Energy Level Tuning of Polythiophene Derivative by Click Chemistry-Type Postfunctionalization of Side-Chain Alkynes

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Received 11 September 2010; accepted 14 October 2010 DOI: 10.1002/pola.24443 Published online 11 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A polythiophene derivative substituted with electronrich alkynes as a side chain was synthesized using the Suzuki polycondensation reaction. The electron-rich alkynes underwent the "click chemistry"-type quantitative addition reaction with strong acceptor molecules, such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), resulting in the formation of donor-acceptor chromophores. All polymers showed excellent solubilities in the common organic solvents as well as good thermal stabilities with their 5% decomposition temperatures exceeding 230 °C. The TCNE-/TCNQ-adducted polymers displayed well-defined charge-transfer (CT) bands in the low energy region. The CT energy of the TCNE-adducted polymer was 2.56 eV (484 nm), which was much greater than that of the TCNQ-adducted polymer [1.65 eV (750 nm)]. This result was supported by the electrochemical measurements.

INTRODUCTION Polythiophene derivatives have been extensively investigated as an organic semiconducting polymer, which can be used in many organic devices, such as field effect transistors, photovoltaic cells, biosensors, and electrochromic devices.¹ To achieve a good device performance, it is important to design polymer structures with energy levels suitable for a specific application. One of the most straightforward and promising approaches is the modification of the side-chain groups of the polythiophenes.² The introduction of electron-donating or electron-accepting groups directly or via a π -spacer into the polythiophene main chain dramatically altered the energy levels. For example, it is reported that the introduction of electron-accepting side chains resulted in an enhanced hole mobility and accordingly, good energy conversions in bulk heterojunction solar cells.³

Click chemistry is the concept of achieving the target functional materials using highly efficient addition reactions. This definition suggests that the reactions should be performed under mild conditions and yield no by-products.⁴ Therefore, it is reasonable to apply click chemistry reactions to the postThe electrochemical band gaps of the TCNE-adducted polymers were much greater than those of the corresponding TCNQ-adducted polymers. Furthermore, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, determined from the first oxidation and first reduction peak potentials, respectively, decreased with the increasing acceptor addition amount. All these results suggested that the energy levels of the polythiophene derivative can be tuned by varying the species and amount of the acceptor molecules using this postfunctionalization method. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 225–233, 2011

KEYWORDS: charge transfer; conjugated polymers; electrochemistry; polythiophenes; postfunctionalization

functionalization of polymers, as the desired moieties and undesired moieties in a single polymer cannot be separated by any methods.⁵ The most well-known click chemistry reaction is the Cu(I)-catalyzed azide-alkyne cycloaddition reaction (CuAAC), which forms a 1,4-triazole ring. There are indeed numerous reports on the click postfunctionalization of polythiophene derivatives by using CuAAC.⁶ For example, various functional groups, such as electron-donating ferrocene and electron-deficient benzoimide moieties, were efficiently attached to the polythiophene derivatives.⁷ However, it is suggested that CuAAC has a limitation regarding the application to conjugated polymers. This is because the formed 1,4-triazole rings do not serve as a powerful π -spacer for electronic communication between the two substituents.⁸ Thus, the introduction of electron-donating or electron-accepting groups using CuAAC does not seem to significantly affect the energy levels of the polythiophene main chains.

To solve this problem, we recently reported a new click chemistry-type reaction.⁹ The reaction includes [2 + 2] cycloaddition between electron-rich alkynes and cyano-

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 49, 225-233 (2011) © 2010 Wiley Periodicals, Inc.

containing strong acceptor molecules, such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) derivatives, followed by the ring opening of the formed cyclobutene intermediate, resulting in donor-acceptor chromophores.¹⁰ When dialkylanilino groups, ferrocene, and other specific donors are used as an activator of alkynes, the reactions proceeds under mild conditions and the yields are quantitative.¹¹ When compared with CuAAC, this class of reactions requires no metal catalysts, and the energy levels of the products can be tuned by the strength of the donor-acceptor interactions. Previously, we succeeded in controlling the lowest unoccupied molecular orbital (LUMO) levels of an aromatic polyamine by applying this click chemistry-type reaction to the postfunctionalization of the side-chain alkynes.¹² As more TCNE was added, the LUMO levels were more significantly lowered. However, the energy variation was not remarkable because of the presence of the sp³-hybridized nitrogen atoms in the polymer main chain.

