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Synthesis of Conjugated Polymers with Controlled Terminal Structures by Direct Arylation Polycondensation and Correlation Between Terminal Structures and Emission Properties

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Conjugated polymers are promising semiconducting materials for applications in organic electronic devices such as organic light-emitting diodes (OLEDs). Recent advances in direct arylation polycondensation have enabled the synthesis of defect-free polymers in the main chain; however, terminal groups have not been fully investigated. This research focuses on the synthesis of polymers with controlled terminal groups and the evaluation of their effects on photophysical and OLED properties. Investigation of the monomer feed ratio and terminal treatment methods allows the synthesis of three polymers with different terminal groups. The terminal groups affect the photoluminescence quantum yield in the thin-film state and the external quantum efficiency in OLEDs. These findings indicate that a small percentage of terminal groups in the polymer material has a significant impact on the device properties.

1. Introduction

With the development of semiconducting polymers, the properties of organic electronic devices have improved significantly.[1–8] Organic light-emitting diodes (OLEDs),[2–4] organic photovoltaics (OPVs),[5–7] and organic field-effect transistors (OFETs)[7,8] are representative semiconducting-polymer applications. These semiconducting polymers have mainly been synthesized by polycondensation using cross-coupling reactions such as the Suzuki–Miyaura[9] and Migita–Kosugi-Stille coupling reactions.[10] In recent years, polycondensation via direct arylation (C–H/C–X coupling, X = halogen) has been developed as an alternative to conventional methods.[11] Direct arylation polycondensation has advantages in terms of short synthetic processes and environmental impacts because the reaction does not require organometallic monomers and, therefore, gives no metal-containing by-products. In direct arylation polycondensation, there are several potential risks associated with the formation of structural defects in the polymer main chain. The reaction of the undesired C–H moieties causes branching or crosslinking defects.[12–16] Additionally, side reactions involving the C–H/C–H or C–Br/C–Br homocoupling reactions cause defects in the alternating structure, which are referred to as homocoupling defects.[12,14,16–22] These defect structures degrade the semiconducting properties.[17,18,21] Detailed optimization of the reaction conditions by several research groups over a decade succeeded in avoiding the formation of such defect structures in direct arylation polycondensation.[11,16,23–30] Indeed, the direct arylation polycondensation yields polymers with fewer defect structures than the conventional Migita–Kosugi–Stille polycondensation, which causes 10% homocoupling defects.[30] In contrast to intensive research on the accuracy of the main chain, control of the terminal structure has received relatively little attention in direct arylation polycondensation,[27,31] although the terminal structures of the polymer materials affect their physical properties such as crystallinity,[32,33] hole mobility,[34–36] and photoelectric conversion properties.[32,36–39] In our previous study, luminescence properties were affected by the terminal defect structure caused by side reactions.[31] The purpose of this study was to synthesize semiconducting polymers with controlled terminal structures and defect-free main chains using direct arylation polycondensation. An investigation of the monomer feed ratio and terminal treatment methods enabled

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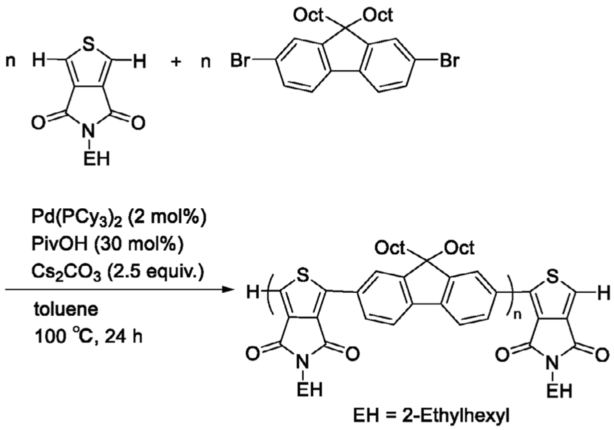


Scheme 1. Polycondensation of TPD and Br_2-DOF.

the synthesis of three polymers with nearly complete control of both terminals. The influence of the terminals on the photophysical properties was elucidated by evaluating the optical and OLED properties of polymers with the same main-chain structure but different terminal groups.

