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# Synthesis of EDOT-containing polythiophenes and their properties in relation to composition ratio of EDOT

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Polythiophenes composed of 3,4-ethylenedioxythiophene (**EDOT**) and 3-hexylthiophene with different composition ratios of **EDOT** in a repeat unit of a polymer backbone are synthesized by polycondensation reactions. The optical and electrochemical properties of the polymers are compared with those of poly(3,4-ethylenedioxythiophene) and poly(3-hexylthiophene), and they are found to be well correlated with the **EDOT** composition ratio. In addition, the charge transport properties of the polymer films measured using the *in-situ* conductivity technique are discussed in terms of the **EDOT** composition ratio, regioregularity, and the doping level.

## Introduction

Since polyacetylene was successfully obtained as a film state and the bromine-doped film was found to show high electrical conductivities,[1] π-conjugated polymers with various kinds of chemical structures have attracted a great deal of attention from many researchers because these polymers exhibit not only the metallic nature at the doped (oxidized or reduced) state, but also the semiconducting nature at the neutral state.[2] While doped polymers were originally studied to understand the mechanism of the electrical conduction from the fundamental aspects, neutral polymers are well-studied for the last few decades from the viewpoints of the applications to many types of plastic electronics, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs) which enable low-cost, large-area and flexible devices. Since it was found that poly(3,4-ethylenedioxythiophene) (**PEDOT**), a derivative of polythiophene, shows the high electrical conductivity by chemical or electrochemical doping and the doped **PEDOT** can be applied to transparent conductive materials[3] and organic thermoelectrics[4], the doped polymers have started to attract attention again in very recent years. However, **PEDOT** is not soluble in common organic solvents because of the rigid backbone, which restricts their industrial applications. To improve the processability, **PEDOT** and its related polymers having 3,4-alkylenedioxythiophenes in a repeat unit have been enthusiastically developed, but chemical structures of most of the polymers synthesized by chemical or electrochemical oxidation of their corresponding monomers were not well-defined.[3b,5]

Recently, we have succeeded in the synthesis of polythiophenes containing 3,4-ethylenedioxythipohene (**EDOT**) in a repeat unit, poly(3´,4´-ethylenedioxy-2,2´:5´,2´´-terthiophene) (**polyTET**) and poly(3,3´´´´-dihexyl-3´,4´,3´´´,4´´´-diethylenedioxy-2,2´:5´,2´´:5´´,2´´´:5´´´,2´´´´-quinquethiophene) (**polyHE5T**) (Fig. 1).[6] These polymers were soluble in common organic solvents, so that their chemical structures could be characterized well by $^1$H NMR and MS spectroscopies, and GPC analysis. Furthermore, the electrical conductivities of these polymers were found to be controlled from $10^{-7}$ to $10^{1}$ S cm$^{-1}$ by changing the chemical structure and doping level.

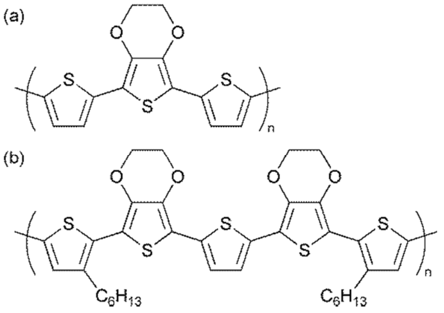

**Fig. 1** Chemical structures of (a) **polyTET** and (b) **polyHE5T**.

In this paper, three kinds of polythiophenes containing **EDOT** and 3-hexylthiophene (**3HT**) with different **EDOT** composition ratios were synthesized by polycondensation reactions using the direct C-H arylation and Stille-coupling, and their optical, electrochemical, and electrical properties were discussed with those of **PEDOT** and poly(3-hexylthiophene) (**P3HT**). In

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*Electronic Supplementary Information (ESI) available: Electronic absorption spectra in o-dichlorobenzene and films, and spectroelectrochemistry of polymer films. See DOI: 10.1039/x0xx00000x* particular, the charge transport properties of these polythiophene films were investigated in relation to the **EDOT** composition ratio, the primary structure (regioregularity) of the polymers, and the extent of oxidation of a polymer chain (doping level).

## Experimental

### Materials and Instrumentation

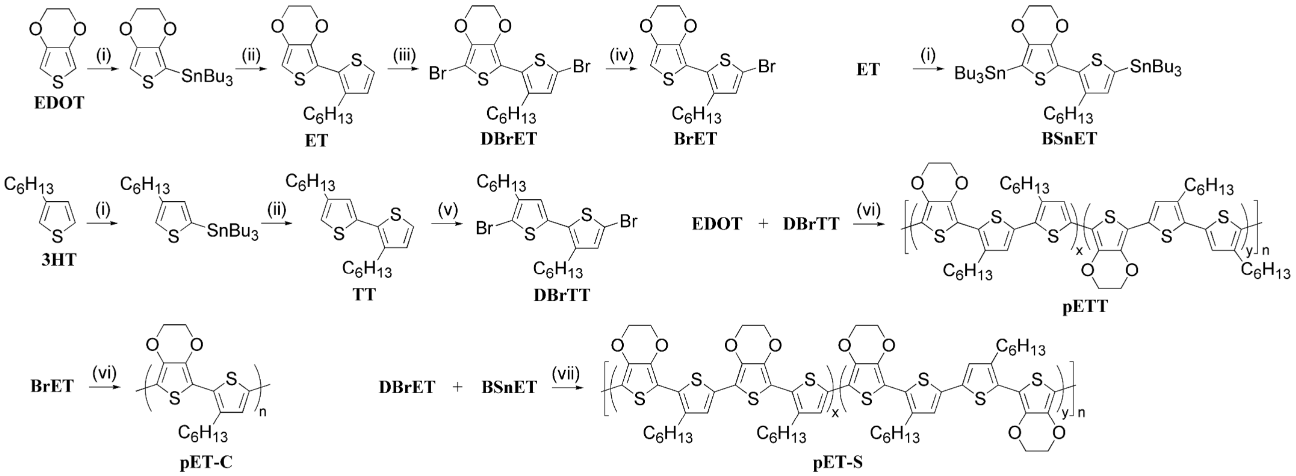
*n*-Hexane, toluene, tetrahydrofuran (THF), acetic acid (AcOH), chloroform, dichloromethane, *o*-dichlorobenzene and acetonitrile were purified by standard methods and used immediately after purification. Tetraethylammonium perchlorate (TEAP) and *N*-bromosuccinimide (NBS) were purified by recrystallization from ethanol and benzene, respectively, and dried under vacuum. **EDOT** and 3-bromothiophene were purchased from Tokyo Chemical Industry and used without further purification. **P3HT** used in this study was regiorandom (regioregularity of 54 % determined by $^1$H NMR). 2-Tributylstannyl-3,4-ethylenedioxythiophene,[6b] **3HT**[7] and 2-bromo-3-hexylthiophene[8] were synthesized according to the literatures.

