

ORIGINAL ARTICLE

Creation of persistent charge-transfer interactions in TCNQ polyester

Yusuke Washino¹, Kimie Murata², Minoru Ashizawa¹, Susumu Kawauchi¹ and Tsuyoshi Michinobu^{2,3}

A 7,7,8,8-tetracyanoquinodimethane polyester was converted into a strongly colored polyester with low-energy charge-transfer (CT) bands by treatment with electron-rich alkyne molecules under mild conditions. The post-functionalization was monitored by its ultraviolet-visible-near infrared (IR) spectra, which suggested a quantitative addition reaction without any side reactions. This result was further supported by ¹H and ¹³C nuclear magnetic resonance, IR and elemental analyses. The functionalized polymer retained a high thermal stability with a decomposition onset temperature of ~200 °C and ~63% residual soot at 500 °C. The CT chromophores in the polymer showed a clear positive solvatochromism and redox behaviors in both anodic and cathodic directions. The HOMO and LUMO levels estimated from the first oxidation potential ($E_{\text{ox},1}$) and the first reduction potential ($E_{\text{red},1}$), respectively, were markedly elevated by this post-functionalization. The extent of HOMO elevation (1.45 eV) was more significant than that of LUMO elevation (0.44 eV).

Polymer Journal (2011) 43, 364–369; doi:10.1038/pj.2011.2; published online 2 February 2011

Keywords: addition reaction; charge transfer; electrochemistry; post-functionalization

INTRODUCTION

Since the pioneering work on conducting polyacetylene films,¹ p-type doping of conjugated polymers has been investigated for creating conducting and magnetic organic polymers.^{2–5} For example, the addition of p-type doping reagents, such as tetracyanoethylene, 7,7,8,8-tetracyanoquinodimethane (TCNQ) and their derivatives, to electron-rich polymers produces open-shell polymers because of the charge-transfer (CT) complexation.^{6–10} However, a similar approach using the combination of n-type doping reagents and electron-deficient polymers is rare, probably because of the difficulty of preparing precursor polymers, namely electron-deficient conjugated polymers, and the limited chemical stability of the n-doped polymers at room temperature.

To improve the chemical stability of doped polymers, chemical reactions using cyano-containing p-type doping reagents rather than redox reactions were recently proposed.¹¹ The chemical reactions include the thermal [2+2] cycloaddition between electron-rich alkynes and electron-deficient ethene moieties of acceptor molecules, such as tetracyanoethylene and TCNQ, followed by ring opening of the cyclobutene intermediates formed, yielding the donor–acceptor chromophores, as exemplified in Scheme 1 (see ref. 12). Application of these reactions to polymer reactions corresponds to the post-functionalization of polymers. After post-functionalization, the resulting polymers are chemically stable because of their closed-shell structures, and they possess more intense CT bands than the intermolecular CT complexes because of the strong intramolecular donor–acceptor

interactions. Such polymers are promising for optical applications, such as electro-optic materials. The post-functionalization of electron-rich polymers, namely aromatic polyamines, thiophene polymers and various anilino-functionalized polymers, has previously been demonstrated.^{13–18}

In this paper, the post-functionalization of electron-deficient polymers using the high-yielding addition reaction between electron-rich alkynes and TCNQ moieties is reported for the first time. Because it is known that the preparation of electron-deficient conjugated polymers is difficult, TCNQ polyester¹⁹ was used as an n-type precursor polymer and a dianilino-substituted acetylene molecule as a p-type reactant. A persistent CT band appeared in the low-energy region. A detailed comparison with the model reaction of small molecules suggested that a quantitative post-functionalization was achieved under mild reaction conditions.

EXPERIMENTAL PROCEDURE

Materials

All reagents were purchased from Kanto (Tokyo, Japan), Wako (Osaka, Japan), Tokyo Kasei (Tokyo, Japan) and Aldrich (St Louis, MO, USA), and used without further purification. Solvents for the reactions were distilled before use.