In this study, we applied this postfunctionalization method to a polythiophene derivative substituted with the electronrich alkynes as a side chain, and report for the first time, the remarkable large shift of the LUMO levels and control of both the highest occupied molecular orbital (HOMO) and LUMO levels. The maximum difference in the energy levels caused by this postfunctionalization method was 2.39 eV.

EXPERIMENTAL

Materials

All reagents were purchased from Kanto, Tokyo Kasei, Wako, and Aldrich and used as received. Tetrahydrofuran (THF) was distilled over sodium and benzophenone under $N_{\rm 2}$ before use.

General Measurements

 $^1\mathrm{H}$ NMR and $^{13}\mathrm{C}$ NMR spectra were measured on a JEOL model AL300 spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from SiMe₄, using the solvent's residual signal as an internal reference. The resonance multiplicity is described as s (singlet), br (broad), d (doublet), t (triplet), g (quartet), and m (multiplet). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. MALDI-TOF-MS spectrum was measured on an Applied Biosystems model Voyager-DE STR in the reflect mode. Gel permeation chromatography (GPC) was measured on a Shodex system equipped with polystyrene gel columns using THF as an eluent at a flow rate of 1.0 mL min⁻¹. Relative molecular weights were determined by comparison with the calibrated standard polystyrenes. Elemental analysis was performed on a Perkin-Elmer 2400-SeriesII CHNS/O Analyzer. UV/vis spectra were recorded on a JASCO V-670 spectrophotometer using a 10-mm-thick cuvette. Thermogravimetric analysis (TGA) was carried out on a Seiko SII TG 6220 under nitrogen flow at the scanning rate of 10 °C min⁻¹. Electrochemical measurements of the polymer thin films were carried out at 20 °C in dehydrated CH₃CN containing 0.1 M $(nC_4H_9)_4NClO_4$ in a classical three-electrode cell. The working, reference, and auxiliary electrodes were a glassy carbon disk electrode (2 mm in diameter), Ag/Ag⁺/CH₃CN/ $(nC_4H_9)_4NClO_4$, and a platinum wire, respectively. All potentials were referenced to the fericinium/ferrocene (Fc $^+$ /Fc) couple and used as an internal standard.

Monomer Synthesis

Trimethyl(thiophen-3-ylethynyl)silane (1)

In a 500-mL flask, 3-bromothiophene (10.0 mL, 107 mmol) was dissolved into diisopropylamine (230 mL) and the solution was bubbled with argon for 30 min. After that, trime-thylsilylacetylene (18.1 mL, 128 mmol), $PdCl_2(PPh_3)_2$ (1.54 g, 2.14 mmol), and CuI (0.41 g, 2.14 mmol) were added to the solution under nitrogen flow. The reaction mixture was heated to 60 °C for 8 h. After cooling to 20 °C, the mixture was passed through a short plug. Removal of the solvent *in vacuo* followed by column chromatography (SiO₂, hexane) yielded the desired compound **1** (15.6 g, 81%) as yellow oil.

¹H NMR (300 MHz, CDCl₃): δ 0.24 (s, 9 H), 6.87 (q, J = 3.0 Hz, 1 H), 6.98 (q, J = 3.0 Hz, 1 H), 7.23 ppm (q, J = 3.0 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 0.41, 93.87, 99.92, 122.34, 125.18, 129.62, 130.10 ppm. IR (neat): v 3106.6, 2959.0, 2893.9, 2147.4, 1516.8, 1410.0, 1360.8, 1254.1, 1155.6, 1106.4, 942.9, 872.3, 843.5, 781.0, 758.4, 707.6, 628.6 cm⁻¹.

