

Article

Atom-economical Synthesis and Characterization of Poly(oxindolidene thienylene vinylene) Based on Aldol Polycondensation Reaction

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Abstract: It is known that π -conjugated polymers can be easily synthesized using monomers which possess metals or halogen atoms as well as transition-metal catalysts. However, in the polymer materials synthesized by such reactions, small amounts of halogens and transition-metal-catalysts remain, often negatively affecting their optoelectronic device performances. Herein, we report a new polycondensation method based on the aldol condensation reaction utilizing the intramolecular resonance effect of the anionic monomer through π -conjugation. We have designed a novel AB type monomer to synthesize the semiconducting poly(oxindolidene thienylene vinylene) (POTV) using the proposed system. Indeed, the polymerization readily proceeded by adding 5-nitro-2-thiophenecarbaldehyde as an initiator after the α -proton abstraction of the oxindole group by the reaction of the monomer precursor with lithium hexamethylsilazide (LiHMDS)/12-crown-4. As a result, the objective POTV with $M_n = 3700$ and $D_M = 1.47$ could be obtained with a good yield (65%). In addition, an organic field effect transistor (OFET) was based on POTV exhibited p-type characteristics, with a hole mobility of $2.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Keywords: atom-economical synthesis; aldol condensation reaction; condensation polymerization; π -conjugated polymers; organic field effect transistor

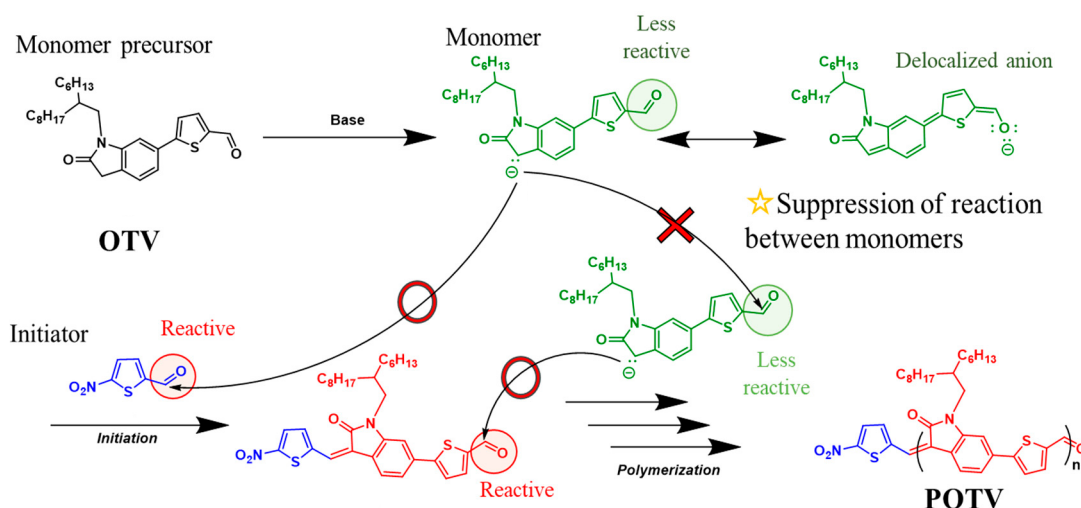
1. Introduction

Organic electronics, such as organic photovoltaics (OPVs) and organic field effect transistors (OFETs), have been well studied in recent years, because they have several advantages, such as a high mechanical flexibility and solution processability [1,2]. Therefore, the development of π -conjugated polymers employed in such organic electronic devices has been actively conducted [3–5]. Moreover, π -conjugated polymers used for such devices can be easily synthesized by transition-metal-catalyzed cross-coupling polycondensations. The cross-coupling reactions include, for example, the Mizoroki–Heck [6,7], Kumada–Tamao [8], Sonogashira [9], Negishi [10,11], Migita–Kosugi–Stille [12,13], and Suzuki–Miyaura [14,15] reactions, and they are well known as the most practical methods for the formation of aryl–aryl bonds over the past four decades. For the synthesis of semiconducting polymers applicable to organic electronics, the Migita–Kosugi–Stille cross-coupling polycondensation has often been employed. However, these synthetic methods usually have some issues. First, expensive organometallic reagents are required for the synthesis of functionalized monomers, followed by troublesome purification steps. Second, the stoichiometric quantities of organometallic by-products,

such as toxic trialkylstannanes, are produced after the polymerizations [16]. Third, in the polymer materials synthesized by such cross-coupling reactions, small amounts of halogen (F, Cl, Br or I) and transition-metal-catalysts (Pd or Ni) would remain even after purification, often negatively affecting their optoelectronic device performances. In fact, Kuwabara et al. reported that terminal halogen groups and transition-metal-catalyst residues led to a decrease in the conversion efficiency of the OPVs [17]. Based on these reports, economical and environmentally friendly methods without requiring organometallic functional groups, halogens and transition-metal-catalysts are needed for the preparation of π -conjugated polymers.