2. Results and Discussion

2.1. Polymerization and Terminal Structure Control

5-(2-Ethylhexyl)thieno[3,4-c]-pyrrole-4,6-dione (TPD) was selected as the monomer for this investigation owing to its favorable reactivity of the C—H bonds for direct arylation.[27,40,41] Our group reported the optimal reaction conditions for TPD using a low-polarity solvent with a PCy_3 (tricyclohexylphosphine) ligand.[27] The use of the Pd(0) catalyst, $Pd(PCy_3)_2$, instead of a combination of $Pd(OAc)_2$ and PCy_3 is important for preventing homocoupling defects during the initiation of the catalytic reaction.[29] To modify both polymer terminals with TPD units, polycondensation reactions of TPD with 2,7-dibromo-9,9-dioctylfluorene (Br_2-DOF) were performed with excess TPD (**Scheme 1**, **Table 1**). The reaction with excess TPD yielded polymers with suppressed molecular weights, in accordance with the Carothers equation.[42] Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) provides direct information on terminal structures. The mass spectra of the polymers synthesized in Entries 1 and 2 show peaks corresponding to the alternating structure with both TPD terminals (Figures S1 and S2, Supporting Information). These results indicate that the polycondensation reaction can be used to synthesize polymers with no structural defects in the main chain, unified terminals, and controlled molecular weights. Interestingly, even in the case of polymerization with a 1:1 molar ratio (Table 1, Entry 3), TPD-terminated structures were dominant (Figure S3, Supporting Information). In principle, both the TPD and fluorene terminals should be observed. Such selective modification of both terminals occurs when a Pd catalyst is transferred intramolecularly and reacts sequentially.[43–45] In this case, after the reaction with one Br group of Br_2-DOF proceeds, the Pd catalyst may transfer to the other Br through a fluorene unit and react sequentially. To confirm the intramolecular catalyst transfer, polycondensation reactions of TPD and Br_2-DOF under conditions with an excess of Br_2-DOF were performed because polycondensation involving intramolecular catalyst transfer would give a high-molecular-weight polymer, even in the presence of excess amounts of Br_2-DOF (Table S1, Supporting Information Entry 1). Polymerization gave polymers of higher molecular weight than the calculated molecular weight from the Carothers equation, confirming that the intramolecular catalytic transfer occurred. However, the reaction with a large excess of Br_2-DOF (Table S1, Supporting Information Entry 2) yielded a relatively low-molecular-weight polymer with bromofluorene terminals, indicating that the intramolecular catalytic transfer is preferentially occurred, but a certain percentage of intermolecular reactions also occurred.

Table 1. Results of polycondensation.

Entry	TPD:Br_2-DOF	Yield[a)]	M_n (M_w/M_n)
1	1.05:1	42%	14 500 (1.5)
2	1.01:1	96%	70 000 (2.3)
3	1:1	91%	98 700 (2.0)

[a)] Yields of the $CHCl_3$-soluble and hexane-insoluble parts.

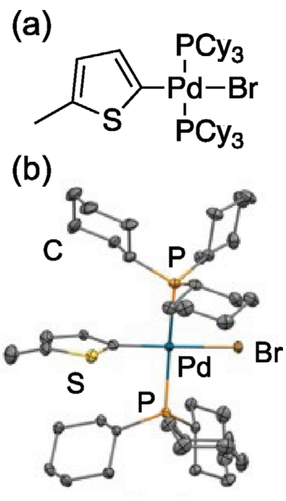


Figure 1. a) Chemical structure and b) crystal structure of the Pd(II) catalyst precursor. One of the disordered structures is presented.

2.2. Modification of Terminals with Methylthiophene

For the modification of the TPD terminals, methylthiophene was selected as the electron-rich terminal group to compare the properties of the electron-poor TPD terminal group. Although Pd(0) catalysts are effective in preventing side reactions,[29] they are unstable in air and difficult to handle. To smoothly introduce the methylthiophene units at the chain terminals, a new Pd(II) catalyst precursor bearing a methylthiophene moiety was synthesized (**Figure 1**; Scheme S1, Supporting Information). This catalyst is stable and easy to handle in the air, facilitating the addition of a Pd catalyst for terminal modification during the reaction.[46] The Pd(II) catalyst precursor should generate an active Pd(0) species when reacting with the C—H terminals of the polymer.

