Direct arylation polycondensation for synthesis of bithiophene-based alternating copolymers

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ABSTRACT:

Direct arylation polycondensation reactions using a simple catalytic system gave eight kinds of bithiophene-based alternating copolymers. The conditions for the reactions of 3,3′,4,4′-tetramethylbithiophene with dibromoarylenes were optimized to obtain high-molecular-weight polymers without formation of cross-linked structures. In the reaction of a dibromoarylene containing a reactive C–H bond, a short reaction

time (1.5 h) was suitable for preventing side reactions. In contrast, a long reaction time (6 h) gave high-molecular-weight polymers from dibromoarylene monomers without a reactive C–H bond. This polycondensation reaction enables the synthesis of polymers containing dye structures such as diketopyrrolopyrrole and isoindigo, which are applicable as materials for polymer solar cells.

Introduction

A bithiophene unit is one of the most important components of π-conjugated polymers for optoelectronic materials because it gives good charge mobility to the corresponding polymers[1] and serves as an appropriate donor unit in donor–acceptor polymers with a low bandgap.[2] A considerable number of bithiophene-based polymers have therefore been developed as materials for polymer solar cells (PSCs),[2] organic light-emitting diodes,[3] and organic field-effect transistors (OFETs).[4] In particular, bithiophene-based polymers containing dye structures such as diketopyrrolopyrrole derivatives exhibit high performances in PSCs[5] and OFETs.[6] Although bithiophene-based polymers can be synthesized by chemical or electrochemical oxidation reactions, most bithiophene-based polymers for optoelectronic materials are synthesized by polycondensation via cross-coupling reactions such as the Suzuki–Miyaura and Migita–Kosugi–Stille cross-coupling reactions.[7]

Polycondensation via dehydrohalogenative cross-coupling reactions, so-called direct arylation,[8] has recently become widely recognized as a method for synthesizing π-conjugated polymers.[9–15] We previously reported the direct arylation polycondensation of an alkylated bithiophene with dibromofluorene analogs using a simple catalytic system; the reaction with $Pd(OAc)_2$ and pivalic acid in a phosphine-free system for 3 h gave the corresponding polymer with a high molecular weight in good yield.[13a] Since direct arylation polycondensation does not require prior preparation of organometallic monomers and does not produce stoichiometric amounts of metal-containing wastes, direct arylation polycondensation is expected to be an efficient synthetic method for a variety of functional bithiophene-based conjugated polymers, compared with polycondensation using conventional cross-coupling reactions. However, this synthetic method is difficult to completely avoid a side reaction at unexpected C-H bonds, which leads to formation of branched or cross-linked structures because all aromatic C-H bonds in a monomer have a potential for direct arylation reactions.[12-14] Since the number of expected C–H bonds for direct arylation decreases with increasing degree of polymerization, a reaction for too long time causes the overreactions at unexpected C–H bonds. Therefore, appropriate reaction time is needed to be determined in direct arylation polycondensation to avoid overreactions and

to obtain high-molecular-weight polymers. We investigated optimization of the reaction conditions, especially in terms of reaction time, for the synthesis of bithiophene-based conjugated polymers. Base on the results, dye-containing polymers were synthesized and evaluated as materials for PSCs.

Results and Discussion

Optimization of Reaction Conditions and Synthesis. In a previous report, the polycondensation reaction of 3,3′,4,4′-tetramethylbithiophene with 2,7-dibromo-9,9-dioctylfluorene for 3 h gave **Polymer 1** with a high molecular weight (M_n = 31 800) in good yield (91%)[13a] (Scheme 1; Table 1, entry 1) The methyl groups on the bithiophene monomer provided selective direct arylation at its α position. To adapt this method for use with a variety of monomers, including dye-containing monomers, the reaction conditions, especially reaction time, were re-examined. The reaction for synthesis of **Polymer 1** in a shorter reaction time was investigated because large amounts of polymeric products were precipitated out from the reaction mixture before the reaction time reached 3 h. Using the same catalytic system, the reaction for 1.5 h gave **Polymer 1** with a molecular weight of 32 100 in 93% yield (Table 1, entry 2). This result, which was similar to that obtained for a reaction time of 3 h, showed that

