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New luminescent 1,2,4-triazole/thiophene alternating copolymers: Synthesis, characterization, and optical properties

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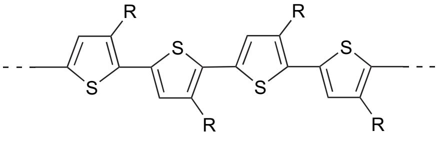
Abstract

New five-membered ring heteroaromatic copolymers composed of 1-alkyl-1*H*-1,2,4-triazole and thiophene or bithiophene units were prepared by palladium-catalyzed polycondensation. The copolymers were soluble in organic solvents, and showed number-average molecular weights of 6200–23,700 in the GPC analysis. NMR spectroscopy revealed that the copolymers had a regio-random molecular structure. The optical properties, as well as the electrochemical properties, of the copolymers in solutions and films were determined. The polymers exhibited blue photoluminescence (PL) with an emission peak at about 420 nm and quantum yields of 36–43% in solutions, and the PL peak shifted to 470–480 nm in films. X-ray diffraction data suggested that the polymers formed a π-stacked structure in solid state.

Keywords: π-Conjugated polymer; 1,2,4-Triazole; Optical properties

1. Introduction

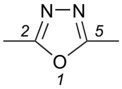
The design and synthesis of new π-conjugated polymers with high potential for electronic and optoelectronic applications have received considerable attention [1–4]. Among π-conjugated polymers, those composed of five-membered rings with alkyl side chains such as head-to-tail type poly(3-alkylthiophene)s (HT-P3RThs) are a class of materials that have shown interesting optical and electronic properties [5,6].



HT-P3RTh

Recently, one research interest has been devoted to the modification of the electronic properties of π-conjugated polymers by the introduction of electron-deficient *N*-containing heteroaromatic rings (so-called azaheterocycles) [7–14].

Low-molecular-weight compounds consisting of 1,3,4-oxadiazole [15] or 1,2,4-triazole [16,17] unit serve as a good electron-transporting and hole-blocking material in organic light-emitting diodes (OLEDs), because of the electron-accepting capabilities of the unit associated with an electron-withdrawing imine −C=N− group in the unit [18,19]. In this context, many π-conjugated polymers containing a 1,3,4-oxadiazole unit have been reported [7,20–24].



1,3,4-Oxadiazole-2,5-diyl

However, solution-processable polymers with a 1,2,4-triazole moiety have received much less attention (Chart 1) [12,25,26].

Previously, we reported the preparation of π-conjugated 4-alkyl-4*H*-1,2,4-triazole/thiophene (4RTaz/Th) alternating copolymers (Eq. (1)) [12].

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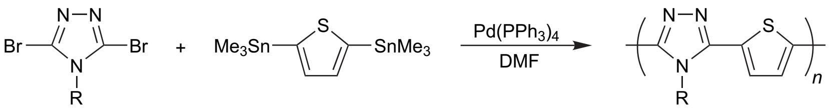


4RTaz/Th copolymer

(1)

Chart 1. Two kinds of 1,2,4-triazole repeating unit.

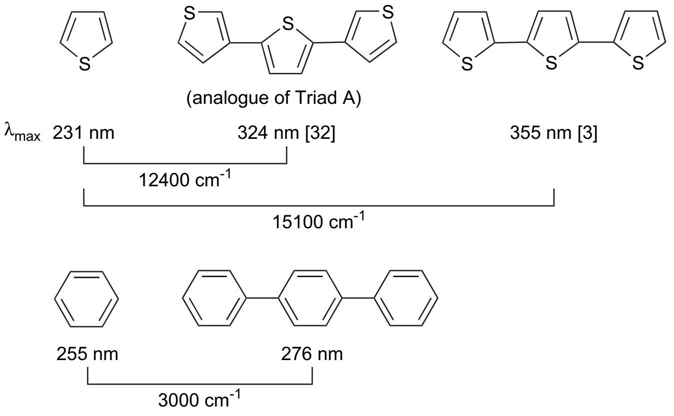
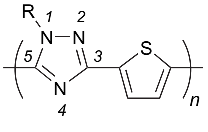


Chart 2. Degree of shift of UV–vis peak induced by expansion of π-electron system.

However, the influence of the 1,2,4-triazole unit on the optical and electrochemical properties of these polymers has not been sufficiently studied.

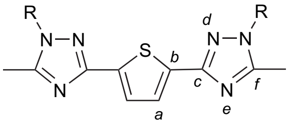
To obtain further information on the structure–property relationships of the above-mentioned polymers, we have prepared a new series of 1-alkyl-1*H*-1,2,4-triazole/thiophene (1RTaz/Th) alternating copolymers by introducing an alkyl substituent at the 1-position of the 1*H*-1,2,4-triazole unit, instead of at the 4-position of the 4*H*-1,2,4-triazole.



1RTaz/Th copolymer

Herein, we report the results of the preparation of new polymers and optical and electrochemical properties of these polymers. 1RTaz/Th copolymers had a higher solubility in organic solvents than the aforementioned 4RTaz/Th copolymers, and gave a higher quantum yield in photoluminescence (PL) than 4RTaz/Th copolymers.

1RTaz/Th copolymers have a relatively short π-conjugation system, e.g., an 8π-electron system in the following triad.



Triad-A

The π-conjugation system is formally broken by two consecutive single bonds (e.g., b–c and c–e bonds), and is considered to have a feature of the cross-π-conjugation system [27–31], which may enable a partial expansion of the π-electron system. Actually, UV–vis data of the following thiophene trimer with a similar π-electron system suggest the expansion of the π-electron system to some extent [32], although the degree of expansion of the π-electron system is smaller than the degree of expansion of the π-electron system in fully π-conjugated 2,2′:5′,2″-terthiophene (Chart 2).

The chemical and physical properties of oligomeric and polymeric systems with a cross-conjugated π-framework are a subject of recent interest [27–31]. Because of the moderate (or a smaller degree of) expansion of the π-conjugation system and the electron-deficient nature of the 1-alkyl-1*H*-1,2,4-triazole-3,5-diyl (1RTaz) unit, the 1RTaz unit is regarded as a new interesting building block for tuning the electronic and optical functions of π-conjugated polymers. Polymers with a moderately expanded π-conjugation system may be advantageous for emission of blue light. However, such a 1RTaz-containing functional polymer has no precedent to our knowledge. 1-Alkyl-1*H*-1,2,4-triazole derivatives have recently been attracting interest in energy [33,34], similar to alkylimidazole derivatives.