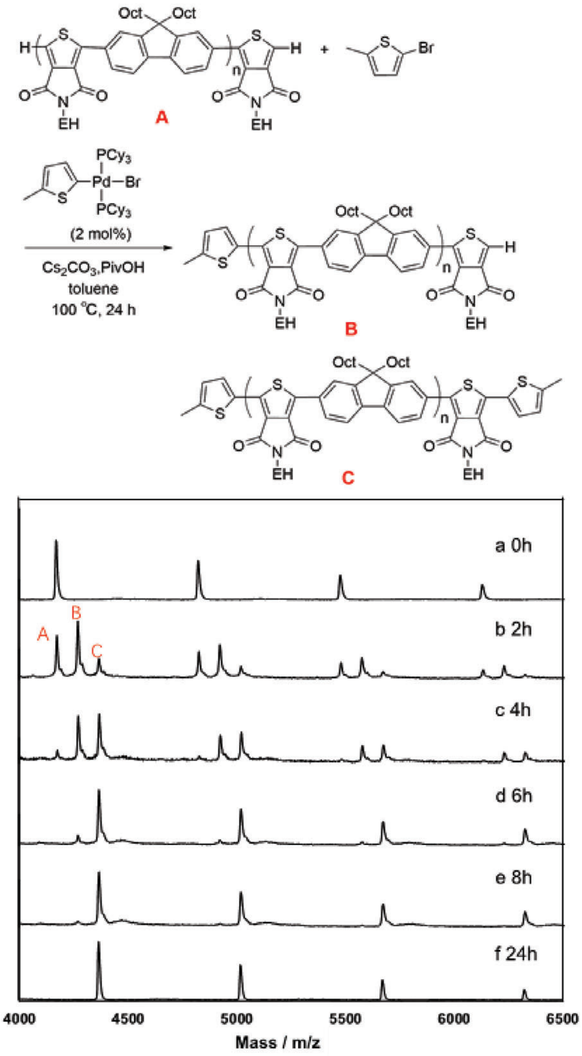
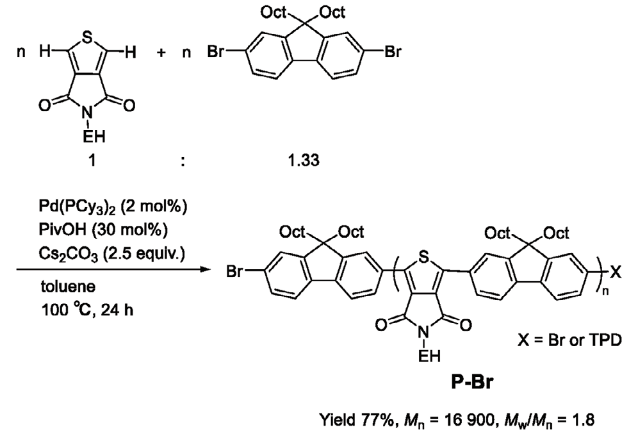


Figure 2. MALDI-TOF-MS tracking the terminal modification process.

Single-crystal X-ray diffraction analysis confirmed the expected structures (Figure 1b).

The catalytic activity of the Pd(II) catalyst precursor was investigated for terminal modification of the TPD-terminated polymer synthesized in the previous section (Table 1, Entry 1). The progress of terminal modification was tracked using MALDI-TOF-MS (**Figure 2**). Before modification, the spectrum showed only peaks corresponding to the TPD-terminated polymer (A). The spectrum of the sample after the reaction for 2 h showed peaks corresponding to polymers with one terminal modified (B) and polymers with both terminals modified (C). The intensity of peak C increased with time, and eventually, only peak C was observed. The structure of the terminally modified polymer was confirmed by ^{1}H NMR spectroscopy (Figure S4, Supporting Information). Similar results were obtained when the modification was conducted with Pd(PCy$_3$)$_2$, which is highly active but unstable in the air (Figure S5, Supporting Information). The Pd(II) catalyst precursor exhibited a terminal modification comparable to that of the Pd(0) catalyst, with the added advantages of air stability and ease of handling. The Pd(II) catalyst precursor facilitated both polycondensation and terminal modification, producing the corresponding polymers with methylthiophene terminals (Scheme S2, Supporting Information). Although there are many examples of terminal modification in polycondensation reactions using conventional cross-coupling reactions,[47–49] a unique feature of this system is that both terminals can be modified nearly completely. Complete terminal modification is possible because the C—H bond is more stable than the carbon–metal bond used in conventional cross-coupling reactions and does not decompose during the reaction. Direct arylation reactions can be used to synthesize polymers with well-controlled terminals.



Scheme 2. Synthesis of Br-terminated polymer (**P-Br**).

2.3. Synthesis of the Polymers with Different Terminal Units

To evaluate the effect of terminal groups on the physical properties, a polymer with bromofluorene terminals was prepared. Normally, a reaction with a small excess of Br$_2$-DOF would yield a polymer with bromofluorene terminals; however, owing to the aforementioned intramolecular catalyst transfer, the formation of the TPD terminal takes precedence. Several trials revealed that a large excess of Br$_2$-DOF (1.33 times) was required to obtain a polymer with the desired terminal structure (**Scheme 2**). Because of the large excess of monomers, the molecular weight was only 16 900. MALDI-TOF MS revealed the presence of polymers with both bromofluorene terminals and polymers with one TPD terminal (**Figure 3**).