the polycondensation reaction proceeded to completion in 1.5 h. In contrast to the reaction of 2,7-dibromo-9,9-dioctylfluorene, the polycondensation reaction of 2,7-dibromo-*N*-octadecylcarbazole for 3 h gave insoluble products as well as the soluble **Polymer 2** in low yield (Table 1, entry 3). The formation of insoluble products indicates the presence of cross-linked structures caused by undesired side-reactions at C–H bonds.[12–14] High reactivities of the C–H bonds at the 3 and 6 positions in carbazole derivatives in direct arylation have been reported,[16] so reactions at these C–H bonds were likely to form cross-linked structures. The large polydispersity ($M_w/M_n >$ 5) of the soluble fraction was consistent with the predicted cross-linked structures. In the reaction for 1.5 h, **Polymer 2** with a molecular weight of 26 000 was obtained in 96% yield without formation of insoluble products (Table 1, entry 4). Negligible branched structures were detected by MALDI-TOF-MS (See Supporting Information, Figure S1). This improved result indicates that direct arylation at the aromatic C–H bonds in the 3,3′,4,4′-tetramethylbithiophene moiety proceeded preferentially over those at the C–H bonds in the carbazole moiety, in the early stage of the reaction, i.e., before 1.5 h. Since the number of aromatic C–H bonds in the 3,3′,4,4′-tetramethylbithiophene moiety decreases with increasing degree of polymerization, the undesirable reactions at C–H bonds in the carbazole moiety occur at relatively high frequencies in the late stage

of the polycondensation reaction, resulting in the formation of cross-linked structures. The reaction time is therefore an important factor in direct arylation polycondensation to avoid overreactions at unexpected C–H bonds. The reaction of 3,6-dibromo-*N*-octadecylcarbazole for 3 h yielded **Polymer 3** with a moderate molecular weight (7300), without formation of insoluble products (Table 1, entry 5). The extension of the reaction time to 6 h increased the yield and the molecular weight of the polymer (Table 1, entry 6). A similar trend was observed in the syntheses of **Polymers 4** and **5** (Table 1, entries 7–10). The nitrogen atoms at the *para* position to the C–Br group are likely to decrease the reaction rate. Although 1,4-dibromo-2,5-dioctylbenzene possesses steric hindrance of the octyl groups at the *ortho* position to the C–Br group, the polycondensation reaction with 3,3′,4,4′-tetramethylbithiophene yielded the soluble **Polymer 6** in moderate yield (Table 1, entry 11). The reaction for 6 h provided a higher molecular weight and yield than that for 3 h (Table 1, entry 12).

Since these simple dibromoarylenes can be used as monomers for direct arylation polycondensations, polycondensation reactions of dibromoarylenes containing diketopyrrolopyrrole[17] and isoindigo[18] structures were conducted to synthesize materials for PSCs. The polycondensation reaction of the dibromo-substituted

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diketopyrrolopyrrole derivative gave **Polymer 7** with a molecular weight of 18 100 in 96% yield (Table 1, entry 13). Since **Polymer 7** had low solubility in *N,N*-dimethylacetamide (DMAc), the product was precipitated out in 0.5 h at the standard concentration (0.30 M). The details for optimization of the concentration are shown in the Supporting Information (Table S-1). The reaction was therefore conducted under diluted conditions (0.15 M). **Polymer 7** was purified by Soxhlet extraction to remove the oligomeric products, which were of low solubility and difficult to remove by simple washing. A polymer with an isoindigo moiety, **Polymer 8**, was obtained using the polycondensation reaction under the optimized conditions (Table 1, entry 14).

   Characterization. The characterizations of **Polymers 1–4** and **Polymer 6** were reported in a previous study.[13a] The ^{1}H NMR spectra of the polymers, synthesized under the modified conditions, were almost identical to the reported spectra (see Supporting Information). The optimization of the reaction conditions provided polymers with higher molecular weights in increased yields without changing the structures. The newly synthesized polymers, **Polymer 5**, **7**, and **8**, were characterized using ^{1}H and ^{13}C{^{1}H} NMR spectroscopies. Figure 1 shows the ^{1}H NMR spectrum of

Polymer 7. Each signal can be assigned to the repeating unit, and the signal of the terminal units was observed at 6.98 ppm. These results indicate that **Polymer 7** has a linear structure without defects such as branched or cross-linked structures. Characterization of **Polymer 7** was also conducted using MALDI-TOF-MS (Figure S2). The spectrum exhibits peaks corresponding to alternating structures with terminal C–H groups in the 3,3′,4,4′-tetramethylbithiophene moiety and terminal C–Br groups in the diketopyrrolopyrrole moiety. There are no peaks corresponding to a branched structure in the mass spectrum, supporting the proposed linear structure of **Polymer 7**. In contrast, the mass spectrum of **Polymer 8** exhibits peaks corresponding to a branched structure; this structure may be caused by direct arylation reactions at the C–H bonds in the isoindigo moiety (Figure S3).