Microwave reactions were conducted using a Monowave 300 (Anton Paar GmbH). $^1$H NMR spectra were recorded by 500 MHz spectrometers (Varian Inc., NMR System 500) and by a 600 MHz spectrometer (JEOL Ltd., JNM-ECA600). Molecular weights of the resulting polymers were analyzed by a GPC coupled with an UV detector (Shimadzu Corp., SPD-10A). Combination of Shodex KF-801 (30 cm, exclusion limit: $M_n$ = $1.5 \times 10^3$, polystyrene) KF-802 (30 cm, exclusion limit: $M_n$ = $5.0 \times 10^3$, polystyrene) and KF-803L (30 cm, exclusion limit: $M_n$ = $7.0 \times 10^4$, polystyrene) columns (linear calibration down to $M_n$ = 100) were used for molecular weight analysis with THF (1.0 $dm^3$ $min^{-1}$) as an eluent. Measurements of mass spectroscopy and the elemental analysis were made using a LTQ Orbitrap XL™ Hybrid Ion Trap-Orbitrap Mass Spectrometer (Thermo Fisher Scientific Inc.) and an Elemental Analyzer (Perkin Elmer, 2400 Series II CHNS/O), respectively. UV-Vis absorption spectra were measured by a spectrophotometer (Shimadzu Corp., UV-3150). Cyclic voltammetry and *in-situ* conductivity measurements were carried out using a potentiostat/galvanostat (Hokuto Denko Corp., HAB-151 or HZ-3000) with an X-Y recorder (Riken Denshi Co., Ltd., F-57), a coulometer (homemade), and a function generator (Iwatsu Electric Co., Ltd., SG-4105).

### Synthesis

The synthetic routes of the monomers and polymers are shown in Scheme 1 and the detailed synthetic processes are described below.

**3,4-Ethylenedioxy-3´-hexyl-2,2´-bithiophene (ET).** To a solution of **EDOT** (0.70 g, 4.9 mmol) in THF (15 mL) at −78 °C was added 1.8 mL (4.9 mmol) of *n*-butyllithium (2.7 M in *n*-hexane) by syringe. The mixture was stirred at −78 °C for 1 h. Tri(*n*-butyl)tin chloride (1.8 g, 5.6 mmol) was added to the solution, and the resulting mixture was stirred at −78 °C for 30 min, warmed to room temperature, and stirred further for 1 h. The solvent was removed *via* rotary evaporation, and *n*-hexane was added to the residue. The soluble fraction was extracted by filtration. The filtrated solution was added to a solution of tetrakis(triphenylphosphine)palladium (0.27 g, 0.23 mmol) and 2-bromo-3-hexylthiophene (1.2 g, 4.9 mmol) in toluene (30 mL). The solution was stirred at 80 °C for 7 h. The mixture was poured into sat. aq. $Na_2CO_3$ and extracted with dichloromethane. The extract was then successively washed with water. After being dried over anhydrous $Na_2SO_4$, the solvent was evaporated and the crude product was purified by column chromatography on silica gel with a mixed solvent of *n*-hexane and toluene (*v*/*v* = 1/2) as an eluent to afford a yellow liquid (0.80 g, 2.6 mmol). Yield: 53 %. $^1$H NMR (500 MHz, $(CD_3)_2CO$, *δ*, ppm): 0.86 (t, *J* = 6.82 Hz, 3H, $C\boldsymbol{H}_3$), 1.22-1.36 (m, 6H, thienyl-$(CH_2)_2(C\boldsymbol{H}_2)_3CH_3$), 1.59 (tt, *J* = 7.80, 7.80 Hz, 2H, thienyl-$CH_2C\boldsymbol{H}_2$), 2.68 (t, *J* = 7.80 Hz, 2H, thienyl-$C\boldsymbol{H}_2$),



**Scheme 1.** Synthetic procedures of the monomers and polymers: (i) *n*-BuLi, dry THF, $Bu_3SnCl$; (ii) 2-bromo-3-hexylthiophene, $Pd(PPh_3)_4$, toluene; (iii) NBS, $CHCl_3$/AcOH; (iv) MeMgBr, dry THF; water; (v) NBS, THF; (vi) $Pd(dba)_2$, $P(o\text{-Tol})_3$, $Cs_2CO_3$, pivalic acid, THF, and (vii) $Pd(PPh_3)_4$, toluene.

4.23-4.31 (m, 4H, $\mathrm{OC}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}_2\mathrm{O}$), 6.51 (s, 1H, EDOT-***H***), 6.99 (d, *J* = 5.32 Hz, 1H, thienyl-***H***) , 7.38 (d, *J* = 5.32 Hz, 1H, thienyl-***H***). HRMS (APCI) *m*/*z* calcd for $C_{16}H_{21}O_2S_2$ ($[M+H]^+$) 309.0978, found 309.0983.

**5,5´-Dibromo-3,4-ethylenedioxy-3´-hexyl-2,2´-bithiophene (DBrET).** To a $CHCl_3$/AcOH (75 mL/75 mL) solution of **ET** (1.2 g, 4.0 mmol), a $CHCl_3$/AcOH (175 mL/175 mL) solution of NBS (1.6 g, 9.1 mmol) was slowly added in the dark at 0 °C. The reaction mixture stirred in the dark at 0 °C for 2 h was poured into water, and extracted two times with chloroform. The organic extracts were washed with sat. aq. $Na_2CO_3$ and water, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by column chromatography on silica gel with a mixed solvent of acetone and dichloromethane (*v*/*v* = 1/1) to afford a yellow viscous liquid (1.1 g, 2.3 mmol). Yield: 56 %. $^1$H NMR (500 MHz, $(CD_3)_2CO$, *δ*, ppm): 0.87 (t, *J* = 6.88 Hz, 3H, $\mathrm{C}\boldsymbol{H}_3$), 1.24-1.38 (m, 6H, thienyl-$(\mathrm{CH}_2)_2(\mathrm{C}\boldsymbol{H}_2)_3\mathrm{CH}_3$), 1.59 (tt, *J* = 7.83, 7.83 Hz, 2H, thienyl-$\mathrm{CH}_2\mathrm{C}\boldsymbol{H}_2$), 2.65 (t, *J* = 7.83 Hz, 2H, thienyl-$\mathrm{C}\boldsymbol{H}_2$), 4.36 (s, 4H, $\mathrm{OC}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}_2\mathrm{O}$), 7.07 (s, 1H, thienyl-***H***). HRMS (APCI) *m*/*z* calcd for $C_{16}H_{18}O_2Br_2S_2$ ($M^+$) 463.9110, found 463.9110.