Polymers with methylthiophene (**P-Th**) and TPD terminals (**P-TPD**) bearing molecular weights similar to **P-Br** were synthesized using the method described in the previous section. **P-TPD** was obtained via the polycondensation under the condition of a 5% excess TPD monomer (**Scheme 3**). **P-Th** was prepared via polycondensation and subsequent terminal modification in a one-pot manner. The molecular weights from GPC measurements and yields are listed in **Table 2**. The molecular weight of **P-Th** (17600) was calculated from the integral ratio of the main chain and terminal unit in the ^{1}H NMR spectrum. This value is in good agreement with that obtained from GPC (17900). The terminal structures were confirmed using MALDI-TOF-MS (Figure 3). These results indicate that the three polymers have the same

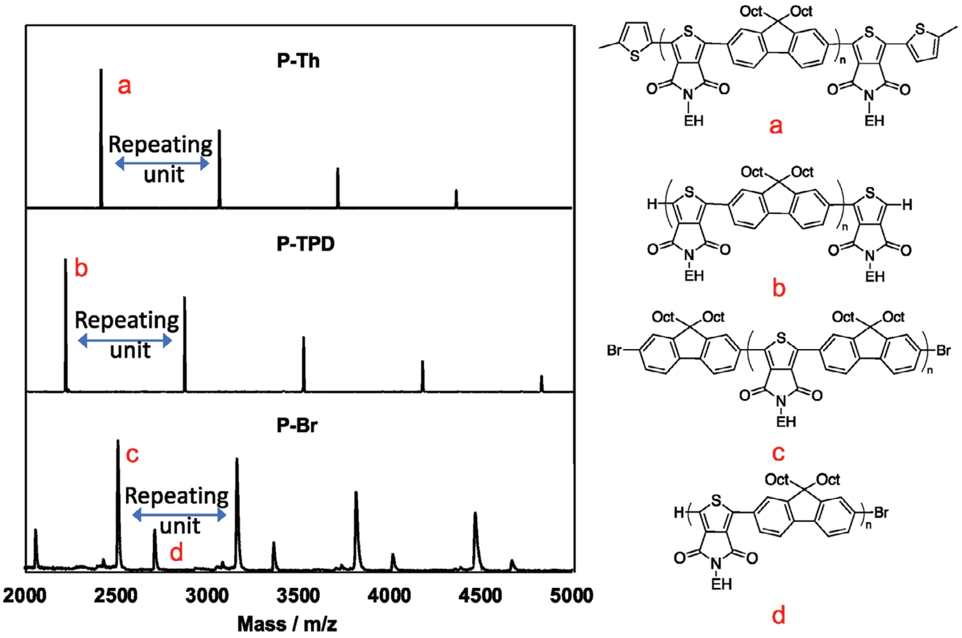
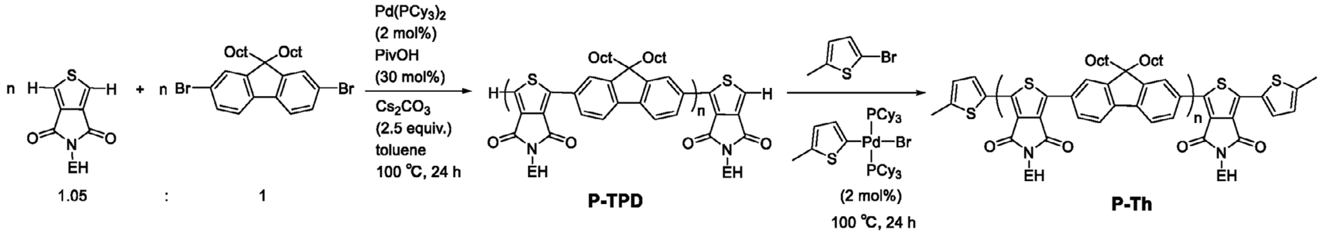


Figure 3. MALDI-TOF-MS for **P-Th**, **P-TPD**, and **P-Br**.



Scheme 3. Synthesis of **P-TPD** and **P-Th**.

Table 2. Molecular weight and yield of the polymers.

	Terminal structure	M_n	M_w/M_n	Yield
P-Th	Methylthiophene	17 900	1.9	84%
P-TPD	TPD	17 500	2.0	77%
P-Br [a)]	Br	16 900	1.8	65%

[a)] **P-Br** contains minor TPD terminal units.

main chain, are free of defects, and contain controlled terminal groups with similar molecular weights.

2.4. Evaluation of Photophysical Properties and Device Performance

The UV–vis absorption and photoluminescence (PL) spectra of the three polymers were measured in solution and thin-film states. The absorption spectra of the polymers are nearly identical (Figure S12, Supporting Information). The PL spectra in the solution state are very similar because the emission is predominantly from the main chain (**Figure** 4a). In contrast, the spectra in the thin-film state show different ratios of the first (495 nm) and second (530 nm) maximum peaks (Figure 4b). Although the mechanism by which the terminal structures affect the intensity ratio of the two peaks derived from the vibrational structure is unknown, but it is found that the effects of the terminals are pronounced in the film state. In terms of photoluminescence quantum yield (PLQY), **P-Th** had a relatively low value (**Table** 3). The three polymers have identical optical bandgap (2.53 eV) and HOMO level (−6.2 eV), which are estimated from the absorption edges in the thin film states and by photoelectron yield spectroscopy (PYS), respectively. These identical values reveal that the main chain structure dominantly determines the energy levels and that the terminal structures have minimal effect.