Photophysical Properties. Table 2 summarizes the photophysical properties of **Polymers 1**–**8**. **Polymers 1**–**6** have similar absorptions in the solution and thin-film states. In contrast, **Polymers 7** and **8** exhibit red shifts of their absorptions in the film state compared with the solution state, presumably as a result of donor–acceptor structures leading to strong π–π stacking interactions. Figure 2 shows the UV-Vis absorption spectra of **Polymers 1**, **7**, and **8** in the solution state. The introduction of

dye moieties into the main chain resulted in absorptions in the long-wavelength region. Polymers with similar structures to those of **Polymers 7** and **8** have been reported in the literature (**DPP-DT** and **IID-DT**, Figure 3).[17a,18a] These polymers have a bithiophene unit instead of the 3,3′,4,4′-tetramethylbithiophene unit. The maximum absorption wavelengths of **DPP-DT** and **IID-DT** are 580 and 701 nm in thin film state, respectively; these are at longer wavelengths than those of **Polymers 7** and **8** (520 and 580 nm), respectively.[17a,18a] These observations indicate that the methyl groups on the tetramethylbithiophene induce a twisted structure as a result of their steric hindrance, leading to decreases in the coplanarities and the conjugation lengths of the polymers. In particular, the difference between the maximum absorption wavelengths of **Polymer 8** and **IID-DT** was significant (121 nm). These results indicate that the impact on the absorption properties of donor–acceptor interactions between the bithiophene unit and the isoindigo unit through π-conjugation is more significant than interactions between the bithiophene and diketopyrrolopyrrole units.

Electrochemical Properties and Photovoltaic Performances. The electrochemical properties of **Polymers 7** and **8** were investigated using cyclic voltammetry (Figure S4). The oxidation-onset potentials of **Polymers 7** and **8** were

0.67 V and 0.70 V vs. the ferrocene/ferrocenium couple, respectively.   On the basis of

these potentials, the highest occupied molecular orbital (HOMO) energy levels of

Polymers 7 and **8** were estimated to be −5.47 and −5.50 eV.[17a]   These values are close

to those obtained from photoelectron spectroscopy measurements (Table 3).   Similarly,

the lowest unoccupied molecular orbital (LUMO) energy levels were estimated to be

−3.15 and −3.51 eV from the cyclic voltammograms.   The electrochemical bandgaps

of **Polymers 7** and **8** were larger than those of the corresponding reference polymers

(**DPP-DT** and **IID-DT**).[17a,18a]   These trends are consistent with the absorption

properties of the polymers.

Since **Polymers 7** and **8** have wide absorptions in the visible region and

low-energy HOMO levels, these polymers are expected to be suitable as materials for

PSCs.[19]   The photovoltaic performances of **Polymers 7** and **8** were investigated in

bulk heterojunction solar cells with the configuration glass/indium tin oxide

(ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/**Polymer**

7 or **8**:methyl[6,6]phenyl-C61-butylate (PC61BM)/TiO$_x$/Al.   The details of the devices

are described in the Experimental Section.   The photovoltaic results are shown in

Figure 4 and Table 4.   The edges of the external quantum efficiency (EQE) curves of

the devices are in accordance with the absorption edges of the polymers.   The

similarities of the EQE responses and the absorption properties demonstrate that

Polymers 7 and **8** served as active materials for exciton formation by light absorption.

Although the power conversion efficiency (PCE) values are lower than those of typical

P3HT-based devices,[2] these results are important for the point that direct arylation

polycondensation can be used to synthesize materials for PSCs.[14c]   It is notable that the

devices with **Polymer 7** or **8** both showed a high open-circuit voltage (V_{oc}) of 1.01 V.