Recently, Zhang et al. demonstrated the transition-metal-catalyst-free and halogen-free synthetic method, based on the aldol condensation reaction for the atom-economical synthesis of π -conjugated polymers [18]. Onwubiko et al. also reported the synthesis of n-type semiconducting polymers through a similar approach [19]. In these methods, the by-product during the polymerization is only water. However, since they are based on a step-growth polycondensation system, the primary structures of the obtained polymers are not very controlled regarding molecular weight and molecular weight distribution. The control of the primary structure of the polymer materials is an important aspect for realizing high-performance organic electronic device applications [20,21]. The controlled polymerization methods proceeding in a chain-growth manner include the Kumada–Tamao catalyst-transfer polycondensation [22,23] and Negishi catalyst-transfer polycondensation systems [24–27]; but in such methods, it was essential to use monomers having halogen groups, as well as transition-metal catalysts. Our group succeeded in the synthesis of poly(3-alkylthienylene vinylene), with a controlled number-average molecular weight (M_n) and low molar-mass dispersity (D_M) based on the Horner–Wadsworth–Emmons polycondensation, utilizing the reactivity difference between monomer-to-monomer and polymer-to-monomer, triggered by the cancellation of the delocalization of the monomer anion through a resonance effect during the propagation reaction [28]. In this system, both transition metals and halogens are unnecessary. However, the condensate of phosphates is eliminated during polymerization. Therefore, the development of another polymerization method with a further low environmental load system is desired.

In this study, we have proposed the atom-economical synthetic methodology of poly(oxindolidene thienylene vinylene) (POTV) based on the aldol condensation reaction, attempting to utilize the intramolecular resonance effect of the anionic monomer through π -conjugation and expecting the chain-growth polycondensation system (Scheme 1). We have designed a novel AB type monomer precursor, *N*-(2-ethylhexyl)oxindolidene thienylene vinylene (OTV), having a formyl group and an oxindole moiety, to synthesize a semiconducting polymer using the developed system. First, OTV reacts with a base catalyst for the α -proton abstraction to afford an anionic monomer. The monomer is expected not to self-polymerize by the deactivation of the formyl group, due to the resonance effect. Next, by reacting the monomer with an initiator, 5-nitro-2-thiophenecarboxaldehyde, by having a reactive formyl group, the formyl group of the monomers is expected to be reactivated by cancelling the resonance effect. This initiation step is thought to be a trigger reaction; thereby, the polycondensation of the monomer may possibly proceed in a chain-growth manner. Based on this polymerization method, the objective POTV with $M_n = 3700$ and $D_M = 1.47$ could be obtained in a good yield (65%). In addition, polymer electronic properties were also evaluated by incorporating conjugated POTV as the active semiconducting layer in the OFET device.



Scheme 1. Expected mechanism for the preparation of poly(oxindolidene thienylene vinylene) by the aldol condensation reaction.

2. Results and Discussion

2.1. Polymerizations

According to the successful polymerization method based on the Horner–Wadsworth–Emmons reaction reported by Goto et al., we tried to suppress the unwanted step-growth propagation reaction by adding a variety of bases to OTV in THF at -78°C . All the polymerizations were initiated with 5-nitro-2-thiophenecarboxaldehyde and allowed to stand for 24 h, targeting an M_n value of 10,800. The results are summarized in Table 1.

Table 1. Polymerization of *N*-(2-ethylhexyl)oxindolidene thienylene vinylene (OTV) based on the aldol condensation reaction.

Run ^a	Base	Solvent	Temp.	M_n ^b	$\bar{D}_M$	Yield (%)
1	sodium hexamethyldisilazide (NaHMDS)/15-crown-5	Tetrahydrofuran (THF)	-40°C	1300	1.17	71 ^c
2	NaHMDS/15-crown-5	THF	<i>r. t.</i>	2100	1.97	58 ^c
3	NaHMDS/15-crown-5	Toluene/THF ^f	<i>r. t.</i>	2600	1.46	~100 ^d
4	lithium hexamethyldisilazide (LiHMDS)/12-crown-4	Toluene/THF ^g	<i>r. t.</i>	2500	1.37	66 ^c
5 ^e	LiHMDS/12-crown-4	Toluene/THF ^g	<i>r. t.</i>	3000	1.45	73 ^c
6 ^e	LiHMDS/12-crown-4	Toluene/THF ^g	30°C	3700 (5300) ^h	1.47 (1.57) ^h	65 ^c (40) ^h

(a) Polymerizations for Runs 1–6 were conducted for 24 h, targeting the same M_n of 10,800 without fractionation. (b) Determined by size exclusion chromatography (SEC) using polystyrene standards. (c) Determined by gravimetry after precipitation and drying under vacuum. (d) Crude yield. (e) The amount of 12-crown-4 was 0.1 equivalent of monomer. (f) Toluene/THF = 20.0/0.17 by vol. was used. (g) Toluene/THF = 20.0/0.30 by vol. was used. (h) After Soxhlet extraction.