Measurements

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were measured on a JEOL (Tokyo, Japan) model AL300 spectrometer at 20 °C. Chemical shifts are reported in p.p.m. downfield from SiMe₄, using the solvent's residual signal as

¹Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan; ²Global Edge Institute, Tokyo Institute of Technology, Tokyo, Japan and ³PRESTO, Japan Science and Technology Agency, Tokyo, Japan

Correspondence: Dr T Michinobu, Global Edge Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

E-mail: michinobu.t.aa@m.titech.ac.jp

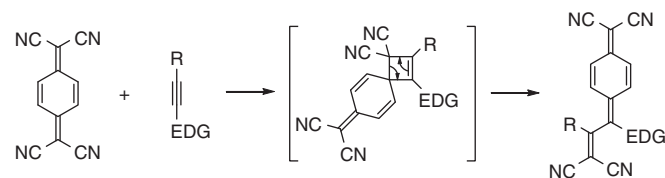
Received 14 October 2010; revised 14 December 2010; accepted 23 December 2010; published online 2 February 2011

an internal reference. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet) and m (multiplet). Attenuated total reflectance Fourier transform infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer (JASCO, Tokyo, Japan). Gel permeation chromatography was measured on a JASCO system equipped with polystyrene gel columns using tetrahydrofuran 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. Matrix-assisted laser desorption/ionization–time of flight mass spectrometry spectra were measured on a Shimadzu/Karatos (Kyoto, Japan) AXIMA-CFR mass spectrometer using dithranol as a matrix. Melting points (m.p.) were measured in open capillaries with a Büchi Melting Point apparatus (Büchi, Flawil, Switzerland) and are uncorrected. Elemental analysis was carried out on a PerkinElmer 2400-Series II CHNS/O Analyzer (PerkinElmer, Boston, MA, USA). Thermogravimetric analysis and differential scanning calorimetry were carried out on a Rigaku ThermoPlus TG8120 and DSC8230 (Rigaku, Tokyo, Japan), respectively, under flowing nitrogen at a scanning rate of 10 °C min⁻¹. Ultraviolet-visible-near infrared spectra were recorded on a JASCO V-670 spectrophotometer at 20 °C. Cyclic voltammetry measurements were taken at 20 °C in dehydrated CH₂Cl₂ containing 0.1-M (nC₄H₉)₄NClO₄ in a classic three-electrode cell. The working, reference and auxiliary electrodes were a glassy carbon disk electrode (2 mm in diameter), Ag/AgCl/CH₃CN/(nC₄H₉)₄NPF₆ and a platinum wire, respectively. All potentials are referenced to the ferricinium/ferrocene (Fc⁺/Fc) couple used as an internal standard.

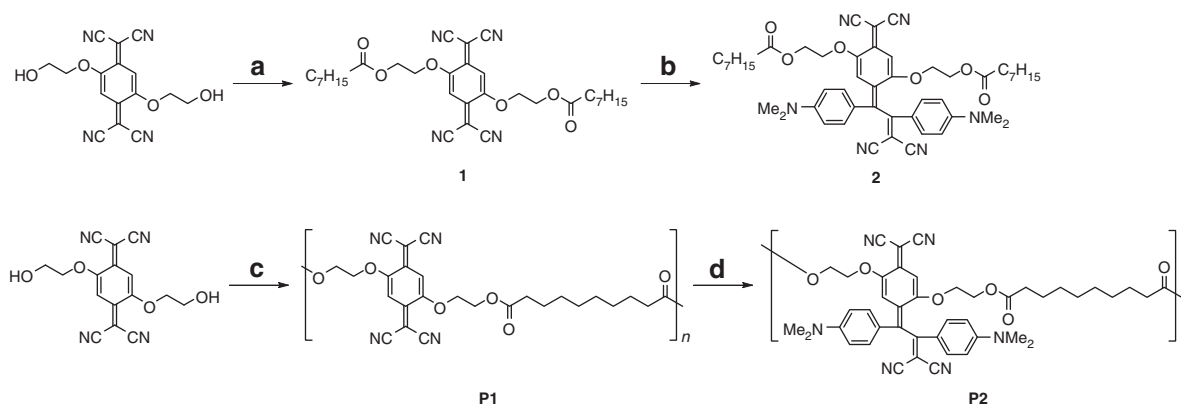
Synthesis

[3,6-Bis(dicyanomethylidene)cyclohexa-1,4-diene-1,4-diyl]bis(oxyethane-2,1-diyl) dioctanoate (1). To 2,2'-[2,5-bis(2-hydroxyethoxy)cyclohexa-2,5-diene-1,4-diylidene]dipropanedinitrile (5.5 mg, 17.0 μmol) in dehydrated dimethyl formamide (1 ml) was added octanoyl chloride (20 μl, 0.13 mmol), and the solution was stirred at 20 °C for 6.5 h. Column chromatography (SiO₂, CH₂Cl₂/acetone 20:1) yielded the desired compound (5.1 mg, 52%).