[(2,5-Dibromothiophen-3-yl)ethynyl](trimethyl)silane (2)

In a 200-mL flask, **1** (4.00 g, 22.2 mmol) was dissolved into anhydrous THF (40 mL) and cooled to -40 °C. A hexane solution of *n*-butyllithium (22.3 mmol) was added to the solution and the mixture was stirred at -40 °C for 5 h. Then, a THF solution of CF₂BrCF₂Br (22.6 g, 86.9 mmol) was added to the mixture at -40 °C. After stirring for 0.5 h, an aqueous solution of Na₂S₂O₃ was added, and the product was extracted three times with chloroform. The organic phase was washed with brine and dried over MgSO₄. After filtration and removal of the solvent, the crude product was purified by column chromatography (SiO₂, hexane), yielding the desired compound **2** (5.65 g, 75%) as brown oil.

¹H NMR (300 MHz, CDCl₃): δ 0.25 (s, 9 H), 6.93 ppm (s, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 0.42, 96.96, 99.86, 110.88, 116.90, 125.35, 132.33 ppm. IR (neat): v 3303.3, 3096.0, 2959.1, 2899.4, 2158.1, 1647.4, 1525.1, 1413.0, 1324.9, 1249.9, 1175.2, 1114.0, 1022.4, 985.1, 937.4, 845.7, 757.3, 699.5, 652.1, 563.7 cm⁻¹.

2,5-Dibromo-3-ethynylthiophene (3)

To a 200-mL flask, **2** (1.56 g, 4.60 mmol), K_2CO_3 (1.91 g, 13.8 mmol), and methanol (30 mL) were added, and the mixture was stirred at 20 °C for 3 h. The mixture was diluted with dichloromethane and the organic phase was washed three times with water. After drying over Na_2SO_4 , the solution was filtered. Removal of the solvent *in vacuo* and column chromatography (SiO₂, hexane) yielded the desired compound **3** (1.17 g, 95%) as a scarlet solid.

¹H NMR (300 MHz, CDCl₃): δ 3.30 (s, 1 H), 6.96 ppm (s, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 76.12, 81.68, 110.96, 117.08, 123.97, 132.22 ppm. IR (KBr): v 3286.8, 3082.4, 2114.9, 1647.7, 1516.8, 1410.0, 1319.9, 1172.3, 1016.3, 909.6, 827.8, 671.9, 615.1, 565.9 cm⁻¹.

4-[(2,5-Dibromothiophen-3-yl)ethynyl]-N, N-dihexadecylaniline (4)

In a 200-mL flask, **3** (1.42 g, 5.40 mmol) and 4-iodo-*N*,*N*-dihexadecylaniline (2.4 g, 5.4 mmol) were dissolved in diisopropylamine (70 mL), and the solution was bubbled with argon for 30 min. $PdCl_2(PPh_3)_2$ (66 mg, 0.094 mmol) and CuI (32 mg, 0.20 mmol) were added under nitrogen flow, and the mixture was stirred at 20 °C for 18 h. The mixture was passed through a short plug. Removal of the solvent *in vacuo* followed by column chromatography (SiO₂, hexane) yielded the desired compound **4** (2.78 g, 64%).

¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, J = 6.9 Hz, 6 H), 1.26 (s, 52 H), 1.56 (t, J = 10.5 Hz, 4 H), 3.27 (t, J = 7.8 Hz, 4 H), 6.55 (d, J = 9.3 Hz, 2 H), 6.98 (s, 1 H), 7.35 ppm (d, J = 9.3 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ 14.12, 22.69, 26.99, 27.09, 27.14, 29.36, 29.50, 29.60, 29.66, 29.68, 29.70, 31.92, 53.41, 75.21, 79.82, 107.53, 110.42, 111.05, 113.91, 131.97, 132.98, 137.58, 148.20 ppm. IR (KBr): v 2926.4, 2851.1, 2205.3, 1606.7, 1535.9, 1511.3, 1497.6, 1465.3, 1425.1, 1399.1, 1368.3, 1294.5, 1248.3, 1191.5, 1148.3, 1115.9, 1014.5, 931.6, 823.8, 811.6, 800.8 cm⁻¹. MALDI-TOF MS (matrix: dithranol): m/z: calcd for C₄₄H₇₁Br₂NS⁺: 805.1; found 806.6 [M + H]⁺.

