Direct Arylation Polymerization Toward a Narrow Bandgap Donor–Acceptor Conjugated Polymer of Alternating 5,6-Difluoro-2,1,3benzothiadiazole and Alkyl-Quarternarythiophene: From Synthesis, Optoelectronic Properties to Devices

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ABSTRACT: Direct arylation polymerization (DAP) enabled facile synthesis of a narrow bandgap donor-acceptor conjugated polymer (PDFBT-Th₄) composed of alternating 5,6-difluoro-2,1,3-benzothiadiazole and alkyl-quaternarythiophene. The optimized reaction condition of DAP catalyzed with Pd(OAc)₂/(*o*-MeOPh)₃P/PivOH/K₂CO₃ in *o*-xylene led to the target polymer with a number-average molecular weight (M_n) of 14.6 kDa without noticeable homocoupling or β -branching defects. UVvis absorption spectra of PDFBT-Th₄ indicate strong interchain aggregation in films. While the C-H selectivity and the alternating polymer structure of PDFBT-Th₄ synthesized via DAP are comparable to those of the same type polymers synthesized

INTRODUCTION Conjugated semiconducting polymers with tunable optoelectronic properties, mechanical flexibility, and solution processability are attractive for a new generation of flexible organic electronic devices such as organic field-effect transistors (OFETs),¹⁻⁶ organic photovoltaics (OPVs),⁷⁻¹² and organic light emitting diodes (OLEDs).^{13,14} Conventionally, π conjugated polymers are synthesized via transition metalcatalyzed polycondensation reactions, such as Suzuki-Miyaura and Migita-Kosugi-Stille couplings.¹⁵⁻¹⁸ Despite their great versatility and choice in the synthesis of conjugated polymers, these protocols require the preparation of highpurity organometallic functionalized monomers such as arylene diboronic acid/diboronic ester (for Suzuki coupling) and distannyl arylenes (for Stille coupling) using flammable and toxic precursors. In addition, these polycondensation reactions could produce a stoichiometric amount of toxic byproducts such as trialkyltin compound, which would become a key issue in the future commercialization of conjugated polymers for organic electronics applications. Recently, much attention has been paid to a new coupling chemistry called direct (C-H) arylation polymerization (DAP) for

via Stille coupling, the batch of PDFBT-Th₄ synthesized via optimal DAP, despite its lower M_n , showed higher hole mobility in field effect transistors and larger power conversion efficiency in organic solar cell devices. These results further demonstrate the promising potential of DAP for efficient synthesis of high-performance D-A conjugated polymers for broad optoelectronic applications. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

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synthesis of π -conjugated polymers because it involves the coupling of an aryl halide monomer directly with another arene monomer without the need of preactivating C-H bonds using organometallic reagents that are either flammable (e.g. n-BuLi) or highly toxic (e.g. organo-tin).^{19–21} Therefore, DAP is an economically efficient and environmentally benign approach compared with the traditional coupling methods (such as Stille and Suzuki couplings).^{22–39}

5,6-Difluoro-2,1,3-benzothiadiazole (**DFBT**) has been sought as an attractive building block for the construction of highperformance π -conjugated polymers.^{12,40-43} The electronwithdrawing nature of fluorine substituents in conjugated backbone of the polymer resulted in lower energy level of the highest occupied molecular orbital (HOMO) and thus larger open circuit voltage (V_{oc}) in bulk heterojunction (BHJ) solar cells.^{40,44-46} In addition, fluorination of 2,1,3-benzothiadiazole could improve planarity of the polymer backbone, and therefore the effective π -conjugation length of the polymer.⁴⁷ However, most of the DFBT-based conjugated polymers were synthesized by traditional coupling techniques such as Stille coupling and Suzuki coupling. Only a few

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DFBT-based conjugated polymers have been recently synthesized via DAP coupling.^{48–50} For instance, Marder and coworkers reported the synthesis of small molecules based on 4,7-diaryl-5,6-difluoro-2,1,3-benzothiadiazole.⁴⁸ Zhang and coworkers reported the synthesis of high molecular weight poly(5,6-difluoro-2,1,3-benzothiadiazole-*alt*-9,9-dioctylfluorene) using Pd(OAc)₂ as a catalyst via DAP.⁵⁰ Recently, DFBTbased D-A conjugated polymer poly(5,6-difluoro-2,1,3-benzothiadiazole-*alt*-quarternary thiophene(Th₄)) (denoted as **PDFBT-Th**₄) synthesized through a traditional coupling method of Stille polymerization have shown power conversion efficiency (PCE) as high as 10% in single-junction OPVs and a hole mobility of 1.92 cm² V⁻¹ s⁻¹ in OFETs.^{51,52}

In this article, we report an atom-efficient and ecologicallybenign synthesis of this high-performance DFBT-based D-A conjugated polymer **PDFBT-Th**₄ via direct arylation polymerization (DAP). The synthesis of **PDFBT-Th**₄ polymers via DAP was investigated under a series of catalytic conditions including different Pd-catalysts, ligands, solvents, and reaction temperatures. The chemical structures, optoelectronic properties and performances in both OFET and OPV devices involving **PDFBT-Th**₄ synthesized under the optimal condition of DAP were examined, and compared with the same type of polymer synthesized *via* Stille coupling as a control.

EXPERIMENTAL

Materials

Unless stated otherwise, all chemicals and solvents were obtained from commercial sources and used without further purification.4,7-dibromo-5,6-difluorobenzo[c] [1,2,5]thiadiazole (**DBrDFBT**) were obtained from Derthon optoelectronics materials and 3-(2-octyldodecyl) thiophene were prepared according to the reported procedures.^{53,54}

Photovoltaic Device Fabrication and Characterization

A pre-patterned ITO-coated glass substrate (sheet resistance of \sim 15 Ω /square) was used as a substrate. It was cleaned by sequential sonication in soap DI water, DI water, acetone and isopropanol for 15 min at each step. After ultraviolet/ ozone treatment for 15 min, a ZnO as an electrontransporting layer was spin coated at 2,500 rpm for 1 min and then it was backed at 200 °C for 1 h. The active layer solutions (PDFBT-Th₄: PC71BM in ratio of 1:1.2) with 9 mg mL⁻¹ concentration of **PDFBT-Th₄** polymer were prepared in chlorobenzene:1,2-dichlorobenzene (1:1 v/v) with 3% of 1,8-diiodooctane (DIO) as an additive. Before spin coating the active layer, both the active layer solution and ITO substrate were preheated on a hot plate at 110 °C for 5 min. The warm solution of the active layer was spin coated on the preheated substrate at 800 rpm. The polymer/fullerene films were then annealed at 80 °C for 10 min before being transferred to the vacuum chamber of a thermal evaporator. A thin layer of MoO₃ (10 nm) was deposited as the anode interlayer, followed by deposition of Ag (100 nm) as the top electrode. Device current (J)-voltage (V) characteristics was measured under AM1.5G (100 mWcm⁻²) solar simulator. J–V characteristics were recorded using a Keithley SCS-4200 Semiconductor parameter analyzer. All OPVs fabrication and measurement were done in the air without any protective atmosphere.