First, 1.05 equivalents of sodium hexamethyldisilazide (NaHMDS) / 15-crown-5 as a base to OTV was used. The polymerization was then performed at $-40\text{ }^{\circ}\text{C}$ for 24 h (Run 1). The 15-crown-5 was expected to capture the sodium cation of NaHMDS, and increase the reactivity of the monomer anions. Unfortunately, the polymerization hardly proceeded ($M_n = 1300$). Therefore, we attempted to accelerate the reactivity of the monomer anions by increasing the reaction temperature to room temperature without changing the other conditions (Run 2). As a result, the molecular weight was slightly improved ($M_n = 2100$), probably due to the increased reactivity between the polymer chain end and incoming monomers at the elevated temperature from $-40\text{ }^{\circ}\text{C}$ to room temperature. Next, the solvent used for the polymerization was optimized. Actually, THF was changed to the mixed solvent of toluene / THF = 20.0 / 0.17 by vol. (Run 3) and a slight improvement was noted in the molecular weight ($M_n = 2600$, $D_M = 1.46$). This is considered to be due to the suppressed inactivation of the formyl group of the monomer based on the lower resonance effect in the more apolar solvent. Therefore, toluene / THF = 20.0 / 0.17 by vol. was adopted as the solvent, then the base was optimized. Lithium hexamethylsilazide (LiHMDS) was previously used in the successful synthesis of the well-defined polyamide [29]. Thus, LiHMDS was employed as a base for the α -proton abstraction. Under this condition, the molecular weight of the obtained POTV was not improved, showing a value similar to that for Run 3. On the other hand, the molecular weight distribution was slightly improved (Run 4, $M_n = 2500$, $D_M = 1.37$). The SEC curves for the resulting polymers are shown in Figure 1. They indicated that the monomer was mostly consumed under the conditions using LiHMDS (Runs 4–6). The result may be derived from the atomic radius size of the cation. The smaller the atomic radius of the cation, the closer the distance between the anionic monomers and counter cation. Therefore, the lithium cation with a small atomic radius was close to the monomer and reduced the effect of the resonance stabilization, to improve the reactivity of the formyl group of OTV. Since LiHMDS was determined to be an effective base, the amount of 12-crown-4 was optimized (Run 5). Reducing the amount of 12-crown-4 from 1.05 to 0.1 equivalent to OTV further improved the molecular weight ($M_n = 3000$, $D_M = 1.45$). It was postulated that the reduction of the crown ether amount enhanced the contact ion pair between the anionic monomer and Li cation, resulting in a lower resonance effect and further increasing the reactivity of the formyl group of OTV. Finally, the reaction temperature was raised to $30\text{ }^{\circ}\text{C}$, to improve the reactivity of the monomer (Run 6). As a result, POTV with the highest M_n value was obtained, although the D_M value was not very low ($M_n = 3700$, $D_M = 1.47$). This improvement in molecular weight is again probably due to the enhanced reactivity between the polymer chain end and monomers at the elevated temperature. Eventually, POTV with $M_n = 5300$, $D_M = 1.57$ could be obtained by the Soxhlet extraction of POTV (Run 6) with methanol, hexane and acetone, followed by recovering with chloroform. It should be noted that there are several sharp peaks in the lower molecular weight region of the SEC curves for all Runs. They may possibly be derived from the linear and/or cyclic oligomers, which are hardly removed by the Soxhlet extraction. The presence of oligomers suggests the partial step-growth mechanism for the proposed polymerization, which are coincident with the fact that the resulting POTVs were obtained in relatively high yields, while having lower M_n values than expected.