M.p. 82–84 °C; ¹H NMR (300 MHz, CDCl₃, 293 K) δ 0.87 (t, J=9 Hz, 6 H), 1.29 (m, 16 H), 1.61 (m, 4 H), 2.34 (t, J=7.5 Hz, 4 H), 4.37–4.52 (m, 8 H), 6.46 p.p.m. (s, 2 H); ¹³C NMR (75 MHz, CDCl₃, 293 K) δ 14.0, 22.5, 24.6, 28.8, 29.0, 31.6, 33.9, 60.5, 68.7, 82.8, 103.5, 112.6, 113.1, 147.5, 154.8, 173.5 p.p.m.;



Scheme 1 Reaction mechanism of a high-yield addition reaction between alkyne activated by electron-donating groups (EDGs) and 7,7,8,8-tetracyanoquinodimethane.



Scheme 2 Synthesis and reaction of 7,7,8,8-tetracyanoquinodimethane diester and polyester. (a) Octanoyl chloride, dimethyl formamide, 20 °C, 6.5 h, 52%; (b) Me₂NPhC≡CPhNMe₂, 1,2-dichloroethane, 60 °C, 8 days, 100%; (c) sebacoyl chloride, *N,N*-dimethylacetamide, 20 °C, 48 h; (d) Me₂NPhC≡CPhNMe₂, 1,2-dichloroethane, 80 °C, 3 days.

IR (neat): ν 2922, 2853, 2361, 2338, 2203, 1735, 1588, 1537, 1468, 1418, 1364, 1157, 942, 819 cm⁻¹; matrix-assisted laser desorption/ionization–time of flight mass spectrometry (dithranol): *m/z*: calcd. for C₃₂H₄₀N₄O₆: 576.29 g mol⁻¹; found: 575.63 g mol⁻¹ [M–H]⁺; elemental analysis calcd. (%) for C₃₂H₄₀N₄O₆ (576.68): C 66.65, H 6.99, N 9.72; found: C 66.87, H 7.29, N 9.90.

[(3Z)-3{3,3-dicyano-1,2-bis[4-(dimethylamino)phenyl]prop-2-en-1-ylidene}-6-(dicyanomethylidene)cyclohexa-1,4-diene-1,4-diyl]bis(oxyethane-2,1-diyl) dioctanoate (2). Compound **1** (6.61 mg, 25.0 μmol) and 4,4'-(ethyne-1,2-diyl)-bis(*N,N*-dimethylaniline) (14.4 mg, 25.0 μmol) in 1,2-dichloroethane (12 ml) were heated to 60 °C for 8 days. After cooling to 20 °C, the solvent was removed *in vacuo*, yielding the desired product (21.0 mg, quant.).

M.p. 152–153 °C; ¹H NMR (300 MHz, CDCl₃, 293 K) δ 0.87 (t, J=7 Hz, 6 H), 1.25–1.27 (m, 16 H), 1.60–1.62 (m, 4 H), 2.34 (t, J=7.5 Hz, 4 H), 3.08 (s, 6 H), 3.09 (s, 6 H), 3.92–4.45 (m, 8 H), 6.33 (s, 1 H), 6.55 (s, 1 H), 6.60 (d, J=9 Hz, 2 H), 6.68 (d, J=9 Hz, 2 H), 7.25 (d, J=9 Hz, 2 H), 7.72 p.p.m. (d, J=9 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃, 293 K) δ 14.1, 22.6, 24.7, 28.91, 28.92, 29.0, 31.6, 33.9, 34.0, 39.9, 40.0, 53.4, 61.2, 61.3, 67.1, 67.6, 77.2, 83.8, 102.0, 110.5, 111.3, 111.9, 114.7, 115.5, 115.7, 116.2, 120.7, 124.7, 126.3, 132.2, 133.7, 149.4, 149.9, 152.0, 153.1, 158.3, 172.8, 173.7, 173.9 p.p.m.; IR (neat): ν 2922, 2852, 2361, 2338, 2203, 1736, 1588, 1537, 1492, 1418, 1364, 1157, 942, 820 cm⁻¹; matrix-assisted laser desorption/ionization–time of flight mass spectrometry (dithranol): *m/z*: calcd. for C₅₀H₆₀N₆O₆: 840.5 g mol⁻¹; found: 838.8 g mol⁻¹ [M–H]⁺; elemental analysis calcd. (%) for C₅₀H₆₀N₆O₆ (841.05): C 71.40, H 7.19, N 9.99; found: C 69.20, H 7.11, N 9.49.

