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Facile One-pot Access to π-Conjugated Polymers via Sequential Bromination/Direct Arylation Polycondensation

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The synthesis of π-conjugated polymers starting from unfunctionalized aromatic monomers via sequential bromination/direct arylation polycondensation was investigated. The developed protocol provides a step-economical access to the polymers in a one-pot fashion, without the need for prior preparation and purification of dibrominated aromatic monomers or organometallic monomers. Benzyltrimethylammonium tribromide was effective for the bromination of 10-(2-octyldodecyl)phenothiazine and 4,4'-didodecyl-2,2'-bithiophene, and the obtained dibrominated aromatic monomers were used for the subsequent direct arylation polycondensation without isolation and purification. The direct arylation polycondensation reaction yielded the corresponding donor-acceptor-type π-conjugated polymers in moderate to good yields. The sequential protocol was also applicable to the synthesis of poly(3-hexylthiophene-2,5-diyl) from 3-hexylthiophene. The obtained polymers served as semiconducting materials in organic light-emitting diodes and organic photovoltaics.

Introduction

π-Conjugated polymers have been extensively investigated as materials for organic optoelectronic devices such as organic photovoltaics (OPVs), organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and sensors.[1,2] While considerable attention has been focused on developing high-performance materials over the past decades, the synthetic accessibility influencing material cost for the π-conjugated polymers has also received attention in recent years because of their impact on the commercial viability of organic optoelectronic devices.[3] In order to design an environmentally benign and cost-effective synthetic route, recently, the preparation of π-conjugated polymers via a dehydrohalogenative cross-coupling reaction, also called direct arylation, has been actively investigated.[4] This protocol serves as a practical tool for the construction of π-conjugated polymers because it avoids the use of organometallic monomers and reduces the undesired waste originating from organometallic reagents. Many efficient strategies have been reported for the direct arylation polycondensation; however, the reaction uses brominated aromatic monomers as coupling partners, and thus requires extra steps for their prior preparation and purification.

The consecutive one-pot strategy is a useful technique in synthetic organic chemistry because it can reduce solvent use, time, and the number of workup procedures compared with individual multi-step syntheses.[5] We have previously attempted to develop a facile synthesis of fluorene-based π-conjugated polymers via sequential bromination/direct arylation polycondensation.[6] The protocol eliminates the prior preparation and purification of a dibrominated fluorene monomer, and gives the cross-coupling polymeric products in a one-pot manner, thereby enabling facile access to π-conjugated polymers starting from unfunctionalized aromatic compounds (Scheme 1a). However, this process was limited to fluorene derivatives; other aromatic monomers have not been examined. This prompted our interest in establishing the protocol as a reliable synthetic method for π-conjugated polymers. In this work, two strategies were envisioned to extend the one-pot approach. At first, we focused on the bromination of electron-sufficient heteroaromatic compounds, used as starting monomers, which generally occurs under mild conditions. The bromination of electron-sufficient heteroaromatic monomers followed by direct arylation polycondensation with electron-deficient aromatic monomers could yield donor-acceptor (D-A)-type low band gap π-conjugated polymers, which would be applicable to OPVs and OFETs.[2] Next, we applied this protocol to the synthesis of poly(3-hexylthiophene-2,5-diyl) (P3HT)[7] from 3-hexylthiophene. This could expand the usability of the protocol to the polycondensation of dissymmetrical AB-type monomers (Scheme 1b). Finally, the obtained polymers were investigated as materials for OLEDs and OPVs to prove the utility of this synthetic method for the construction of organic semiconducting materials.

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a) Sequential bromination and AA-BB type polycondensation

b) Sequential bromination and A-B type polycondensation
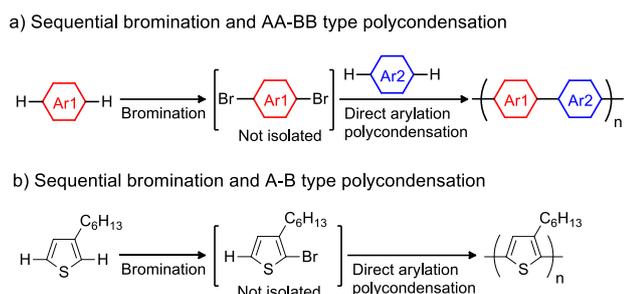
Scheme 1 Synthesis of π-conjugated polymers via sequential bromination and direct arylation.

Results and discussion

Synthesis of D-A-type polymers via a sequential procedure.
For the synthesis of D-A-type polymers by sequential reactions, 10-(2-octyldodecyl)phenothiazine (PTZ) and 4,4'-didodecyl-2,2'-bithiophene (BT) were adopted as electron-sufficient monomers because there have been several reports on the synthesis of π-conjugated polymers consisting of phenothiazine and thiophene derivatives and their use for the fabrication of optoelectronic devices.[8,9] In order to achieve a sequential process, the bromination step should efficiently yield the corresponding dibrominated compounds regioselectively, and the bromination residues and byproducts should have negligible impact on the subsequent polymerization step. Our previous study revealed that benzyltrimethylammonium tribromide (BTMA Br$_3$)[10] was

preferable for our protocol because benzyltrimethylammonium bromide (BTMA Br), a byproduct of the bromination, did not inhibit the polycondensation step.[6] Thus, BTMA Br$_3$ was used for the bromination of PTZ and BT, which proceeded smoothly in the presence of K$_2$CO$_3$ as a base and afforded 3,7-dibromo-10-(2-octyldodecyl)phenothiazine and 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene, respectively, in quantitative yields and with high regioselectivity (Scheme S1). The addition of a Lewis acid (ZnCl$_2$), which was necessary for the bromination of fluorene in our previous work,[6] was not required in this case, presumably because of the electron-sufficient feature of the PTZ and BT moieties.[10b,10c]