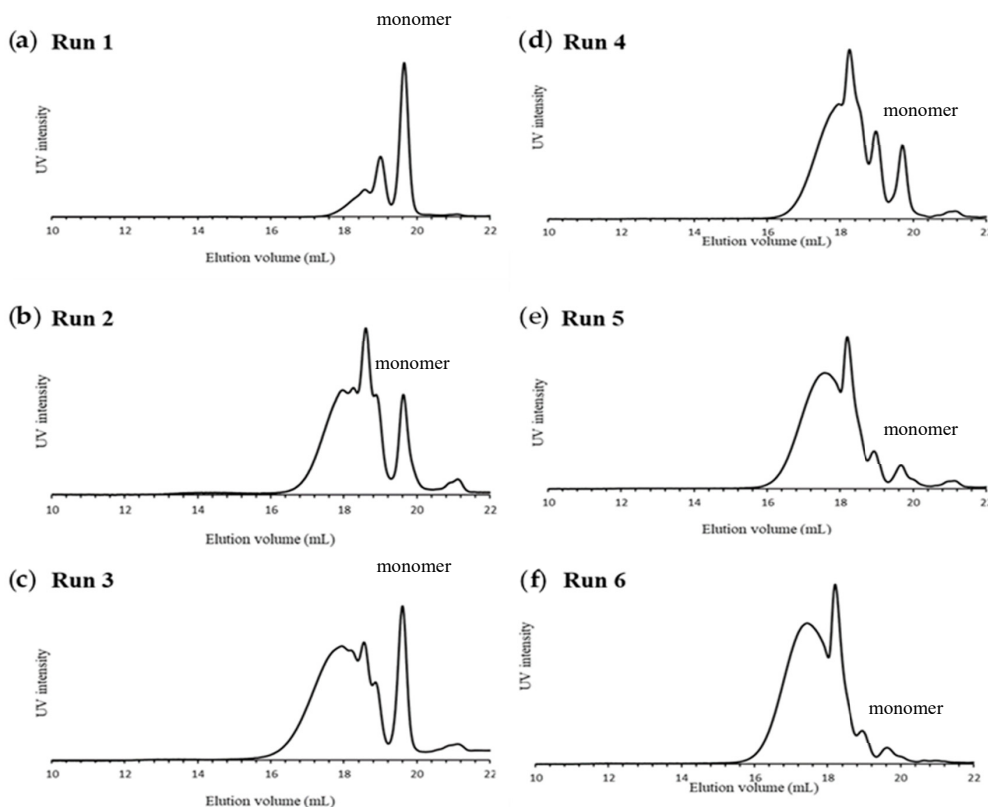


Figure 1. SEC UV traces of poly(oxindolidene thienylene vinylene) (POTV) samples (a) Run 1, (b) Run 2, (c) Run 3, (d) Run 4, (e) Run 5 and (f) Run 6.

2.2. Optical Properties and Microstructures

The normalized UV-vis absorption spectra of POTV in both the solution and film states (Run 6) are shown in Figure 2. The optical characteristics are summarized in Table 2. POTV exhibited a multiband spectrum that is often observed for donor-acceptor (D-A) polymers. The high-energy region corresponds to the π - π^* transition, while the low-energy region is attributed to the intra- and intermolecular charge transfer (ICT) band (0-1 and 0-0) between the D-A units. It is obvious that the $\lambda_{\max}$ shifted to the longer wavelength region from the solution to film states. This is probably because of the enhanced ICT effect, caused from the more coplanar structures in the film state than in the solution, inducing the polymer intermolecular interactions. Based on the absorption onset, the optical band gaps of POTV were calculated to be 1.66 eV and 1.64 eV for the as-cast and annealed films, respectively. The results suggest that the annealing treatment improves the planarity of the molecules and further enhances the intermolecular interaction in the solid state.

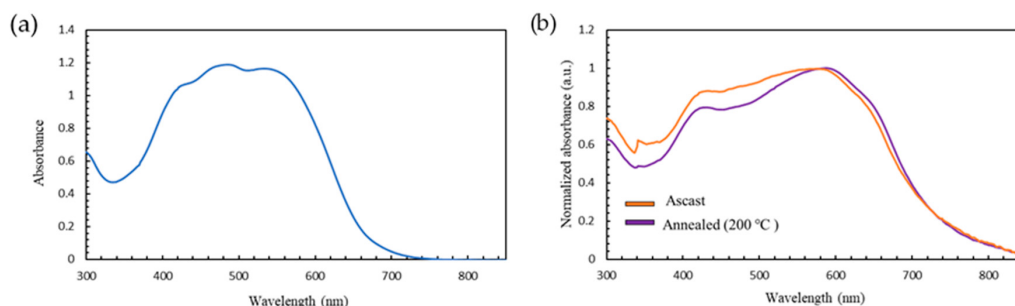


Figure 2. UV-vis absorption spectra of POTV (a) in chloroform and (b) in the films drop-cast from chloroform and annealed at 200 °C at 10 min.

Table 2. Optical parameters of POTV.

Conditions	$\lambda_{\max}$ (nm)	ϵ (L/mol/cm)	λ_{onset} (nm)	E_g (eV)
Solution	486	2.47×10^4	677	1.82
As-cast	433, 577	-	740	1.66
Annealed at 200 °C	431, 588	-	748	1.64

To provide further an insight into the crystalline structures and the morphology of the POTV thin films, the grazing-incidence wide-angle X-ray scattering (GIWAXS) was examined. The 2D-GIWAXS images and the corresponding diffractogram profiles of the polymer films (as-cast, and annealed at 200 °C) are shown in Figure 3. The as-cast film of POTV exhibited out-of-plane (100), (200), and (300) diffraction peaks along the q_z axis. Additionally, the in-plane (010) reflection peak along the q_y axis was clearly observed (Figure 3a,b). Such crystalline lattices can be assigned similarly to the representative semiconducting polymer of regioregular head-to-tail poly(3-hexylthiophene) [30]. These results indicated that the as-cast thin film of POTV favored the edge-on orientation on the substrate. On the other hand, the crystalline structures and orientation of the annealed film of POTV at 200 °C significantly changed, exhibiting an out-of-plane (010) diffraction peak along the q_z axis, and the in-plane reflection peak became rather complicated, showing multispots derived from higher order crystal structures (Figure 3c,d). The π - π stacking distances of the POTV as-cast film and its annealed film were determined to be 3.98 Å and 3.59 Å, respectively, from the (010) diffraction peaks. The result indicates that the annealing treatment enhanced the intermolecular interaction to decrease the π - π stacking distance. Remember that, in the UV-vis spectroscopy, the $\lambda_{\max}$ value of the as-cast film shifted to the longer wavelength region, implying the occurrence of a more effective ICT, which is coincident with the behavior of the π - π stacking distance observed by GIWAXS, as already mentioned.