TCNQ polyester (P1). 2,2'-[2,5-Bis(2-hydroxyethoxy)cyclohexa-2,5-diene-1,4-diylidene]dipropanedinitrile (302 mg, 0.932 mmol) and sebacoyl chloride (0.200 ml, 0.937 mmol) were stirred in dehydrated *N,N*-dimethylacetamide (10 ml) at 20 °C for 48 h. The solution was poured into MeOH, and the precipitate was collected. Reprecipitation into MeOH yielded the desired TCNQ polyester (302 mg, 92%).

Gel permeation chromatography (tetrahydrofuran) *M*_w 5000, *M*_n 4400; ¹H NMR (300 MHz, CDCl₃, 293 K) δ 1.27 (s, 8n H), 1.59 (m, 4n H), 2.36 (t, J=7.5 Hz, 4n H), 4.00–4.80 (m, 8n H), 6.45 p.p.m. (s, 2n H); ¹³C NMR (75 MHz, CDCl₃, 293 K) δ 24.6, 28.9, 29.0, 33.9, 60.6, 68.8, 82.8, 103.6, 112.7, 113.2, 147.6, 154.9, 173.5 p.p.m.; IR (neat): ν 2915, 2849, 2359, 2217, 1727, 1562, 1527, 1457, 1369, 1332, 1239, 1173, 1153, 1042, 993, 843, 801, 719 cm⁻¹; elemental analysis calcd. (%) for (C₂₆H₂₆N₄O₆)_n: C 63.66, H 5.34, N 11.42; found: C 62.82, H 5.22, N 11.42.

Donor–acceptor polyester (P2). **P1** (51.6 mg, 0.105 mmol) and 4,4'-(ethyne-1,2-diyl)bis(*N,N*-dimethylaniline) (27.1 mg, 0.103 mmol) in 1,2-dichloroethane (7 ml) were heated to 80 °C for 3 days. After cooling to 20 °C, the solvent was removed *in vacuo*, yielding the desired polymer (78.7 mg, quant.).

Gel permeation chromatography (tetrahydrofuran) *M*_w 4500, *M*_n 3700; ¹H NMR (300 MHz, CDCl₃, 293 K) δ 1.26 (m, 8n H), 2.31 (m, 4n H), 3.06 (s, 6 H), 3.07 (s, 6 H), 3.61 (m, 4n H), 3.93–4.23 (m, 8n H), 6.30 (s, n H), 6.54–6.89

(m, 5n H), 7.25 (s, 2n H), 7.69 p.p.m. (s, $J=4.4$ Hz, 2n H); ^{13}C NMR (75 MHz, CDCl_3 , 293 K) δ 24.7, 29.0, 29.1, 29.6, 33.8, 34.0, 39.9, 40.0, 40.3, 61.2, 61.3, 67.1, 67.6, 77.2, 102.0, 110.7, 111.3, 111.9, 114.8, 115.6, 115.7, 116.3, 120.6, 124.6, 126.3, 133.8, 134.0, 149.4, 149.7, 150.0, 152.1, 153.1, 158.4, 172.8, 173.6, 173.8 p.p.m.; IR (neat): ν 2925, 2359, 2341, 2202, 1732, 1586, 1530, 1487, 1414, 1362, 1333, 1207, 1155, 1060, 943, 819, 731, 650 cm^{-1} ; elemental analysis calcd. (%) for $(\text{C}_{44}\text{H}_{46}\text{N}_6\text{O}_6)_n$: C 70.01, H 6.14, N 11.13; found: C 68.21, H 6.27, N 10.58.

RESULTS AND DISCUSSION

Synthesis and characterization

A precursor polymer, the TCNQ polyester, was prepared by polycondensation between sebacoyl chloride and the commercially available TCNQ derivative with two OH groups, according to a

previous report on a similar TCNQ polyester synthesis¹⁹ (Scheme 2). Although the previous report did not describe the molecular weights of the TCNQ polymers obtained, the molecular weights of **P1** were measured by gel permeation chromatography. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were 5000 and 4400, respectively, corresponding to a monomer repeat unit (n) of ~ 8 . The relatively low polydispersity (M_w/M_n) suggests the partial adsorption of **P1** on the polystyrene gel.