P1

A mixture of **4** (161 mg, 0.200 mmol), 2,2'-bithiophene-5,5'dibronic acid bis(pinacol) ester (86.2 mg, 0.200 mmol), and Pd(PPh₃)₄ (0.010 g, 0.010 mmol) in THF (10 mL) was stirred at 20 °C for about 0.5 h under argon. Then, an aqueous solution of K₂CO₃ (0.60 mmol; purged with argon) was added, and the mixture was further stirred at 80 °C for 36 h. After cooling to 20 °C, the reaction mixture was poured into an excess amount of methanol. The precipitate was collected by filtration, washed with methanol twice, and dried under vacuum, yielding a red solid (130 mg, 80%).

GPC (THF): $M_n = 6600 \ (M_w/M_n = 1.80)$. ¹H NMR (300 MHz, CDCl₃): δ 0.88 (br, 6n H), 1.25 (br, 52n H), 1.58 (br, 4n H), 3.28 (br, 4n H), 6.52–7.83 ppm (m, 9n H). IR (KBr): ν 2931.5, 2852.3, 2194.2, 1737.1, 1614.8, 1523.4, 1466.7, 1401.5, 1368.2, 1187.9, 1126.8, 812.4, 791.7, 726.0, 629.6, 619.3, 526.7 cm⁻¹.

P2 (x = 1)

To a solution of **P1** (35.7 mg, 0.0440 mmol per repeat unit) in 1,2-dichloroethane (20 mL), TCNE (5.68 mg, 0.0440 mmol) was added, and the mixture was stirred at 20 °C for 5 min. Removal of the solvent *in vacuo* yielded the brown solid **P2** (x = 1; 41.4 mg, 100%).

GPC (THF): $M_n = 6100 \ (M_w/M_n = 2.40)$. ¹H NMR (300 MHz, CDCl₃): δ 0.87 (br, 6n H), 1.23 (br, 52n H), 1.63 (br, 4n H), 3.36 (br, 4n H), 6.67–7.68 ppm (m, 9n H). IR (KBr): ν 2924.5, 2852.2, 2216.5, 1606.3, 1486.4, 1464.5, 1414.1, 1367.1, 1337.2, 1294.9, 1260.6, 1210.2, 1183.7, 1112.2, 802.1, 693.6, 616.7 cm⁻¹. ELEM. ANAL calcd for (C₅₈H₇₅N₅S₃)_n: C 74.23, H 8.06, N 7.46; found: C 71.1, H 7.57, N 7.46%.

P3 (x = 1)

To a solution of **P1** (30 mg, 0.037 mmol per repeat unit) in 1,2-dichlorobenzene (20 mL), TCNQ (7.55 mg, 0.0370 mmol)



SCHEME 1 Synthesis of alkyne-substituted thiophene monomer. (a) $HC\equiv CSiMe_3$, $PdCl_2(PPh_3)_2$, Cul, $(iPr)_2NH$, 60 °C, 81%; (b) 1. *n*BuLi, THF, -40 °C, 2. CF₂BrCF₂Br, THF, -40 °C, 75%; (c) K₂CO₃, methanol, 95%; (d) 4-iodo-*N*,*N*-dihexadecylaniline, $PdCl_2(PPh_3)_2$, Cul, $(iPr)_2NH$, 20 °C, 64%.

was added under nitrogen, and the mixture was stirred at 160 °C for 4 h. After cooling to 20 °C, the solvent was removed *in vacuo*, yielding the green solid **P3** (x = 1; 37.5 mg, 100%).

GPC (THF): $M_n = 7200 \ (M_w/M_n = 2.01)$. ¹H NMR (300 MHz, CDCl₃): δ 0.89 (s, 6n H), 1.25 (br, 52n H), 1.65 (br, 4n H), 3.28 (br, 4n H), 6.53–7.99 (m, 13n H). IR (KBr): ν 2923.7, 2852.1, 2202.4, 2179.5, 1737.1, 1580.3, 1515.6, 1464.3, 1401.6, 1360.5, 1262.5, 1180.5, 1019.8, 908.4, 795.9, 719.8, 542.4 cm⁻¹. ELEM. ANAL calcd for (C₆₄H₇₉N₅S₃)_n: C 75.77, H 7.85, N 6.90; found: C 68.5, H 7.07, N 7.17%.