Next, the synthesis of D-A-type polymers via a sequential approach was examined. The polycondensation step was conducted under the optimal conditions for electron-deficient C-H monomers providing defect-free alternating polymers,[6,11] in which the dibrominated aromatic monomers were used without isolation and purification, and the results are summarized in Table 1. The sequential reaction of PTZ with 5-(2-ethylhexyl)-thieno-[3,4-c]-pyrrole-4,6-dione (TPD) gave Polymer **1** with a molecular weight of 15,000 in 91% yield (Table 1, Entry 1). In the reaction protocol, a small amount of PTZ was added to the reaction mixture after the bromination step to consume trace amount of BTMA Br$_3$ residues (see Experimental Section). Because the unreacted PTZ did not affect the following reaction, the direct arylation polycondensation reaction was carried out subsequently. The chemical structure of Polymer **1** was determined by NMR spectroscopy and MALDI-TOF-MS. In the ^{1}H NMR spectrum shown in Fig. 1, each signal was assigned to the repeating unit,

Table 1 Sequential bromination and direct arylation polycondensation starting with electron rich heteroaromatic compounds
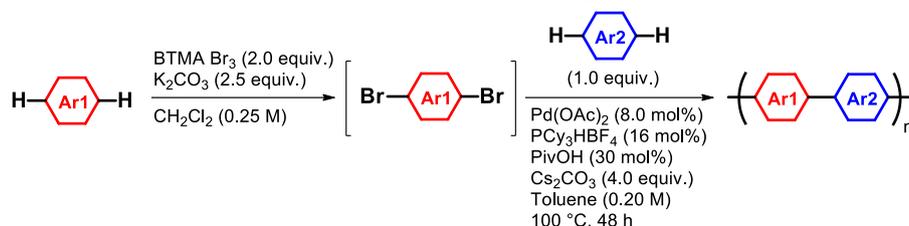
Entry	Ar1	Ar2	Product	Yield (%)[a]	M_n (kDa)[b]	PDI[b]
1	PTZ	TPD	Polymer **1**	91	15.0	1.8
2	PTZ	OFB	Polymer **2**	72	15.3	1.7
3	BT	TPD	Polymer **3**	65[c]	14.9[d]	1.7[d]
4	BT	OFB	Polymer **4**	66	21.6	1.5

[a] The products were obtained by reprecipitation from chloroform / methanol. [b] Estimated by GPC calibrated with polystyrene standards using CHCl$_3$ as an eluent at 40 °C. [c] The product was obtained by reprecipitation from o-dichlorobenzene (100 °C) / methanol. [d] Estimated by GPC calibrated with polystyrene standards using o-dichlorobenzene as an eluent at 140 °C.
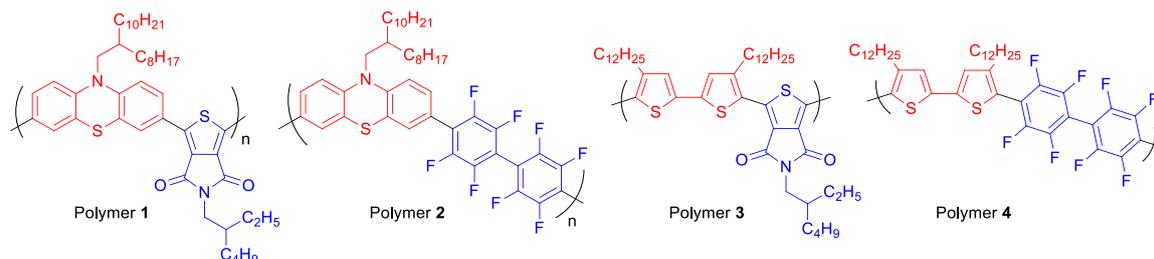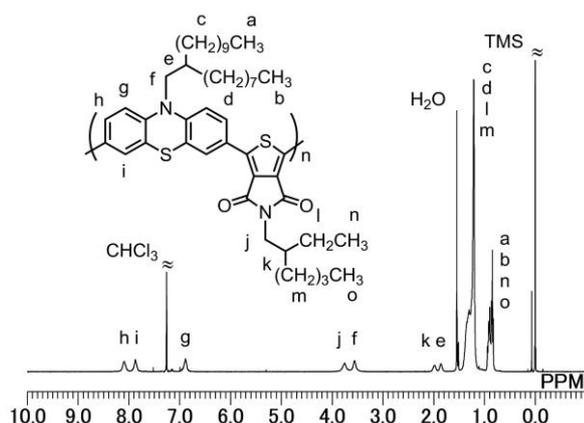
Fig. 1 ^{1}H NMR spectrum of Polymer **1** (400 MHz, CDCl$_3$).

and the integral ratios of the signals agreed with the assignments and were consistent with the alternating structure of the polymer. The ^{1}H NMR spectrum essentially agreed with that of the polymer obtained from the isolated pure 3,7-dibromo-10-(2-octyldodecyl)phenothiazine (Scheme S2 and Fig. S1). All ^{13}C{^{1}H} NMR signals were also assignable to the carbons in the recurring unit (Fig. S2). The MALDI-TOF-MS spectrum exhibited peaks at regular intervals in the measurable molecular weight range, corresponding to the alternating structure (Fig. S3).