A monomer unit **1** was also prepared for comparison with **P1**. The addition reaction of **1** with $\text{Me}_2\text{NPhC}\equiv\text{CPhNMe}_2$ was first conducted in CH_2Cl_2 at 20 °C. A slight coloration occurred after stirring overnight, but no isolatable amount of **2** was obtained. On the basis of the quantitative addition yield of $\text{Me}_2\text{NPhC}\equiv\text{CPhNMe}_2$ to TCNQ at

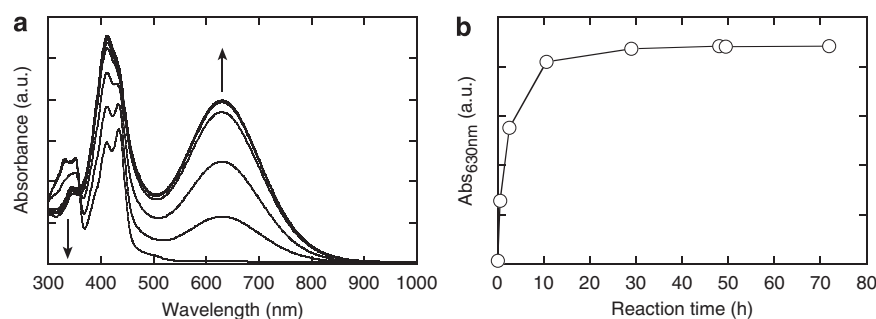


Figure 1 (a) Ultraviolet-visible-near infrared spectral change during the preparation of **P2** from **P1** and an equivalent amount of 4,4'-(ethyne-1,2-diyl)bis(*N,N*-dimethylaniline) in 1,2-dichloroethane at 80 °C. (b) Plots of time versus intensities of the charge-transfer band at 630 nm.

