Synthesis of Conjugated Polymer Consisting of Three-Component Aromatic Units via Two-Step Cross-Dehydrogenative-Coupling Reactions

Chie Tanaka [a], Junpei Kuwabara [a], Takeshi Yasuda [b], and Takaki Kanbara [a]*

[a] Tsukuba Research Center for Energy Materials Science (TREMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

[b] Research Center for Functional Materials, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

*Corresponding author. Tel.: +81-29-853-5066, fax: +81-29-853-4490,

E-mail address: kanbara@ims.tsukuba.ac.jp

Abstract

A Pd-catalyzed two-step cross-dehydrogenative-coupling sequence enabled the synthesis of a π-conjugated polymer consisting of three-component aromatic units, without the use of prefunctionalized starting substrates. When using 1,2,4,5-tetrafluorobenzene as the starting substrate, the cross-coupling reactions proceeded efficiently and the undesired homocoupling reaction was suppressed, producing a new donor-acceptor π-conjugated polymer. The introduction of a 4H-cyclopenta[2,1-b:3,4-b']-dithiophenediyl unit between the tetrafluorophenylene units enhanced coplanarity along the polymer chain, thus lowering the energy gap of the polymer. The obtained polymer was also evaluated for use as an emitting material in organic light-emitting diodes.

1. Introduction

Catalytic direct arylation of aromatic compounds via C–H bond cleavage has attracted increasing attention as a simple method that helps eliminate the need for prior preparation of organometallic reagents [1-6]. Several groups have attempted to utilize this strategy in polycondensation for the synthesis of π-conjugated polymers, which are considered promising materials for optoelectronic devices such as organic photovoltaic cells, field-effect transistors, and light-emitting diodes (Scheme 1a) [7-13]. Recently, strategies for direct sp^2 C-H functionalization toward the synthesis of π-conjugated polymers have been expanded to cross-dehydrogenative-coupling polycondensation (Scheme 1b) [14-17]. The protocol is based on the direct C-H/C-H cross-coupling reaction between two kinds of aromatic monomers, which provides straightforward access to alternating π-conjugated polymers, without the need for the prior preparation of dibrominated aromatic monomers or organometallic monomers. This protocol also allows us to eliminate the end-capping treatment of the terminal reactive functional groups of the polymer, which is known to degrade the semiconducting performance [18-21]. However, the synthetic examples are currently very specific. Previous studies indicated that the use of polyfluorobenzenes as a targeting aromatic monomer was crucial to control the selectivity in the successive C-H metalation steps and suppress undesired homocoupling reactions [14,17]. To expand the applicability of the synthetic protocol, we herein focused on the synthesis of π-conjugated polymers via a two-step cross-dehydrogenative-coupling sequence (Scheme 2). This protocol furnished a π-conjugated polymer consisting of three-component aromatic units, without the use of prefunctionalized starting substrates. The introduction of an aromatic unit between the tetrafluorophenylene units was expected to improve the coplanarity along the polymer chain. The optical properties of the polymer and its performance in an organic light-emitting diode (OLED) were also evaluated.

<Scheme 1>

<Scheme 2>

2. Experimental

2.1. Materials

1,2,4,5-Tetrafluorobenzene, 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, 3,3′-dihexyl-2,2′-bithiophene, and other chemicals were received from commercial suppliers and used without further purification. Anhydrous DMF and DMSO were purchased from Kanto chemical and used as a dry solvent.

2.2. General measurements and characterization

NMR spectra were recorded on Bruker AVANCE-600 and AVANCE-400 NMR spectrometers. Gel permeation chromatography (GPC) measurements were carried out using a SHIMADZU prominence GPC system equipped with polystyrene gel columns, using CHCl$_3$ as an eluent after calibration with polystyrene standards at 40 °C. Ultraviolet visible absorption spectra and photoluminescence (PL) spectra were recorded on a JASCO V-630 and a Hitachi F-2700 spectrophotometers, respectively. The quantum yields of the emission (φ) from polymers in films were measured using a JASCO FP-6500 spectrofluorometer with an integrating sphere. The HOMO energy

level was estimated by photoelectron yield spectroscopy (PYS) using a Riken Keiki AC-3 spectrometer. Elemental analyses were carried out with a PerkinElmer 2400 CHN Elemental Analyzer. All the manipulations for the reactions were carried out under a nitrogen atmosphere using a glove box or standard Schlenk technique.