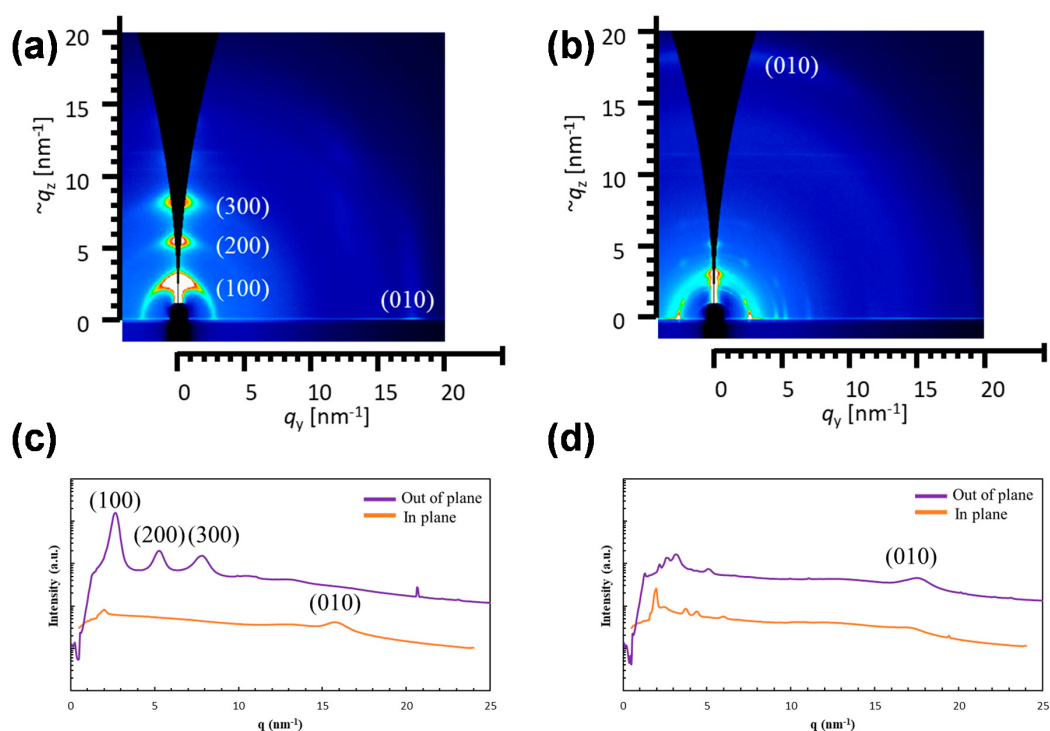


Figure 3. 2D grazing-incidence wide-angle X-ray scattering (GIWAXS) images and 1D-GIWAXS profiles of the thin film of POTV. (a,c) as-cast film, (b,d) annealed at 200 °C.

2.3. OFET Performances

The OFET devices with bottom-gate top-contact architectures were fabricated for elucidating the semiconducting characteristics of POTV (Run 6), after Soxhlet extraction. Hole mobilities were measured on devices prepared on PETS-passivated substrates. It is noted that the presence of hydroxyl groups on the bare SiO₂ surface may act as charge traps. Measurements were performed at nitrogen atmosphere in the solution-sheared film. Figure 4 depicted the exemplary transfer curves for the POTV OFET device. The POTV OFET exhibited a good hole-transporting behavior, with a maximum hole mobility of $2.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, despite its relatively low molecular weight $M_n = 5300$ (Table 3). The I_d of the device is of the order of 10^{-11} A , when it is in the OFF state, and increase up to 10^{-7} A when it is turned to the ON state, thus indicating an ON/OFF current ratio of 1.92×10^4 .

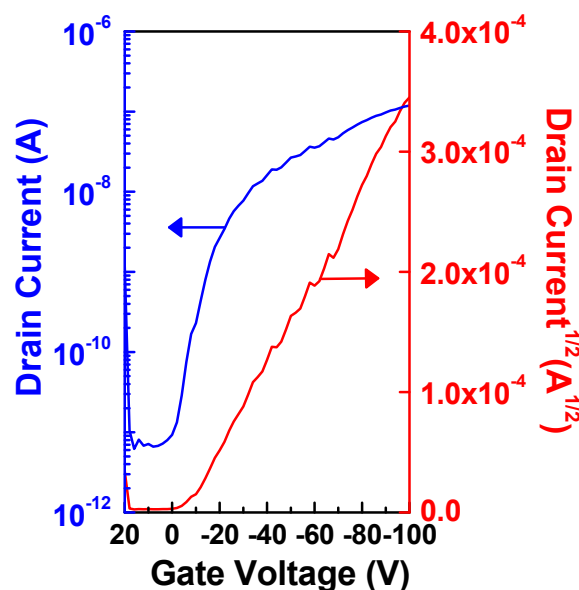


Figure 4. Transfer curve of POTV OFET device.