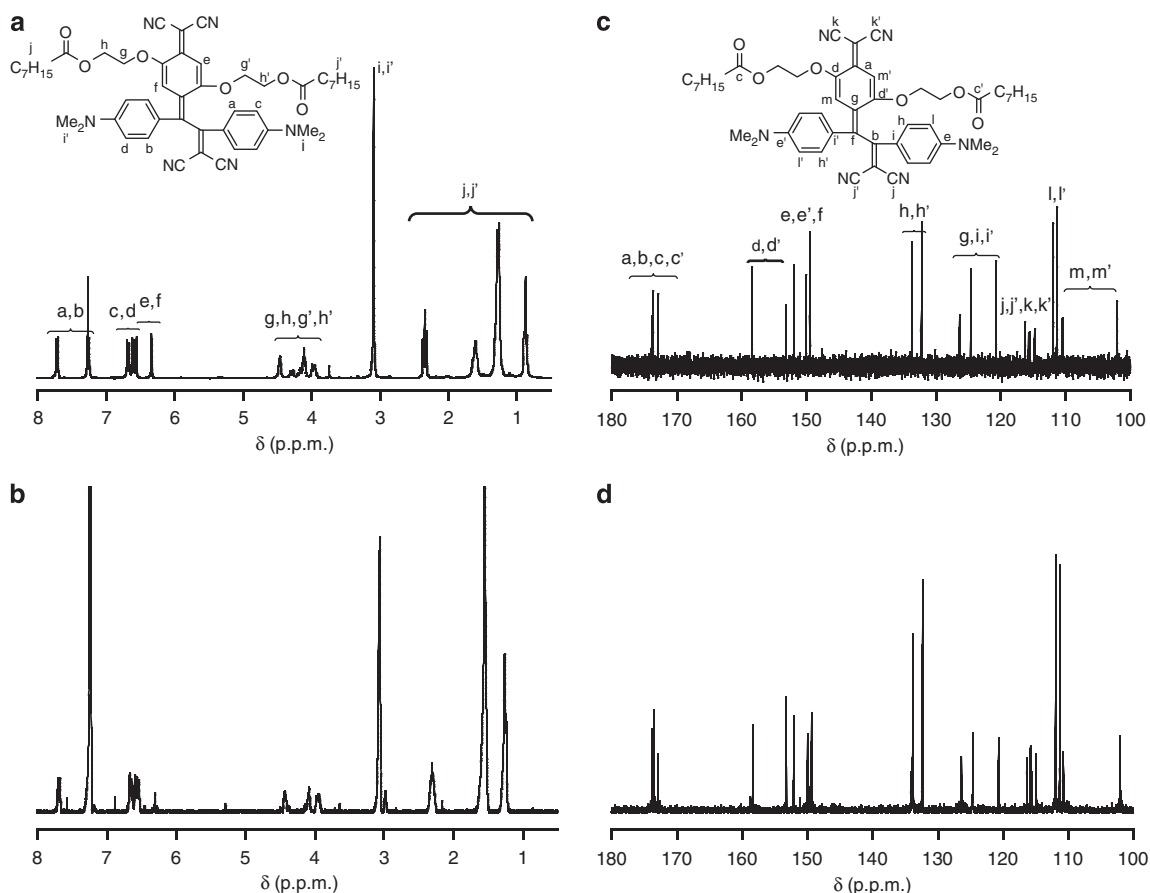


Figure 2 ^1H nuclear magnetic resonance (NMR) spectra of (a) **2** and (b) **P2** in CDCl_3 at 20 °C and the aromatic region of ^{13}C NMR spectra of (c) **2** and (d) **P2** in CDCl_3 at 20 °C.

20 °C (see ref. 20), it was probably caused by the decreased reactivity of the TCNQ moiety because of the substitution of the two electron-donating alkoxy groups. Replacement of the solvent by 1,2-dichloroethane and slight heating started to change the solution color from orange to green. After a sufficient reaction time, the desired product **2** was quantitatively obtained. On the basis of this knowledge, the post-functionalization of **P2** was attempted. The heating of **P2** and Me₂NPhC≡CPhNMe₂ in 1,2-dichloroethane to 80 °C (near boiling point) gradually changed the solution color, implying that the reaction was occurring. The time-dependent spectral change in the ultraviolet-visible-near infrared absorption was monitored (Figure 1a). **P1** possessed absorption maxima at 434 and 412 nm, which are ascribed to the dialkoxy-substituted TCNQ moieties. When the post-functionalization occurred, the intensity of these peaks started to increase and they fused into a single broad peak. In contrast, the weak peaks at

<360 nm decreased. The presence of the isosbestic point at 360 nm indicated that there were no undesired side reactions during post-functionalization. In addition, a well-defined low-energy band appeared at 630 nm, which is ascribed to the CT transition from the dimethyl-anilino donors to the cyano-based acceptor moieties. The intensity of this CT band was plotted against the reaction time (Figure 1b). The plots suggest that the reaction was almost completed after 30 h, and prolongation did not result in any degradation of the donor-acceptor chromophores formed.

The obtained donor-acceptor chromophores were fully characterized. In the ¹H and ¹³C NMR spectra of **2**, all peaks were assigned to the single chemical structure, despite the possibilities of *E*- and *Z*-isomers (Figures 2a and c). To estimate the relative stability of these isomers, computational calculations were carried out for the simplified model structures at the ωB97XD/6-31G* level (see Supplementary Information). These calculations suggested that the *Z*-form is energetically preferred by 11.4 kJ mol⁻¹ compared with the *E*-form. Therefore, the obtained product is assumed to be the *Z*-isomer. The matrix-assisted laser desorption/ionization-time of flight mass spectrometry and elemental analysis were also consistent with the chemical structure. The ¹H NMR spectrum of **P2** was similar to that of **2**, although some peaks were broader because of the polymer effect (Figure 2b). The number of ¹³C NMR peaks in the aromatic region agreed with that of **2** or with the chemical structure of the monomer repeat unit (Figure 2d). The IR spectra of **P1** and **P2** revealed the difference in the cyano vibrational peak positions. The cyano peak of **P1** detected at 2217 cm⁻¹ completely disappeared after the post-functionalization, and a new cyano peak appeared at 2202 cm⁻¹ (Figure 3). This shift is consistent with the previous report.¹⁵ All these results support the clean post-functionalization of the TCNQ polyester by an addition reaction with electron-rich alkyne molecules.

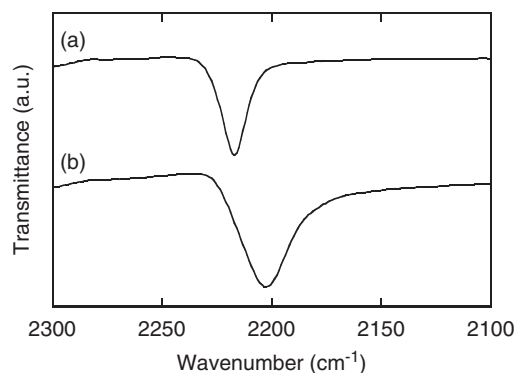


Figure 3 Attenuated total reflectance Fourier transform infrared spectra (neat) of (a) **P1** and (b) **P2**.