2.3. Monomer synthesis

A mixture of $Pd(OAc)_2$ (10.1 mg, 0.045 mmol), Ag_2CO_3 (1.49 g, 5.4 mmol), acetic acid (206 μL, 3.6 mmol), 1,2,4,5-tetrafluorobenzene (1.89 mL, 18 mmol), and 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (725 mg, 1.8 mmol) was stirred in a mixture of anhydrous DMSO (6.0 mL) for 1 h at 120 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was extracted by $CHCl_3$. The $CHCl_3$ solution was washed with 1 M HCl and dried with sodium sulfate. After filtration, the resulting crude product was purified by chromatography on silica gel with $CHCl_3$ to afford 2,6-bis(2,3,5,6-tetrafluorophenyl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene, **M1**, as an orange oil (579.8 mg, 46% yield). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 7.52 (t, J = 3.8 Hz, 2H), 7.03-6.94 (m, 2H), 2.04-1.90 (m, 4H), 1.07-0.86 (m, 18H), 0.71 (td, J = 6.8, 1.1 Hz, 6H), 0.62 (td, J = 7.4, 1.5 Hz, 6H). ^{19}F NMR (376 MHz, 298 K, $CDCl_3$): δ -140.2--140.4 (m), -141.4--141.6 (m). ^{13}C{^{1}H} NMR (150 MHz, 298 K, $CDCl_3$) δ158.6, 146.7 (dm, J_{C-F} = 208 Hz), 143.5 (dm, J_{C-F} = 250 Hz), 140.1, 128.3, 125.6, 116.0, 103.5 (t, J_{C-F} = 23.1 Hz), 54.5, 43.3, 35.5, 34.5, 28.8, 27.6, 22.9, 14.0, 10.8. Anal. Calcd. for $C_{37}H_{38}F_8S_2$: C, 63.59; H, 5.48. Found: C, 63.53; H, 5.66.

2.4. Polymer synthesis

A mixture of $Pd(OAc)_2$ (2.25 mg, 0.010 mmol), Ag_2CO_3 (165 mg, 0.60 mmol), PivOH (45.1 μL, 0.40 mmol), K_2CO_3 (82.9 mg, 0.60 mmol), **M1** (140 mg, 0.20 mmol), and 3,3′-dihexyl-2,2′-bithiophene (66.9 mg, 0.20 mmol) was stirred in a mixture of anhydrous DMF (1.6 mL) and DMSO (0.08 mL) for 48 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and extracted by $CHCl_3$. After filtration, the $CHCl_3$ solution was thoroughly washed with 5% aqueous solution of HNO_3 to dissolve residual Ag, an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8) to remove residual Pd, and distilled water. After filtration through a plug of Celite, the solution was concentrated and reprecipitated into methanol. The precipitates were thoroughly washed with methanol and hexane, and dried under reduced pressure. **P1** was isolated as a reddish solid (135 mg, 66% yield). M_n =17,300, M_w/M_n =1.82. ^{1}H NMR (600 MHz, 373 K, $C_2D_2Cl_4$): δ: 7.62 (m, 4H), 2.72 (t, J = 7.5 Hz, 4H), 2.07 (m, 4H), 1.73-1.68 (m, 4H), 1.35 (m, 12H), 1.13-0.93 (m, 18H), 0.94 (t, J = 7.0 Hz, 6H), 0.81 (t, J = 6.8 Hz, 6H), 0.73 (t, J = 7.5 Hz, 6H). ^{19}F NMR (376 MHz, 298 K, $CDCl_3$): δ -141.8. ^{13}C{^{1}H} NMR (150 MHz, 373 K, $C_2D_2Cl_4$): δ159.0, 145.2 (m, overlap), 143.2, 140.1, 132.0, 131.3, 128.5, 128.2 125.5, 113.3, 112.0 (m), 54.6, 43.6, 35.8, 34.6, 31.5, 30.4, 29.0, 28.9, 28.8, 27.6, 22.7, 22.4, 13.8, 13.7, 10.6. Anal. Calcd. for $C_{57}H_{64}F_8S_4$: C, 66.51; H, 6.27. Found: C, 66.86; H, 6.17.