General Synthesis Procedure of Compound 1 Via Direct C-H Arylation Couplings

4,7-Bis(4-(2-octyldodecyl)thiophen-2-yl)-5,6 Difluoro[2,1,3] Benzothiadiazole (1)

4,7-Dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole

(DBrDFBT) (0.4 mmol, 131.98 mg), 3-(2-octyldodecyl) thiophene, Pd2(dba)3 (20 μ mol, 18 mg), tris(2-methoxyphenyl)-phosphine ((*o*-MeOPh)3P, 40 μ mol, 14 mg), potassium carbonate (K₂CO₃, 1.4 mmol, 193 mg), pivalic acid (PivOH, 0.12 mmol, 12 mg), and 1,2-dimethylbenzene (*o*-xylene, 2 mL) were added under a nitrogen atmosphere in a reaction vial with a magnetic stirring bar. The vial was sealed with an aluminum cap with PTFE/silicone septum and then heated in a preheated oil bath for 24 h. After being cooled to room temperature, the reaction mixture was diluted with chloroform and then filtered to remove the insoluble species. The filtrate was concentrated and purified by column chromatography with hexane as an eluent.

Entry 1: 3-(2-Octyldodecyl)thiophene (2.92 g, 8 mmol, 20 equiv.) an orange color oil, to give 200 mg of Compound 1 in 55.7% yield; ¹H-NMR (300 MHz, CDCl₃) δ (ppm): 8.09 (s, 2H), 7.18 (s, 2H), 2.66 (d, J = 6.9 Hz, 4H), 1.69 (s, 2H), 1.56 – 1.25 (m, 80H), 0.87 (t, J = 12.9 Hz, 12H).

Entry 2: 3-(2-Octyldodecyl)thiophene (1.46 g, 4 mmol, 10 equiv.) an orange color oil, to give 220 mg of Compound 1 in 61.0% yield; ¹H-NMR (300 MHz, CDCl₃) δ (ppm): 8.09 (s, 2H), 7.18 (s, 2H), 2.66 (d, *J* = 6.9 Hz, 4H), 1.69 (s, 2H), 1.56 – 1.25 (m, 80H), 0.87 (t, *J* = 12.9 Hz, 12H); ¹³C-NMR (300 MHz, CDCl₃) δ (ppm): 151.5, 151.3, 148.9, 148.8, 148.1, 147.8, 142.2, 132.7, 131.01, 124.8, 111.65, 111.63, 111.58, 111.52, 39.0, 34.89, 33.39, 32.00, 30.12, 29.79, 29.75, 29.45, 26.71, 22.76, 14.18.

4,7-Bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-5,6-Difluoro[2,1,3]Benzothiadiazole (2)

N-bromosuccinimide (92.71 mg, 0.521 mmol) was added in portion to a solution of 4,7-bis(4-(2-octyldodecyl)thiophen-2-yl)–5,6-difluoro [2,1, 3]benzothiadiazole (1) (220 mg, 0.245 mmol) in 10 mL of THF at room temperature. After the mixture was stirred for 24 h, 50 mL water was added and the mixture was extracted with dichloromethane for three times. The organic phases were combined, washed with brine, and dried over anhydrous MgSO₄. The filtrate was concentrated and purified by column chromatography with hexane as an eluent to afford 230 mg orange solid in 89% yield; ¹H-NMR (300 MHz, CDCl₃) δ (ppm): 7.93 (s, 2H), 2.6 (d, *J* = 7.0 Hz, 4H), 1.74 (s, 2H), 1.25 (m, 80H), 0.86 (t, *J* = 12 Hz, 12H).

General Synthesis Procedure for PDFBT-Th₄ Polymer via Direct Arylation Polymerization (DAP)

A mixture of 4,7-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-5,6-difluoro[2,1,3] benzothiadiazole (2) (1 equiv.) and

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TABLE 1 DAF	reaction	optimization	entries	for the	synthesis	of PDFBT-	Th₄ polymer
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Entry no.	Catalyst	Solvent/Base	Ligand	Time (h)	Yield (%)	<i>M</i> _n (kDa) ^a	$M_{\rm w}/M_{\rm n}$
E1	Pd ₂ (dba) ₃	o-Xylene/K ₂ CO ₃	(<i>o</i> -MeOPh)₃P	24	11 ^b	6.4	2.8
E2 ^c	Pd ₂ (dba) ₃	o-Xylene/K ₂ CO ₃	(<i>o</i> -MeOPh)₃P	24	14 ^{b)}	6.7	3.4
E3c	Pd(OAc) ₂	o-Xylene/K ₂ CO ₃	(<i>o</i> -MeOPh) ₃ P	24	85 ^d	6.6	2.8
E3b	Pd(OAc) ₂	o-Xylene/K ₂ CO ₃	(<i>o</i> -MeOPh) ₃ P	48	83 ^d	6.4	1.6
E3a	Pd(OAc) ₂	o-Xylene/K ₂ CO ₃	(<i>o</i> -MeOPh) ₃ P	72	81 ^b	14.6	2.6
E4	Pd(OAc) ₂	o-Xylene/K ₂ CO ₃	PCy ₃ .HBF ₄	24	-е	-	-
E5	Pd(OAc) ₂	o-Xylene/Cs ₂ CO ₃	(<i>o</i> -MeOPh) ₃ P	24	81 ^d	9.8	2.4
E6	Herrmann	o-Xylene/K ₂ CO ₃	(<i>o</i> -MeOPh)₃P	24	67 ^d	3.0	2.4
E7	Pd ₂ (dba) ₃	DMAc/K ₂ CO ₃	(<i>o</i> -MeOPh) ₃ P	24	-е	-	-
E8	Pd ₂ (dba) ₃	CB/K ₂ CO ₃	(o-MeOPh) ₃ P	24	79 ^d	4.2	2.2
Stille-B1	Pd ₂ (dba) ₃	<i>o</i> -Xylene	P(o-tolyl) ₃	72	56 ^b	25.0	2.3

 a Measured by GPC with polystyrene as standard and CHCl_3 as eluent at 80 $^\circ\text{C}.^{55}$