**5´-Bromo-3,4-ethylenedioxy-3´-hexyl-2,2´-bithiophene (BrET).** To a solution of **DBrET** (0.93 g, 2.0 mmol) in THF (10 mL) was added 2.0 mL (2.0 mmol) of methylmagnesium bromide (1.0 M in THF) by syringe. The mixture was stirred at reflux temperature for 3.5 h. The solvent was removed *in vacuo*. Water and dichloromethane were added to the residue, and the organic phase was extracted and dried over anhydrous $Na_2SO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with a mixed solvent of *n*-hexane and toluene (*v*/*v* = 2/1) as an eluent to afford a yellow solid (0.60 g, 1.5 mmol). Yield: 75 %. $^1$H NMR (500 MHz, $(CD_3)_2CO$, *δ*, ppm): 0.87 (t, *J* = 6.97 Hz, 3H, $\mathrm{C}\boldsymbol{H}_3$), 1.24-1.38 (m, 6H, thienyl-$(\mathrm{CH}_2)_2(\mathrm{C}\boldsymbol{H}_2)_3\mathrm{CH}_3$), 1.59 (tt, *J* = 7.76, 7.76 Hz, 2H, thienyl-$\mathrm{CH}_2\mathrm{C}\boldsymbol{H}_2$), 2.67 (t, *J* = 7.76 Hz, 2H, thienyl-$\mathrm{C}\boldsymbol{H}_2$), 4.24-4.34 (m, 4H, $\mathrm{OC}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}_2\mathrm{O}$), 6.55 (s, 1H, EDOT-***H***), 7.04 (s, 1H, thienyl-***H***). HRMS (APCI) *m*/*z* calcd for $C_{16}H_{19}O_2BrS_2$ ($M^+$) 386.0004, found 386.0001.

**3,4´-Dihexyl-2,2´-bithiophene (TT).** To a solution of **3HT** (0.63 g, 3.7 mmol) in THF (15 mL) at −78 °C was added 1.5 mL (4.0 mmol) of *n*-butyllithium (2.7 M in *n*-hexane) by syringe. The mixture was stirred at −78 °C for 1 h. Tri(*n*-butyl)tin chloride (1.6 g, 4.7 mmol) was added to the solution, and the resulting mixture was stirred at −78 °C for 30 min, warmed to room temperature, and stirred further for 1 h. The solvent was removed *via* evaporation, and *n*-hexane was added to the residue. The soluble fraction was extracted by filtration. The filtrated solution was added to a solution of tetrakis(triphenylphosphine)palladium (0.22 g, 0.19 mmol) and 2-bromo-3-hexylthiophene (0.93 g, 3.7 mmol) in toluene (30 mL). The solution was stirred at 90 °C for 12 h. The mixture was poured into sat. aq. $Na_2CO_3$ and extracted with chloroform. The extract was then successively washed with water. After being dried over anhydrous $Na_2SO_4$, the solvent was evaporated and the crude product was purified by column chromatography on silica gel with a mixed solvent of *n*-hexane and toluene (*v*/*v* = 30/1) as an eluent to afford a yellow liquid (0.55 g, 1.6 mmol). Yield: 44 %. $^1$H NMR (500 MHz, $(CD_3)_2CO$, *δ*, ppm): 0.87 (t, *J* = 7.15 Hz, 3H, $\mathrm{C}\boldsymbol{H}_3$), 0.88 (t, *J* = 7.15 Hz, 3H, $\mathrm{C}\boldsymbol{H}_3$), 1.26-1.42 (m, 12H, thienyl-$(\mathrm{CH}_2)_2(\mathrm{C}\boldsymbol{H}_2)_3\mathrm{CH}_3$), 1.63 (tt, *J* = 7.85, 7.85 Hz, 2H, thienyl-$\mathrm{CH}_2\mathrm{C}\boldsymbol{H}_2$), 1.65 (tt, *J* = 7.64, 7.64 Hz, 2H, thienyl-$\mathrm{CH}_2\mathrm{C}\boldsymbol{H}_2$), 2.63 (t, *J* = 7.64 Hz, 2H, thienyl-$\mathrm{C}\boldsymbol{H}_2$), 2.76 (t, *J* = 7.85 Hz, 2H, thienyl-$\mathrm{C}\boldsymbol{H}_2$), 7.01 (d, *J* = 5.26 Hz, 1H, thienyl-***H***), 7.03 (d, *J* = 1.46 Hz, 1H, thienyl-***H***), 7.09 (d, *J* = 1.46 Hz, 1H, thienyl-***H***), 7.32 (d, *J* = 5.26 Hz, 1H, thienyl-***H***). HRMS (APCI) *m*/*z* calcd for $C_{20}H_{31}S_2$ ($[M+H]^+$) 335.1862, found 335.1866.