These high V_{oc} values provably result from the low HOMO levels of **Polymers 7** and **8**,

because the V_{oc} value is known to be proportional to the difference between the energies

of the LUMO level of PC61BM and the HOMO level of a p-type polymer.[19]   The low

short-circuit current density (J_{sc}) and fill factor may be attributed to the twisted structure

of the polymer, which is identified from the absorption properties, as described above,

because a twisted structure is unfavorable for carrier transport.[20]   Indeed, a

DPP-DT-based device of similar configuration had a PCE of 1.67% with a J_{sc} of 7.8

mA/cm^2.[17a]   The calculations also support the suggestion that steric hindrance of the

methyl groups on the tetramethylbithiophene unit causes the twisted structure of the

main chain (Figure S5).[21]   These methyl groups were introduced to prevent side

reactions at the relatively active C–H bonds at the β positions of the bithiophene

moieties.[13a]   These results clarify the next challenge; high regioselectivity is needed to

be developed in the development of direct arylation polycondensations, to enable rational design of π-conjugated polymers.

Conclusions

Direct arylation polycondensation reactions using a simple catalytic system gave eight kinds of bithiophene-based alternating copolymers. Reaction time was an important factor for obtaining high-molecular-weight polymers without the formation of cross-linked structures. This polycondensation reaction gave dye-containing polymers that are applicable as materials for PSCs. To obtain high-performance materials efficiently, further development of this methodology, especially in terms of C–H bond selectivity, is underway.

Experimental Section

Materials. 2,7−dibromo−9,9−dioctylfluorene, Pd(OAc)$_2$, K$_2$CO$_3$, and other chemicals were received from commercial suppliers and used without further purification. Anhydrous DMAc were purchased from Kanto Chemical and used as a dry solvent. PC61BM was purchased from Frontier Carbon Corporation. PEDOT:PSS (CleviosTM P VP AI 4083) were purchased from Heraeus.

3,3′,4,4′−tetramethylbithiophene,[22]   2,7−dibromo−*N*−octadecylcarbazole,[13a]

3,6−dibromo−*N*−octadecylcarbazole,[13a]

2,8−dibromo−10,10−dioctyl−*N*−methylphenazasiline,[23]   3,7−dibromo−10−

(2−ethylhexyl)phenothiazine,[24]   1,4−dibromo−2,5−dioctylbenzene,[25]   2,5−di−

(2−ethylhexyl)−3,6−bis(4−bromophenyl)pyrrolo[3,4−*c*]pyrrole−1,4−dione,[26]   and   (E)

−6,6'−dibromo−1,1'−bis(2−hexyldecyl)−[3,3'−biindolinylidene]−2,2'−dione[27]   were

prepared according to the literature methods.

General Methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker

AVANCE−400 NMR spectrometer and Bruker AVANCE−600 NMR spectrometer,

respectively. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured with tetramethylsilane

(TMS) as internal standard.   Gel permeation chromatography (GPC) measurements

were carried out on a SHIMADZU prominence GPC system equipped with polystyrene

gel columns, using $CHCl_3$ as an eluent after calibration with polystyrene standards.

All manipulations for the reactions were carried out under nitrogen atmosphere using a

standard Schlenk technique.   Column chromatography was carried out with silica gel

60 (Kanto, 40−100 μm, neutral).   MALDI−TOF−MS spectra were recorded on AB

SCIEX MALDI TOF/TOF 5800 using dithranol as a matrix.   The measurements of the

ionization potential were carried out on Riken Keiki Co., Ltd.; AC−2. Electrochemical measurements were performed by ALS Model 1200A Electrochemical Analyzer (BAS Inc.) with a standard three−electrode configuration. The polymer−coated ITO glass electrode was used as the working electrode. Bu_4NPF_6 (0.10 M) in acetonitrile was used as a supporting electrolyte with a platinum plate auxiliary electrodes. All measurements were carried out under a nitrogen atmosphere, and potentials were related to an Ag/Ag^+ reference electrode. The potentials were calibrated with ferrocene/ferrocenium redox couple. Molecular geometries were fully optimized at the B3LYP/3−21G* level with the Gaussian09 program.[21]

Synthesis of Polymer 5. A mixture of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), pivalic acid (0.017 mL, 0.15 mmol), K_2CO_3 (173 mg, 1.3 mmol), 3,7−dibromo−10− (2−ethylhexyl)phenothiazine (234 mg, 0.50 mmol), 3,3′,4,4′−tetramethylbithiophene (111 mg, 0.50 mmol) were stirred in anhydrous DMAc (1.67 mL) for 6 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred overnight at room temperature. The precipitate was separated by filtration and washed with 0.1 M HCl solution, distilled water, MeOH, and

hexane.   The precipitate was dissolved in CHCl$_3$ and the solution was filtered through

a plug of Celite to remove insoluble material.   A reprecipitation from CHCl$_3$/MeOH

gave **Polymer 5** as pale yellow solid in 98% yield. M_n = 21 000, M_w/M_n = 2.80.   [1]H