OLEDs containing these polymers were fabricated with the same configuration (details are provided in the Experimental section). **Figure** 5 shows the current density–voltage plots and external quantum efficiency (EQE)–current density characteristics of the fabricated OLEDs. The results are summarized in Table 3. The device with **P-TPD** exhibited a higher EQE than those with **P-Th** and **P-Br**. The low EQE of the OLED with **P-Th** was probably owing to its low PLQY (Table 3). Although the PLQYs of **P-Br** and **P-TPD** were similar, the OLED with **P-Br** exhibited a lower EQE than the OLED with **P-TPD**. In the current density–voltage plots, the OLED with **P-Br** showed a relatively low current density at the same voltage compared with the others (Figure 5a), which

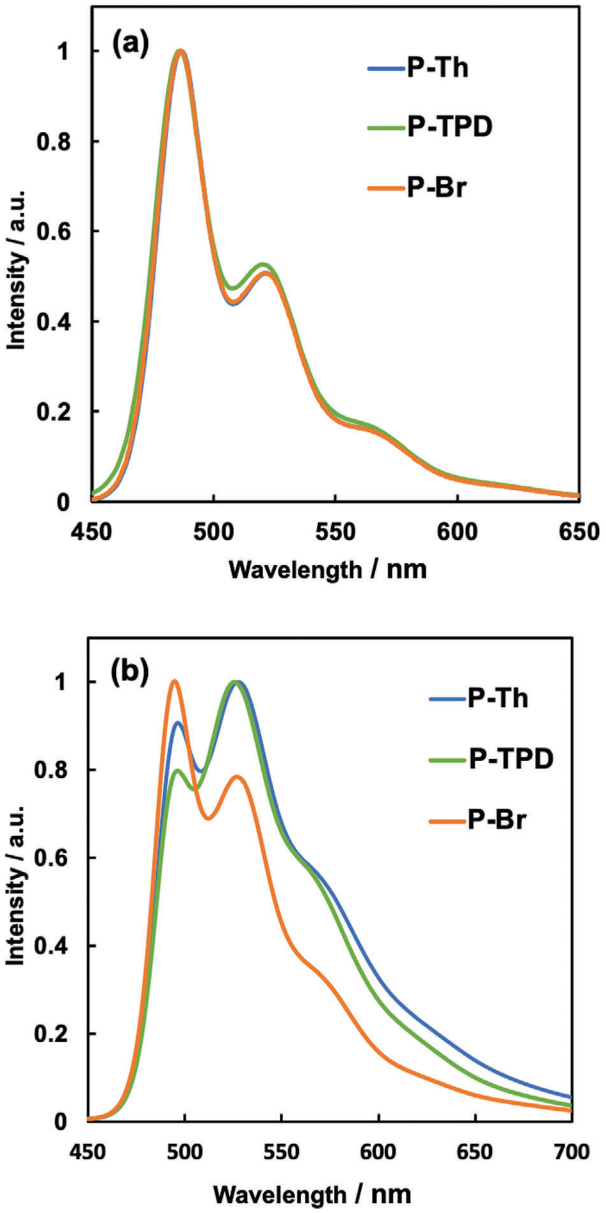


Figure 4. a) PL spectra of **P-Th**, **P-TPD**, and **P-Br** in solution state ($CHCl_3$, 5 µM, $\lambda_{ex} = 400$ nm) and b) in thin-film state ($\lambda_{ex} = 440$ nm).

Table 3. PLQY in the thin film state and OLED properties.

	PLQY [a)] / %	EQE [b)] / %	Max luminance [c)] / cd m^{-2}
P-Th	22	1.05	9760
P-TPD	27	1.25	9740
P-Br	28	1.01	2970

[a)] Photoluminescence quantum yield in the thin film state; [b)] External quantum efficiency of the OLEDs. Configuration: glass/ITO/PEDOT:PSS (40 nm)/ poly(9-vinylcarbazole) (PVK) (30 nm)/Polymer (30 nm)/ 2,2′,2′′-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) (30 nm)/LiF (1 nm)/Al (100 nm); [c)] Maximum luminance of the OLEDs.