2. Experimental

2.1. Synthesis of monomers

2.1.1. Synthesis of 3,5-dibromo-1H-1,2,4-triazole (**1**)

A mixture of 1,2,4-triazole (6.91 g, 100 mmol), distilled water (80 mL), and chloroform (40 mL) in a flask was stirred in an ice bath. Bromine (33.6 g, 210 mmol) and an aqueous solution of sodium hydroxide (14.0 g, 350 mmol) were simultaneously added slowly, and the mixture was stirred overnight at room temperature. Then, it was acidified with concentrated hydrochloric acid (ca. 10 mL) to obtain a white precipitate. The precipitate was separated by filtration, washed with water (twice), and dried in vacuum to give a white solid of **1** (yield = 19.5 g, 86%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 15.2 (br). IR (KBr, cm^{-1}): 3104, 2901, 2741, 1609, 1517, 1427, 1342, 1270, 1252, 1129, 1014, 985, 832, 702, 655. Anal. Calcd for $C_2HBr_2N_3$: C, 10.59%; H, 0.44%; Br, 70.44%; N, 18.52%. Found: C, 10.60%; H, 0.35%; Br, 70.42%; N, 18.48%.

2.1.2. Synthesis of 3,5-dibromo-1-butyl-1H-1,2,4-triazole (**2a**)

To a stirred mixture of **1** (1.13 g, 5.0 mmol) and K_2CO_3 (1.11 g, 8.0 mmol) in DMF (40 mL) was slowly added 1-bromobutane (0.75 g, 5.5 mmol) at 70 °C. The mixture was stirred for 24 h at 70 °C, cooled to room temperature, and then poured into a large amount of water. The product was extracted with chloroform (three times), washed with water, and dried over anhydrous sodium sulfate. After filtration and evaporation, the product was dried under vacuum with heating to give a light-yellow oil of **2a** (yield = 1.16 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.12 (t, $J = 7.2$ Hz, 2H), 1.83 (m, 2H), 1.34 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H). IR (NaCl, cm^{-1}): 2960, 2933, 2873, 1460, 1435, 1419, 1352, 1308, 1261, 1135, 1051, 988, 833, 753, 701. Anal. Calcd for $C_6H_9Br_2N_3$: C, 25.47%; H, 3.21%; Br, 56.48%; N, 14.85%. Found: C, 25.74%; H, 3.10%; Br, 56.73%; N, 15.11%.

The monomers **2b**–**2e** were prepared analogously. The spectroscopic and analytical data of the compounds are described below.

2.1.3. 3,5-Dibromo-1-hexyl-1H-1,2,4-triazole (**2b**)

Yield = 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.11 (t, $J = 7.2$ Hz, 2H), 1.84 (m, 2H), 1.32–1.23 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H). IR (NaCl, cm^{-1}): 2955, 2930, 2858, 1461, 1434, 1419, 1377, 1360, 1261, 1177, 1137, 1058, 988, 727, 701. Anal. Calcd for $C_8H_{13}Br_2N_3$: C, 30.89%; H, 4.21%; Br, 51.38%; N, 13.51%. Found: C, 31.17%; H, 4.10%; Br, 51.07%; N, 13.60%.

2.1.4. 3,5-Dibromo-1-nonyl-1H-1,2,4-triazole (**2c**)

Yield = 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.10 (t, $J = 6.8$ Hz, 2H), 1.84 (m, 2H), 1.30–1.25 (m, 12H), 0.87 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.83, 129.12, 50.26, 31.83, 29.34, 29.29, 29.18, 28.98, 26.27, 22.68, 14.14. IR (NaCl, cm^{-1}): 2953, 2925, 2855, 1461, 1435, 1418, 1376, 1360, 1261, 1128, 1052, 988, 722, 701. Anal. Calcd for $C_{11}H_{19}Br_2N_3$: C, 37.42%; H, 5.42%; Br, 45.26%; N, 11.90%. Found: C, 37.63%; H, 5.41%; Br, 45.44%; N, 11.87%.

2.1.5. 3,5-Dibromo-1-dodecyl-1H-1,2,4-triazole (**2d**)

Yield = 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.10 (t, $J = 7.2$ Hz, 2H), 1.84 (m, 2H), 1.30–1.24 (m, 18H), 0.86 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.76, 129.05, 50.20, 31.86, 29.55, 29.45, 29.29, 29.21, 28.92, 26.21, 22.65, 14.08. IR (NaCl, cm^{-1}): 2925, 2853, 1461, 1435, 1418, 1376, 1354, 1261, 1129, 1052, 987, 722, 701. Anal. Calcd for $C_{14}H_{25}Br_2N_3$: C, 42.55%; H, 6.38%; Br, 40.44%; N, 10.63%. Found: C, 42.87%; H, 6.38%; Br, 40.14%; N, 10.54%.

2.1.6. 3,5-Dibromo-1-(2-ethylhexyl)-1H-1,2,4-triazole (**2e**)

Yield = 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.99 (d, $J = 6.8$ Hz, 2H), 1.97 (m, 1H), 1.35–1.21 (m, 8H), 0.91–0.86 (m, 6H). IR (NaCl, cm^{-1}): 2960, 2930, 2860, 1459, 1435, 1420, 1382, 1360, 1260, 1126, 1055, 988, 754, 727, 701. Anal. Calcd for $C_{10}H_{17}Br_2N_3$: C, 35.42%; H, 5.05%; Br, 47.13%; N, 12.39%. Found: C, 35.72%; H, 5.13%; Br, 48.12%; N, 12.52%.

2.2. Polymerization

The polymers **3a**–**3e** and **4** were prepared via a palladium-catalyzed Stille-coupling reaction. A typical procedure for polycondensation is given below. The obtained polymers contained both an agglomerating fraction and a powdery fraction, and they gave essentially the same NMR, IR, and UV–vis data.

2.2.1. Synthesis of **3a**

To a solution of 2,5-bis(trimethylstannyl)thiophene (1230 mg, 3.00 mmol) and **2a** (849 mg, 3.00 mmol) in dry DMF (25 mL) was added $Pd(PPh_3)_4$ (170 mg, 0.15 mmol) as the catalyst. After being stirred for 48 h at 90 °C under N_2, the reaction mixture was added to an aqueous solution (ca. 5%) of potassium fluoride. The precipitated polymer was separated by filtration and washed with aqueous ammonia, water, and methanol (twice) in this order. Drying under vacuum gave a yellow powder of **3a** (yield = 0.51 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76–7.50 (m, 2H), 4.41 (br, 2H), 1.98 (br, 2H), 1.47 (br, 2H), 0.99 (br, 3H). IR (KBr, cm^{-1}): 3078, 2957, 2931, 2871, 1564, 1468, 1359, 1285, 1204, 1169, 1113, 985, 930, 818, 745. Anal. Calcd for $(C_{10}H_{11}N_3S\cdot 0.3H_2O)_n$: C, 57.01%; H, 5.55%; N, 19.94%; S, 15.22%. Found: C, 56.86%; H, 5.38%; N, 19.57%; S, 15.18%; Br, 0%. Number-average molecular weight (M_n) = 16,600; M_w/M_n (M_w = weight-average molecular weight) = 3.1.