NMR (400 MHz, CDCl$_3$): δ 0.87 (t, J = 7.2 Hz, 6H), 0.91 (t, J = 7.2 Hz, 6H), 1.20−1.61

(br, 8H), 1.99 (br, 1H), 2.12 (s, 6H), 2.22 (s, 6H), 3.77 (br, 2H), 6.91 (d, J = 8.4 Hz, 2H),

7.26 (br, 4H).   ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 144.6, 137.2, 137.0, 133.3, 129.2,

128.2, 128.1 127.9, 125.4, 115.7, 51.0, 35.8, 30.7, 28.6, 24.0, 23.1, 14.4 14.1, 14.0,

10.5.

Synthesis of Polymer 7.   The polycondensation reaction of 2,5−di−

(2−ethylhexyl)−3,6−bis(4−bromophenyl)pyrrolo[3,4−c]pyrrole−1,4−dione (335 mg, 0.50

mmol) and 3,3′,4,4′−tetramethylbithiophene (111 mg, 0.50 mmol) was carried out by

according to the above mentioned method.   The product was subjected to Soxhlet

extraction with hexane and CHCl$_3$.   A reprecipitation of the CHCl$_3$ fraction in MeOH

gave **Polymer 7** as red solid in 96% yield. M_n = 18 100, M_w/M_n = 2.35.   ^{1}H NMR (400

MHz, CDCl$_3$): δ 0.75 (t, J = 7.4 Hz, 6H), 0.81 (t, J = 7.2 Hz, 6H), 1.00−1.30 (br, 16H),

1.50−1.60 (br, 2H), 2.18 (s, 6H), 2.33 (s, 6H), 3.82 (s, 4H), 7.65 (d, J = 8.4 Hz, 4H),

7.89 (d, J = 8.0 Hz, 4H).   ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)   δ 162.9, 148.2, 137.84,

137.80, 137.5, 137.2, 134.7, 129.2, 129.0, 127.2, 110.0, 45.1, 38.6, 30.4, 28.3, 23.8,

22.9, 14.42, 14.37, 14.0, 10.5.

Synthesis of Polymer 8. The polycondensation reaction of (E)−6,6'−dibromo−1,1'−bis(2−hexyldecyl)−[3,3'−biindolinylidene]−2,2'−dione (322 mg, 0.5 mmol) and 3,3′,4,4′−tetramethylbithiophene (111 mg, 0.50 mmol) was carried out by according to the above mentioned method for **Polymer 5** giving **Polymer 8** as pale green solid in 82% yield. M_n = 11 300, M_w/M_n = 2.76. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.90 (t, J = 6.6 Hz, 6H), 0.96 (t, J = 7.2 Hz, 6H), 1.20−1.55 (br, 16H), 1.80−2.00 (br, 2H), 2.19 (s, 6H), 2.35 (s, 6H), 3.73 (s, 4H), 6.92 (s, 2H), 7.19 (d, J = 8.4 Hz, 2H), 9.21 (d, J = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 168.7, 145.4, 138.7, 138.2, 138.1, 134.9, 132.4, 129.8, 129.3, 122.7, 120.7, 108.5, 44.3, 37.8, 30.9, 28.9, 24.2, 23.1, 14.6, 14.5, 14.1, 10.9.

Photovoltaic Device Fabrication.

A dispersion of PEDOT:PSS in water (Clevios[TM] P VP AI 4083) was spun cast onto a clean ITO substrate, which was washed with acetone and irradiated under UV light and ozone gas for 20 min to decompose the impurities, and then baked at 200 °C for 10 min. To a polymer (1.0 wt %) solution of o−dichlorobenzene were added PC61BM (double weight vs polymer), then the mixture was stirred for 1 h at ambient temperature. The

resulting solution was applied to the surface of a PEDOT:PSS coated ITO plate by the

spincoating method at a thickness of ca. 100 nm.   After drying under vacuum for 20

min, titanium(IV) isopropoxide solution (0.35wt% in isopropanol) was spincoated.

The resulting plate was placed in a vacuum chamber and the surface was coated with

the aluminum electrode (100 nm) by evaporation at 10^{-4} Pa at room temperature.