Table 3. The organic thin-film transistor performances of POTV (Run 6)

	$I_{\text{ON}}/I_{\text{OFF}}$	Max mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Threshold voltage (V)	W/L
POTV (Run 6)	1.92×10^4	2.24×10^{-4}	−21.6	25

3. Experimental

3.1. Materials

Tetrahydrofuran (THF, 99.5%, stabilizer-free, Kanto Chemical Co., Inc., Tokyo, Japan) was purified by refluxing over sodium benzophenone under nitrogen for 2 h, followed by distillation just before use. Other reagents purchased from Sigma-Aldrich Japan K.K., Tokyo Chemical Industry Co., Ltd., Kanto Chemical Co., Inc. or FUJIFILM Wako Pure Chemical Industries, Ltd., were used as received. Furthermore, (2-phenylethyl)trichlorosilane (PETS) for the self-assembly monolayer (SAM) treatment was purchased from Gelest, Inc.

3.2. Synthesis of OTV

3.2.1. 1-Bromo-2-hexyldecane (1)

Triphenylphosphine (14.2 g, 54.2 mmol) was placed in a 200 mL two-necked flask purged with N₂. After dissolving in dichloromethane (86.0 mL), the solution was cooled down to 0 °C before addition of Br₂ (2.78 mL, 54.2 mmol). Then, 2-Hexyl-1-decanol (15.0 mL, 51.6 mmol) was added dropwise

over 30 min and the reaction was stirred at room temperature overnight. The reaction was quenched by adding a saturated aqueous solution of Na_2SO_3 , then extracted with dichloromethane. After the organic phase was dried over anhydrous magnesium sulfate, the filtered solution was removed under the reduced pressure. The resulting residue was washed with hexane, and the precipitates were filtered. The filtrate was concentrated under the reduced pressure, yielding the title compound as a pale-yellow oil (12.3 g, 83%). ^1H NMR (400 MHz, CDCl_3): δ 3.44 (d, J = 4.4 Hz, 2H), 1.64–1.53 (m, 1H), 1.48–0.98 (m, 24H), 0.93–0.62 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 39.44, 32.54, 31.91, 31.82, 29.81, 29.57, 29.47, 29.33, 26.55, 26.52, 22.69, 22.66, 14.10, 14.08.

3.2.2. 6-Bromo-(*N*-2-hexyldecyl)isatin (2)

A compound 1 (7.63 g, 25.0 mmol), 6-bromoisatin (5.00 g, 22.1 mmol) and anhydrous potassium carbonate (3.66 g, 26.5 mmol) were placed in a 200 mL two-necked flask purged with N_2 . After dissolving the mixture in *N,N*-dimethylformamide (140 mL), it was heated to 60 °C and allowed to stand for 20 h. After cooling down to room temperature, the reaction mixture was extracted with ethyl acetate and washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate, filtered, rotary evaporated, and purified by silica gel chromatography, using hexane/ethyl acetate (9/1) as an eluent to afford the title compound as an orange solid (8.14 g, 82%). ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, J = 7.6 Hz, 1H), 7.27 (dd, J = 8.0, 1.6 Hz, 1H), 7.02 (d, J = 1.2 Hz, 1H), 3.57 (d, 8.0 Hz, 2H), 1.83 (s, 1H), 1.41–1.06 (m, 24H), 0.94–0.75 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 182.04, 158.03, 152.02, 133.25, 126.51, 126.04, 116.00, 113.77, 44.58, 40.28, 39.45, 39.20, 35.67, 32.33, 31.65, 31.56, 31.11, 30.71, 29.89, 29.72, 29.56, 29.40, 29.31, 29.08, 26.67, 26.30, 26.00, 25.98, 22.46, 13.92, 13.88.

3.2.3. 6-Bromo-(*N*-2-hexyldecyl)oxindole (3)

A compound 2 (7.95 g, 17.7 mmol) was placed in a 100 mL two-necked flask purged with N_2 . After dissolving it in dimethyl sulfoxide (65.0 mL), hydrazine (5.50 mL, 177 mmol) was added. The mixture was heated to 140 °C and allowed to stand for 40 min. After cooling down to 0 °C, the reaction was quenched by adding a 6 M HCl aq. (2.5 mL). The quenched solution was extracted with ethyl acetate and washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate, filtered, rotary evaporated and purified by silica gel chromatography using hexane/ethyl acetate (8.5/1.5) as an eluent to afford the title compound as a viscous yellow oil (6.16 g, 80%). ^1H NMR (400 MHz, CDCl_3): δ 7.14 (dd, J = 8.0, 1.6 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 1.6 Hz, 1H), 3.54 (d, J = 7.2 Hz, 2H), 3.45 (s, 1H), 1.83 (s, 1H), 1.48–1.04 (m, 24H), 0.95–0.74 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 174.82, 146.26, 125.39, 124.60, 124.17, 123.21, 121.12, 111.75, 44.37, 35.68, 35.12, 31.74, 31.67, 31.46, 31.28, 30.80, 29.98, 29.85, 29.64, 29.52, 29.40, 29.23, 29.18, 26.76, 26.73, 26.19, 26.15, 22.53, 13.99, 13.96.