2.2.2. Compound **3b**

Yield = 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76–7.50 (m, 2H), 4.40 (br, 2H), 1.98 (br, 2H), 1.37–1.18 (br, 6H), 0.89 (br, 3H). IR (KBr, cm^{-1}): 3079, 2953, 2926, 2855, 1566, 1467, 1359, 1285, 1216, 1161, 1100, 988, 929, 818, 745. Anal. Calcd for $(C_{12}H_{15}N_3S\cdot 0.3H_2O)_n$: C, 60.37%; H, 6.50%; N, 17.60%; S, 13.43%. Found: C, 60.69%; H, 6.39%; N, 17.16%; S, 12.92%; Br, 0%. $M_n = 19{,}200$; $M_w/M_n = 1.4$.

2.2.3. Compound **3c**

Yield = 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77–7.50 (m, 2H), 4.39 (br, 2H), 1.99 (br, 2H), 1.42–1.27 (br, 12H), 0.85 (br, 3H). IR (KBr, cm^{-1}): 3089, 2924, 2853, 1568, 1468, 1361, 1286, 1205, 1101, 986, 930, 819, 745. Anal. Calcd for $(C_{15}H_{21}N_3S\cdot 0.7H_2O)_n$: C, 62.55%; H, 7.84%; N, 14.59%; S, 11.13%. Calcd for $BrC_{11}H_{19}N_3(C_{15}H_{21}N_3S\cdot 0.5H_2O)_{33}Br$: C, 62.40%; H, 7.71%; N, 14.67%; S, 10.87; Br, 1.64%. $M_n = 9440$. Found: C, 62.47%; H, 7.21%; N, 14.48%; S, 10.84%; Br, 2.33%. $M_n = 9600$; $M_w/M_n = 1.8$.

2.2.4. Compound **3d**

Yield = 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78–7.50 (m, 2H), 4.39 (br, 2H), 1.99 (br, 2H), 1.42–1.25 (br, 18H), 0.85 (br, 3H). IR (KBr, cm^{-1}): 3093, 2923, 2851, 1562, 1467, 1359, 1289, 1204, 1101, 987, 930, 818, 745. Anal. Calcd for $(C_{18}H_{27}N_3S\cdot 0.6H_2O)_n$: C, 65.85%; H, 8.66%; N, 12.80%; S, 9.77%. Calcd for $BrC_{14}H_{25}N_3(C_{18}H_{27}N_3S\cdot 0.3H_2O)_{19}Br$: C, 65.48%; H, 8.48%; N, 12.87%; S, 9.33%; Br, 2.45%. $M_n = 6430$. Found: C, 65.66%; H, 7.95%; N, 12.62%; S, 9.72%; Br, 2.28%. $M_n = 6200$; $M_w/M_n = 1.8$.

2.2.5. Compound **3e**

Yield = 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76–7.50 (m, 2H), 4.29 (br, 2H), 2.12 (br, 1H), 1.39–1.29 (br, 8H), 0.87 (br, 6H). IR (KBr, cm^{-1}): 3077, 2957, 2927, 2858, 1567, 1466, 1398, 1361, 1285, 1204, 1164, 1096, 1045, 977, 930, 905, 746. Anal. Calcd for $(C_{14}H_{19}N_3S\cdot0.5H_2O)_n$: C, 62.19%; H, 7.46%; N, 15.54%; S, 11.86%. Calcd for $BrC_{10}H_{17}N_3(C_{14}H_{19}N_3S\cdot0.3H_2O)_{46}Br$: C, 62.28%; H, 7.34%; N, 15.66%; S, 11.70%; Br, 1.27%. $M_n = 12{,}360$. Found: C, 62.14%; H, 6.88%; N, 15.00%; S, 11.36%; Br, 1.11%. $M_n = 12{,}500$; $M_w/M_n = 2.7$.

2.2.6. Compound **4**

5,5′-Bis(trimethylstannyl)-2,2′-bithiophene was used instead of 2,5-bis(trimethylstannyl)thiophene. Yield = 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (br, 1H), 7.49 (br, 1H), 7.40–7.20 (m, 2H), 4.29 (br, 2H), 2.12 (br, 1H), 1.50–1.20 (br, 8H), 1.00–0.80 (m, 6H). FT-IR (KBr, cm^{-1}): 3071, 2957, 2927, 2858, 1749, 1557, 1472, 1431, 1403, 1360, 1217, 1198, 1164, 1097, 1055, 973, 943, 875, 800, 746. Anal. Calcd for $(C_{18}H_{21}N_3S_2)_n$: C, 62.94%; H, 6.16%; N, 12.23%; S, 18.67%. Found: C, 63.21%; H, 6.27%; N, 12.09%; S, 18.64%; Br, 0%. $M_n = 23{,}700$; $M_w/M_n = 6.0$.

2.3. Measurements

NMR and IR spectra were recorded on a JEOL EX-400 spectrometer and a JASCO FT/IR-460 Plus spectrometer, respectively. Elemental analyses were carried out with an LECO CHNS-932 analyzer and a Yanaco YS-10 SX-Elements microanalyzer. GPC traces were obtained with a Shimadzu LC-9A chromatograph equipped with Shodex 80M columns (eluent = $CHCl_3$; polystyrene standards). Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 analyzer. UV–vis absorption and photoluminescence spectra were measured with a Shimadzu UV-3100 spectrometer and a Hitachi F-4010 spectrophotometer, respectively. The cyclic voltammetry of films of polymers cast on a Pt plate was performed in a CH_3CN solution of $[(C_2H_5)_4N]BF_4$ (0.10 M) with a Pt counter electrode and an Ag^+/Ag reference electrode, using a Toyo Technica Solartron SI 1287 electrochemical interface.