**5,5´-Dibromo-3,4´-hexyl-2,2´-bithiophene (DBrTT).** To a THF (6 mL) solution of **TT** (0.40 g, 1.2 mmol), a THF (6 mL) solution of NBS (0.46 g, 2.6 mmol) was slowly added in the dark at 0 °C. The reaction mixture was stirred in the dark at 0 °C for 3 h. The solvent was removed *in vacuo*. Water and chloroform were added to the residue, and the organic phase was extracted and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by column chromatography on silica gel with *n*-hexane as an eluent to afford a pale yellow viscous liquid (0.48 g, 0.98 mmol). Yield: 81 %. $^1$H NMR (500 MHz, $(CD_3)_2CO$, *δ*, ppm): 0.87 (t, *J* = 7.09 Hz, 3H, $\mathrm{C}\boldsymbol{H}_3$), 0.88 (t, *J* = 7.09 Hz, 3H, $\mathrm{C}\boldsymbol{H}_3$), 1.24-1.42 (m, 12H, thienyl-$(\mathrm{CH}_2)_2(\mathrm{C}\boldsymbol{H}_2)_3\mathrm{CH}_3$), 1.61 (tt, *J* = 7.82, 7.82 Hz, 2H, thienyl-$\mathrm{CH}_2\mathrm{C}\boldsymbol{H}_2$), 1.63 (tt, *J* = 7.64, 7.64 Hz, 2H, thienyl-$\mathrm{CH}_2\mathrm{C}\boldsymbol{H}_2$), 2.60 (t, *J* = 7.64 Hz, 2H, thienyl-$\mathrm{C}\boldsymbol{H}_2$), 2.70 (t, *J* = 7.82 Hz, 2H, thienyl-$\mathrm{C}\boldsymbol{H}_2$), 6.99 (s, 1H, thienyl-***H***), 7.10 (s, 1H, thienyl-***H***). HRMS (APCI) *m*/*z* calcd for $C_{20}H_{29}Br_2S_2$ ($[M+H]^+$) 491.0072, found 491.0079.

**Poly(3,4-ethylenedioxy-3´,3´´-dihexyl-2,2´:5´,2´´-terthiophene) (pETT).** Bis(dibenzylideneacetone) palladium (5.7 mg, 0.01 mmol), tris(*o*-methoxyphenyl) phosphine (3.5 mg, 0.01 mmol), $Cs_2CO_3$ (0.14 g, 0.43 mmol), pivalic acid (30 mg, 0.30 mmol) were placed in a 10-mL microwave vessel with a magnetic stir bar. A THF (2 mL) solution of **EDOT** (28 mg, 0.20 mmol) and **DBrTT** (99 mg, 0.20 mmol) was added and the resulting solution was bubbled by dry nitrogen to remove dissolved oxygen. The vessel was sealed and placed in the microwave reactor. The solution was heated at 100 °C for 1 h. The mixture was poured into methanol, and the formed precipitate was washed with methanol and acetone and extracted with chloroform and THF by Soxhlet extraction. After purification with a metal scavenger (Silia*MetS* DMT, SiliCycle Inc.), a black powder (57 mg, 0.12 mmol (per repeating unit)) was obtained. Yield: 60 %. $^1$H NMR (600 MHz, THF-$d_6$, 50 °C, *δ*, ppm): 0.84-0.94 (br, 6H, $\mathrm{C}\boldsymbol{H}_3$), 1.22-1.48 (br, 16H, thienyl-$\mathrm{CH}_2(\mathrm{C}\boldsymbol{H}_2)_4\mathrm{CH}_3$), 2.73-2.86 (br, 4H, thienyl-$\mathrm{C}\boldsymbol{H}_2$), 4.26-4.45 (br, 4H, $\mathrm{OC}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}_2\mathrm{O}$), 6.95-7.05 (br, 1H, thienyl-***H***), 7.05-7.15 (br, 1H, thienyl-***H***). Anal. Calcd. for $C_{26}H_{32}O_2S_3$: C, 66.06; H, 6.82; S, 20.35. Found: C, 64.65; H, 6.95; S, 20.45.

**Poly(3,4-ethylenedioxy-3´-hexyl-2,2´-bithiophene) (pET-C) prepared by direct C-H arylation.** **BrET** (77 mg, 0.20 mmol), bis(dibenzylideneacetone)palladium (5.7 mg, 0.01 mmol), tris(*o*-methoxyphenyl)phosphine (3.5 mg, 0.01 mmol), $Cs_2CO_3$ (0.14 g, 0.43 mmol), pivalic acid (30 mg, 0.30 mmol) were placed in a 10-mL microwave vessel with a magnetic stir bar. THF (2 mL) was added and the resulting solution was bubbled by dry nitrogen to remove dissolved oxygen. The vessel was sealed and placed in the microwave reactor. The solution was heated at 100 °C for 20 min. The mixture was poured into methanol, and the formed precipitate was washed with methanol and acetone and extracted with chloroform and THF by Soxhlet extraction. After purification with a metal scavenger (Silia*MetS* DMT, SiliCycle Inc.), a black powder (21 mg, 0.069 mmol (per repeating unit)) was obtained. Yield: 34 %. $^1$H NMR (600 MHz, THF-$d_6$, 50 °C, $\delta$, ppm): 0.86-0.94 (br, 3H, C$\boldsymbol{H}_3$), 1.26-1.46 (br, 8H, thienyl-$CH_2$(C$\boldsymbol{H}_2$)$_4$$CH_3$), 2.71-2.81 (br, 2H, thienyl-C$\boldsymbol{H}_2$), 4.27-4.40 (br, 4H, OC$\boldsymbol{H}_2$C$\boldsymbol{H}_2$O), 7.06-7.13 (br, 1H, thienyl-$\boldsymbol{H}$). Anal. Calcd. for $C_{16}H_{18}O_2S_2$: C, 62.71; H, 5.92; S, 20.93. Found: C, 62.86; H, 6.53; S, 16.74.