RESULTS AND DISCUSSION

The key monomer, 4-[(2,5-dibromothiophen-3-yl)ethynyl]-N,N-dihexadecylaniline 4, was prepared by the repeated Sonogashira cross-coupling and the silyl-deptrotection protocol (Scheme 1). Starting from the commercially available 3bromothiophene, the bromo group was substituted by trimethylsilylacetylene under the Sonogashira conditions to yield **1**. Subsequently, the 2,5-positions of the thiophene ring were selectively brominated according to a reported procedure.¹³ Deprotection of the trimethylsilyl group of **2** with K_2CO_3 followed by the Sonogashira coupling with 4-iodo-N,N-dihexadecylaniline afforded the desired monomer 4. It should be noted that the introduction of a dialkylanilino group must be preceded by the bromination reaction, as aniline rings are readily brominated. The reaction yields of each step are moderate to good, and the total yield of the four steps amounted to 37%. The chemical structure of 4 was fully characterized by ¹H and ¹³C NMR, IR, and MALDI-TOF MS analyses. As an example, the identified ¹H NMR spectrum of **4** measured in $CDCl_3$ is shown in Figure 1.



FIGURE 1 ¹H NMR spectrum of 4 in CDCl₃ at 20 °C.

There is, to the best of our knowledge, only a limited number of reports on the polymerization of 3-alkyne-substituted thiophene monomers.¹⁴ For example, Yamamoto and coworkers¹⁵ synthesized a series of polythiophene derivatives by the Stille and Suzuki polycondensation. Li and coworkers¹⁶ also reported the synthesis of such polythiophene derivatives by the Grignard metathesis method. However, it is also suggested that the coordination of a nickel catalyst to the 3-alkyne moiety of the thiophene monomers partially prevents the polymerization mechanism.¹⁷ In this study, we used the Suzuki polycondensation between 4 and the 2,2'bithiophene-5,5'-dibronic acid bis(pinacol) ester to prepare the precursor polymer P1 (Scheme 2). After the polymerization at 80 °C for 36 h, P1 was obtained as a red powder in 80% yield. The obtained polymer showed very good solubilities in the common organic solvents, such as THF, dichloromethane, benzene, and somewhat in hexane, because of the two long alkyl chains. Therefore, the chemical structure was characterized by ¹H NMR and IR spectroscopies (vide infra). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of **P1**, determined by GPC (eluent: THF), were 6600 and 1.80, respectively. As the polymerization results were reproducible, there were no significant side reactions in this case.

Subsequently, the postfunctionalization of the side-chain alkynes of **P1** was attempted by using the TCNE/TCNQ addition reactions. To estimate the progress of the reactions as well as the presence of side reactions, the UV-vis-NIR spectra were monitored during the stepwise addition of the acceptor molecules. The absorption spectrum of **P1** in 1,2-dichlorobenzene possessed the longest wavelength absorption (λ_{max}) at 488 nm (2.54 eV) as a shoulder peak. When a TCNE solution in 1,2-dichloroethane was added, the



SCHEME 2 Synthesis of polythiophene derivative and the postfunctionalization by TCNE/TCNQ addition.

ARTICLE



FIGURE 2 UV-vis-NIR spectral change of P1 during the titration of (a) TCNE in 1,2-dichloroethane and (b) TCNQ in 1,2-dichlorobenzene. The titration experiments of TCNE and TCNQ were performed at 20 °C and 160 °C, respectively. All spectra were taken at 20 °C.

intensities of the longer wavelength absorptions at about 484 and 425 nm quickly increased, while the shorter wavelength band at 347 nm decreased [Fig. 2(a)]. The increased absorptions were charge-transfer (CT) bands originating from the intramolecular donor-acceptor interactions, because these bands displayed solvatochromic behaviors from 480 and 426 nm in CH₂Cl₂ to 456 and 410 nm in hexane. The spectral change continued at 20 °C until an equivalent amount of TCNE relative to the polymer repeat unit was added. The presence of the isosbestic point at 382 nm indicated the absence of any undesired side reactions. All these results suggest the occurrence of the click postfunctionalization of P1. When compared with the compact acceptor molecule of TCNE, the postfunctionalization using the TCNQ addition required heating. Based on the TGA of P1 and the products (vide infra), the reaction temperature was determined to be 160 °C. Similar to the TCNE addition, a new CT band of lower energy was observed at 750 nm and the intensity gradually increased with the increasing amount of TCNQ addition up to 1.0 eq. [Fig. 2(b)]. Despite the higher reaction temperature, a smooth postfunctionalization without any side reactions was suggested from the isosbestic point at 376 nm.