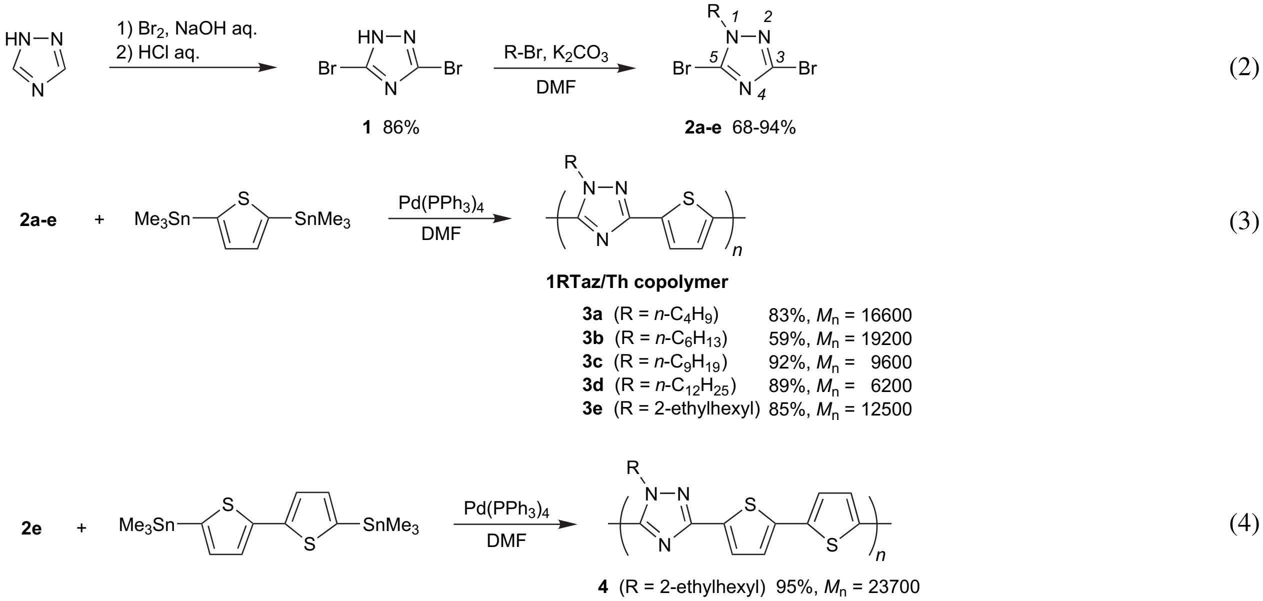
The electroluminescence (EL) spectra of the polymers were measured at Sumitomo Chemical Co., Ltd. The EL devices used were fabricated as follows. A hole-injection layer of poly(3,4-ethylenedioxythiophene) doped with sulfonated polystyrene (PEDOT–PSS) was spin-coated on top of an ITO glass substrate using a dispersion of PEDOT–PSS in water, and dried at 200 °C for 10 min. A 1RTaz/Th polymer layer was spin-coated on the hole-injection layer from a toluene solution of the polymer. Finally, a metal cathode (Ca) was deposited onto the polymer layer. The current–voltage characteristics and luminance of the devices were measured with a Photo Research SpectraScan PR650 meter and a Keithley 2000-type multimeter.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of the dibromo monomers (**2a**–**2e**) and their corresponding polymers is outlined in Scheme 1. Although 1*H*-1,2,4-triazole is in tautomeric equilibrium with 4*H*-1,2,4-triazole [34], no such tautomerism with an alkyl migration between the 1- and 4-position was observed with the alkylated dibromo monomers **2a**–**2e**.

Fig. 1 shows comparison of the ^{1}H and ^{13}C NMR spectra of 3,5-dibromo-4-dodecyl-4*H*-1,2,4-triazole shown in Eq. (1) in Section 1 and the corresponding **2d**. As shown in Fig. 1c, the symmetrical monomer, 3,5-dibromo-4-dodecyl-4*H*-1,2,4-triazole gives only one aromatic ^{13}C NMR signal at δ 130.2. On the other hand, the ^{13}C NMR spectrum of **2d** exhibits two aromatic signals at δ 139.8 and 129.1, as shown in



Scheme 1. Synthetic route of 1-alkyl-1*H*-1,2,4-triazole-based copolymers.

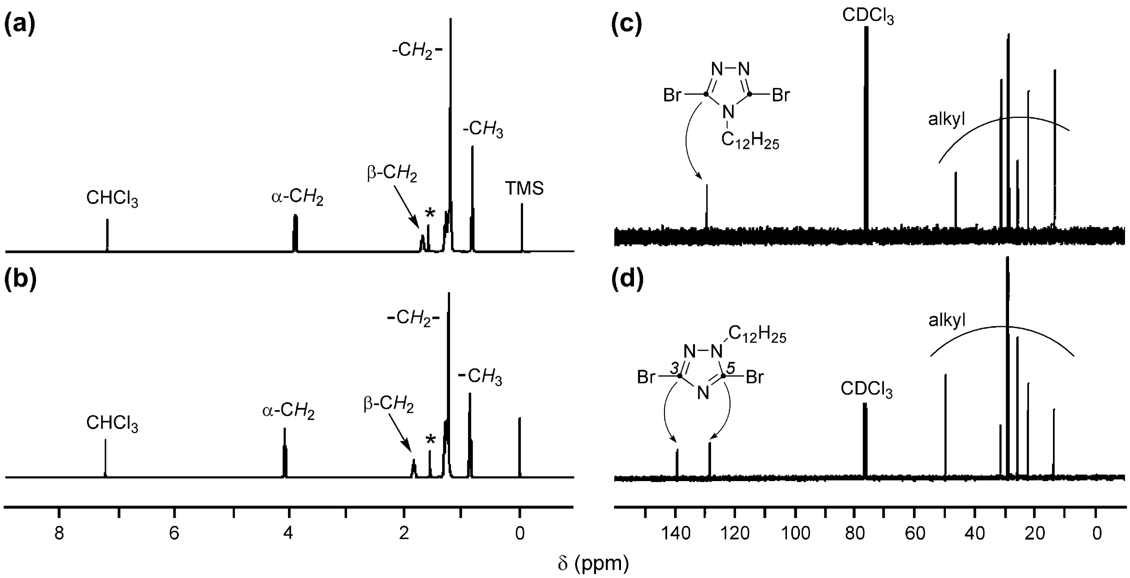


Fig. 1. ^{1}H NMR spectra of (a) 3,5-dibromo-4-dodecyl-4*H*-1,2,4-triazole (cf. Eq. (1)) and (b) **2d**; ^{13}C NMR spectra of (c) 3,5-dibromo-4-dodecyl-4*H*-1,2,4-triazole and (d) **2d** in $CDCl_3$. The peak with * is due to H_2O.

Fig. 1d. The ^{1}H NMR spectrum of **2d** was unchanged after leaving the solution for 1 week at room temperature, indicating that the structure of **2d** was stable in the $CDCl_3$ solution. The IR spectra of the two monomers also differ from each other [12].