The same reaction protocol was used for the polycondensation of 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (OFB) as an Ar2 monomer and BT as an Ar1 monomer (Table 1, Entries 2-4), which yielded the corresponding polymers (Polymers **2**-**4**) in moderate to good yields. In the case of the bromination of BT, 2-methylthiophene was added to consume the BTMA Br$_3$ residues (see Experimental Section). The GPC measurement of Polymer **3** was conducted with a high-temperature GPC system using o-dichlorobenzene as an eluent because of the low solubility of the polymer in chloroform at room temperature. Polymers **2**-**4** were characterized by NMR spectroscopy and MALDI-TOF-MS (Figs. S4-S14), and ^{19}F NMR spectra were also recorded for Polymers **2** and **4** (Figs. S5 and S12). The results were consistent with the trend observed in the synthesis of Polymer **1**. In the case of Polymer **3**, because the brominated 2-methylthiophene could take part in the direct arylation, the terminal 2-methylthiophene unit was observed in ^{1}H NMR and MALDI-TOF-MS spectra (Figs. S8 and S10). These results indicate that the sequential protocol is applicable to the synthesis of D-A-type π-conjugated polymers.

Synthesis of P3HT via a sequential procedure.
Several groups have demonstrated the synthesis of P3HT with high molecular weight and/or high regioregularity via direct arylation polycondensation of 2-bromo-3-hexylthiophene.[4b,12] Thus, to evaluate the applicability of the sequential protocol to the polycondensation of dissymmetrical AB-type monomers, the synthesis of P3HT from 3-hexylthiophene was carried out. For the success of the sequential reaction process, the bromination of 3-hexylthiophene should efficiently give 2-

bromo-3-hexylthiophene. However, the bromination reaction of 3-hexylthiophene with BTMA Br$_3$ resulted in the formation of 2,5-dibromo-3-hexylthiophene as a minor product under the similar reaction conditions described in the previous section (Table S1, Entry 1). Alternatively, the use of tetra-n-butylammonium tribromide (TBA Br$_3$) as a brominating agent[13] reduced the formation of the dibrominated product and gave 2-bromo-3-hexylthiophene in higher yield (Table S1, Entry 2).

Subsequently, in order to examine the effect of tetra-n-butylammonium bromide (TBA Br), the byproduct of the bromination, on the following polycondensation reaction, the Pd-catalyzed direct arylation polycondensation of isolated pure 2-bromo-3-hexylthiophene was examined under various conditions.[4b,12d] The results revealed that the addition of TBA Br considerably reduced the catalytic activity under the representative reaction conditions (Scheme S3).[14] In contrast, the polycondensation reaction of 2-bromo-3-hexylthiophene proceeded smoothly even in the presence of TBA Br (1.0 equiv.) with Pd(OAc) (0.1 mol%), pivalic acid (PivOH, 1.0 equiv.), K$_2$CO$_3$ (2.5 equiv.) in THF (0.5 M of monomer) at 60 °C for 96 h; the reaction gave P3HT with a molecular weight of 10,900 (regioregularity of 95%) in 80% yield (Scheme S4). The effect of concentration and amount of catalyst loading was also evaluated, and the results are summarized in Table S2.

The established reaction conditions were applied to the sequential protocol, and the bromination reaction mixture was used directly for the subsequent polycondensation step (Scheme 2). The sequential bromination/polycondensation gave P3HT with a molecular weight of 19,800 and 93% regioregularity in 88% yield; the chemical structure and regioregularity were elucidated by ^{1}H NMR spectroscopy (Fig. S15). The regioregularity of the product was somewhat lower than that of P3HT prepared by direct arylation polycondensation of isolated pure 2-bromo-3-hexylthiophene under the established reaction conditions, which was due to the formation of small amount of 2,5-dibromothiophene in the bromination step, but higher than that of P3HT prepared by the conventional oxidative polymerization of 3-hexylthiophene.[15,16] In the ^{1}H NMR spectrum, no evidence of
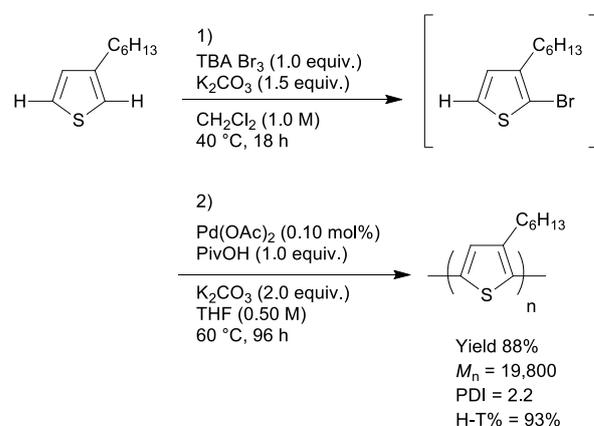
Scheme 2 Sequential bromination of 3-hexylthiophene and direct arylation polycondensation.