Finally, the solar cell was completed by encapsulation.   The PCE values were obtained

using Bunko Keiki CEP−2000 (AM1.5G, 100 mW/cm^2).

Author Information

Notes

The authors declare no competing financial interest.

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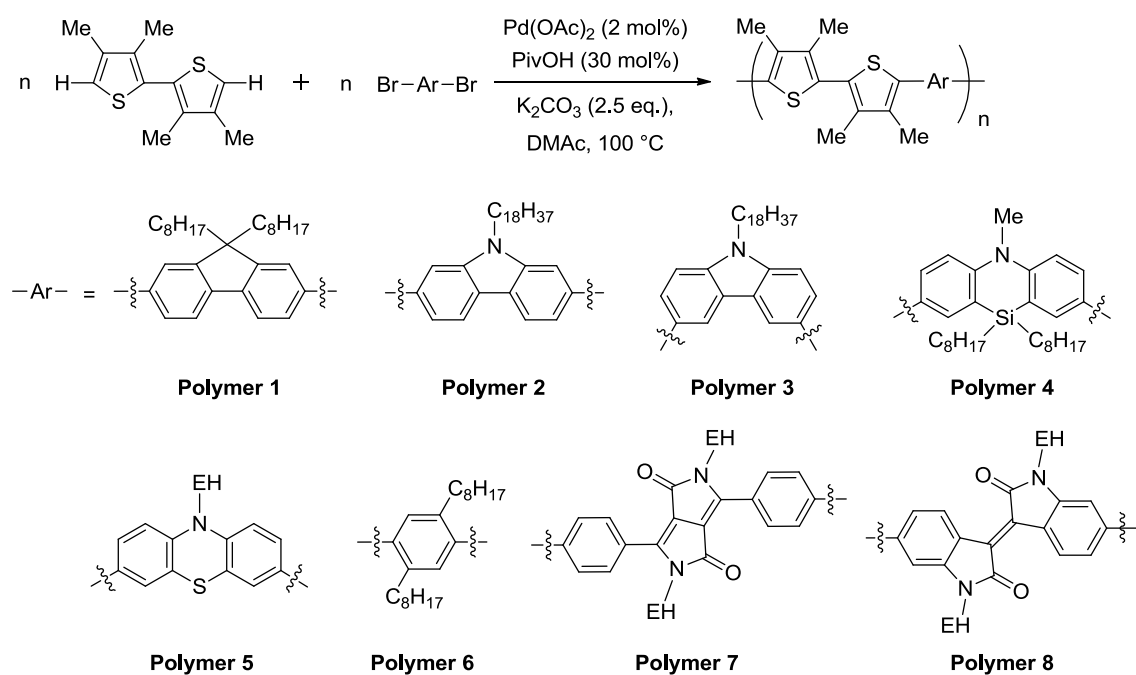
Scheme 1 Polycondensation of 3,3′,4,4′−tetramethylbithiophene and various dibromo−aromatic compounds.　EH indicates a 2−ethylhexyl group.

Table 1. Results of the polycondensation reactions[a]

Entry	Polymer	Reaction time(h)	M_n[b]	M_w/M_n[b]	Yield (%)[c]
1 [g]	**Polymer 1**	3 h	31 800	2.46	91
2	**Polymer 1**	1.5 h	32 100	2.34	93
3 [g]	**Polymer 2**	3 h	32 900	5.36	47
4	**Polymer 2**	1.5 h	26 000	2.76	96
5 [g]	**Polymer 3**	3 h	7 300	2.13	81
6	**Polymer 3**	6 h	11 700	1.93	99
7 [g]	**Polymer 4**	3 h	19 200	2.90	88
8	**Polymer 4**	6 h	27 100	2.82	98
9	**Polymer 5**	3 h	14 400	2.44	86
10	**Polymer 5**	6 h	21 000	2.80	98
11 [g]	**Polymer 6**	3 h	13 500	1.95	65
12	**Polymer 6**	6 h	15 000	1.69	88[d]
13 [f]	**Polymer 7**	6 h	18 100	2.35	96[e]
14	**Polymer 8**	6 h	11 300	2.76	82

[a] Reactions were carried out at 100 °C using $Pd(OAc)_2$ (2 mol%), PivOH (30 mol%) and K_2CO_3 (2.5 equiv.) in DMAc. [b] Estimated by GPC calibrated on polystyrene standards. [c] The products were obtained by reprecipitation from $CHCl_3$/MeOH and washing with hexane. [d] Without washing with hexane. [e] Yield after Soxhlet extraction with hexane and acetone. [f] The concentration of the monomer was 0.15 M. [g] reference 13a.