New copolymers constituted of alternating 1-alkyl-1*H*-1,2,4-triazole/thiophene (Eq. (3)) and 1-alkyl-1*H*-1,2,4-triazole/bithiophene (Eq. (4)) units were prepared via the palladium-catalyzed Stille-coupling reaction in high yields. All the polymers obtained were soluble in organic solvents such as 1,1,2,2-tetrachloroethane, $CHCl_3$, THF, NMP (*N*-methyl-2-pyrrolidinone), and CF_3COOH at room temperature. By contrast, the previously reported 4RTaz/Th copolymers shown in Eq. (1) were completely soluble in only a limited number of solvents such as CF_3COOH and hexafluoro-2-propanol.

The number-average molecular weights (M_ns) of the polymers estimated from GPC ranged from 6200 to 23,700 (vs. polystyrene standards), which corresponds to the degree of polymerization in the range of about 20–80 based on the repeating unit.

As depicted in Fig. 2, the ^{1}H NMR spectra of polymers **3a**–**3e** showed four aromatic peaks in the range of δ 7.5–7.8, suggesting that the polymers do not have a regio-controlled backbone structure. No characteristic peak due to an $-SnMe_3$ group at δ 0.35 [35,36] was observable after the polymerization. For **3a**, **3b**, and **4** having M_n values higher than 15,000, no Br was detected in the elemental analysis either, as described in Section 2.

In the case of **3a**, **3b**, and **4**, the polymer formed may have a polymer–Pd–Ln (Ln: ligand) terminal group as the main terminal group, and the terminal group is considered to be converted into a polymer–H terminal group during the work-up of the polymer. In relation to this, it has been reported that the dehalogenative polycondensation of dibromoaromatic compounds with a zerovalent nickel complex often affords a Br-free polymer with a polymer–H terminal group; this group is also considered to be derived from polymer–Ni–Ln terminal groups during the work-up of the polymer [4,37]. For **3c**–**3e** with relatively low M_n values, Br was detected and data from elemental analysis suggest that these polymers had –Br group at both ends (cf. Section 2).

The $-SnMe_3$ group has a higher reactivity than the –Br group in an analogous Stille-type polycondensation between a dibromo monomer and a bis(stannyl)-monomer and the polymer obtained has the –Br group as the major polymer terminal

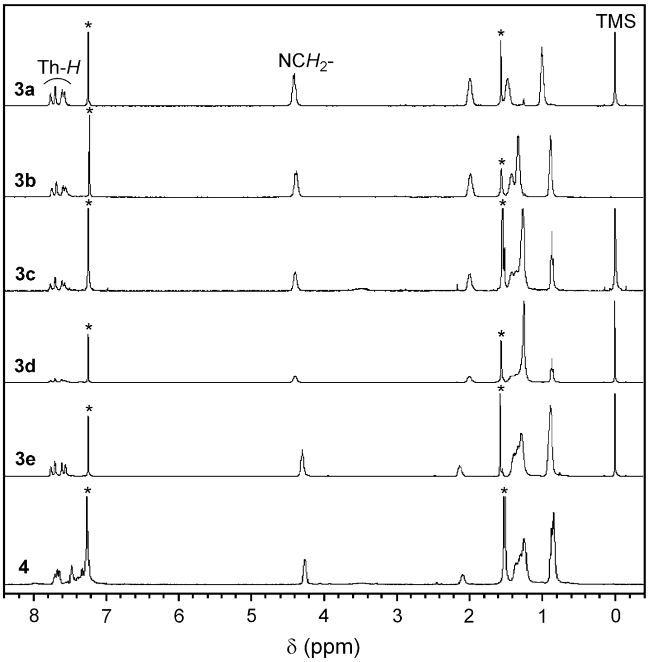
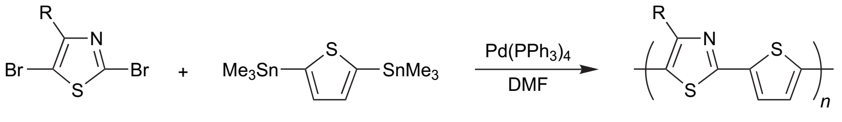


Fig. 2. ^{1}H NMR spectra of **3a**–**3e** and **4** in $CDCl_3$. Peaks with * denote resonances from $CHCl_3$ and H_2O.

[35,36]. Although factors controlling the M_n of the polymers obtained by Stille-type polycondensation have not been clarified yet, the M_n and Br content of the polymers obtained in this study suggest that the reactivity of the propagating polymer–Br species toward the Pd catalyst (or the oxidative addition of the polymer–Br bond in the propagating species to Pd) is an important factor for controlling M_n. The reactivity of the polymer–Br species may be affected by the delicate electronic and steric effects of the R group in the 1RTaz unit, and a larger M_n would be attained when the polymer–Br species have a higher reactivity toward Pd. Such polymer–Br species with a higher reactivity are considered to have a better chance of propagating via the formation of a polymer–Pd–polymer species and of giving a Br-free polymer. The large M_w/M_n of 6.0 observed with **4** may be due to the occurrence of both reductive elimination and acidolysis on the propagating active Pd species, similar to the case of Ni-promoted dehalogenative polycondensation [38,39].

If **3a–3e** adopt a regio-random structure, the polymers should possess two kinds of bonds between 1,2,4-triazole and thiophene units, which results in the following three triad regioisomers i.e., Triad-A, Triad-B, and Triad-C in Chart 3 in the polymer chain. Consequently, the protons of thiophene rings would have four different chemical environments (H^a through H^d in Chart 3) in a mixture of three possible configurational triads. Polymers **3a–3e** give rise to four ^{1}H NMR peaks in the aromatic region, and this supports the regio-random structure of **3a–3e**. The ^{1}H NMR spectrum of **4** exhibited a complex peak pattern for the thiophene protons owing to the regio-random structure. The ^{1}H NMR peak area ratio between the signals in the aromatic and aliphatic regions agrees with the structure of the polymers. Polymer **3b** gave a similar ^{1}H NMR spectrum in $CDCl_2CDCl_2$ and the ^{1}H NMR spectrum showed no significant change in the temperature range from 25 °C to 100 °C.

The regio-selective reaction occurs in a similar polycondensation between 2,5-dibromo-4-alkylthiazole and 2,5-bis(trimethylstannyl)thiophene to produce the following PTz(R)/Th [10,11] having a similar molecular shape composed of similar five-membered rings and alkyl side chain (Eq. (5)). The regio-selectivity in PTz(R)/Th formation is considered to arise from the formation of energetically stable π-stacked assemblies in the polymerization reaction, assisted by the charge-transferred (CT) electronic structure between the electron-donating thiophene and electron-accepting thiazole units [10,11]. However, such a regio-selective polymerization does not seem to proceed in the present preparation of **3a–3e**.