β-branching structure in P3HT was identified.[12c,12f,17]

Optical and electronic properties.

The UV-vis absorption spectra of Polymers **1**-**4** and P3HT are shown in Fig. 2. The absorption bands of Polymers **2** and **4** appear at shorter wavelengths than those of Polymers **1** and **3** because of their limited π-conjugation due to the steric hindrance of the fluorine atoms in the OFB unit. The absorption spectrum of P3HT displays a shoulder peak at around 600 nm, indicating interchain interactions among regioregular P3HT chains.[18a] The optical band gaps of Polymers **1**-**4** were determined to be 2.3, 3.0, 1.8, and 2.7, respectively. The highest occupied molecular orbital (HOMO) energy levels of Polymers **1** and **3** were determined to be -5.60 and -5.24 eV, respectively, by photoelectron yield spectroscopy.

Because Polymer **1** film exhibits orange emission (λ_{max} = 608 nm, quantum yield (φ) = 18%) when excited at 450 nm (Fig. 3(a)), the electroluminescent properties of Polymer **1** were evaluated in OLED devices, and the results are shown in Fig. 3 (see Experimental Section for details of OLED fabrication). The electroluminescence spectrum was consistent with the photoluminescence spectrum of Polymer **1**, and the coordinates of the CIE chromaticity diagram were x = 0.61, y = 0.39 at 0.2 mA cm^{-2}. These results indicate that Polymer **1** serves as the emitting material of the OLED device. The electroluminance reached 2510 cd m^{-2} at a current of 250 mA cm^{-2}, and the external quantum efficiency (EQE) of the OLED was 0.84% at 23 mA cm^{-2}, which was comparable or higher than that reported for OLEDs using related phenothiazine-based π-conjugated polymers as emitting materials.[9]

Polymer **1** and P3HT were also examined as active materials in OPVs, and the photovoltaic properties of the fabricated OPVs are summarized in Table 2. The details of OPV fabrication and results of *J-V* curves and incident-photon-to-current conversion efficiency (IPCE) spectra were described in Experimental Section and Supporting Information (Fig. S16). The IPCE spectra of the OPVs overlapped with the absorption spectra of the polymers and PCBM or PC$_{70}$BM (Fig. S16b), indicating that these polymers served as active materials in the OPVs for exciton formation by light absorption. An OPV cell with a P3HT:PCBM (1:0.8) active blend layer gave a PCE of 3.5 ± 0.3%, which was comparable to the values reported for OPVs using P3HT prepared by other synthetic methods.[18] The low PCE value of the OPVs using Polymer **1** (0.91 ± 0.05%) can be attributed to a significant phase separation of the Polymer **1**:PC$_{70}$BM blend film (Fig. S17).

Conclusions

In summary, the synthesis of π-conjugated polymers via sequential bromination/Pd-catalyzed direct arylation polycondensation was demonstrated. Since bromination of electron-sufficient heteroaromatic monomers occurs under mild conditions, appropriate choices of monomers allow that this sequential protocol could be applied to the preparation of D-A-type π-conjugated polymers in a one-pot fashion, without the need for prior preparation and purification of

Fig 3 (a) Photoluminescence spectrum of thin film of Polymer **1** and electroluminescence spectrum of OLED using Polymer **1** at 3.9 V and (b) Luminance vs current density plots for OLED using Polymer **1**.

Fig. 2 Absorption spectra of Polymers **1**-**4** and P3HT in the thin-film state.

Table 2 Photovoltaic properties of Polymer **1** and P3HT[a]

BHJ layer	Solvent	Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
Polymer **1** : PC$_{70}$BM (1:4)	CHCl$_3$	81	2.6±0.1	0.86±0.02	0.40±0.01	0.91±0.05
P3HT : PCBM (1:0.8)	o-DCB[b]	223	10.4±0.7	0.64±0.0008	0.52±0.02	3.5±0.3

[a] OPV configuration: ITO/ PEDOT:PSS/ BHJ layer/ LiF(1nm)/ Al(80nm). The average values with standard deviations were calculated from the results of six OPV. [b] 1,2-Dichlorobenzene.

dibrominated aromatic monomers or organometallic monomers. The methodology was extended to the polycondensation of dissymmetrical AB-type monomers, and a one-pot access to P3HT from 3-hexylthiophene was achieved. OLED and OPV devices were fabricated using Polymer **1** and P3HT, and the role of the polymers as active materials in the devices was demonstrated. The practical applications of the synthesis of π-conjugated polymers have been limited by the high cost of workup and purification procedures;[3b] thus, optimization of the synthetic route to minimize the number of workup and purification steps was highly desirable. Concatenating bromination and direct arylation reactions into a one-pot sequence represents a superior strategy to conventional synthetic methods from the atom- and step-economical points of view; thus, this methodology should provide one of practical solutions on this matter.