**Poly(3,4-ethylenedioxy-3´-hexyl-2,2´-bithiophene) (pET-S) prepared by Stille coupling.** To a solution of **ET** (0.37 g, 1.2 mmol) in THF (6 mL) at −78 °C was added 1.7 mL (4.6 mmol) of *n*-butyllithium (2.7 M in *n*-hexane) by syringe. The mixture was stirred at −78 °C for 2 h. Tri(*n*-butyl)tin chloride (1.6 g, 4.9 mmol) was added to the solution, and the resulting mixture was stirred at −78 °C for 30 min, warmed to room temperature, and stirred further for 1 h. The solvent was removed *via* rotary evaporation, and *n*-hexane was added to the residue. The soluble fraction was extracted by filtration. The bis-stannylated **ET** (**BSnET**) obtained by the evaporation of the filtrated solution was added to a solution of tetrakis(triphenylphosphine)palladium (69 mg, 0.06 mmol) and **DBrET** (0.56 g, 1.2 mmol) in toluene (3.2 mL). The solution was stirred at 90 °C for 24 h. The mixture was poured into methanol, and the formed precipitate was washed with methanol and acetone and extracted with chloroform and THF by Soxhlet extraction. After purification with a metal scavenger (Silia*MetS* DMT, SiliCycle Inc.), a black powder (230 mg, 0.75 mmol (per repeating unit)) was obtained. Yield: 63 %. $^1$H NMR (600 MHz, THF-$d_6$, 50 °C, $\delta$, ppm): 0.86-0.94 (br, 3H, C$\boldsymbol{H}_3$), 1.26-1.46 (br, 8H, thienyl-$CH_2$(C$\boldsymbol{H}_2$)$_4$$CH_3$), 2.72-2.81 (br, 2H, thienyl-C$\boldsymbol{H}_2$), 4.27-4.42 (br, 4H, OC$\boldsymbol{H}_2$C$\boldsymbol{H}_2$O), 7.00-7.12 (br, 1H, thienyl-$\boldsymbol{H}$). Anal. Calcd. for $C_{16}H_{18}O_2S_2$: C, 62.71; H, 5.92; S, 20.93. Found: C, 60.99; H, 5.90; S, 19.55.

**Poly(3,4-ethylenedioxythiophene) (PEDOT) prepared by electrolytic polymerization.** **PEDOT** film was prepared by cycling a potential between −1.5 and 0.9 V *vs.* Ag/Ag$^+$ at sweep rate of 20 mV sec$^{-1}$ in an acetonitrile solution containing TEAP (0.1 mol dm$^{-3}$) and **EDOT** (0.01 mol dm$^{-3}$). After polymerization, the polymer film was dedoped at 1.5 V *vs.* Ag/Ag$^+$. Since the resulting polymer was insoluble in common organic solvents, the polymer was used as prepared.

### Conductivity measurements

*In-situ* conductivity measurements were made in acetonitrile solution of TEAP (0.1 mol dm$^{-3}$) by the two-probe method.[9] A solution of each polymer in *o*-dichlorobenzene (15 mg mL$^{-1}$) was spin-coated (1000 rpm for 1 min) on a micro-array Pt electrode (ALS Co., Ltd., 65 lines, separation distance = 5 µm, total width = 260 mm) or a two-band Pt electrode (homemade, separation distance = 100 µm, width = 7 mm). Film thickness of the polymer was found to be around 50 nm by a 3D laser microscope (Keyence Corp., VK-9700). The polymer film on the micro-array or two-band Pt electrode was electrochemically oxidized with Pt wire and Ag/$AgClO_4$ (0.01 mol dm$^{-3}$ in acetonitrile) as counter and reference electrodes, respectively. The amounts of charges during electrochemical oxidation (doping) and reduction (dedoping) of the polymer film were measured with a coulometer by stepping a potential from –0.5 V vs. Ag/Ag$^+$ to a desired potential and back to –0.5 V vs. Ag/Ag$^+$, respectively. Doping levels, defined as the number of charges per thiophene ring, were estimated from the doping/dedoping charges, a weight of a polymer film, and a molecular weight of the repeating unit. Apparent mobilities ($\mu$) of charge carriers in the polymer film at various doping levels (electrode potentials) were calculated from the equation, $\mu = \sigma / n\, e$, where $\sigma$, $n$, and $e$ denote the electrical conductivity at an electrode potential, the density of charge carriers estimated from the doping/dedoping charges, and the elementary electric charge, respectively.

## Results and Discussion

### Synthesis of Monomers

Scheme 1 shows a synthetic route of monomers. **ET** and **TT** were synthesized by the Stille coupling reaction of 2-bromo-3-hexylthiophene with 2-(tributylstannyl)-3,4-ethylenedioxythiophene and 2-(tributylstannyl)-4-hexylthiophene prepared from **EDOT** and **3HT**, respectively. Bromination of **ET** and **TT** with 2 eq. of NBS gave **DBrET** and **DBrTT**. The yield of the latter is reasonable (81 %), while that of the former is not so high (56 %). The plausible reason of the low yield is that **ET** or **DBrET** will decompose by $Br_2$ formed during the reaction.[10] A Grignard reagent, 5-(3,4-ethylenedioxy-3´-hexyl-2,2´-bithienyl)magnesium bromide, was predominantly obtained by the metal-halogen exchange reaction between **DBrET** and 1 eq. of methylmagnesium bromide, which was confirmed by $^1$H NMR spectroscopy. The obtained Grignard reagent was decomposed by water to give **BrET**.

### Polycondensation

In the previous paper, we have found that the polycondensation reaction using direct C-H arylation reaction was the effective way to obtain the **EDOT**-containing polythiophene with moderately high molecular weight.[6b] Using this method, **pETT** and **pET-C** were obtained by the copolymerization of **EDOT** and **DBrTT**, and by the homopolymerization of **BrET**, respectively. It was found that the utilization of microwave heating gave the polymers with higher molecular weight.

Polythiophene with the same composition ratio of **EDOT** as that of **pET-C** and the different regioregularity (**pET-S**) was synthesized by polycondensation using the Stille coupling reaction between **BSnET** and **DBrET**, although the direct C-H arylation polymerization of **ET** and **DBrET** could not proceed.

The molecular weights of polymers were estimated by GPC and the results are summarized in Table 1. It was found that the molecular weights of **pET-C** and **pET-S** are almost the same although the polycondensation methods are different, whereas that of **pETT** is higher by one-order magnitude than those of **pET-C** and **pET-S**. This may be caused by the difference in solubility between the polymers.

Fig. 2 shows the $^1$H NMR spectra of the aromatic protons in the polymers. While **pET-C** showed only one broad peak at 7.10 ppm, **pET-S** showed two peaks at 7.10 and 7.04 ppm, whose integral ratio is around 1 : 1. These peaks at 7.10 and 7.04 ppm can be ascribed to the protons in the two kinds of repeat structures, "-***ET-ET***-" and "-***ET-TE***-" (***E***: **EDOT** unit, ***T***: **3HT** unit), H$^a$ and H$^b$ as shown in Fig. 3, respectively, whose characterizations were supported by the estimation of the chemical shifts of $^1$H NMR spectra for two types of tetramers of **ET** with "-***ET-ET***-" and "-***ET-TE***-" structures as model compounds using the density functional theory (DFT) calculation with the Gaussian 09 software at the Becke three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional (B3LYP) with a polarized 6-31G(d) basis set.[11] These results suggest that the regioregularity of **pET-C** is almost 100 %, while that of **pET-S** is around 50 %. **pETT** exhibited two broad peaks at 7.01 and 7.09 ppm, which are ascribed to two types of protons, H$^c$ and H$^d$ as shown in Fig. 3(c). Although it is possible that **pETT** contains two different regiostructures as shown in Fig. 3(c), these difference could not be distinguished from the spectrum. Reflecting that the molecular weights of **pET-C** and **pET-S** are lower than that of **pETT**, aromatic protons of the terminal groups were clearly observed at 7.08 ppm for **pET-C** and at 7.08 and 7.02 for **pET-S**, respectively. The integral ratio of protons in the main chain and the terminal group did not contradict the molecular weights estimated by GPC.