Based on the titration experiments of TCNE and TCNQ, the fully postfunctionalized polymers **P2** and **P3** with x = 1were readily prepared from P1 in a click chemistry fashion. The GPC profiles of **P2** (x = 1) and **P3** (x = 1) suggested almost the same molecular weights with slightly wider polydispersities compared with **P1**, which were probably caused by the decreased solubilities of the polymers in the eluent and the concomitant adhesion to the polystyrene gel columns (Table 1). The ¹H NMR spectrum of **P1** displayed reasonable peaks ascribed to the hexadecyl chains and aromatic protons [Fig. 3(a)]. The latter peaks were complicated because of the uncontrolled regioregularity of the side-chain positions. After the TCNE addition, the alkyl chain protons of **P2** (x = 1) did not significantly change, whereas the aromatic ring protons became equivocal probably because of the steric hindrance of the 1,1,4,4-tetracyanobutadiene (TCBD) acceptor moieties. This effect was more significant when the cyclohexa-2,5-diene-1,4-diylidene-expanded larger

acceptor moieties were introduced by the TCNQ addition. Thus, **P3** (x = 1) exhibited much broader original aromatic ring protons as well as relatively sharp quinone protons. The acceptor additions were also confirmed by the IR spectra (Fig. 4). The precursor polymer P1 displayed a weak peak at 2194.2 cm^{-1} , which was ascribed to the alkyne vibration of the side chains. After the TCNE and TCNQ additions, this peak completely disappeared. The TCNE-adducted polymer **P2** (x = 1) showed a new and stronger peak ascribed to the cyano vibration at 2216.5 cm^{-1} . The TCNQ-adducted polymer **P3** (x = 1) similarly displayed the cyano peak at 2202.4 cm^{-1} together with a small side band at 2179.5 cm^{-1} . The absence of the cyano peaks of TCNE and TCNQ, which were observed at 2257 cm⁻¹ and 2227 cm⁻¹, respectively, indicated no residual unreacted acceptor molecules in the polymer samples. The position and relative intensities of these peaks were consistent with previous reports.¹⁸ The nitrogen contents of P2 (x = 1) and P3 (x = 1) determined by elemental analysis also revealed good agreement with the theoretical values.

It is reported that the construction of donor-acceptor chromophores by the postfunctional TCNE/TCNQ additions sometimes improves the thermal and chemical stabilities of polymers.¹⁸ To estimate the decomposition temperatures of the obtained polymers, TGA measurements were performed at the heating rate of 10 °C min⁻¹ under flowing nitrogen. The

 TABLE 1
 Summary of Molecular Weights,

 Decomposition Temperatures, and Optical Properties
 of Polythiophene Derivatives

	<i>M</i> _n ^a	M _w /M _n ^a	<i>T</i> d5% (°C) ^b	λ _{max} [nm (eV)] ^c	λ _{end} [nm (eV)] ^c
P1	6600	1.80	252	488 (2.54) ^d	578 (2.15)
P2 (<i>x</i> = 1)	6100	2.40	262	484 (2.56) ^d	810 (1.53)
P3 (<i>x</i> = 1)	7200	2.01	236	750 (1.65)	1116 (1.11)

^a Measured by GPC (eluent: THF).

^b Temperature at which 5% weight loss occurred on heating.

^c Measured in 1,2-dichloroethane.

^d Shoulder.



FIGURE 3 ¹H NMR spectra of (a) **P1**, (b) **P2** (x = 1), and (c) **P3** (x = 1) in CDCl₃ at 20 °C.

onset decomposition temperatures of all the polymers exceeded 180 °C, which ensured no decomposition during the postfunctionalization (Fig. 5). The TGA curve of the TCNE-adducted polymer **P2** (x = 1) actually showed a slightly enhanced thermal stability compared with the precurosor polymer **P1**. The 5% weight loss temperature ($T_{d5\%}$) of **P2** (x = 1) was 262 °C, which was 10 °C higher than that of **P1** (Table 1). The $T_{d5\%}$ of **P3** (x = 1) was, on the contrary, lower than that of **P1**.