Experimental section

Materials

Palladium acetate (Pd(OAc)$_2$), tricyclohexylphosphine tetrafluoroborate (PCy$_3$·HBF$_4$), PivOH, Cs$_2$CO$_3$, K$_2$CO$_3$, 10*H*-phenothiazine, 4,4′-dibromo-2,2′-bithiophene, TBA Br, and other chemicals were received from commercial suppliers and used without further purification. Anhydrous dichloromethane, toluene, *N,N*-dimethylacetamide (DMAc), and THF were purchased from Kanto Chemical and used as a dry solvent. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP AI 4083) was purchased from Heraeus. PC$_{70}$BM (purity 99%) was purchased from Solenne. 2,2′,2′′-(1,3,5-Benzenetriyl)tris(1-phenylbenzimidazole) (TPBi) was purchased from Luminescence Technology Corp. BTMA Br$_3$ and TBA Br$_3$ were purchased from TCI and purified by recrystallization from dichloromethane/diethylether. 2-Bromo-3-hexylthiophene and 3-hexylthiophene were purchased from TCI and purified by column chromatography. TPD was synthesized according to the literatures[19] and purified by recrystallization from hexane. The synthesis of PTZ and BT were described in supporting information.

General methods

^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra were recorded on Bruker AVANCE-400 and AVANCE-600 NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured with tetramethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were measured with hexafluorobenzene as an external standard (-162.9 ppm). Regioregularity of P3HT was quantified by ^{1}H NMR according to the literature.[4o] 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. The high-temperature GPC measurement was conducted using a HLC-8321 GPC/HT (TOSOH, Tokyo, Japan) with *o*-dichlorobenzene as the eluent after calibration with polystyrene standards. MALDI-TOF-MS spectra were recorded on an AB SCIEX MALDI TOF/TOF 5800 in linear mode using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Elemental Analyzer. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a JASCO V-630 spectrometer or a Hitachi U-3010 spectrometer. Photoluminescence spectrum was recorded on a JASCO FP-6500 spectrometer. The HOMO energy levels were estimated by photoelectron yield spectroscopy (PYS) using an AC-3 spectrometer (Riken Keiki). The surface morphologies of the BHJ films were observed using AFM (5100N, Hitachi High Tech Science). All of the manipulations for the reactions performed under a nitrogen atmosphere using Schlenk techniques.

Synthesis of Polymer 1 via sequential protocol

A mixture of PTZ (144 mg, 0.30 mmol), K$_2$CO$_3$ (104 mg, 0.75 mmol), dichloromethane (1.2 mL), and BTMA Br$_3$ (234 mg, 0.60 mmol) was stirred for 24 h at room temperature under a nitrogen atmosphere. Then, PTZ (14.4 mg, 0.030 mmol) and dichloromethane (0.30 mL) were added to the mixture, and the reaction continued for further 24 h. After the bromination, anhydrous toluene (1.5 mL), Cs$_2$CO$_3$ (391 mg, 1.2 mmol), Pd(OAc)$_2$ (5.39 mg, 0.024 mmol) and PCy$_3$·HBF$_4$ (17.7 mg, 0.048 mmol) were added to the mixture. After stirring for 15 min, TPD (79.6 mg, 0.30 mmol) and PivOH (0.0102 mL, 0.090 mmol) were added to the mixture. The resulting mixture was heated to 100 °C under nitrogen gas steam and stirred for 1 h. Then, the reaction vessel was sealed, and the reaction continued for further 47 h. After cooling to room temperature, toluene was removed under vacuum. The product was dissolved in THF (5 mL), and resulting mixture was poured into distilled water (300 mL). The precipitate was washed with 0.1 M aqueous solution of ethylenediaminetetraacetic acid disodium salt (EDTA 2Na) (pH 8), distilled water, methanol, and hexane. The polymeric product was dissolved in CHCl$_3$, and the solution was filtered through a Celite plug. A reprecipitation from CHCl$_3$ / methanol gave poly[[10-(2-octyldodecyl)phenothiazine-3,7-diyl]-(5-octylthieno[3,4-*c*]pyrrole-4,6-dione-1,3-diyl)] (Polymer **1**) as a red solid in 91% yield (M_n = 15,000, PDI = 1.8). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.10 (br, 2H), 7.88 (br, 2H), 6.89 (br, 2H), 3.75 (br, 4H), 3.56 (br,

4H), 1.98 (br, 1H), 1.86 (br, 1H), 1.30-1.21 (br m, 40H), 0.94-0.83 (m, 12H). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 163.3, 146.2, 143.1, 129.3, 127.6, 126.7, 125.6, 125.3, 116.0, 51.7, 42.6, 38.2, 34.8, 32.0, 31.9, 31.5, 30.6, 30.0, 29.7, 29.5, 29.4, 29.3, 28.7, 26.2, 23.9, 23.1, 22.7, 14.1, 10.5. Anal. calcd. for C$_{46}$H$_{64}$N$_2$O$_2$S$_2$: C 74.55, H 8.70, N 3.78; found C 74.33, H 8.72, N 3.86.