^b Yield of the polymer from chloroform fraction.;

 $^{\rm c}$ The reaction was carried out at 140 $^{\circ}\text{C}.$

2,2'-bithiophene (BT) (1equiv.), palladium source, ligand, base, PivOH, and solvent (0.2 M) 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 °C except for Entry **E2** heated at 140 °C. After being cooled to room temperature, the reaction mixture was diluted with CHCl₃ and added dropwise to 150 mL of methanol. Precipitates were collected by filtration and then subjected to Soxhlet extraction with methanol, acetone, hexane, and chloroform sequentially each for 24 h. The hexane and/or chloroform fraction was concentrated and precipitated into methanol. The precipitates were collected by filtration and dried under vacuum before further characterization.

Entry E1: $Pd_2(dba)_3$ (5 mol%), (*o*-MeOPh)₃P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and *o*-xylene solvent (0.2 M) at 100 °C. Yield: 11% form CHCl₃ fraction.

Entry E2: $Pd_2(dba)_3$ (5 mol%), (o-MeOPh)₃P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and *o*-xylene solvent (0.2 M) at 140 °C. Yield: 14% form CHCl₃ fraction.

Entry 3a: $Pd(OAc)_2$ (5 mol%), (*o*-MeOPh)₃P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and *o*-xylene solvent (0.2 M) at 100 °C with reaction time of (72 h, see Table 1). Yield: 81% form CHCl₃ fraction.

Entry 3b: $Pd(OAc)_2$ (5 mol%), (*o*-MeOPh)₃P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and *o*-xylene solvent (0.2 M) at 100 °C with reaction time of (48 h, see Table 1). Yield: 83% form hexane fraction.

Entry 3c: $Pd(OAc)_2$ (5 mol%), (*o*-MeOPh)₃P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and *o*-xylene solvent (0.2 M) at 100 °C with reaction time of (24 h, see Table 1). Yield: 85% form hexane fraction.

^d Yield of the polymer from hexane fraction ad no polymer in chloroform fraction.

^e No precipitate in methanol.

For all entries, PiVOH was used as additive; monomer concentration = 0.2 M; reaction temperature: 100 $^\circ C.$

Entry E4: $Pd(OAc)_2$ (5 mol%), $PCy_3.HBF_4$ (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and *o*-xylene solvent (0.2 M) at 100 °C. no polymerization.

Entry E5: $Pd(OAc)_2$ (5 mol%), $PCy_3.HBF_4$ (10 mol%), Cs_2CO_3 (4 equiv.), PivOH (50 mol%), and *o*-xylene solvent (0.2 M) at 100 °C. Yield: 81% form hexane fraction.

Entry E6: Herrmann's catalyst (5 mol%), $(o\text{-MeOPh})_3P$ (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and *o*-xylene solvent (0.2 M) at 100 °C. Yield: 67% form hexane fraction.

Entry E7: $Pd_2(dba)_3$ (5 mol%), (*o*-MeOPh)₃P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and DMAc solvent (0.2 M) at 100 °C. no polymerization.

Entry E8: $Pd_2(dba)_3$ (5 mol%), (*o*-MeOPh)₃P (10 mol%), K_2CO_3 (4 equiv.), PivOH (50 mol%), and chlorobenzene solvent (0.2 M) at 100 °C. Yield: 79% form hexane fraction.

Synthesis of PDFBT-Th₄ Polymer via Stille Polymerization

A mixture of 4,7-Bis(5-bromo-4-(2-octyl dodecyl)thiophen-2yl)-5,6-difluoro[2,1,3]benzo thiadiazole (2) (80 mg, 0.0758 mmol, 1 equiv.), 5,5-bis(trimethyl stannyl)-2,2-bithiophene (37. 29 mg, 0.0758 mmol, 1 equiv.), $Pd_2(dba)_3$ (3.28 mol%, 2.27 mg), and (*o*-tolyl)₃P (19.7 mol%, 4.55 mg) were added to a 50 mL flask under nitrogen atmosphere. After three cycles of degassing and purging with nitrogen, 3 mL of anhydrous *o*-xylene was added and then the flask was charged with nitrogen after three cycles of freeze-pump-thaw. The solution was heated to reflux for 72 h. The mixture was poured into methanol. The precipitated solid was placed in a Soxhlet thimble, and extracted sequentially with methanol (12 h), acetone (12 h), ethyl acetate (12 h), hexane (24 h), dichloromethane (12 h), and chloroform (12 h), respectively. The chloroform fraction was precipitated in methanol, and





SCHEME 1 The synthesis of **PDFBT-Th**₄ via DAP versus Stille polymerization. The synthesis of **PDFBT-Th**₄ via DAP includes the one-step direct arylation to generate Compound **1**. Thus the synthesis of **PDFBT-Th**₄ is enabled in only 3 steps via DAP, while the synthesis of **PDFBT-Th**₄ requires at least 4 steps via Stille coupling. Conditions are as follows: (i) $Pd_2(dba)_3$, ((*o*-MeOPh)₃P, K₂CO₃, PivOH, o-xylene, 61.0% yield; (ii) NBS, THF, 89% yield; (iii) n-BuLi, THF, -78 °C, SnMe₃Cl; (iv) DAP Protocol (Table 1); (v) P(*o*-tol)₃, $Pd_2(dba)_3$, *o*-xylene, 56% yield. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 1 ¹H-NMR (300 MHz) spectra of the **PDFBT-Th₄** polymers synthesized *via* DAP, **E3a** (a) and **Stille-B1** (b) at 100 °C in $C_2D_2Cl_4$. [Color figure can be viewed at wileyonlinelibrary.com]

then filtered and dried under vacuum to give 34 mg of the final product as a black solid. Yield: 56% for **Stille-B1**. The molecular weight of the obtained **Stille-B1** polymer was measured using GPC at 80 °C with CHCl₃ as the eluent:⁵⁵ $M_{\rm n} = 25$ kDa; $M_{\rm w}/M_{\rm n} = 2.3$.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of PDFBT-Th₄ Polymers

Compound **1** (Scheme 1) was synthesized via $Pd_2(dba)_3$ -catalyzed direct arylation coupling between **DBrDFBT** and thiophene attached with a branched alkyl chain to ensure solubility of the target polymer. Decreasing the feed ratio (by moles) of alkyl thiophene/**DBrDFBT** from 20 to 10 resulted in an improved yield of Compound **1** from 55.7% to 61.0%, which was comparable to that obtained by Stille coupling as reported in the literature.^{51,56,57} The subsequent bromination Compound **1** using N-bromosuccinimide (NBS) gave Compound **2** in a yield of 89%. The purity of both Compound **1** and **2** was confirmed with ¹H- and ¹³C-NMR spectra (Supporting Information Figure S4).