3.2.4. 5-Iodothiophene-2-carbaldehyde (4)

Thiophene-2-carbaldehyde (5.00 g, 44.6 mmol), *N*-iodosuccinimide (11.0 g, 49.1 mmol) and *p*-toluenesulfonic acid monohydrate (0.848 g, 4.46 mmol) were placed in a 200 mL two-necked flask purged with N_2 . After dissolving the mixture in ethanol (90.0 mL), it was heated to 50 °C in the dark and allowed to stand for 10 min. After cooling down to room temperature, the reaction was quenched by adding a 1 M HCl aq. (45.0 mL), then extracted with diethyl ether and washed with saturated aqueous solutions of $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2CO_3 . The organic phase was dried over anhydrous magnesium sulfate, filtered, and rotary evaporated, yielding the title compound as a yellow solid (9.61 g, 90%). ^1H NMR (400 MHz, CDCl_3): δ 9.77 (s, 1H), 7.39 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 181.00, 149.16, 138.06, 137.12, 87.93, 77.32, 77.00, 76.67.

3.2.5. 5-(Trimethyltin)thiophene-2-carbaldehyde (5)

A compound 4 (1.90 g, 8.00 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.462 g, 0.40 mmol) were placed in a 100 mL two-necked flask purged with N_2 . After dissolving the mixture in

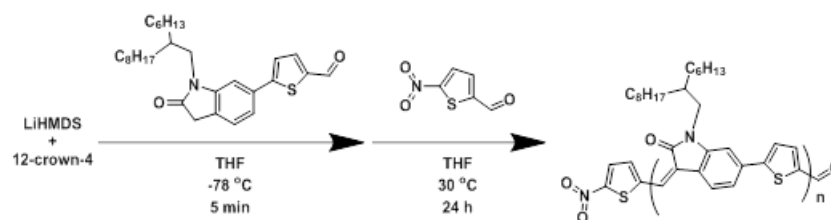
toluene (40.0 mL), hexamethylditin (2.50 mL, 12.0 mmol) was added, and the mixture was heated to 85 °C and allowed to stand for 8 h. After cooling down to room temperature, the reaction mixture was filtered through celite. It was then extracted with hexane and washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate, filtered, rotary evaporated and purified by sublimation, yielding the title compound as a white crystalline solid (1.22 g, 55%). ¹H NMR (400 MHz, CDCl₃): δ 9.94 (s, 1H), 7.83 (d, *J* = 3.6 Hz, 1H), 7.28 (d, *J* = 3.2 Hz, 1H), 0.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃): δ 181.93, 151.84, 149.02, 136.72, 135.90, −8.21.

3.2.6. *N*-(2-hexyldecyl)oxindolidene thienylene vinylene (OTV)

The compounds of **3** (1.81 g, 4.14 mmol) and **5** (1.14 g, 4.14 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.190 g, 0.207 mmol) and tri(*o*-tolyl)phosphine (0.317 g, 1.04 mmol) were placed in a 100 mL two-necked flask purged with N₂. After dissolving the mixture in toluene (40.0 mL), it was heated to 100 °C and allowed to stand for 2 h. After cooling down to room temperature, the reaction mixture was filtered through celite. It was then extracted with hexane and washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate, filtered, rotary evaporated and purified by silica gel chromatography using hexane/ethyl acetate (7/3) as and eluent to afford OTV as an orange solid (1.22 g, 63%). ¹H NMR (400 MHz, CDCl₃): δ 9.90 (s, 1H), 7.75 (d, *J* = 4.4 Hz, 1H), 7.38 (d, *J* = 4.0 Hz, 1H), 7.35 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 3.63 (d, *J* = 7.2 Hz, 2H), 3.57 (s, 2H), 1.89 (s, 1H), 1.44–1.02 (m, 24H), 0.95–0.66 (m, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 182.79, 175.11, 154.09, 146.10, 142.54, 137.42, 132.98, 126.15, 125.03, 124.22, 120.47, 106.32, 44.60, 36.08, 35.65, 31.93, 31.87, 31.64, 30.05, 29.73, 29.61, 29.37, 26.53, 22.73, 14.20. Anal. Calcd. for C₂₉H₄₁NO₂S (%): C, 74.03; H, 8.84; N, 2.99; S, 6.85. Found (%): C, 74.56; H, 9.43; N, 3.01; S, 6.56.