Synthesis of Polymer 3 via sequential protocol

A mixture of BT (75.4 mg, 0.15 mmol), K$_2$CO$_3$ (51.8 mg, 0.38 mmol), dichloromethane (0.6 mL), and BTMA Br$_3$ (117 mg, 0.30 mmol) was stirred for 24 h at 40 °C under a nitrogen atmosphere. Then, a solution of 2-metylthiophene in dichloromethane (0.10 M, 60 µL, 6.0µmol) was added to the mixture, and the reaction continued for further 1 h. After the bromination, anhydrous toluene (0.75 mL), Cs$_2$CO$_3$ (195 mg, 0.60 mmol), Pd(OAc)$_2$ (2.69 mg, 0.012 mmol) and PCy$_3$·HBF$_4$ (8.84 mg, 0.024 mmol) were added to the mixture. After stirring for 15 min, TPD (39.8 mg, 0.15 mmol) and PivOH (5.08 µL, 0.045 mmol) were added to the mixture. The resulting mixture was heated to 100 °C under nitrogen gas steam and stirred for 1 h. Then, the reaction vessel was sealed, and the reaction continued for further 47 h. After cooling to room temperature, toluene was removed under vacuum. The product was washed with 0.1 M aqueous solution of EDTA 2Na (pH 8), distilled water, methanol, and hexane. The polymeric product was dissolved in o-dichlorobenzene at 100 °C, and the solution was filtered through a Celite plug. The hot solution was poured into vigorously stirred methanol at room temperature, giving Poly[[5-(2-ethylhexyl)-5,6-dihydro-4,6-dioxothieno[3,4-c]pyrrole-1,3-diyl](4,4´-didodecyl[2,2´-bithiophene]-5,5´-diyl)] as a dark purple solid in 65% yield (M_n = 14,900, PDI = 1.7). ^1H NMR (600 MHz, C$_2$D$_2$Cl$_4$, 373 K): δ 7.22 (s, 2H), 3.60 (d, J = 6.8 Hz, 2H), 2.87 (t, J = 7.5 Hz, 4H), 1.94-1.90 (m, 1H), 1.79-1.74 (m, 4H), 1.42-1.35 (m, 44H), 0.98-0.94 (m, 12H). $^{13}C\{^1H\}$ NMR (150 MHz, C$_2$D$_2$Cl$_4$, 373 K): δ 162.1, 145.4, 138.1, 136.0, 130.8, 127.1, 124.9, 42.6, 38.3, 31.6, 30.8, 30.0, 29.8, 29.3, 29.1, 29.0, 28.5, 24.2, 22.7, 22.3, 13.7, 10.4. Anal. calcd. for C$_{46}$H$_{69}$NO$_2$S$_3$: C 72.29, H 9.10, N 1.83; found C 71.80, H 9.07, N 1.51.

Synthesis of P3HT from 3-hexylthiophene via sequential protocol

A mixture of 3-hexylthiophene (0.179 mL, 1.0 mmol), K$_2$CO$_3$ (207 mg, 1.5 mmol), dichloromethane (1.0 mL) and BTMA Br$_3$ (482 mg, 1.0 mmol) was stirred for 18 h at 40 °C under a nitrogen atmosphere. After the bromination, dichloromethane was evaporated at 60 °C. After cooling to room temperature, K$_2$CO$_3$ (276 mg, 2.0 mmol), PivOH (0.113 mL, 1.0 mmol), and THF (1.9 mL) were added. The mixture was stirred for 2 h at 60 °C. Then, a solution of Pd(OAc)$_2$ in THF (0.010 M, 0.10 mL, 1.0 µmol) was added. The resulting mixture was stirred at 60 °C for 96 h. After cooling to room temperature, the mixture was diluted with small amount of THF, and poured into distilled water (500 mL). The precipitate was washed with 0.1 M aqueous solution of EDTA 2Na (pH 8), distilled water, methanol, and hexane. The polymeric product was dissolved in CHCl$_3$, and the solution was filtered through a Celite plug. A reprecipitation from CHCl$_3$ / methanol gave P3HT as a dark purple solid in 88% yield (M_n = 19,800, PDI = 2.2, H-T% = 93%). ^1H NMR (400 MHz, CDCl$_3$): δ 6.98 (s, 1H), 2.80 (t, J = 7.7 Hz, 2H), 1.74-1.67 (m, 2H), 1.46-1.31 (m, 6H), 0.91 (t, J = 7.0 Hz, 3H). Anal. calcd. for C$_{10}$H$_{14}$S: C 72.23, H 8.49; found C 72.20, H 8.98.

Notes and references

1   (a) A. Facchetti, *Chem. Mater.*, 2011, **23**, 733; (b)X. Guo, M. Baumgarten and K. Müellen, *Prog. Polym. Sci.*, 2013, **38**, 1832; (c) P. P. Khlyabich, B. Burkhart, A. E. Rudenko and B. C. Thompson, *Polymer*, 2013, **54**, 5267; (d) H. Benten, D. Mori, H. Ohkita and S. Ito, *J. Mater. Chem. A*, 2016, **4**, 5340; (e) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897; (f) A. Alvarez, A. Salinas-Castillo, J. M. Costa-Fernández, R. Pereiro and A. Sanz-Medel, *TrAC Trends Anal. Chem.*, 2011, **30**, 1513; (g) G. Fukuhara, *Polym. J.*, 2015, **47**, 649.

2   (a) C. Duan, F. Huang and Y. Cao, *J. Mater. Chem.*, 2012, **22**, 10416; (b) R. S. Kularatne, H. D. Magurudeniya, P. Sista, M. C. Biewer and M. C. Stefan, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 743; (c) C. Liu, K. Wang, X. Gong and A. J. Heeger, *Chem. Soc. Rev.*, 2016, **45**, 4825; (d) K.-J. Baeg, M. Caironi and Y.-Y. Noh, *Adv. Mater.*, 2013, **25**, 4210.