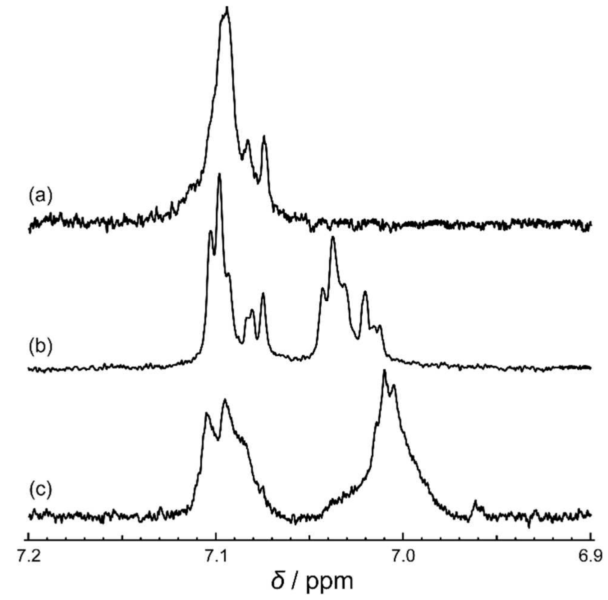


**Fig. 2** $^1$H NMR spectra of (a) **pET-C**, (b) **pET-S**, and (c) **pETT**.

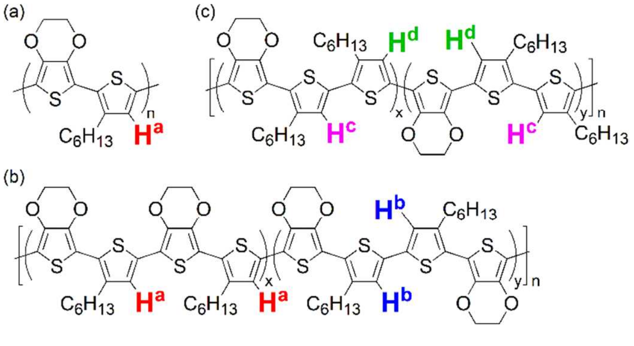


**Fig. 3** Assignments of aromatic protons in (a) **pET-C**, (b) **pET-S**, and (c) **pETT**.

### Optical Properties

The electronic absorption spectra of the polymer films are depicted in Fig. 4, and the spectroscopic data of the polymers in the film state and in *o*-dichlorobenzene are included in Table 1. The spectra of the polymer films exhibit a single absorption band due to π-π* transition at 454, 487, 512, 515, and 597 nm for **P3HT**, **pETT**, **pET-C**, **pET-S**, and **PEDOT**, respectively. As is clearly seen in the inset of Fig. 4, the peak wavelength is correlated well with the composition ratio of **EDOT** in a repeat unit of the polymer ($R_{\mathrm{EDOT}}$). We note also that all the film spectra show a broadening compared to the solution spectra (Fig. 1S, ESI†), suggesting that the polymers are somewhat π-stacked in the film state.[12] Furthermore, in comparison with the solution spectra, the film absorption peak of **pET-C** is red-shifted by 28 nm, which is greater than those of **P3HT** (14 nm), **pETT** (0 nm) and **pET-S** (19 nm). This implies that the **pET-C** film is most tightly packed among the four polymers, reflecting the highest regioregularity of **pET-C**.

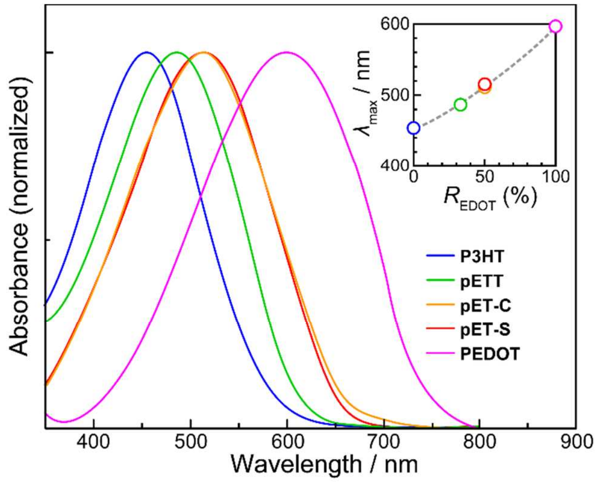


**Fig. 4** Electronic absorption spectra of polymer films (inset depicts correlation between $R_{EDOT}$ and absorption maximum ($\lambda_{max}$)).