Br-Tz(R)-Br

PTz(R)/Th

(HT of PTz(R)/Th is controlled [10])

(5)

3.2. Thermal stability

As shown in Fig. 3, TGA showed that the 5% weight-loss temperature of the polymers was higher than 420 °C, and a residual weight range of 20–50% was observed at 900 °C. The good thermal stability is advantageous for use in electronic and optical devices. The thermal decomposition at about 420 °C seems to be related to the degradation of alkyl side chains because **3** with a longer alkyl group gives a larger weight loss. The polymers are considered to contain a small

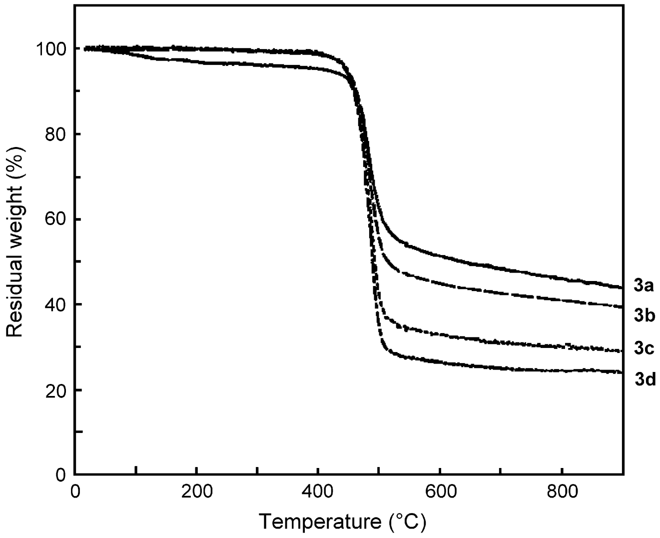
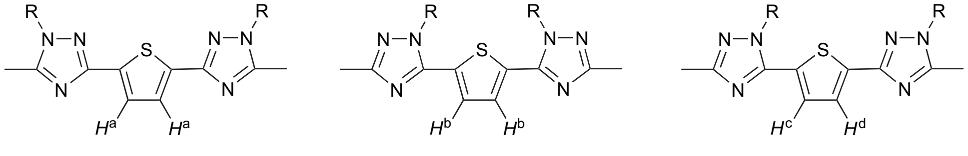


Fig. 3. TGA curves of **3a–3d** in N_2 at heating rate of 10 °C min^{-1}.



Triad-A
(one Th-*H* peak)

Triad-B
(one Th-*H* peak)

Triad-C
(two Th-*H* peaks)

Chart 3. Possible triad regioisomers in **3a–3e**.

amount of water because of the presence of hydrophilic nitrogens (cf. Section 2), and a weight loss due to hydrated water was observed at approximately 100–200 °C in the TGA curves for some polymers. It was difficult to remove hydrated water completely.

3.3. X-ray diffraction data

The powder X-ray diffraction (XRD) patterns of the polymers are shown in Fig. 4. Although the observed XRD peaks are rather broad, the XRD data suggest that at least a portion of **3a** and **4** assumes an ordered π-stacked structure in the solid state to give a distinct peak at $d_1 = 3.6$ Å. This peak may be assigned to the face-to-face packing distance between the stacked polymers, which is often observed with five-membered π-conjugated polymers [1–6] such as HT-P3RTh described in Section 1.

The XRD peak, however, is less sharp than those observed in the regio-controlled HT-P3RTh and PTz(R)/Th (cf. Eq. (5)), presumably because of a lower order of π-stacking due to the non-regio-controlled structure of 1RTaz/Th. The π-stacked structure may be formed with the non-regio-controlled part, as shown in Chart 4. However, such a π-stacked structure is considered to be formed preferentially with a regio-controlled part that is locally formed.

When highly planar π-conjugated polymers such as HT-P3RTh and PTz(R)/Th form a face-to-face π-stacked assembly, it usually gives an XRD peak corresponding to an interplane distance of about $d = 3.6$–3.8 Å [4–6,10,11]. A broad shoulder peak at about 4.5 Å is assigned to a side-to-side distance between loosely packed alkyl chains [40]. In the cases of regio-controlled HT-P3RTh and PTz(R)/Th, a sharp XRD peak is observed in a low-angle region [1–6,10,11], and the peak is considered to correspond to the distance between polymer main chains separated by alkyl side chains, e.g., for HT-P3RTh shown in Chart 5.

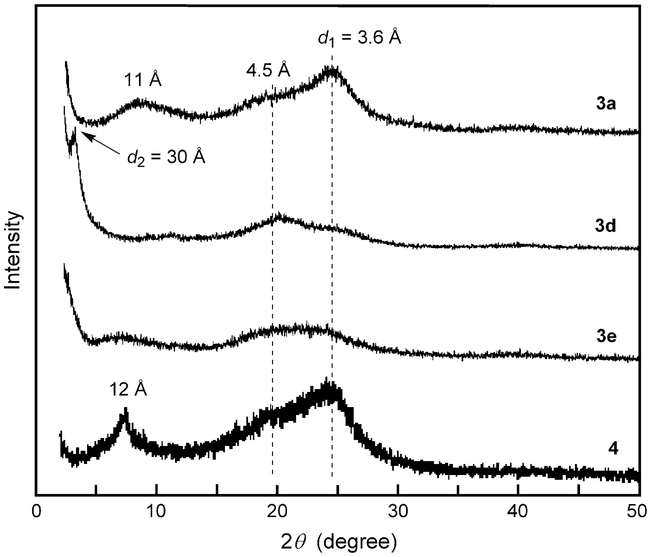


Fig. 4. X-ray diffraction patterns of **3a**, **3d**, **3e**, and **4**.

Polymers **3a** and **3d** show broad XRD peaks at $d_2 = 11$ Å and 30 Å, respectively, and these peaks may correspond to similar distances. The $d_2 = 30$ Å of **3d** is comparable to those of HT-P3DodTh (R = dodecyl in HT-P3RTh; $d_2 =$ ca. 28 Å [41]) and PTz(Dod)/Th (cf. Eq. (5), $d_2 =$ ca. 31 Å [10]) with the same dodecyl side chain, and suggests the formation of an end-to-end type packing with a locally formed regio-regular part (cf. Chart 6). Even non-regio-controlled P3RTh can form an ordered structure locally [41], and the formation of such a packing mode as shown in Chart 6 has been reported for PTz(R)/Th [10]. The d_2 of **3d** is considerably shorter than

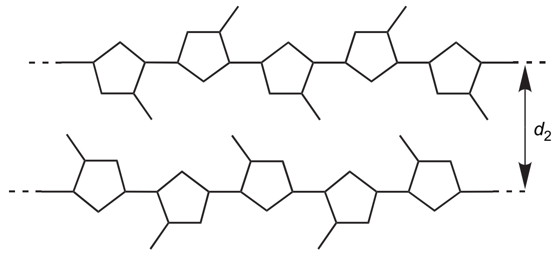


Chart 5. End-to-end packing of HT-P3RTh.