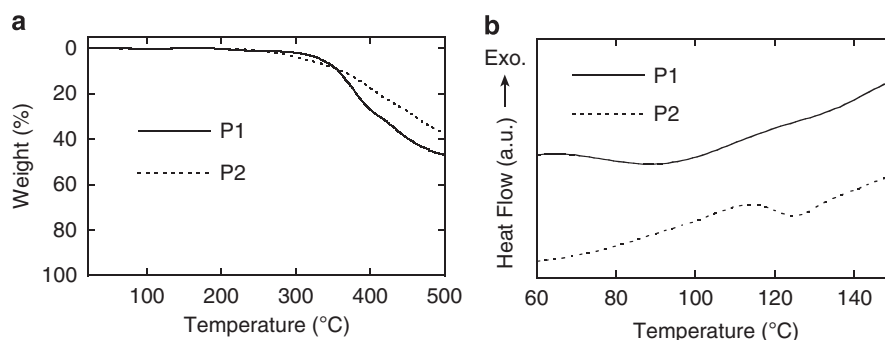


Figure 4 (a) Thermogravimetric analysis and (b) differential scanning calorimetry thermograms (second heating) of **P1** and **P2** at the scanning rate of 10 °C min⁻¹ under nitrogen flow.

Table 1 Summary of λ_{\max} values in different solvents at 20 °C

Solvent	$E_{T(30)}/\text{kcal mol}^{-1}$	$1/nm$ (eV)	$2/nm$ (eV)	$P1/nm$ (eV)	$P2/nm$ (eV)
Cyclohexane	30.9	426 (2.91)	555 (2.23)	425 (2.92)	— ^a
Benzene	34.3	440 (2.82)	608 (2.04)	426 (2.91)	591.5 (2.10)
Diethyl ether	34.5	420 (2.95)	581 (2.13)	430.5 (2.88)	— ^a
Tetrahydrofuran	37.4	433 (2.86)	609.5 (2.03)	434 (2.86)	614 (2.02)
Dichlorobenzene	38.0	441 (2.81)	629 (1.97)	440 (2.82)	633 (1.96)
Ethyl acetate	38.1	429.5 (2.89)	625.5 (1.98)	426.5 (2.91)	— ^a
Chloroform	39.1	433 (2.86)	620 (2.00)	434 (2.86)	625.5 (1.98)
Dichloromethane	40.7	432.5 (2.87)	625.5 (1.98)	433.5 (2.86)	628.5 (1.97)

^aInsoluble.

Thermal properties

The obtained polymers were chemically and thermally stable. The thermogravimetric analysis of **P1** and **P2** was carried out at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under flowing nitrogen. Both polymers showed no decomposition at least up to $200\text{ }^{\circ}\text{C}$, suggesting that the high thermal stability was retained after the post-functionalization (Figure 4a). This result is consistent with the previous results for the post-functionalization of p-type-conjugated polymers.^{13,17} The residual soot amount of **P2** (63%) was greater than that of **P1** (53%), reflecting the aromatic contents in the polymers. The enhanced intermolecular interactions of **P2** with additional aromatic rings were implied by the melting points of the small molecules (**1**: $82\text{--}84\text{ }^{\circ}\text{C}$, **2**: $152\text{--}153\text{ }^{\circ}\text{C}$). The weak intermolecular interactions based on the $\pi\text{--}\pi$ interactions and dipolar interactions might also be associated with the increased amount of soot at $500\text{ }^{\circ}\text{C}$. Both polymers **P1** and **P2** displayed a glass transition temperature (T_g) at 87 and $123\text{ }^{\circ}\text{C}$, respectively, in the differential

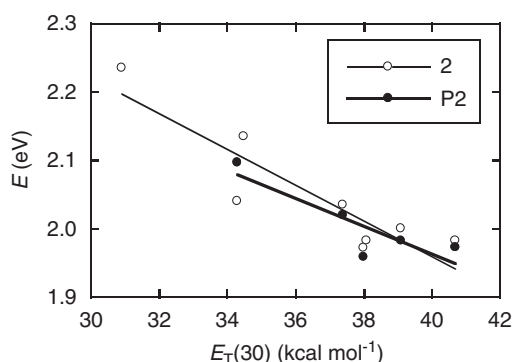


Figure 5 Relationship between the solvent polarity parameter $E_T(30)$ and the charge-transfer band maxima of **2** and **P2**.

scanning calorimetry thermograms (Figure 4b). It is thought that the higher T_g of **P2** is also derived from the enhanced intermolecular interactions.