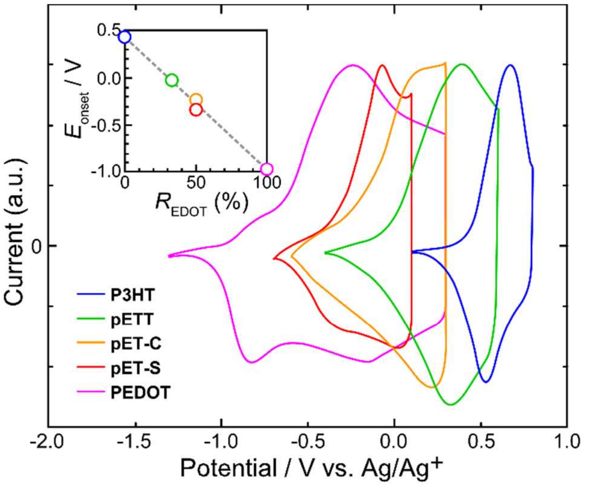


**Fig. 5** Cyclic voltammograms of polymer films (inset depicts correlation between $R_{EDOT}$ and $E_{ox}$).

**Table 1** Characterization of polymers

| Polymer | $R_{EDOT}$ (%) | Molecular weight | | | Absorption maximum / nm | | $E_{ox}$ / V *vs.* Ag/Ag$^+$ |
|---|---|---|---|---|---|---|---|
| | | $M_n$ / kg mol$^{-1}$ | $M_w$ / kg mol$^{-1}$ | $M_w$ / $M_n$ | $\lambda_{max}^{sol}$ a) | $\lambda_{max}^{film}$ b) | |
| **PEDOT** | 100 | - c) | - c) | - c) | - c) | 597 | -0.99 |
| **pET-S** | 50 | 3.9 | 6.4 | 1.64 | 496 | 515 | -0.34 |
| **pET-C** | 50 | 4.2 | 7.3 | 1.75 | 485 | 512 | -0.23 |
| **pETT** | 33 | 16.9 | 29.4 | 1.74 | 487 | 487 | -0.03 |
| **P3HT** | 0 | 34.8 | 168 | 4.83 | 441 | 454 | 0.43 |

a) absorption in *o*-dichlorobenzene. b) absorption of films. c) unmeasurable due to low solubility of **PEDOT** in solvents.

## Electrochemical Properties

Cyclic voltammetry of the polymer films was carried out (Fig. 5) and the onset potentials of anodic oxidation ($E_{ox}$s) are summarized in Table 1. It is known that the alkoxy group introduced at the $\beta$-position of thiophene ring can stabilize the positive charge formed by the anodic oxidation reaction.[13] Thus, with increasing $R_{EDOT}$, the $E_{ox}$s are shifted to the negative direction reflecting the enhanced electron-donating natures (inset of Fig. 5).

## Spectroelectrochemical Properties

To characterize the redox states of polymers, spectroelectrochemistry was investigated. Fig. 6 depicts the difference spectra of **pETT** film, which were obtained by subtracting the spectrum of the neutral polymer as reference from the spectra of polymers electrochemically oxidized at different electrode potentials. When the **pETT** film was oxidized at 0 V *vs.* Ag/Ag$^+$, the intensity of the absorption band at ca. 500 nm was decreased and two absorption bands newly appeared at around 800 and 1600 nm, and their intensities were gradually increased by increasing the potential up to 0.3 V. These new absorption bands were ascribable to the one-electron oxidized species (polaron and/or π-dimer). On further oxidation of **pETT**, one broad absorption band appeared at around 1500 nm, which can be ascribed to the two-electron oxidized species (bipolaron). Other polymers showed spectra similar to those of **pETT** (Fig. 2S, ESI†), except that the one-electron oxidized species began to appear at –1.2, –0.4 and 0.275 V for **PEDOT**, **pET-S**, and **P3HT**,[14] respectively, reflecting their higher electron-donating nature.

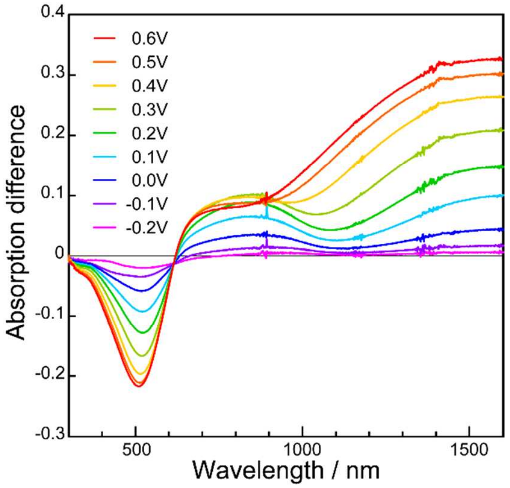


**Fig. 6** Spectroelectrochemistry of **pETT** film.

### Electrical Properties

Doping levels and electrical conductivities of the polymer films were measured by using the *in-situ* electrochemical technique[6,7] in order to investigate the electrical properties of the polymers. Fig. 7a depicts semilogarithmic plots of doping level against electrode potential for the polymer films. In concert with the electrochemical oxidation of the films, the doping levels gradually increased and finally reached around 20 ~ 30 %, suggesting that one positive charge is formed on every three to five thiophene rings. The maximum value of the doping levels tends to increase with increasing $R_{\mathrm{EDOT}}$, reflecting the stabilization of the positive charge introduced by the electrochemical oxidation due to the electron-donating ethylenedioxy group in **EDOT** unit. The plot of log(doping level) *vs.* electrode potential fits a straight line in a low doping region, and its slope values are around 190, 310, 180 and 289, and 60 mV decade$^{-1}$ for **PEDOT**, **pET-C**, **pET-S**, **pETT**, and **P3HT**,[14,15] respectively. The slope values except for **P3HT** are much larger than 60 mV decade$^{-1}$ expected for a common one-electron transfer process at room temperature. We have already clarified that the slope value is a measure of distribution of effective π-conjugation length in conjugated oligomers and polymers, and wider distribution leads to a larger slope value.[9b,d,16] We also note that the slope value of **pET-C** is larger than that of **pET-S**. This can be explained by more widely distributed conjugation length because of the higher polydispersity ($M_{\mathrm{w}}/M_{\mathrm{n}}$) of **pET-C**.

The electrical conductivities of polymers increased with increasing the electrode potentials, and showed maximum values of 320, 16, 2.4, 1.4, and 1.0 S cm$^{-1}$ for **PEDOT**, **pET-S**, **pET-C**, **pETT**, and **P3HT**,[14,15] respectively (Fig. 7b). This result suggests that the conductivities of doped polymer films tend to increase with $R_{\mathrm{EDOT}}$. Although $R_{\mathrm{EDOT}}$s in **pET-S** and **pET-C** are the same, the maximum conductivity of **pET-S** is 7 times higher than that of **pET-C**. We have already found that the electrical conductivities are affected by the disordered structure of π-conjugated polymers and oligomers.[14,15,16] In view of this, more disordered structure of **pET-C** may lead to the reduction of the electrical conductivity.