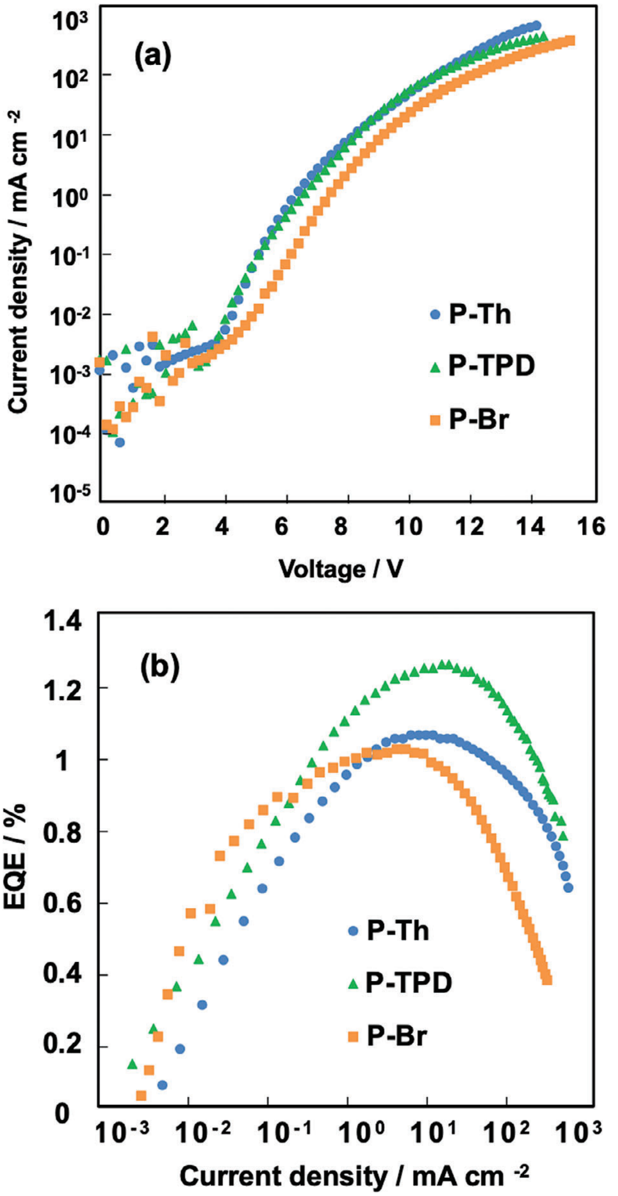


Figure 5. a) Current density–voltage plots and b) EQE–current density characteristics of the OLEDs fabricated with glass/ITO/PEDOT:PSS (40 nm)/PVK (30 nm)/Polymer (30 nm)/TPBi (30 nm)/LiF (1 nm)/Al (100 nm).

implies that **P-Br** has a large resistance. As has been previously reported,[34,36–38] the Br terminals are likely to be carrier trapping sites, which lead to high resistivity and exciton quenching due to carrier-exciton interactions, resulting in the low EQE.[50] Related to this, the OLED with **P-Br** has a lower maximum luminance value (Table 3; Figure S13, Supporting Information). The TPD terminals in **P-TPD** were superior to the other terminals in terms of the PLQY and efficient carrier transport, resulting in the highest EQE and contributing to the lower driving voltage. Notably, the same polymer with high molecular weight (M_n

= 176 800) was evaluated in the same device configuration and showed a high EQE (2.04%) in a previous study.[31] This suggests that all the terminal groups can have negative effects on device performance, and high-molecular-weight materials are desirable in OLED materials to reduce the number of terminal units.

3. Conclusion

We successfully synthesized conjugated polymers with defect-free main chains and controlled their terminal structures via direct arylation polycondensation. A Pd(II) catalyst precursor was developed and used as an air-stable catalyst for terminal modification. An investigation of the optical and OLED properties of the three polymers with nearly complete control of both terminals revealed that the terminal structures affected the PLQY in the thin-film state and carrier transport properties in the OLEDs. The small percentage of terminal groups in the polymer material can produce a 20% difference in EQE of OLEDs. This research highlights the potential for improving device properties through terminal group control and provides valuable insights for the future development of organic optoelectronic materials.

4. Experimental Section

Materials: $Pd(PCy_3)_2$ was purchased from BLDpharm and stored under a N_2 atmosphere. Anhydrous toluene was purchased from Kanto Chemical and used as a dry solvent. Other chemicals were received from commercial suppliers and used without further purification. 5-(2-Ethylhexyl)thieno[3,4-c]-pyrrole-4,6-dione (TPD) was prepared according to previously reported methods.[51,52]