Table 2. Optical properties and energy level of polymers

Polymer	λ_{max}(nm)[a] (solution)	λ_{max}(nm) (thin film)	λ_{eg}(nm)[b] (thin film)	λ_{em} (nm)[a, c] (solution)	E_g^{opt} (eV)[d]
Polymer 1	368	364	414	468	2.99
Polymer 2	370	370	414	467	2.99
Polymer 3	319	319	390	460	3.18
Polymer 4	359	359	412	463	3.01
Polymer 5	310	310	418	430	2.97
Polymer 6	328	[e]	381	484	3.25
Polymer 7	502	520	600	586	2.07
Polymer 8	574	585	713	[f]	1.74

[a] In $CHCl_3$. [b] Absorption edge. [c] Maximum emission wavelength. [d] Optical bandgap from the absorption edge. [e] Broad absorption. [f] Negligible emission.

Table 3. Electrochemical properties of **Polymer 7**, **8** and the reference polymers

Polymer	E_{HOMO} (eV) [a]	E_{HOMO}^{CV} (eV) [b]	E_{LUMO}^{CV} (eV) [b]	E_g^{CV} (eV)
Polymer 7	-5.46	-5.47	-3.15	2.32
DPP−DT[17a]		-5.4	-3.5	1.9
Polymer 8	-5.55	-5.50	-3.51	1.99
IID−DT[18a]		-5.65	-3.78	1.87

[a] The value of E_{HOMO} was obtained from ionization potential. [b] The value of E_{HOMO}^{CV} and E_{LUMO}^{CV} were obtained from cyclic voltammograms vs Fc/Fc$^+$ (E_{HOMO} = -4.80 eV).

Table 4. Photovoltaic properties of **Polymer 7** and **8**

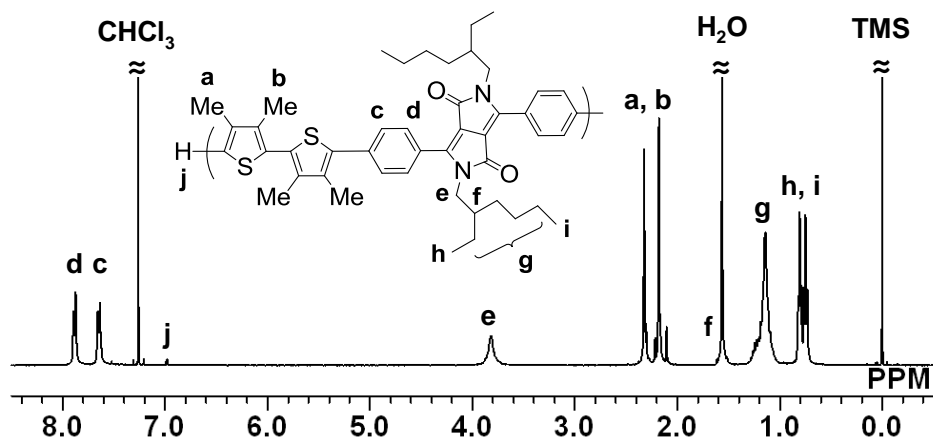| Polymer	V_{oc} / V	J_{SC} / mA cm^{-2}	FF / %	PCE / %
Polymer 7	1.01	2.93	0.30	0.89
Polymer 8	1.01	1.53	0.25	0.39

Figure 1. ^{1}H NMR spectrum of **Polymer 7** (400 MHz, CDCl$_3$).
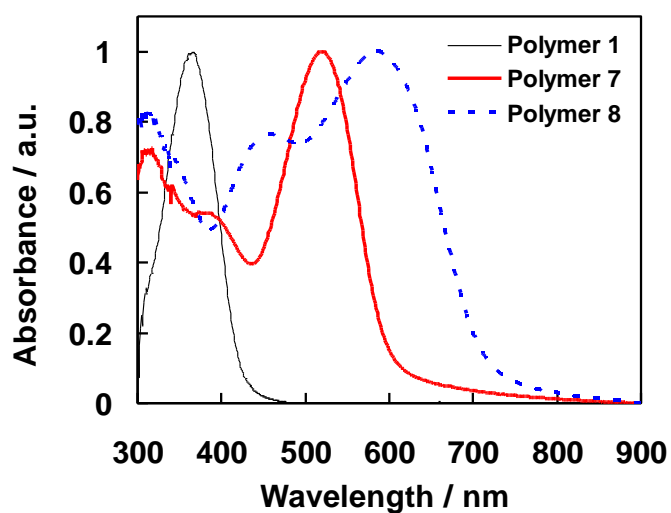