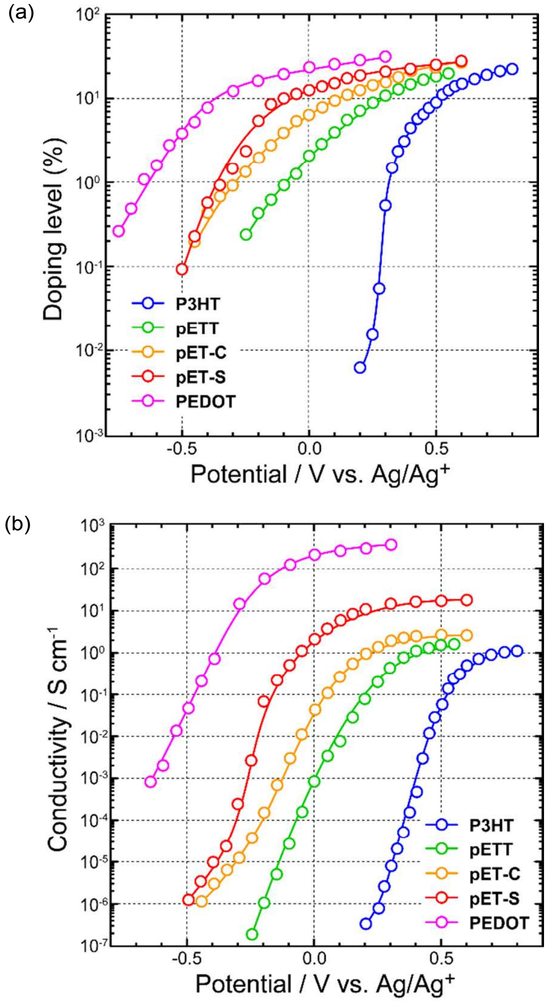


**Fig. 7** (a) Doping levels and (b) electrical conductivities of polymer films as a function of electrode potential, measured in acetonitrile containing TEAP (0.1 mol dm$^{-3}$). Plots for **P3HT** are reproduced from Figs. 2 and 3 in Ref. 15.

To further discuss the charge transport mechanisms of the polymer films, apparent mobilities of charge carriers were estimated by combining the data of doping level and conductivity shown in Fig. 7. The mobilities are plotted in Fig. 8 as a function of doping level. At doping levels as low as or below 1 %, where the interchain hopping transport of monocation radicals (polarons) is a principal route of a charge transport, the mobilities for the **P3HT**, **pET-C**, and **pET-S** films are constant at around 10$^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$.[17] The mobility plots showed maxima at doping levels of 10 – 15 %, where two-electron oxidized (diamagnetic) species predominantly prevail and the intrachain charge transport is a main conduction mechanism.[17] The maximum mobility values ($\mu_{\mathrm{max}}$) are plotted against $R_{\mathrm{EDOT}}$ (Fig. 8, inset). It was found that the $\mu_{\mathrm{max}}$ increased with increasing $R_{\mathrm{EDOT}}$. A plausible reason may be explained by the electron donating nature of **EDOT** unit in the polymer: it becomes difficult for the positive charge to move along the polymer chains because of a Coulombic repulsion, but the degree of the Coulombic repulsion will become smaller when the electron-donating alkoxy groups are introduced. Thus, the mobilities become higher with the increase of $R_{\mathrm{EDOT}}$. It is worth noting here that the $\mu_{\mathrm{max}}$ values for the two types of polymers having the same **ET** repeat unit, i.e., the same $R_{\mathrm{EDOT}}$ values, differ much from each other: 0.1 and 0.02 $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ for **pET-S** and **pET-C**, respectively. The $\mu_{\mathrm{max}}$ value for **pET-S** larger than that for **pET-C** appears to be strange when we remember that the former has a regioregularity lower than the latter. According to our previous study, however, the regioregular nature of the polymer film affects mainly the mobilities of charge carriers at low doping levels where the hopping transport of polarons is the main charge transport mechanism. In view of this, the relatively low $\mu_{\mathrm{max}}$ value for **pET-C** may be ascribed to the disordered structure of the **pET-C** film inferred from its greater $M_{\mathrm{w}}/M_{\mathrm{n}}$ value, which is supported by the large slope value for **pET-C** compared with that for **pET-S**, as shown in Fig. 7a.

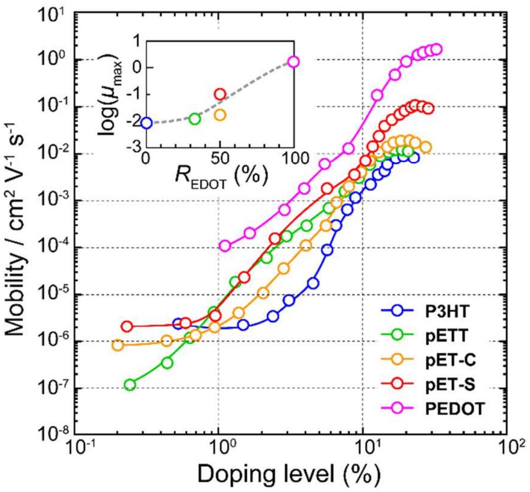


**Fig. 8** Apparent mobilities of charge carriers in polymer films plotted against doping level (inset depicts correlation between $R_{\mathrm{EDOT}}$ and $\mu_{\mathrm{max}}$). Plot for **P3HT** is reproduced from Fig. 4 in Ref. 15.

## Conclusions

A new family of polythiophenes containing **EDOT** with different composition ratios were synthesized by polycondensation reactions of the corresponding monomers, and their optical, electrochemical, and electrical properties were investigated in relation to the polymer structures. The polymers showed a red-shift of the absorption band and a negative shift of oxidation potential as the ratio of **EDOT** unit in the polymers increased. It was found that the electrical conductivities of polymers could to be successfully controlled by the **EDOT** composition ratio, the regioregularity, and the doping level. The highest electrical conductivities of electrochemically-doped polymers were found to increase with increasing the ratio of **EDOT** in the polymers.

## Acknowledgements

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## *Graphical Abstract*

# Synthesis of EDOT-containing polythiophenes and their properties in relation to composition ratio of EDOT

**Ichiro Imae*, Ryo Ogino, Yoshiaki Tsuboi, Tatsunari Goto, Kenji Komaguchi, and Yutaka Harima**

Polythiophenes composed of 3,4-ethylenedioxythiophene (EDOT) and 3-hexylthiophene with different composition ratios of EDOT are synthesized and their optical, electrochemical and electrical properties are investigated in terms of the EDOT composition ratio.