3   (a) D. J. Burke and D. J. Lipomi, *Energy Environ. Sci.*, 2013, **6**, 2053; (b) T. P. Osedach, T. L. Andrew and V. Bulović, *Energy Environ. Sci.*, 2013, **6**, 711; (c) R. Po, A. Bernardi, A. Calabrese, C. Carbonera, G. Corso and A. Pellegrino, *Energy Environ. Sci.*, 2014, **7**, 925; (d) R. Po, G. Bianchi, C. Carbonera and A. Pellegrino, *Macromolecules*, 2015, **48**, 453.

4   (a) M. Sévignon, J. Papillon, E. Schulz and M. Lemaire, *Tetrahedron Lett.*, 1999, **40**, 5873; (b) Q. Wang, R. Takita, Y. Kikuzaki and F. Ozawa, *J. Am. Chem. Soc.*, 2010, **132**, 11420; (c) W. Lu, J. Kuwabara and T. Kanbara, *Macromolecules*, 2011, **44**, 1252; (d) P. Berrouard, A. Najari, A. Pron, D. Gendron, P.-O. Morin, J.-R. Pouliot, J. Veilleux and M. Leclerc, *Angew. Chem., Int. Ed.*, 2012, **51**, 2068; (e) S. Kowalski, S. Allard and U. Scherf, *ACS Macro Lett.*, 2012, **1**, 465; (f) H. Zhao, C.-Y. Liu, S.-C. Luo, B. Zhu, T.-H. Wang, H.-F. Hsu and H.-h. Yu, *Macromolecules*, 2012, **45**, 7783; (g) S.-W. Chang, H. Waters, J. Kettle, Z.-R. Kuo, C.-H. Li, C.-Y. Yu, M. Horie, *Macromol. Rapid Commun.*, 2012, **33**, 1927; (h) K. Nakabayashi, H. Mori, *Chem. Lett.*, 2013, **42**, 717; (i) R. Matsidik, H. Komber and M. Sommer, *ACS Macro Lett.*, 2015, **4**, 1346; (j) S. Hayashi, Y. Kojima, T. Koizumi, *Polym. Chem.*, 2015, **6**, 881; (k) A. S. Dudnik, T. J. Aldrich, N. D. Eastham, R. P. H. Chang, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2016, **138**, 15699; (l) F. Grenier, K. Goudreau and M. Leclerc, *J. Am. Chem. Soc.*, 2017, **139**, 2816; (m) S. Kowalski, S. Allard, K. Zilberberg, T. Riedl and U. Scherf, *Prog. Polym. Sci.*, 2013, **38**, 1805; (n) K. Okamoto, J. X. Zhang, J. B. Housekeeper, S. R. Marder and C. K. Luscombe, *Macromolecules*, 2013, **46**, 8059; (o) A. E. Rudenko and B. C. Thompson, *J. Polym. Sci.,*

Part A: Polym. Chem., 2015, **53**, 135; (p) S.-L. Suraru, J. A. Lee and C. K. Luscombe, *ACS Macro Lett.*, 2016, **5**, 724; (q) T. Bura, J. T. Blaskovits and M. Leclerc, *J. Am. Chem. Soc.*, 2016, **138**, 10056; (r) J.-R. Pouliot, F. Grenier, J. T. Blaskovits, S. Beaupré and M. Leclerc, *Chem. Rev.*, 2016, **116**, 14225; (s) P.-O. Morin, T. Bura and M. Leclerc, *Mater. Horiz.,* 2016*,* **3**, 11.

5   (a) Y. Hayashi, *Chem. Sci.*, 2016, **7**, 866; (b) H.-Q. Do and O. Daugulis, *J. Am. Chem. Soc.*, 2011, **133**, 13577; (c) N. Kutsumura, Y. Matsubara, K. Niwa, A. Ito and T. Saito, *Eur. J. Org. Chem.*, 2013, 3337; (d) M. A. B. Mostafa, E. D. D. Calder, D. T. Racys and A. Sutherland, *Chem. Eur. J.*, 2017, **23**, 1044.

6   H. Saito, J. Kuwabara and T. Kanbara, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 2198.

7   R. D. McCullough, *Adv. Mater.*, 1998, **10**, 93.

8   (a) H. Padhy, J.-H. Huang, D. Sahu, D. Patra, D. Kekuda, C.-W. Chu and H.-C. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 4823; (b) W. Jang, F. Lyu, H. Park, Q. B. Meng, S.-H. Lee and Y.-S. Lee, *Chem. Phys. Lett.*, 2013, **584**, 119; (c) M.-C. Yuan, M.-Y. Chiu, S.-P. Liu, C.-M. Chen and K.-H. Wei, *Macromolecules*, 2010, **43**, 6936; (d) M.-S. Su, C.-Y. Kuo, M.-C. Yuan, U.-S. Jeng, C.-J. Su and K.-H. Wei, *Adv. Mater.*, 2011, **23**, 3315.