Figure 2. UV−Vis absorption spectrum of **Polymer 1**, **7**, and **8** in the thin film state.
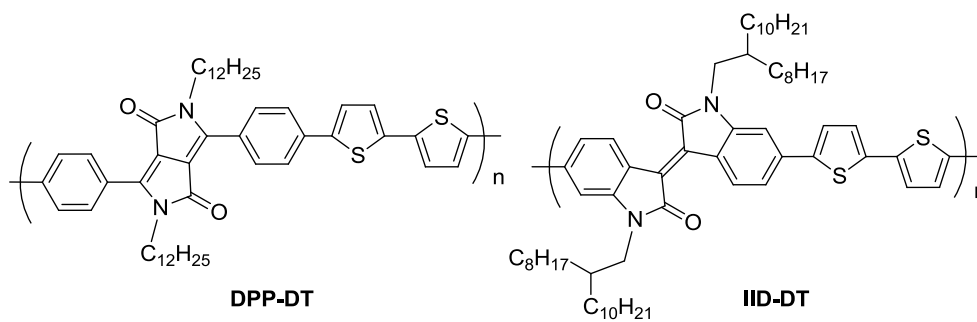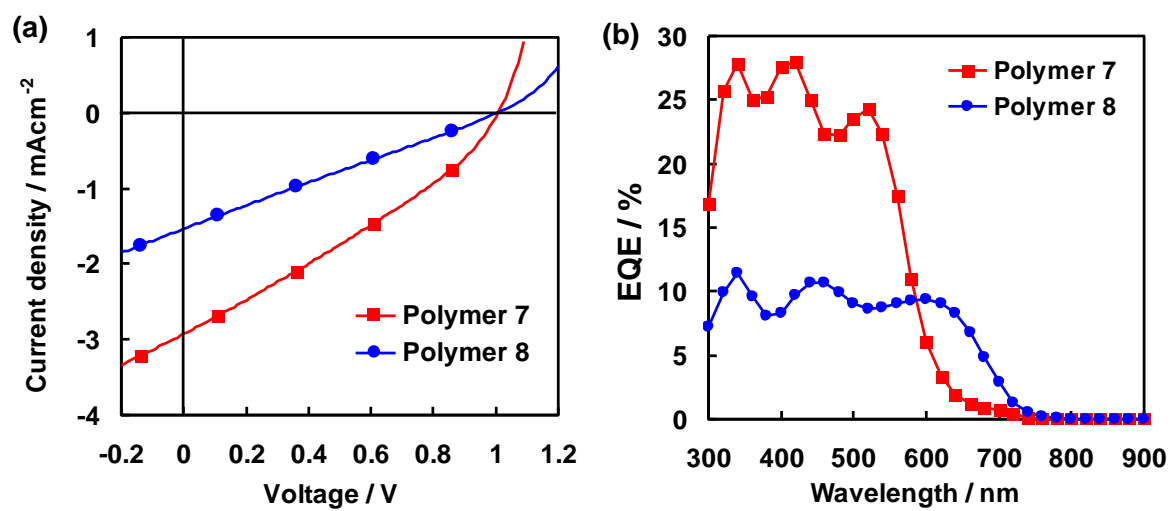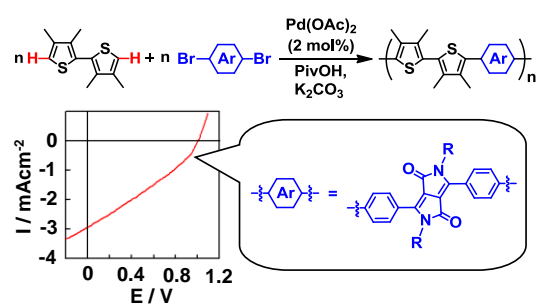

Figure 3. Structures of the reference polymers.

Figure 4. (a) *J−V* and (b) EQE curves of the devices with **Polymer 7** and **Polymer 8**.

Graphical Abstruct

Direct arylation polycondensation gave bithiophene-based conjugated polymers serving as materials for polymer solar cells.