The synthetic route to **PDFBT-Th₄** polymer via DAP is shown in Scheme 1, where Compound 2 and 2,2'-bithiophene were reacted under different DAP reaction conditions aiming to obtain good quality PDFBT-Th₄ polymer with high molecular weights. Therefore, the optimization of DAP reaction was carried out via changing palladium-catalyst, phosphine-ligand, base, solvent, reaction time, and temperature (see Table 1). First, Compound 2 and 2,2'-bithiophene (0.2 M) were reacted in the presence of $Pd_2(dba)_3$ as the catalyst, (o-MeOPh)₃P as the ligand, PivOH as the additive, K_2CO_3 as the base, and o-xylene as the solvent at 100 °C for 24 h (Entry E1), which was previously employed for the synthesis of high molecular weight 2,1,3-benzothidiazole copolymers.⁵⁷ However, in the present system, only a low yield of 11% ($M_{\rm p}$ = 6.4 kDa) was obtained from chloroform fraction. The effort to further increase the yield of chloroform fraction and molecular weight was carried out by increasing the reaction temperature to 140 °C (Entry E2), which gave a polymer with slightly increased molecular weight ($M_n = 6.7$ kDa) but a yield similar to that of E1. This implies that the degree of polymerization was not improved with an increase in reaction temperature. The effect of solvent on the reactivity of Pd₂(dba)₃ catalyst was investigated using DMAc (Entry E7) and chlorobenzene (Entry E8), respectively. No polymer was obtained from the reaction in DMAc, as the reaction mixture did not precipitate in methanol after 24 h reaction time at 100 °C. However, in chlorobenzene, a polycondensation product was obtained mainly from hexane fraction ($M_{\rm n} = 4.2$ kDa). Therefore, it could be inferred that less polar solvents might promote the degree of polymerization.

In order to investigate the effect of a catalyst on DAP reactions between Compound **2** and 2,2'-bithiophene, Herrmann's catalyst (Entry **E6**) was employed to give a polycondensation product mainly from hexane fraction



FIGURE 2 UV-vis absorption spectra of **PDFBT-Th**₄ from chlorobenzene solution (a), thin films before (b), and after (c) being annealed at 100 °C. [Color figure can be viewed at wileyonline-library.com]

(mainly oligomers) with M_n of 3.0 kDa. Therefore, from **E1**, **E2**, **E6**, and **E8**, it could be inferred that palladium catalyst with oxidation sate of Pd(0) is not reactive enough to give high molecular weight



Entry no.	λ _{max} (nm, in CHCl ₃)	λ _{onset} (nm, in CHCl ₃)	λ _{max} ª (nm, in films)	λ _{max} ^b (nm, in films)	λ _{onset} ^a (nm, in films)	E_{g}^{opt} (eV)
E3a	571 ^d /553 ^e	737 ^d /736 ^e	680 ⁰⁻⁰ /625 ⁰⁻¹ /447 ⁰⁻²	680 ⁰⁻⁰ /625 ⁰⁻¹ /446 ⁰⁻²	746 ^a /752 ^b	1.66
Stille-B1	588 ^d /566 ^e	737 ^d /736 ^e	680 ⁰⁻⁰ /625 ⁰⁻¹ /447 ⁰⁻²	680 ⁰⁻⁰ /625 ⁰⁻¹ /446 ⁰⁻²	746 ^a /749 ^b	1.66

TABLE 2 Optical data of **PDFBT-Th₄** polymers

^a Film at room temperature.

^b Film after being annealing at 100 °C.

^c E_g^{opt} (eV) = 1240/ λ_{onset} (nm).

PDFBT-Th₄ polymer. Pd(OAc)₂ has been used in the DAP synthesis of DFBT-based small molecules and high molecular weight copolymers.^{48–50} Therefore, we employed $Pd(OAc)_2$ in the DAP reaction of Compound 2 with 2,2'-bithiophene (0.2 M) in the presence of $(o-\text{MeOPh})_3\text{P}$ as the ligand, PivOH as the additive, K_2CO_3 as the base and o-xylene as the reaction media at 100 °C (Entry E3c). The polymerization over 24 h gave a majority of low molecular weight polymer $(M_{\rm n} = 6.6 \text{ kDa})$ as collected from hexane fraction. Upon increasing the reaction time to 48 h, there was no significant improvement in reaction yield and molecular weight. However, as the reaction time was extended to 72 h (Entry E3a), the color of the reaction mixture changed from dark-red to dark-purple. After precipitation in methanol and Soxhlet extraction, **PDFBT-Th₄** polymer with M_n as high as 14.6 kDa was isolated in 81% yield from chloroform fraction. These results demonstrate that $Pd(OAc)_2$, where Pd in (+2) oxidation state combined with an extended reaction time results in the DAP reaction of Compound 2 with 2,2'-bithiophene towards a high degree of polymerization. The effectiveness of Pd(OAc)₂ for direct arylation coupling involving 5,6difluoro-2,1,3-benzothiadiazole (DFBT) or 2,2'-bithiophene as reactants in a nonpolar solvent such as toluene was also demonstrated by Marder's $\operatorname{group}^{48}$ and Leclerc's $\operatorname{group}^{56}$ as well as by Zhang and coworkers.⁵⁰

The effect of ligand and base on Pd(OAc)₂-catalyzed DAP reaction was studied by using PCy₃•HBF₄ (Entry **E4**) and Cs₂CO₃ as a strong base (Entry **E5**) for 24 h. In **E4** no polycondensation product was obtained, which implies that $(o-\text{MeOPh})_3\text{P}$ is a better ligand than PCy₃•HBF₄. Using a stronger base Cs₂CO₃ as compared to K₂CO₃ (for **E3c**) led to a relatively high molecular weight of **PDFBT-Th**₄ (M_n = 9.8 kDa, yield = 81%) from hexane fraction. Based on the aforementioned results, Pd(OAc)₂/ $(o-\text{MeOPh})_3\text{P}$ /PivOH/K₂CO₃/o-xylene of **E3a** is the best reaction condition to obtain the high molecular weight of **PDFBT-Th**₄ in high yield *via* DAP.