2.5. Fabrication and characterization of OLED

OLED was fabricated in the following configuration: ITO/PEDOT:PSS/light-emitting **P1** layer/electron transporting (hole blocking) TPBi layer/LiF/Al. The patterned indium tin oxide (ITO) glass (conductivity: 10 Ω/square) was precleaned 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 glovebox where it was redried at 110 °C for 10 min on a hot plate. A toluene solution of **P1** (10 mg/1 mL) was subsequently spincoated onto the PEDOT:PSS surface to form the light-emitting layer (47 nm), followed with an annealing process for 10 min at 80 °C. TPBi (40 nm), LiF (1 nm), and Al (100 nm) were then deposited onto the active layer with conventional thermal evaporation 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 6246 DC voltage current source/monitor (ADC CORPORATION) and an LS-100 luminance meter (KONICA MINOLTA JAPAN, INC.), respectively. The electroluminescence (EL) spectra and the coordinates of the CIE chromaticity were measured using an array spectrometer (MCPD-9800-311C, Otsuka Electronics Co, Ltd.).

3. Results and Discussion

3.1. Synthesis and characterization

Monomer **M1** was prepared by the Pd-catalyzed cross-dehydrogenative-coupling of 1,2,4,5-tetrafluorobenzene with 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b′*]dithiophene by referring to literature procedures (Scheme S1) [22]. **M1** was fully characterized by NMR and elemental analyses (Fig. S1). The polycondensation reaction of **M1** with 3,3′-dihexyl-2,2′-bithiophene was conducted under the optimal conditions described in a previous report [14]. The polycondensation reaction afforded the corresponding polymer **P1** with a molecular weight (M_n) of 17,300 in 66% yield (Scheme 3).

<Scheme 3>

The chemical structure of **P1** was characterized by NMR spectroscopy and elemental analysis. Assignment of the NMR signals was performed by comparison with the signals of the monomers and a reference polymer (**P0**, Scheme 4), which was synthesized by cross-dehydrogenative-coupling of 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl with 3,3′-dihexyl-2,2′-bithiophene [14]. As shown in Fig. 1a, the main signals were assigned to the repeating unit. The integral ratios of the signals essentially agreed with the assignments and were consistent with the alternating structure of **P1**. The minor signals at δ 7.03 and 7.37 ppm were assignable to a terminal 3,3′-dihexyl-2,2′-bithiophene unit, whereas the minor signals at δ 7.14 and 7.57 ppm were assigned to structural defects in the polymer chain, which were caused by the homocoupling reaction of the 3,3′-dihexyl-2,2′-bithiophene moiety (Fig. S2). However, the integral ratios between the minor defects and the recurring unit in the ^{1}H NMR spectrum indicated that **P1** included less than 3% of the homocoupling defects. The ^{19}F NMR spectrum supported the alternating structure of **P1** (Fig. 1b). The minor signals at δ -140.3 and -141.5 ppm were assigned to a terminal tetrafluorophenyl unit in the ^{19}F NMR spectrum, but no signal corresponding to the homocoupling defect of the polyfluoroarene unit in the polymer chain was observed. These results are consistent with the trend mentioned in previous reports [14,17,23].

<Scheme 4>

4

<Figure 1>

3.2. Optical properties and OLED behavior

The UV-vis absorption spectra of **P1** and **P0** in the film state are shown in Fig. 2. The absorption of **P1** was redshifted as compared with that of **P0** in CHCl$_3$ solution (Fig. S4) and in the film state. The optical bandgaps (E_g^{opt}) of **P1** and **P0** were determined to be 2.37 and 2.96 eV, respectively, and the corresponding HOMO levels were 5.60 and 6.07 eV, as determined by PYS. While **P0** showed a large distortion of the aromatic rings in the octafluorobiphenylene unit, the introduction of a cyclopenta[2,1-*b*:3,4-*b'*]dithiophenediyl unit between the tetrafluorophenylene units could effectively reduce the torsion angle, as was also confirmed by density functional theory (DFT) calculations (Fig. S5). This enhanced coplanarity along the polymer chain lowered the energy gap of the polymer. Intramolecular donor-acceptor interactions between the tetrafluorophenylene and cyclopenta[2,1-*b*:3,4-*b'*]dithiophenediyl units would also be associated with the lowering of the E_g^{opt} value of **P1** [24,25].