Although the λ_{max} values of **P1** and **P2** (x = 1) were almost the same, the end absorption (λ_{end}) values showed a clear difference between these two polymers. The λ_{end} of **P1** measured in 1,2-dichloroethane was 578 nm (2.15 eV), while **P2** (x = 1) displayed the bathochromically shifted λ_{end} value at 810 nm (1.53 eV). This result suggested that the formation of donor-acceptor chromophores in the polythiophene side chains by the postfunctionalization lowered the polymer band gap. The band gap lowering was more significant when the expanded acceptor of TCNQ was used. Thus, the λ_{end} of **P3** (x = 1) was 1116 nm, corresponding to the optical band gap of 1.11 eV.

To verify the optical band gaps and determine the absolute energy levels, cyclic voltammograms (CVs) were measured in CH₃CN with 0.1 M (nC_4H_9)₄NClO₄ at 20 °C for the polymer thin films cast on a glassy carbon electrode. Several postfunctionalized polymers **P2** and **P3** with different acceptor addition amounts were prepared to elucidate the relationship between the added acceptor amount (x) and the absolute energy levels. The CV curves of all polymers are shown in Figure 6, and the peak top values are summarized in Table 2. **P1** showed the first oxidation peak potential (E_{ox1}) at 0.412 V (vs. Fc/Fc⁺), which was ascribed to the *N*,*N*-



FIGURE 4 IR spectra of (a) **P1**, (b) **P2** (x = 1), and (c) **P3** (x = 1) (KBr pellet).



FIGURE 5 TGA curves of **P1**, **P2** (x = 1), and **P3** (x = 1) at the heating rate of 10 °C min⁻¹ under flowing nitrogen.



FIGURE 6 Cyclic voltammograms of polymer thin films (a) P1, (b) P2 (x = 0.33), (c) P2 (x = 0.66), (d) P2 (x = 1), (e) P3 (x = 0.33), (f) P3 (x = 0.66), and P3 (x = 1) in CH₃CN with 0.1 M (nC_4H_9)₄NCIO₄ at 20 °C, at the scanning rate of 0.1 V s⁻¹.

dihexadecylaniline moieties. Oxidation and reduction of the polythiophene main chain were detected at 1.242 V and -2.318 V, respectively. A stepwise TCNE addition to **P1** grad-

ually changed the oxidation and reduction potentials. The E_{ox1} anodically shifted with the increasing TCNE addition amount. For example, **P2** (x = 0.33) and **P2** (x = 0.66)

TABLE 2 Redox Potentials and Energy Levels of Polythiophene Derivatives^a

	E _{red3} (V)	E _{red2} (V)	E _{red1} (V)	E _{ox1} (V)	E _{ox2} (V)	HOMO (eV) ^b	LUMO (eV) ^b
P1			-2.318	0.412	1.242	-5.21	-2.48
P2 (<i>x</i> = 0.33)		-2.168	-1.708	0.502	1.102	-5.30	-3.09
P2 (<i>x</i> = 0.66)	-1.958	-1.422	-1.178	0.585	1.042	-5.39	-3.62
P2 (<i>x</i> = 1)	-1.728	-1.214	-0.828	0.862		-5.66	-3.97
P3 (<i>x</i> = 0.33)		-0.481	-0.136	0.486	1.071	-5.29	-4.66
P3 (<i>x</i> = 0.66)		-0.396	-0.059	0.531	0.867	-5.33	-4.74
P3 (<i>x</i> = 1)		-0.290	0.066	0.796		-5.60	-4.87

 $^{\rm a}$ All potentials were represented as the peak top value versus ${\rm Fc/Fc^+}.$

^b HOMO and LUMO levels were estimated from E_{ox1} and E_{red1} values, respectively, based on the assumption of Fc/Fc⁺ = -4.80 eV.



