J Chem. 2011;35(6):1327-34.

[62] Almeataq MS, Yi H, Al-Faifi S, Alghamdi AA, Iraqi A, Scarratt NW, et al. Anthracene-based donor–acceptor low band gap polymers for application in solar cells. Chem Commun. 2013;49(22):2252-4.

[63] Thompson BC, Fréchet JM. Polymer–fullerene composite solar cells. Angew Chem Int Ed. 2008;47(1):58-77.

[64] Janietz S, Bradley D, Grell M, Giebeler C, Inbasekaran M, Woo E. Electrochemical determination of the ionization potential and electron affinity of poly (9, 9-dioctylfluorene). Appl Phys Lett. 1998;73(17):2453-5.

Highlights

- Direct arylation polymerization enables facile synthesis of a narrow-bandgap polymer.
- Polymers with alternating strong-donor/strong-acceptors are obtained.
- The charge transport properties are first examined in field effect transistors.