<Figure 2>

A previous report describes the fabrication of an OLED using **P0** with light green emission [14]. Since the **P1** film showed orange emission with a higher emission quantum yield ($\varphi = 16\%$) compared to that of **P0** ($\varphi = 9\%$), the emission properties of **P1** were also evaluated in an OLED. The EL spectrum was consistent with the PL spectrum of **P1** (Fig. 3), and the coordinates of the CIE chromaticity diagram were x = 0.59, y = 0.41, at 7.0 mA cm^{-2} (Fig. S6). The luminance reached 690 cd m^{-2} at a current of 485 mA cm^{-2}; the maximum external quantum efficiency (EQE) was 0.32% in the OLED using **P1** (Fig. S7), which was higher than that (0.12%) in the same OLED using **P0** [14]. While the OLED performance with **P1** is mediocre, these results indicate that **P1** can serve as the emitting material in these devices.

<Figure 3>

4. Conclusion

The synthesis of a π-conjugated polymer via a two-step cross-dehydrogenative-coupling sequence is demonstrated. The protocol furnishes a π-conjugated polymer consisting of three-component aromatic units, without the need for any reactive functional group in the aromatic substrates. The introduction of a third aromatic unit helps tune the energy levels and emission color of the polymer from light green to orange. Therefore, the synthetic protocol can provide easy access to multicomponent semiconducting materials in organic optoelectronic devices with improved step economy. Further studies on extending the usability of the developed synthetic protocol are underway.

JSPS.

**Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1019/j.synthmet.2019.

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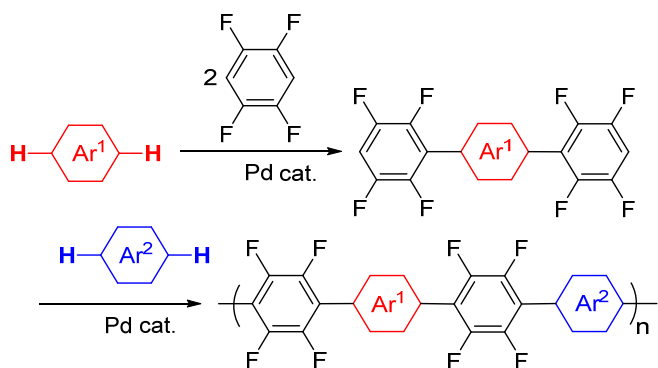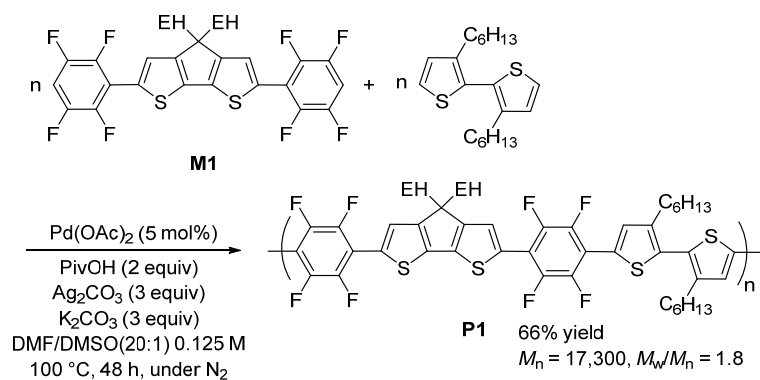
(a) Direct arylation polycondensation
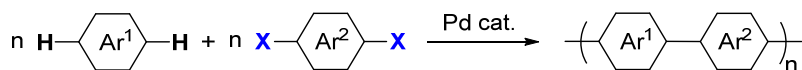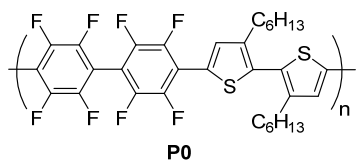

(b) Cross-dehydrogenative-coupling polycondensation
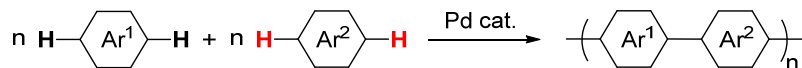
Scheme 1. Synthesis of π-conjugated polymers via sp^2 C-H bond functionalization.