For comparison, **PDFBT-Th**₄ polymer was synthesized via Stille polycondensation of 4,7-dibromo-5,6-difluorobenzo [c] [1,2,5]thiadiazole (Compound **2**) and 5,5'-bis(trimethyl stannyl)-2,2'-bithiophene in the same type of solvent (oxylene) used in DAP (see Scheme 1). **PDFBT-Th**₄ polymers (labeled as **Stille-B1**) with $M_n = 25.0$ kDa and PDI = 2.3 were obtained in a yield of 56%. This result indicates that M_n of **PDFBT-Th**₄ polymer obtained by DAP is still lower than that of Stille polymerization method. However, this ^d In CHCl₃.

^e In chlorobenzene (CB).

work indicates that it could be possible to synthesize **PDFBT-Th**₄ polymer via DAP and an extensive DAP reaction optimization could lead to further increase in its molecular weight. 36,58,59

The chemical structures of representative **PDFBT-Th**₄ polymers synthesized via DAP (**E3a**) were characterized using high temperature (100 °C) ¹H-NMR spectroscopy (Fig. 1) in C₂D₂Cl₄, in comparison with the spectrum of **PDFBT-Th**₄ polymers (**Stille-B1**) synthesized by Stille polymerization method. No evidence of branching could be observed, and the extra little peaks found in the ¹H-NMR spectra could be attributed to different chain-end groups. These results imply that the good selectivity of (α)C-H over (β)C-H bond in 2,2'-bithiophene in the present DAP, which was also reported in the DAP synthesis of other conjugated polymers.⁵⁷⁻⁵⁹

Thermal Properties of PDFBT-Th₄ Polymer

The thermal stability of **PDFBT-Th**₄ polymers was investigated using thermogravimetric analysis (TGA) with a heating rate of 10 °C min⁻¹ under N₂ atmosphere. The decomposition temperature (T_d , corresponding to 5% weight loss) is located at 394 °C for both **PDFBT-Th**₄ polymers obtained by DAP (**E3a**) and Stille coupling (Supporting Information Figure S1), demonstrating their sufficient high thermal stability for application in the organic electronic device.

Optical Properties of PDFBT-Th₄ Polymer

The UV-vis absorption spectra of representative **PDFBT-Th**₄ polymers were acquired from both chloroform and chlorobenzene solutions and spin-cast thin films. The spectra are shown in Figure 2 and S2 (Supporting Information) and the relevant data are summarized in Table 2. Broad absorption bands across the visible region were observed for **PDFBT-Th**₄ in both solution and thin films. The maximal absorption wavelength ($\lambda_{max,abs}$) for **E3a** and **Stille-B1** polymers in chlorobenzene solution [Fig. 2(a)] are located at 553 and 566 nm, respectively. In contrast, the $\lambda_{max,abs}$ in chloroform [Supporting Information Fig. S2(a)] is red shifted by ca.18 and 22 nm for **E3a** and **Stille-B1**, respectively, which could be due to strong aggregation of these polymers in chloroform.

The aggregation and de-aggregation behaviors of **PDFBT-Th**₄ were further reflected from the UV-vis absorption spectra of polymers upon heating and cooling their chlorobenzene solutions. Upon heating from 25 to 70 °C [Supporting Information Fig. S2 (b,d)], the absorption maxima for both **E3a** and



FIGURE 3 Cyclic voltammetry curves for **PDFBT-Th**₄ polymers: (a) **E3a** and (b) **Stille-B1**. [Color figure can be viewed at wileyonlinelibrary.com]

Stille-B1 polymers were blue-shifted due to the deaggregation of **PDFBT-Th**₄ polymers. Upon cooling, reversible red-shifted absorption spectra were observed because of the formation of aggregates [Supporting Information Fig. S2 (c,e)].^{51,52}

The thin films of **PDFBT-Th**₄ polymers exhibited a dramatic red shift of $\lambda_{max,abs}$ (~127 nm for **E3a** and ~114 nm for **Stille-B1**) as compared to their absorption spectra in chlorobenzene [Fig. 2(b)]. The absorption spectra of the polymers in thin films exhibit three well-resolved vibrational peaks at $680^{(0-0)}$, $625^{(0-1)}$, and $447^{(0-2)}$ nm, respectively, for all **PDFBT-Th**₄ polymers, which is an indication for the presence of strong intermolecular aggregation in solid thin films.^{40,51,52} Upon annealing at 100 °C, no significant changes were observed except a slightly enhanced intensity of 0-0 peak for **E3a** polymer [Fig. 2(c)]. The corresponding optical bandgap (E_g^{opt}) was estimated from $\lambda_{abs, onset}$ in thin films at room temperature is 1.66 eV for both **E3a** and **Stille-B1** (see Table 2).

Electrochemical Properties of PDFBT-Th₄ Polymers

The electrochemical properties of **PDFBT-Th₄** polymers were investigated by cyclic voltammetry (CV) analysis using threeelectrode electrochemical workstation (Model CHI006D). A glassy carbon disk coated with a thin layer of polymer film as working electrode, a silver wire as pseudo-reference electrode and a platinum wire as counter electrode were used in 0.1 M anhydrous acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) electrolyte at 25 °C under nitrogen atmosphere with ferrocene as an internal standard (Fig. 3). Table 3 summarizes the CV data for both E3a and Stille-B1 polymers. The HOMO^{ele} and LUMO^{ele} potentials of E3a calculated from its oxidation (E_{ox}) and reduction (E_{red}) onsets are -5.45 and -3.62 eV, respectively, very close to that of **Stille-B1** (HOMO^{ele} = -5.50 eV, LUMO^{ele} = -3.61 eV). The difference of the bandgaps (E_{σ}^{opt} and E_{σ}^{ele}) of these batches of **PDFBT-Th₄** polymers is within experimental error. The LUMO^{opt} calculated by using $LUMO^{opt} = HOMO^{ele} - E_g^{opt}$ (see Table 3), which is similar to the values reported in literature for the same type of polymer.⁵¹