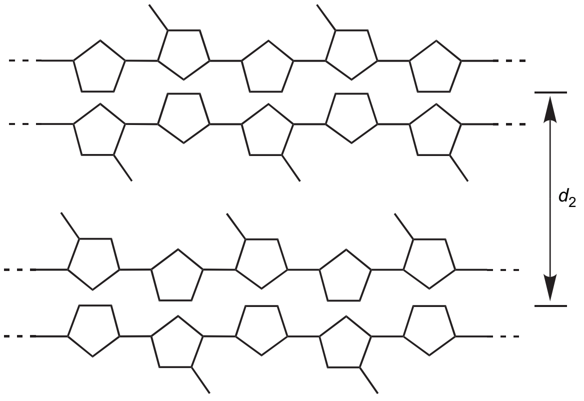


Chart 6. Conceivable packing mode constructed of locally formed regio-regular part.

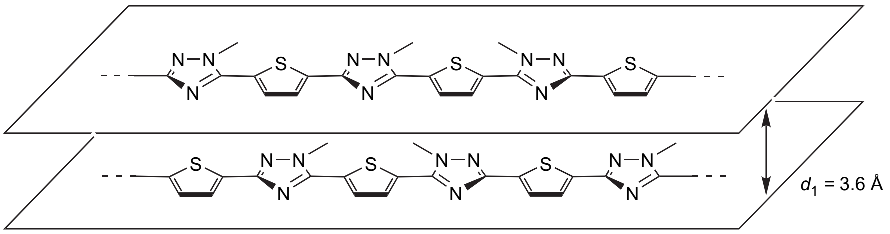
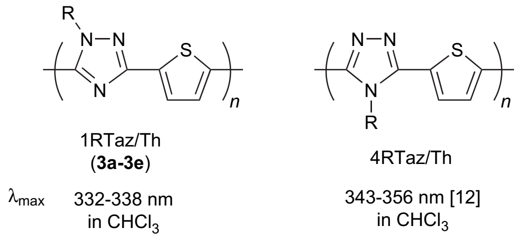


Chart 4. π-Stacked structure of 1RTaz/Th.

that ($d_2 = 19.1$ Å) of the 4RTaz/Th copolymer which is considered to assume an interdigitation packing in solid state [12]. The tilting of the alkyl side chain in the present 1RTaz/Th copolymers seems to make the formation of the interdigitation packing difficult. In the case of **4**, it gives rise to an XRD peak at a shorter length of 12 Å, and this suggests the formation of the interdigitation packing because of the presence of sufficient space between the alkyl side chains.

3.4. UV–vis and photoluminescence data

UV–vis absorption and photoluminescence (PL) data of the polymers are shown in Fig. 5 and Table 1. In $CHCl_3$ solutions, the π–π* absorption maximum (λ_{max}) and PL emission maximum (λ_{em}) of **3a**–**3e** are in the ranges of 332–338 nm and 418–421 nm, respectively (Table 1). The λ_{max} values of **3a**–**3e** are shorter than those of previously reported 4RTaz/Th copolymers [12]. However, the shift in λ_{max} from those of thiophene (231 nm) and 1-alkyl-1*H*-1,2,4-triazole (210 nm) indicates the presence of a moderately expanded π-conjugation system in **3a**–**3e**. The copolymer of bithiophene, **4**, gives a UV–vis absorption peak at a longer wavelength of 387 nm.



Because of the moderate expansion of the π-conjugation system, **3a**–**3e** are suited to the emission of blue light with λ_{em} values of approximately 420 nm in solution and 470–480 nm in film. In contrast, 4RTaz/Th copolymers (Eq. (1)) emit yellow light with λ_{em} at longer wavelengths of about 540–550 nm in films. The PL quantum yields ($\Phi = 36$–43% in Table 1) of **3a**–**3e** are higher than those of the 4RTaz/Th copolymers ($\Phi = 21$–29%) [12] and 1,3,4-oxadiazole-containing π-conjugated polymers ($\Phi = 7$–34%) [7,24].

Table 1
Optical data of polymers

Polymer	UV–vis λ_{max} (nm)		PL λ_{em} (nm)		Φ (%)[a,b]	E_g (eV)[c]
	Solution[a]	Film	Solution[a]	Film		
3a	335	350	419	476, 504	37	3.1
3b	338	348	421	475	36	3.1
3c	335	361	418	472	43	3.1
3d	332	352	418	479, 499	43	3.0
3e	335	348	420	472	38	3.1
4	387	405	436, 465, 496, 529	557	31	2.7

[a] In $CHCl_3$.

[b] PL quantum yield calculated using quinine sulfate as standard ($\Phi = 54.6\%$).

[c] Band-gap energy estimated from onset position of UV–vis spectra in film.

Polymers emitting blue light are considered to be important materials for polymer-based light-emitting diodes [42]. As shown in Fig. 5 and Table 1, the λ_{max} position of the polymers in the $CHCl_3$ solution is shifted by 10–26 nm to a longer wavelength in the film. This shift suggests the presence of some intermolecular electronic interactions between the polymer molecules which are considered to form a stacked structure, as discussed above. The PL spectrum shows a larger shift in λ_{em} to a longer wavelength in films, and this is assigned to the formation of an excimer-like adduct between a photo-activated polymer molecule and the polymer molecule in the ground state; the photo-activated polymer molecule is considered to be stabilized by the formation of an excimer-like adduct for emitting light with a smaller radiation energy.