Scheme 2. Two-step cross-dehydrogenative coupling reaction for synthesis of π-conjugated polymer.

Scheme 3. Synthesis of P1 via cross-dehydrogenative coupling polycondensation.
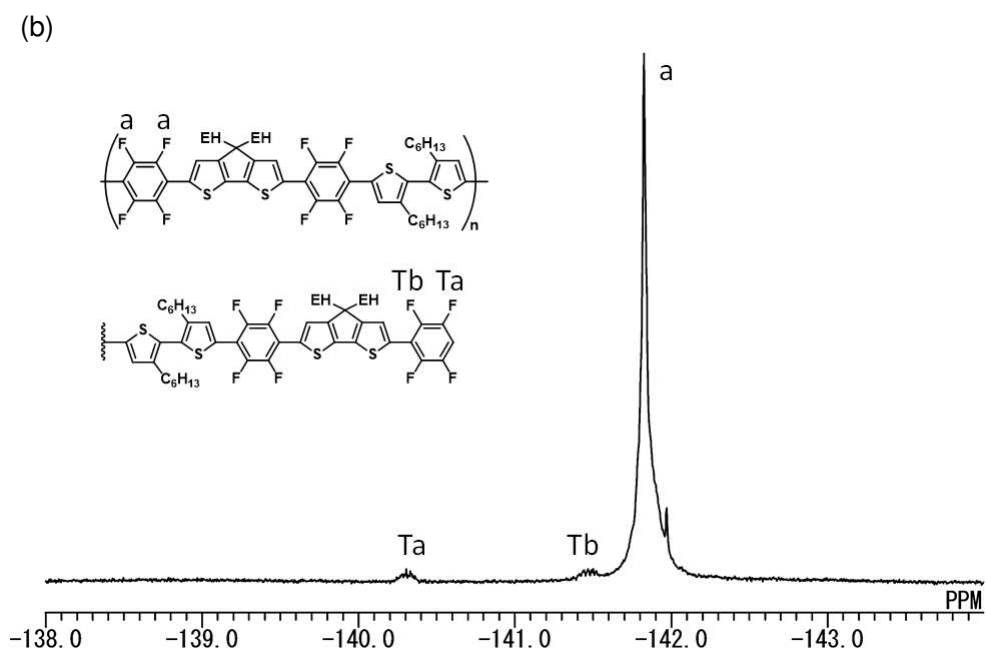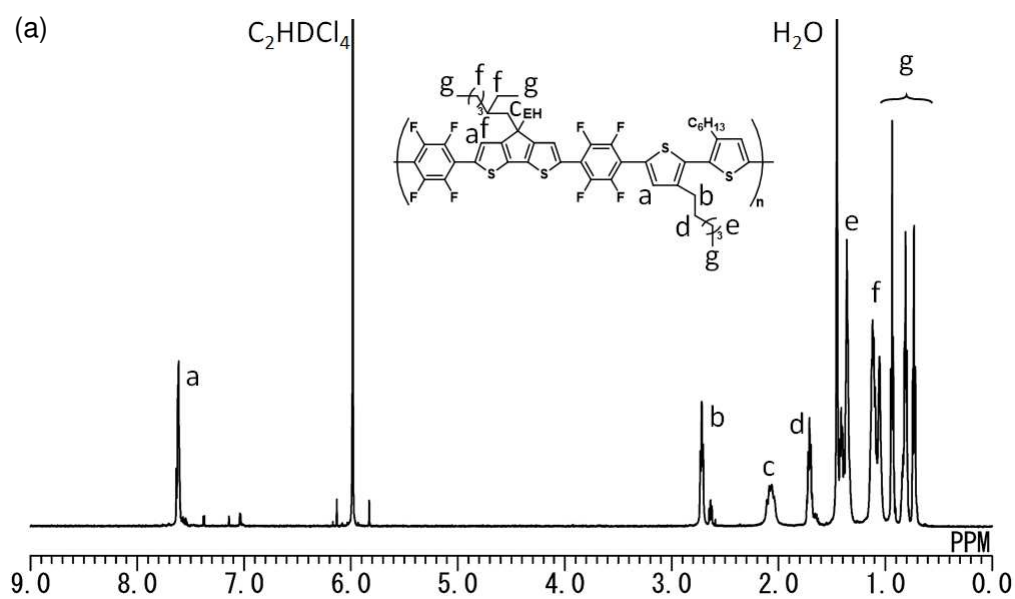