General Measurements and Characterization: NMR spectra were recorded by AVANCE-400 and AVANCE-600 NMR spectrometers (Bruker). Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder at A-Rabbit-Science Japan Co., Ltd. MALDI-TOF-MS spectra were recorded on a MALDI TOF/TOF 5800 (AB SCIEX) using trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. UV–vis absorption spectra in solution states were recorded on a Hitachi U-3900H or a JASCO V-630. PL spectra in solution states were recorded on a Hitachi F-2700 fluorescence spectrophotometer. UV–vis absorption spectra and PL spectra for the spin-coated films were recorded on a Hitachi U-3010 and JASCO FP-6500 spectrophotometer, respectively. PLQYs of the spin-coated films were measured using a JASCO FP-6500 spectrophotometer with an integrating sphere. The HOMO energy levels were estimated by PYS using an AC-3 spectrometer (Riken Keiki). All the manipulations for the reactions were carried out under an N_2 atmosphere using a glove box or standard Schlenk technique. Intensity data for crystal structure determination were collected on a Bruker SMART APEX II ULTRA with Mo $K\alpha$ radiation. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters using the SHELXL-97 program. CCDC 2409877 contains the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Synthesis of the Pd(II) Catalyst Precursor: To a 25 mL Schlenk tube with a stirrer chip were added $Pd_2(dba)_3$ (91.6 mg, 0.10 mmol), PCy_3 (140 mg, 0.50 mmol), dry toluene (6.5 mL), and 2-bromo-5-methylthiophene (68 µL, 0.60 mmol) in a Glove box. The mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the mixture was filtered using a syringe filter. The filtrate was concentrated under reduced pressure. Recrystallization with toluene and diethyl ether gave light yellow crystals. The crystals were dried under vacuum (79.1 mg, 47%).

^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 6.59 (d, $J = 3.1$ Hz, 1H), 6.30 (d, $J = 3.4$ Hz, 1H), 2.43 (s, 3H), 1.98 (m, 22H), 1.64 (m, 22H), 1.14 (m, 22H). $^{13}C\{^1H\}$ NMR spectrum (100 MHz, $CDCl_3$): δ 140.47, 130.35, 126.17, 33.86, 30.31, 27.76, 27.17, 15.42. ^{31}P NMR spectrum (162 MHz, $CDCl_3$): δ 22.61 (s, 2P). Anal Calcd. for $C_{41}H_{71}BrP_2PdS$: C 58.32, H 8.48, S 3.80; found: C 58.25, H 8.53, S 3.69.

*Synthesis of **P-Th***: A solution of $Pd(PCy_3)_2$ (2.7 mg, 0.0040 mmol) in dry toluene (1 mL) was prepared in a glove box. 2,7-Dibromo-9,9-dioctylfluorene (Br_2-DOF) (106.4 mg, 0.194 mmol), Cs_2CO_3 (163 mg, 0.50 mmol), 5-(2-ethylhexyl)-thieno[3,4-c]pyrrole-4,6-dione (TPD) (53 mg, 0.20 mmol) was added to a 25 mL Schlenk tube with a stirrer chip. The solution of the Pd catalyst was added to the Schlenk tube in the glove box. The pivalic acid (6.9 µL, 0.060 mmol) was added under the N_2 atmosphere outside of the glove box. The mixture was stirred at 100 °C for 24 h. The Pd(II) catalyst precursor (6.8 mg, 0.0080 mmol), dry toluene (3.5 mL), and 2-bromo-5-methylthiophene (4.6 µL, 0.040 mmol) were added to the mixture under N_2. The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, volatiles were removed under vacuum. The products were dissolved in $CHCl_3$ (100 mL) and an aqueous solution of sodium diethyldithiocarbamate (0.1 M, 150 mL) was added. The mixture was stirred for 16 h at room temperature. After separation, the organic layer was washed with water (3 times) and brine. The organic layer was dried with Na_2SO_4 and was concentrated. The solution was poured into vigorously stirred MeOH (200 mL) and stirred overnight. The solid was filtered and washed with hexane (150 mL) for 1 h. **P-Th** was isolated as a yellow solid after drying under vacuum (109.4 mg, 84%).

^{1}H NMR spectrum (600 MHz, 373 K, $C_2D_2Cl_4$): δ 8.33 (s, 2H), 8.26 (d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 8.1$ Hz, 2H), 3.72 (br, 2H), 2.23 (br, 4H), 2.01 (t, $J = 6.3$ Hz, 1H), 1.54-1.46 (br, 8H), 1.26-1.21 (br, 20H), 1.07-0.99 (m, 6H), 0.88 (10H, overlapped); Terminal groups: 8.31 (br), 8.23 (br), 7.88 (br), 6.88 (s), 3.67 (br), 2.62 (s) M_n = 17 900, M_w/M_n = 1.9.

*Synthesis of **P-TPD***: A solution of $Pd(PCy_3)_2$ (2.7 mg, 0.0040 mmol) in dry toluene (1 mL) was prepared in a glove box. Br_2-DOF (106.4 mg, 0.194 mmol), Cs_2CO_3 (163 mg, 0.50 mmol), TPD (53 mg, 0.20 mmol) were added to a 25 mL Schlenk tube with a stirrer chip. The solution of the Pd catalyst was added to the Schlenk tube in the glove box. The pivalic acid (6.9 µL, 0.060 mmol) was added under the N_2 atmosphere outside of the glove box. The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, volatiles were removed under vacuum. The products were dissolved in $CHCl_3$ (100 mL) and an aqueous solution of sodium diethyldithiocarbamate (0.1 M, 150 mL) was added. The mixture was stirred for 16 h at room temperature. After separation, the organic layer was washed with water (3 times) and brine. The organic layer was dried with Na_2SO_4 and was concentrated. The solution was poured into vigorously stirred MeOH (200 mL), and stirred overnight. The solid was filtered and washed with hexane (150 mL) for 1 h. **P-TPD** was isolated as a yellow solid after drying under vacuum (101.1 mg, 77%).