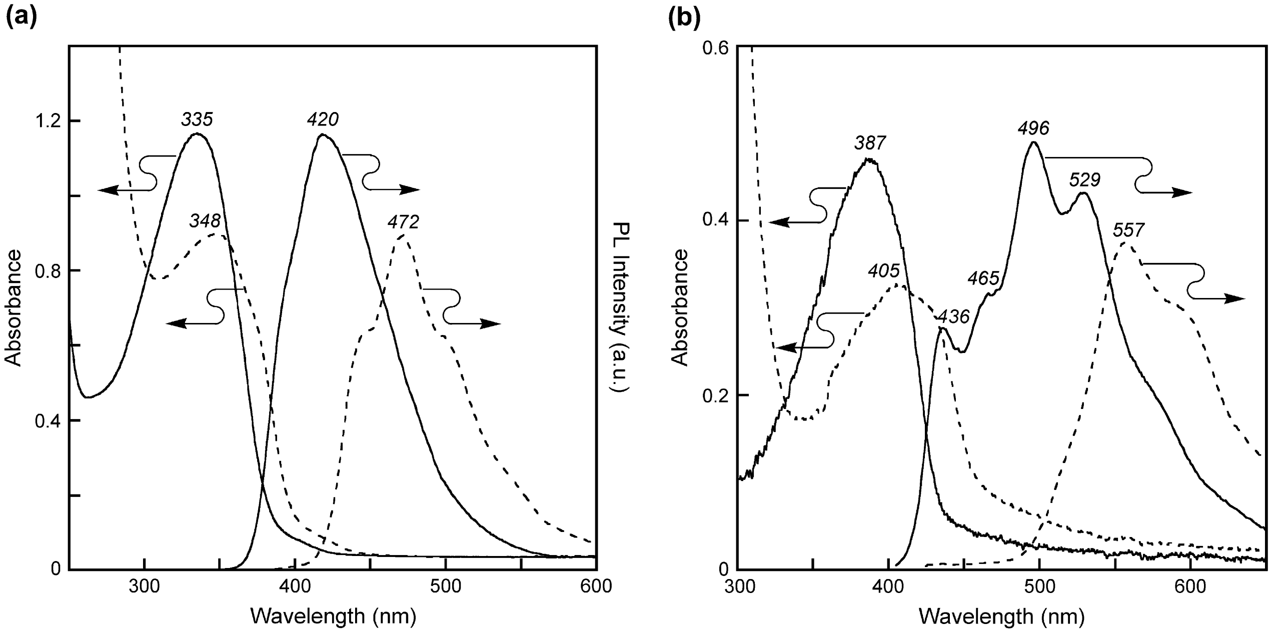


Fig. 5. UV–vis and PL spectra of (a) **3e** and (b) **4** in $CHCl_3$ (solid lines) and thin film (dashed lines).

An EL device, ITO/PEDOT–PSS/**3e**/Ca, started to emit light at about 12 V, and showed an EL spectrum similar to the PL spectrum of **3e** in the cast film, although the EL intensity was low; the EL peak was observed at about 470 nm.

3.5. Electrochemical properties

The redox behavior of thin films of the polymers was determined by cyclic voltammetry (CV). Although **3a**–**3e** showed only electrochemical oxidation with the peak at 1.4 V vs. Ag^+/Ag, **4** with bithiophene unit exhibited both electrochemical oxidation and reduction with peaks at about 1.4 V and −2.4 V vs. Ag^+/Ag, respectively, as shown in Fig. 6a.

The CV chart of **4** exhibits a main oxidation peak at 1.4 V vs. Ag^+/Ag, and the peak locates at a higher potential than those of polythiophenes (about 0.7 V vs. Ag^+/Ag [1–4]) and the 4RTaz/Th copolymers (about 1.1 V vs. Ag^+/Ag in Fig. 6b) because of the incorporation of an electron-accepting 1RTaz unit in the thiophene system and a smaller effective π-conjugation length than that of the 4RTaz/Th copolymers. The oxidation potential is also higher than that of Me-capped bithiophene (about 1.1 V vs. Fc^+/Fc or about 1.3 V vs. Ag^+/Ag) [43].

The reduction peak of **4** is located in a more negative potential region compared to that of the 4RTaz/Th copolymers (−2.2 V vs. Ag^+/Ag). The electrochemical process was accompanied by obvious color changes from yellow to purple on oxidation and to red-brown on reduction, as shown in Fig. 6.

The highest occupied molecular orbital (HOMO) energy level (E_{HOMO}) of **3a**–**3e** and **4** was deduced to be about −5.2 eV from the onset potential of the oxidation wave (about 0.5 V vs. Ag^+/Ag) [44–47]. Accordingly, the lowest unoccupied molecular orbital (LUMO) energy level (E_{LUMO}) of **3a**–**3e** and **4** is estimated to be −2.1 eV using $E_{LUMO} = E_g + E_{HOMO}$ [44–47]. The electrochemical data suggest that the incorporation of an electron-deficient 1,2,4-triazole unit into the polythiophene system leads to an increase in the electron affinities of the polymers, which is important for their use as an electron-transporting material in electronic devices.

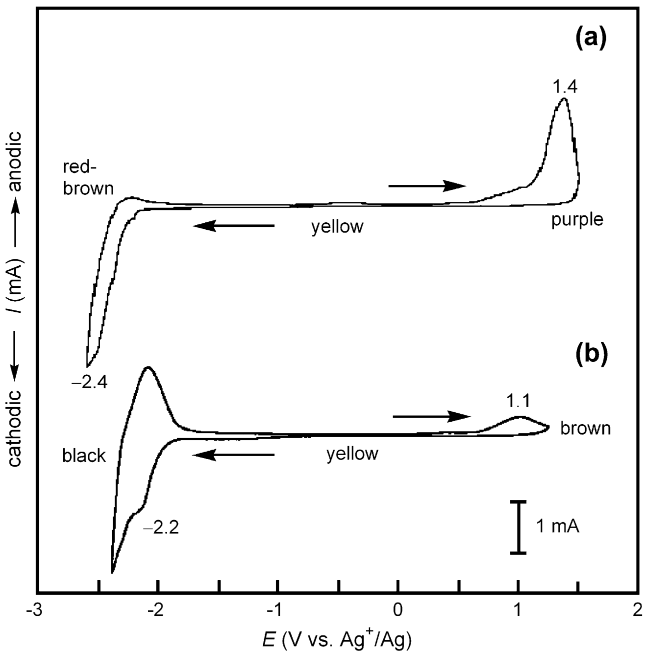


Fig. 6. Cyclic voltammograms of films of (a) **4** and (b) 4RTaz/Th copolymer on Pt plate in CH_3CN solution of $[(C_2H_5)_4N]BF_4$ (0.10 M) in N_2. The sweep rate is 30 mV s^{-1}.

4. Conclusion

New 1-alkyl-1*H*-1,2,4-triazole/thiophene and 1-alkyl-1*H*-1,2,4-triazole/bithiophene alternating copolymers with a moderately expanded π-conjugation system were prepared. The polymers showed good photoluminescent properties with a high quantum yield ($\Phi = 31$–43%) and blue emission ($\lambda_{em} =$ ca. 420 nm in solution and 470 nm in film), and were electrochemically active. The heteroaromatic 1-alkyl-1*H*-1,2,4-triazole unit is regarded as a potentially useful building block for highly luminescent and charge-transporting polymer materials.

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