Scheme 4. The chemical structure of **P0**.

Fig. 1. (a) ^{1}H (600 MHz, $C_2D_2Cl_4$, 373 K) and (b) ^{19}F (376 MHz, $CDCl_3$, 298 K) NMR spectra of **P1**.
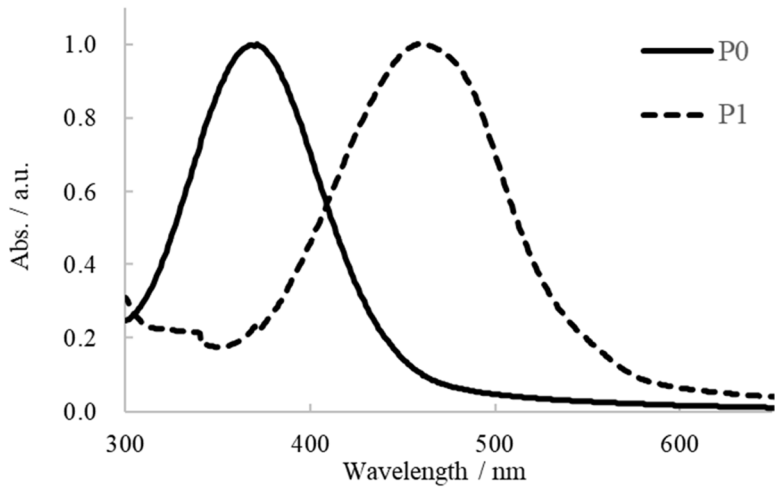
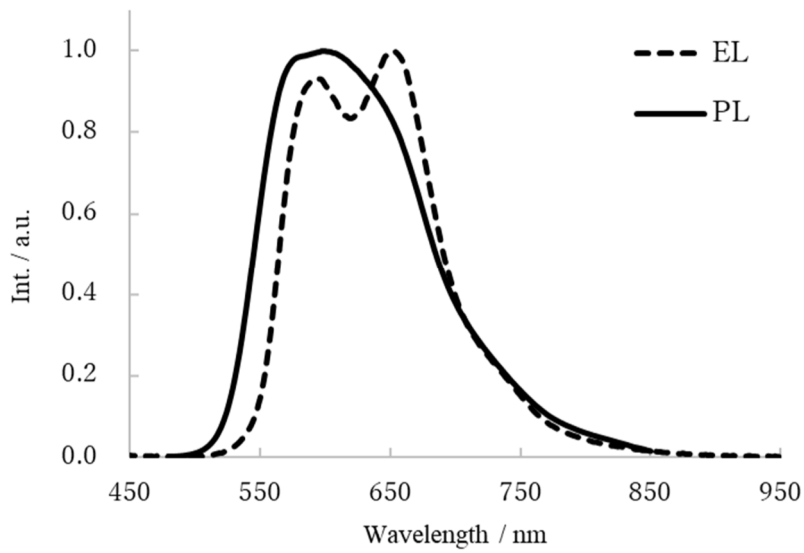Fig. 2. UV-vis absorption spectra of **P1** and **P0** in the film states.

Fig. 3. PL spectrum of thin film of **P1** and EL spectrum of OLED using **P1** at 6.0 V.