Field-Effect Transistors of PDFBT-Th₄ Polymers

The charge-transport properties of PDFBT-Th₄ polymers were studied in bottom-gate, top-contact OTFT devices on octadecyl trichlorosilane (OTS-18) modified Si/SiO2 substrate under ambient conditions. The device performances of three representative polymers (E3a, E5, and Stille-B1) are summarized in Table 4 and their transfer and output curves are shown in Figure 4 and Supporting Information Figure S3, respectively. The hole mobilities (μ_h) derived from the slope of their transfer curves are 1.7 \times 10 $^{-3}$, 1.0 \times 10 $^{-3}$, and 2.3 \times 10⁻³ cm²V⁻¹s⁻¹ for E3a, E5, and Stille-B1 polymers, respectively. After thermal annealing at 100 °C, the two DAP polymers (E3a and E5) showed an increased $\mu_{\rm h}$ to 6.5 \times 10^{-3} and 2.2×10^{-3} cm²V⁻¹s⁻¹, respectively, whereas a comparable μ_h of 2.0×10^{-3} cm²V⁻¹s⁻¹ was observed for Stille-B1. This could be explained by the relatively improved intermolecular interaction as can be seen from its UV-vis absorption spectrum [Fig. 2(c)]. The lower hole mobility of Stille-B1 compared to E3a might be due to stannyl-end groups in the former, which could cause charge trapping in the thin film FETs.⁶⁰ Similar effect of end capping on the structural order and charge transport was also reported in a

TABLE 3 Electrochemical	properties	of PDFBT-Th ₄	polymers
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Entry No.	E_{ox} (V)	Ered (V)	^a HOMO ^{ele} (eV)	^a LUMO ^{ele} (eV)	^b LUMO ^{₀pt} (eV)	^c E ^{ele} (eV)
E3a	1.10	-0.72	-5.45	-3.62	-3.80	1.83
Stille-B1	1.16	-0.73	-5.50	-3.61	-3.85	1.89

^a HOMO^{ele}/LUMO^{ele} = $-(4.8 - E_{1/2, Fc,Fc^+} + E_{ox/red, onset})$. ^b LUMO^{opt} = $E_q^{opt} + HOMO^{ele}$.

^c $E_{q}^{ele} = LOMO^{ele} - HOMO^{ele}$.

Materials



FIGURE 4 Representative transfer curves of the OFET devices involving PDFBT-Th₄ (E3a for (a-b), and Stille-B1 for (c-d)) as the semiconducting layer before (a, c) and after (b, d) being annealed at 100 °C. [Color figure can be viewed at wileyonlinelibrary.com]

donor-acceptor alternating copolymer consisting of dithienogermole and 2,1,3-benzothiadiazole.⁶⁰

Photovoltaic Properties PFFBT-Th₄ Polymers

Figure 5 shows J–V curves of **PDFBT-Th₄** (**E3a-DAP** and **Stille-B1**) polymers under illumination of AM 1.5 G, 100 mWcm⁻² in an inverted BHJ-OPV architecture (indium tin oxide (ITO)/zinc oxide (ZnO)/polymer (**PDFBT-Th₄**):C71-

butyric acid methyl ester (PC71BM)(1:1.2, by moles)/molybdenum trioxide (MoO_3)/silver (Ag)). The photovoltaic performance of **E3a** (synthesized via DAP) as the electron donor partnered with PC71BM as the electron acceptor was examined, using **Stille-B1** (synthesized via Stille coupling) as the control. The device results are summarized in Table 5. The photovoltaic device involving **E3a** tested in the air without any encapsulation gave a power conversion efficiency (PCE)

TABLE 4 Performance characteristics of OFET devices for **PDFBT-Th**₄ polymers (**E3a, E5, and Stille-B1** polymer) semiconductor on OTS-18-treatd substrate fabricated and measured under ambient condition

Entry No.	<i>M</i> _n (kDa)	Annealing temperature (°C)	$\mu_{\rm h} \ [{\rm cm}^2 \ {\rm V}^{-1} \ {\rm s}^{-1}]$	$V_{\rm th}$ (V)	On/off Ratio
E3a	14.6	R.T.	$(1.7\pm 0.3) imes 10^{-3}$	14	10 ⁴
		100	(6.5 \pm 1.2) $ imes$ 10 $^{-3}$	16	$10^3 - 10^4$
E5	9.8	R.T.	$(1.0\pm 0.3) imes 10^{-3}$	13	10 ³
		100	(2.2 \pm 0.4) \times 10 $^{-3}$	18	10 ³
Stille-B1	25.0	R.T.	(2.3 \pm 1.1) \times 10 $^{-3}$	10	$10^3 - 10^4$
		100	$(2.0\pm 0.5) imes 10^{-3}$	10	10 ⁴



FIGURE 5 Current density-voltage curves of photovoltaic devices with active layers of **PDFBT-Th₄** (**E3a-DAP** and **Stille-B1** polymers) as the electron donor and PC71BM as the electron acceptor (1:1.2 by weight) with 3% of DIO additive. [Color figure can be viewed at wileyonlinelibrary.com]

of 4%, with open circuit voltage (V_{oc}) of 0.77 V, a shortcircuit current (J_{sc}) of 12.4 mA cm⁻², and a fill factor (FF) of 45.7%.

Surprisingly, the photovoltaic device involving Stille-B1, despite its larger molecular weight than that of E3a, showed a lower V_{oc} (ca. 0.5 V) and thus poorer PCE (3%), while other conditions for the device fabrication and the performance test were maintained the same. These results are consistent with the improved hole mobility of E3a compared to Stille-B1 in the OFET devices [Fig. 4(a,b)]. Such differences between E3a and Stille-B1 in both OFETs and OPVs might be due to the end-group effect present in polymers synthesized via Stille coupling (Fig. 1),⁶¹⁻⁶⁷ while other factors such as the polymer molecular weight⁶⁸⁻⁷⁰ and structural ordering^{22,71,72} might also play a role. The similar superior photovoltaic performance of phenanthridinone-based conjugated polymers synthesized via DAP versus the same type of polymers synthesized via Suzuki coupling was also recently reported by Leclerc's group.³⁶ Nevertheless, the mechanism underlying the $V_{\rm oc}$ difference between E3a-DAP and Stille-B1 remains unclear and warrants further study.