^{1}H NMR spectrum (600 MHz, 373 K, $C_2D_2Cl_4$): δ 8.32 (s, 2H), 8.26 (d, $J = 8.3$ Hz, 2H), 7.91 (d, $J = 8.1$ Hz, 2H), 3.72 (br, 2H), 2.23 (br, 4H), 2.00 (t, $J = 6.1$ Hz, 1H), 1.52-1.44 (br, 8H), 1.25-1.21 (br, 20H), 1.07-0.98 (m, 6H), 0.91-0.83 (10H, overlapped); Terminal groups: 8.30 (br), 8.20 (br), 7.88 (br), 7.75 (s), 3.65 (br) M_n = 17 500 M_w/M_n = 2.0.

*Synthesis of **P-Br***: A solution of $Pd(PCy_3)_2$ (2.7 mg, 0.0040 mmol) in dry toluene (1 mL) was prepared in a glove box. Br_2-DOF (109.7 mg, 0.20 mmol), Cs_2CO_3 (163 mg, 0.50 mmol), TPD (39.8 mg, 0.15 mmol) were added to a 25 mL Schlenk tube with a stirrer chip. The solution of the Pd catalyst was added to the Schlenk tube in the glove box. The pivalic acid (6.9 µL, 0.060 mmol) was added under the N_2 atmosphere outside of the glove box. The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, volatiles were removed under vacuum. The products were dissolved in $CHCl_3$ (100 mL) and an aqueous solution of sodium diethyldithiocarbamate (0.1 M, 150 mL) was added. The mixture was stirred for 16 h at room temperature. After separation, the organic layer was washed with water (3 times) and brine. The organic layer was dried with Na_2SO_4 and was concentrated. The solution was poured into vigorously stirred MeOH (200 mL), and stirred overnight. The solid was filtered and washed with hexane (150 mL) for 1 h. **P-Br** was isolated as a yellow solid after drying under vacuum (84.5 mg, 65%).

^{1}H NMR spectrum (600 MHz, 373 K, $C_2D_2Cl_4$): δ 8.33 (s, 2H, s), 8.26 (d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 7.7$ Hz, 2H), 3.72 (br, 2H), 2.24 (br, 2H), 2.00 (d, $J = 6.2$ Hz, 1H), 1.55-1.45 (br, 8H), 1.30-1.19 (br, 20H), 1.07-1.00 (m, 6H), 0.89 (10H, overlapped); Terminal groups: 8.31 (br), 8.20 (br), 7.81 (br), 7.66 (d, $J = 8.3$ Hz), 7.59 (s), 7.56 (d, $J = 9.5$ Hz), 7.52 (s) $M_n = 16\,900$, $M_w/M_n = 1.8$.

Fabrication and Characterization of OLEDs: OLEDs were fabricated in the following configuration: Glass/ITO/PEDOT:PSS (40 nm)/PVK (30 nm)/Polymer (30 nm)/TPBi (30 nm)/LiF (1 nm)/Al (100 nm) The patterned indium tin oxide (ITO) glass (conductivity: 10 Ω/square) was pre-cleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated onto the ITO at 3000 rpm and air-dried at 110 °C for 10 min on a hot plate. The substrate was then transferred to a N_2-filled glove box where it was re-dried at 110 °C for 10 min on a hot plate. A chloroform solution of PVK (3 mg 1 mL^{-1}) was subsequently spin-coated onto the PEDOT:PSS surface to form the hole transport layer (30 nm), followed by a baking process for 10 min at 150 °C. A toluene solution of polymer (5 mg 1 mL^{-1}) was subsequently spin-coated onto the PVK surface to form the light-emitting layer (30 nm), followed with an annealing process for 10 min at 80 °C. TPBi was placed in a Mo boat, and LiF and Al in a W boat, and the boats were heated by applying suitable current to the boats. TPBi (30 nm), LiF (1 nm), and Al (100 nm) were then deposited onto the active layer at a chamber pressure lower than 5×10^{-4} Pa, which provided the devices with an active area of 2×2 mm^2. Current-voltage characteristics and luminance of the OLED were simultaneously measured using an ADCMT 6245 DC voltage current source/monitor (ADC CORPORATION) and an LS-100 luminance meter (KONICA MINOLTA, INC.), respectively. The EL spectra were measured using an array spectrometer (MCPD-9800-311C, Otsuka Electronics Co, Ltd.).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

conjugated polymers, direct arylation polycondensation, organic light-emitting diodes, semiconducting polymers, terminal group

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