3.3. Synthesis of POTV

The representative experiment for Run 6 (see Scheme 2) is as follows: A 20 mL two-necked flask was first purged with N₂ and placed with dehydrated toluene (18 mL), 12-crown-4 ether (8.0 μL, 0.05 mmol) and lithium hexamethyldisilazide (1.3 M in THF, 0.40 mL, 0.52 mmol). After cooling down the flask to −78 °C, the OTV solution (232 mg, 0.495 mmol, 2 mL of toluene) was added to the reaction mixture and allowed to stir for 5 min. The initiator of 5-nitro-2-thiophenecarboxaldehyde (3.4 mg, 0.022 mmol, 0.5 mL of toluene) was added to the mixed solution to start the polymerization. The polymerization was performed with stirring at 30 °C for 24 h. To quench the polymerization, a 5 M HCl aq. solution (2 mL) was finally added. The aliquot of the resulted solution was sampled out and extracted with a mixture of chloroform and water. The obtained sample was analyzed by SEC before precipitation. To precipitate the polymer, the rest of the solution was poured into methanol/water (200 mL/ 100 mL). By filtrating and drying the polymer under vacuum, the crude POTV was obtained as a black solid (146 mg, 65%). SEC: *M*_n = 3700, *D*_M = 1.47. (*M*_n = 5700, *D*_M = 1.57, after Soxhlet extraction).



Scheme 2. Synthetic route for POTV (Run 6).

3.4. Measurements and Characterization

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECX400 in chloroform-*d* at 25 °C or 40 °C, calibrated to chloroform as a standard (δ_H 7.26). Size exclusion chromatography (SEC) was recorded on a Jasco GULLIVER 1500, equipped with an absorbance

detector (UV, $\lambda = 254$ nm) and three polystyrene gel columns (Eluent: THF, 1.0 mL/min, 40 °C). The M_n and M_w/M_n values of the polymers were calculated from a calibration curve using eight polystyrene standards. A JASCO V-670 spectrophotometer was used for recording UV-vis spectra. The treatment conditions for preparing the thin film samples for the measurement of UV-vis spectra are as follows: (a) dissolution of the polymer in chloroform (~ 1 mg/mL), (b) drop-cast onto the quartz substrates, and (c) annealing at 200 °C for 10 min. For operating grazing-incidence wide-angle x-ray scattering (GIWAXS), the beamline BL46XU of SPring-8, Japan (proposal No. 2018A1794) was used. The polymer samples for the GIWAXS experiment were prepared as follows: (a) dissolution of the polymer in chloroform (8.0 mg/mL), (b) filtering through PTFE filters (0.45 μ m pore size), and (c) spin-coating onto Si wafers. The samples were irradiated at a fixed incident angle $\alpha_i = 0.12^\circ$, through a Huber diffractometer. The X-ray energy was 12.398 keV (X-ray wavelength $\lambda = 0.10002$ nm). The GIWAXS patterns were recorded on a 2D image detector (Pilatus 300K, sample-to-detector distance = 174.4 mm). The scattering vectors q_y and q_z for GIWAXS are defined in Equation (1).

$$(q_y, q_z) = (2\pi (\sin \psi \cos \alpha_f) / \lambda, 2\pi (\sin \alpha_f + \sin \alpha_i) / \lambda) \quad (1)$$

where ψ is out-of-plane angle, α_f is exit angle. The current-voltage (I - V) characteristics of POTV-based OFETs were analyzed in dark at room temperature conditions by Keithley 4200-SCS instrument.

3.5. OFET Fabrication

POTV thin films were deposited onto the substrates, using a customized solution-shearing apparatus equipped with a top shearing blade and temperature-controlled heating stage. POTV were dissolved in chloroform/*o*-dichlorobenzene (95/5 vol%) co-solvents to prepare the semiconducting ink (10 mg/mL), and then coated onto the PETS-treated Si/SiO₂ substrate for electronic properties characterization. Shearing speed was precisely controlled at 800 μ m/s and heating during coating was achieved at a temperature of 35 °C. Post-annealing was performed under vacuum at 80 °C for 3 h. Gold contacts were deposited onto POTV channel by thermal deposition, at a pressure of 5×10^{-7} Torr, with shadow mask to form the source and drain electrode. OFETs with a channel length of 40 μ m and a width 1000 μ m were used. The field effect mobilities were evaluated in the saturation region using the following equation,

$$\mu = \left(\frac{\partial \sqrt{I_d}}{\partial V_g} \right)^2 \frac{2L}{WC} \quad (2)$$

where I_d is the drain current, V_g gate voltage, L the channel length, W the channel width and C is the capacitance. The slope in $I_d^{1/2}$ versus V_g plots was determined in the saturation region for field effect mobility calculation.

4. Conclusions

In this study, the atom-economical synthesis of a π -conjugated polymer was reported, based on the aldol condensation reaction free of transition-metals and halogens. Indeed, the synthesis of poly(*N*-2-hexyldecyloxindolidene thienylene vinylene) (POTV), with a moderate $M_n = 3700$ and $D_M = 1.47$ ($M_n = 5300$ and $D_M = 1.57$ after Soxhlet extraction), was obtained when using LiHMDS/12-crown-4, OTV, and 5-nitro-2-thiophenecarbaldehyde as a base, monomer, precursor, and initiator, respectively, in toluene/THF at 30 °C. The results of the OFET device indicated that the POTV possesses the potential for organic electronic applications. In the future, toward a better OFET performance, it is expected that a high-molecular-weight POTV with a controllable molecular weight may be obtained by optimizing the polymerization conditions, such as types of the base, temperature, and solvent.

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