It should be noted that all of the FET and OPV devices described above have not been fully optimized yet. Both the spin-coating of the active layer (**PDFBT-Th**₄:PC71BM) and the performance test of non-encapsulated devices were conducted in air. The moderate performances of the OPV devices

TABLE 5 Photovoltaic performance of PDFBT-Th₄ polymers

Entry No.	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%) ^{max}	PCE (%) ^{aver}
E3a-DAP	12.4	0.77	45.7	4.4	4.1
Stille-B1	12.2	0.52	50.8	3.2	3.1



reported here could be further improved, for example, by using **PDFBT-Th**₄ with a higher average molecular weight, more careful morphological control of the active layer, and optimization of the interfacial contact.^{51,52}

CONCLUSION

In summary, direct arylation polymerization (DAP) has been used for the synthesis of a high-performance D-A copolymer, PDFBT-Th₄, consisting of alternating 5,6-difluoro-2,1,3-benzothiadiazole and alkyl-quaternarythiophene. The chemical structures, thermal properties, optical properties, electrochemical properties of the obtained polymers and their performance in OFET and OPV devices are compared with the same type of polymers synthesized by Stille polymerization method. A series of DAP optimization have led to a high $M_{\rm n}$ up to 14.6 kDa under the catalytic condition of Pd(OAc)₂/(o-MeOPh)₃P/PivOH/K₂CO₃/o-xylene. From a series of optimization reactions, Pd catalyst in (+2) oxidation state is more reactive toward a high degree of polymerization than Pd (0) catalyst. PDFBT-Th₄ has displayed a strong interchain aggregation behavior in films, which is greatly enhanced for DAP synthesized polymer after thermal annealing. PDFBT-Th4 synthesized via DAP, despite their lower molecular weight as compared with the same type of polymers synthesized by Stille coupling polymerization, displayed better performances in both OFET and OPV devices tested in the air without any device encapsulation. 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.

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REFERENCES AND NOTES

1 C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu. *Chem. Rev.* 2011, *112*, 2208.

2 Y. Deng, Y. Chen, X. Zhang, H. Tian, C. Bao, D. Yan, Y. Geng, F. Wang. *Macromolecules.* 2012, *45*, 8621.

3 J. Mei, Y. Diao, A. L. Appleton, L. Fang, Z. Bao. *J. Am. Chem. Soc.* **2013**, *135*, 6724.

4 A. Facchetti. Nat. Mater. 2013, 12, 598.

5 H. N. Tsao, K. Müllen. Chem. Soc. Rev. 2010, 39, 2372.

6 Y. Takeda, T. L. Andrew, J. M. Lobez, A. J. Mork, T. M. Swager. Angew. Chem. Int. Ed. 2012, 51, 9042.

7 L. Koster, S. E. Shaheen, J. C. Hummelen. *Adv. Energy Mater.* 2012, *2*, 1246.

8 J. Li, A. C. Grimsdale. Chem. Soc. Rev. 2010, 39, 2399.

9 H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li. *Nat. Photon.* **2009**, *3*, 649.

10 L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li, J. Hou. *Angew. Chem.* **2011**, *123*, 9871.

11 Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao. *Nat. Photon.* **2012**, *6*, 591.

12 J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li. *Nat. Commun.* **2013**, *4*, 1446.

13 A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes. *Chem. Rev.* **2009**, *109*, 897.

14 F. Huang, H. Wu, Y. Cao. Chem. Soc. Rev. 2010, 39, 2500.

15 B. Carsten, F. He, H. J. Son, T. Xu, L. Yu. *Chem. Rev.* **2011**, *111*, 1493.

16 K. Okamoto, C. K. Luscombe. Polym. Chem. 2011, 2, 2424.

17 J. Sakamoto, M. Rehahn, G. Wegner, A. D. Schlüter. *Macro*mol. Rapid Commun. 2009, 30, 653.

18 C. Amatore, A. L. Jutand, G. Duc. *Angew. Chem.* **2012**, *124*, 1408.

19 L. T. Ball, G. C. Lloyd-Jones, C. A. Russell. *Science* 2012, 337, 1644.

20 D. Alberico, M. E. Scott, M. Lautens. *Chem. Rev.* 2007, 107, 174.

21 J. Wencel-Delord, F. Glorius. Nat. Chem. 2013, 5, 369.

22 P. P. Khlyabich, B. Burkhart, A. E. Rudenko, B. C. Thompson. *Polymer* 2013, *54*, 5267.

23 K. Okamoto, J. Zhang, J. B. Housekeeper, S. R. Marder, C. K. Luscombe. *Macromolecules* 2013, *46*, 8059.

24 L. G. Mercier, M. Leclerc. Acc. Chem. Res. 2013, 46, 1597.

25 K. Wang, M. Wang. Curr. Org. Chem. 2013, 17, 999.

26 A. E. Rudenko, B. C. Thompson. J. Polym. Sci. Part A: Polym. Chem. 2015, 53, 135.

27 X. Wang, M. Wang. Polym. Chem. 2014, 5, 5784.

28 K. Wang, G. Wang, M. Wang. *Macromol. Rapid Commun.* 2015, *36*, 2162.

29 J. Shao, G. Wang, K. Wang, C. Yang, M. Wang. *Polym. Chem.* **2015**, *6*, 6836.

30 H. Bohra, J. Shao, S. Huang, M. Wang. *Tetrahedron Lett.* **2016**, *57*, 1497. *t*.

31 J. Huang, K. Wang, S. Gupta, G. Wang, C. Yang, S. H. Mushrif, M. Wang. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 2015.

32 T. Bura, P.-O. Morin, M. Leclerc. *Macromolecules* 2015, *48*, 5614.

33 A. E. Rudenko, P. P. Khlyabich, B. C. Thompson. *ACS Macro Lett.* **2014**, *3*, 387.

34 A. Luzio, D. Fazzi, F. Nubling, R. Matsidik, A. Straub, H. Komber, E. Giussani, S. E. Watkins, M. Barbatti, W. Thiel. *Chem. Mater.* **2014**, *26*, 6233.

35 J. Kuwabara, T. Yasuda, S. J. Choi, W. Lu, K. Yamazaki, S. Kagaya, L. Han, T. Kanbara. *Adv. Funct. Mater.* **2014**, *24*, 3226.

36 M. Guérette, A. Najari, J. Maltais, J. R. Pouliot, S. Dufresne, M. Simoneau, S. Besner, P. Charest, M. Leclerc. *Adv. Energy Mater.* **2016**, *6*, 1502094.

37 A. Efrem, K. Wang, P. N. Amaniampong, C. Yang, S. Gupta, H. Bohra, S. H. Mushrif, M. Wang. *Polym. Chem.* 2016, *7*, 4862.