FIGURE 7 Relationship between the amount of the added acceptor molecules, (a) TCNE and (b) TCNQ, and the HOMO and LUMO levels, determined by the E_{ox1} and E_{red1} , respectively.

displayed the N,N-dihexadecylaniline-centered E_{ox1} at 0.502 V and 0.585 V, respectively. However, the E_{ox2} originating from the polythiophene main chain cathodically shifted from 1.102 V for P2 (x = 0.33) to 1.042 V for P2 (x = 0.66). These two oxidation peaks were fused into a single broad peak with the E_{ox1} of 0.862 V for **P2** (x = 1). In contrast to the oxidation peaks, the origin of the first reduction peak potential (E_{red1}) was changed from the polythiophene main chain to the TCBD moieties when TCNE was added to P1. Thus, the reduction of P1 was facilitated as more TCNE was added. The E_{red1} of P1 detected at -2.318 V bathochromically shifted to -1.708 V, -1.178 V, and -0.828 V for P2with x = 0.33, 0.66, and 1, respectively. The TCBD moieties of P2 displayed the multiple reduction peaks with an improved reversibility in the CVs. The addition of TCNQ instead of TCNE resulted in similar changes in the electrochemical behaviors. The oxidations of the N,N-dihexadecylaniline moieties and polythiophene main chain were detected at different potentials when the TCNQ addition amount (x)was 0.33 and 0.66, whereas a single broad peak was observed at 0.796 V for P3 (x = 1). The bathochromic (positive) shift in the E_{red1} from **P1** to **P3** (x = 0.33) was significant because of the expanded acceptor moiety. A slight bathochromic shift in the E_{red1} was further recorded from -0.136 V for **P3** (x = 0.33) to -0.056 V for **P3** (x = 0.66) and 0.066 V for **P3** (x = 1). It should be noted that the E_{red1} values of P3 suggest a stronger electron-accepting power than TCNQ with the $E^{0'}$ of -0.25 V.¹⁹ This was probably because of the efficient communication of the multiple acceptor moieties through the planar conjugated main chains, such as polythiophenes.

The HOMO and LUMO energy levels of all the polymers were calculated from the $E_{\rm ox1}$ and $E_{\rm red1}$ values, respectively, based on the assumption of Fc/Fc⁺ = -4.80 eV.²⁰ The energy levels were plotted versus the added acceptor amount (*x*; Fig. 7). The data clearly indicated that both the HOMO and LUMO levels decreased as more acceptor molecules were added (Table 2). The extent of the decrease in the LUMO levels was more significant compared with the decreased HOMO levels. Accordingly, the electrochemical band gaps, calculated from the difference between the HOMO and LUMO levels, reasonably decreased after the postfunctionalization. Furthermore, the TCNQ addition resulted in a greater decrease in the LUMO levels compared with the TCNE addition. Thus, **P3** showed much narrower band gaps than the

corresponding **P2**. The electrochemical band gaps of **P2** (x = 1) and **P3** (x = 1) were 1.69 V and 0.86 V, respectively, which were in fair agreement with the corresponding optical band gaps determined from the λ_{end} values [1.53 eV for **P2** (x = 1) and 1.11 eV for **P3** (x = 1)]. As a result, the order of the band gaps decreased in the order of **P1** > **P2** > **P3**.

CONCLUSIONS

It was demonstrated that the click chemistry-type postfunctionalization using the high-yielding addition reactions between electron-rich alkynes and TCNE/TCNQ acceptor molecules lowers the energy levels of the polythiophene derivative. The data suggested that the careful selection of the species and amount of the added acceptor molecules enables fine control of the polymer energy levels. In this study, there was apparently an efficient communication between the side-chain groups because of the highly conjugated polythiophene main chain. Accordingly, the extent of the decrease in the LUMO levels was much greater compared with the previous report for an aromatic polyamine.12 The LUMO level decrease of the polythiophene derivative on the TCNE and TCNQ additions amounted to 1.49 eV and 2.39 eV, respectively. These results provide a promising prospect for applying this methodology to other conjugated polymers and building super acceptor polymers. Further interests also include the regioregularity control of the polythiophene derivatives.

This work was supported, in part, by a Grant-in-Aid for Scientific Research and the Special Coordination Funds for Promoting Science and Technology from MEXT, Japan, the Murata Science Foundation, and the Association for the Progress of New Chemistry.

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