9   (a) X. Kong, A. P. Kulkarni and S. A. Jenekhe, *Macromolecules*, 2003, **36**, 8992; (b) D.-H. Hwang, S.-K. Kim, M.-J. Park, J.-H. Lee, B.-W. Koo, I.-N. Kang, S.-H. Kim and T. Zyung, *Chem. Mater.*, 2004, **16**, 1298; (c) Z. Qiao, J. B. Peng, Y. Jin, Q. L. Liu, J. E. N. Weng, Z. C. He, S. H. Han and D. R. Cao, *Polymer*, 2010, **51**, 1016; (d) S. A. Elkassih, P. Sista, H. D. Magurudeniya, A. Papadimitratos, A. A. Zakhidov, M. C. Biewer and M. C. Stefan, *Macromol. Chem. Phys.*, 2013, **214**, 572.

10 (a) S. Kajigaeshi, T. Kakinami, M. Moriwaki, T. Tanaka, S. Fujisaki and T. Okamoto, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 439; (b) T. Okamoto, T. Kakinami, H. Fujimoto and S. Kajigaeshi, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2566; (c) S. Kajigaeshi, T. Kakinami, H. Tokiyama, T. Hirakawa and T. Okamoto, *Chem. Lett.*, 1987, **16**, 627; (d) S. Kajigaeshi, T. Kakinami, K. Inoue, M. Kondo, H. Nakamura, M. Fujikawa and T. Okamoto, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 597; (e) S. A. Pourmousavi and P. Salehi, *Acta Chim. Slov.*, 2009, **56**, 734.

11 (a) J. Kuwabara, K. Yamazaki, T. Yamagata, W. Tsuchida and T. Kanbara, *Polym. Chem.*, 2015, **6**, 891; (b) J. Kuwabara, Y. Fujie, K. Maruyama, T. Yasuda and T. Kanbara, *Macromolecules*, 2016, **49**, 9388.

12 (a) Q. Wang, M. Wakioka and F. Ozawa, *Macromol. Rapid Commun.*, 2012, **33**, 1203; (b) A. E. Rudenko, C. A. Wiley, J. F. Tannaci and B. C. Thompson, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 2660; (c) A. E. Rudenko and B. C. Thompson, *Macromolecules*, 2015, **48**, 569; (d) A. E. Rudenko, A. A. Latif and B. C. Thompson, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 1492; (e) Y.-Y. Lai, T.-C. Tung, W.-W. Liang and Y.-J. Cheng, *Macromolecules*, 2015, **48**, 2978; (f) J.-R. Pouliot, M. Wakioka, F. Ozawa, Y. N. Li and M. Leclerc, *Macromol. Chem. Phys.*, 2016, **217**, 1493; (g) S.-L. Suraru, J. A. Lee and C. K. Luscombe, *ACS Macro Lett.*, 2016, **5**, 533.

13 (a) R. E. Buckles, A. I. Popov, W. F. Zelezny and R. J. Smith, *J. Am. Chem. Soc.*, 1951, **73**, 4525; (b) J. Berthelot, C. Guette, M. Essayegh, P. L. Desbene and J. J. Basselier, *Synth. Commun.*, 1986, **16**, 1641; (c) M. K. Chaudhuri, A. T. Khan, B. K. Patel, D. Dey, W. Kharmawophlang, T. R. Lakshmiprabha and G. C. Mandal, *Tetrahedron Lett.*, 1998, **39**, 8163; (d) C. J. Teskey, A. Y. W. Lui and M. F. Greaney, *Angew. Chem., Int. Ed.*, 2015, **54**, 11677; (e) F. Mendoza, R. Ruíz-Guerrero, C. Hernández-Fuentes, P. Molina, M. Norzagaray-Campos and E. Reguera, *Tetrahedron Lett.*, 2016, **57**, 5644.

14 X. Wang and M. Wang, *Polym. Chem.*, 2014, **5**, 5784.

15 (a) S. Amou, O. Haba, K. Shirato, T. Hayakawa, M. Ueda, K. Takeuchi and M. Asai, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1943; (b) K. Tsuchiya and K. Ogino, *Polym. J.*, 2013, **45**, 281; (c) W. M. Facchinatto, B. B. M. Torres and D. T. Balogh, *J. Polym. Res.*, 2016, **23**, 187.

16 For high-regioregular oxidative polymerization of other 3-substituted thiophene see: (a) O. Haba, T. Hayakawa, M. Ueda, H. Kawaguchi, T. Kawazoe, *React. Funct. Polym.*, 1998, **37**, 163; (b) T. Hayakawa, K. Fukukawa, M. Morishima, K. Takeuchi, M. Asai, S. Ando, M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 2287; (c) K. Tanaka, T. Mihara, N. Koide, *Polym. J.*, 2004, **36**, 628; (d) L. Ricciotti, F. Borbone, A. Carella, R. Centore, A. Roviello, M. Barra, G. Roviello, C. Ferone, C. Minarini, P. Morvillo, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4351; (e) N. S. Gobalasingham, S. Noh, B. C. Thompson, *Polym. Chem.*, 2016, **7**, 1623.

17 K. Okamoto, J. B. Housekeeper, F. E. Michaelc and C. K. Luscombe, *Polym. Chem.*, 2013, **4**, 3499.

18 (a) Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha and M. Ree, *Nat. Mater.*, 2006, **5**, 197; (b) C. H. Woo, B. C. Thompson, B. J. Kim, M. F. Toney and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2008, **130**, 16324; (c) M. T. Dang, L. Hirsch and G. Wantz, *Adv. Mater.*, 2011, **23**, 3597.

19 C. Piliego, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2010, **132**, 7595.