38 A. S. Dudnik, T. J. Aldrich, N. D. Eastham, R. P. Chang, A. Facchetti, T. J. Marks. *J. Am. Chem. Soc.* **2016**, *138*, 15699.

39 E. lizuka, M. Wakioka, F. Ozawa. *Macromolecules* 2016, 49, 3310.

40 H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu, W. You. Angew. Chem. Int. Ed. 2011, 123, 3051.

41 J. F. Jheng, Y. Y. Lai, J. S. Wu, Y. H. Chao, C. L. Wang, C. S. Hsu. *Adv. Mater.* **2013**, *25*, 2445.

42 J. You, C. C. Chen, Z. Hong, K. Yoshimura, K. Ohya, R. Xu, S. Ye, J. Gao, G. Li, Y. Yang. *Adv. Mater.* **2013**, *25*, 3973.

43 Y.-L. Chen, W.-S. Kao, C.-E. Tsai, Y.-Y. Lai, Y.-J. Cheng, C.-S. Hsu. *Chem. Commun.* **2013**, *49*, 7702.

44 Y. Zhang, S.-C. Chien, K.-S. Chen, H.-L. Yip, Y. Sun, J. A. Davies, F.-C. Chen, A. K.-Y. Jen. *Chem. Commun.* **2011**, *47*, 11026.

45 A. C. Stuart, J. R. Tumbleston, H. Zhou, W. Li, S. Liu, H. Ade, W. You. *J. Am. Chem. Soc.* **2013**, *135*, 1806.

46 S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You. *J. Am. Chem. Soc.* **2011**, *133*, 4625.

47 H. Bronstein, J. M. Frost, A. Hadipour, Y. Kim, C. B. Nielsen, R. S. Ashraf, B. P. Rand, S. Watkins, I. McCulloch. *Chem. Mater.* **2013**, *25*, 277.

48 J. Zhang, W. Chen, A. J. Rojas, E. V. Jucov, T. V. Timofeeva, T. C. Parker, S. Barlow, S. R. Marder. *J. Am. Chem. Soc.* **2013**, *135*, 16376.

49 J. Zhang, T. C. Parker, W. Chen, L. Williams, V. N. Khrustalev, E. V. Jucov, S. Barlow, T. V. Timofeeva, S. R. Marder. *J. Org. Chem.* **2015**, *81*, 360.

50 X. Zhang, Y. Gao, S. Li, X. Shi, Y. Geng, F. Wang. *J. Polym. Sci. Part A: Polym. Chem.* **2014**, *52*, 2367.

51 Z. Chen, P. Cai, J. Chen, X. Liu, L. Zhang, L. Lan, J. Peng, Y. Ma, Y. Cao. *Adv. Mater.* **2014**, *26*, 2586.

52 Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan. *Nat. Commun.* 2014, *5*, 5293.

53 A. Efrem, Y. Lei, B. Wu, M. Wang, S. C. Ng, B. S. Ong. *Dyes* and *Pigm.* 2016, *129*, 90.

54 A. Efrem, C.-J. Lim, Y. Lu, S.-C. Ng. *Tetrahedron Lett.* 2014, 55, 4849.

55 X. Lou, J. L. van Dongen, Y. Braeken, J. Brebels, G. W. van Pruissen, W. Li, M. M. Wienk, R. A. Janssen. *Polym. Chem.* **2014**, *5*, 558.

56 Y. Wang, X. Xin, Y. Lu, T. Xiao, X. Xu, N. Zhao, X. Hu, B. S. Ong, S. C. Ng. *Macromolecules* 2013, *46*, 9587.

57 X. Wang, K. Wang, M. Wang. Polym. Chem. 2015, 6, 1846.

58 P.-O. Morin, T. Bura, B. Sun, S. I. Gorelsky, Y. Li, M. Leclerc. *ACS Macro. Lett.* 2014, *4*, 21.

59 R. Matsidik, H. Komber, A. Luzio, M. Caironi, M. Sommer. *J. Am. Chem. Soc.* **2015**, *137*, 6705.

60 U. Koldemir, S. R. Puniredd, M. Wagner, S. Tongay, T. D. McCarley, G. D. Kamenov, K. Mullen, W. Pisula, J. R. Reynolds. *Macromolecules* **2015**, *48*, 6369.

61 J. K. Park, J. Jo, J. H. Seo, J. S. Moon, Y. D. Park, K. Lee, A. J. Heeger, G. C. Bazan. *Adv. Mater.* **2011**, *23*, 2430.

62 J. S. Kim, Y. Lee, J. H. Lee, J. H. Park, J. K. Kim, K. Cho. *Adv. Mater.* 2010, *22*, 1355.

63 L. Wang, Z. Qiao, C. Gao, J. Liu, Z.-G. Zhang, X. Li, Y. Li, H. Wang. *Macromolecules* **2016**, *49*, 3723.

64 Y. Kim, S. Cook, J. Kirkpatrick, J. Nelson, J. Durrant, D. Bradley, M. Giles, M. Heeney, R. Hamilton, I. McCulloch. J. Phy. Chem. C. 2007, 111, 8137.

65 L. Dou, C.-C. Chen, K. Yoshimura, K. Ohya, W.-H. Chang, J. Gao, Y. Liu, E. Richard, Y. Yang. *Macromolecules* **2013**, *46*, 3384.

66 J. Kuwabara, T. Yasuda, N. Takase, T. Kanbara. ACS Appl. Mater. Interfaces 2016, 8, 1752.

67 C.-M. Chen, T.-H. Jen, S.-A. Chen. ACS Appl. Mater. Interfaces 2015, 7, 20548.

68 P. Ma, S. Wen, C. Wang, W. Guo, L. Shen, W. Dong, J. Lu, S. Ruan. *J. Phy. Chem. C* 2016, *120*, 19513.

69 A. Katsouras, N. Gasparini, C. Koulogiannis, M. Spanos, T. Ameri, C. J. Brabec, C. L. Chochos, A. Avgeropoulos. *Macromol. Rapid Commun.* **2015**, *36*, 1778.

70 L. Lu, T. Zheng, T. Xu, D. Zhao, L. Yu. *Chem. Mater.* 2015, 27, 537.

71 P. M. Beaujuge, J. M. Fréchet. J. Am. Chem. Soc. 2011, 133, 20009.

72 L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao, L. Yu. *Chem. Rev.* 2015, *115*, 12666.