Optical and electrochemical measurements

The formation of stable CT bands was evaluated by ultraviolet-visible-near infrared absorption spectra in various solvents, and the energy levels were estimated from the end absorptions and electrochemical redox potentials.

As shown in Figure 1a, the addition reaction produced a low-energy band in the ultraviolet-visible-near infrared region. These bands were chemically persistent in various solvents, and the λ_{max} values are summarized as a function of solvent polarity $E_T(30)$ (Table 1). Similar to many donor-acceptor chromophores prepared by this class of addition reactions,²¹⁻²³ both **2** and **P2** displayed a positive solvatochromism with a correlation coefficient of ~ 0.90 (Figure 5). In contrast, the λ_{max} values of the precursors **1** and **P1** did not show such behaviors.

To compare the chemical stability of the CT bands with those prepared by the conventional n-type doping, complexation of the TCNQ polyester **P1** with tetrathiafulvalene was attempted. However, **P1** did not react with tetrathiafulvalene even when the solution was heated to the boiling point of CHCl_3 , probably because of the cathodic shift of $E_{\text{red},1}$ of the TCNQ moieties relative to the unsubstituted TCNQ ($E_{\text{red},1} = -0.25\text{ V}$) (see ref. 24; vide infra).

Redox potentials are often used to estimate the energy levels of aromatic compounds. Cyclic voltammograms of the polymers and model monomers were measured in CH_2Cl_2 containing 0.1-M ($n\text{C}_4\text{H}_9$) $_4\text{NClO}_4$ at $20\text{ }^{\circ}\text{C}$. Figure 6 shows the typical cyclic voltammogram curves, and the redox potentials are summarized in Table 2. The redox behaviors of the polymers were basically the same as those of the corresponding monomers. The precursors displayed the only two

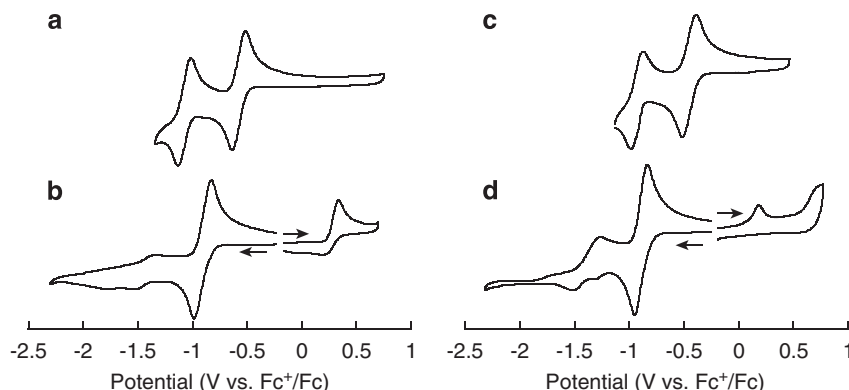


Figure 6 Cyclic voltammograms of (a) **1**, (b) **2**, (c) **P1** and (d) **P2** in CH_2Cl_2 with 0.1-M ($n\text{C}_4\text{H}_9$) $_4\text{NClO}_4$ at the scan rate of 0.1 V s^{-1} under nitrogen.

Table 2 Summary of electrochemical and optical measurements

	$E_{\text{red}2}/\text{V}^a$	$E_{\text{red}1}/\text{V}^a$	$E_{\text{ox}1}/\text{V}^{a,b}$	$\Delta E_{\text{ox}1} - E_{\text{red}1}/\text{V}$	Opt. band gap/eV ^c	HOMO/eV	LUMO/eV ^d
1	-0.93	-0.46	—	—	2.32	-6.61 ^e	-4.29
2	-1.44	-0.90	0.34	1.24	1.41	-5.38 ^d	-3.97
P1	-0.96	-0.47	—	—	2.28	-6.71 ^e	-4.43
P2	-1.29	-0.92	0.19	1.11	1.27	-5.26 ^d	-3.99

^aRedox potentials measured in CH_2Cl_2 with 0.1 M ($n\text{C}_4\text{H}_9$) $_4\text{NClO}_4$ at $20\text{ }^{\circ}\text{C}$. Potentials versus Fc^+/Fc .

^bPeak top values.

^cMeasured in CH_2Cl_2 at $20\text{ }^{\circ}\text{C}$.

^dCalculated from the $E_{\text{ox}1}$ and $E_{\text{red}1}$ values based on the assumed value of $\text{Fc}^+/\text{Fc} = -4.8\text{ eV}$.

^eCalculated from the electrochemically determined LUMO level and optical band gap.

reversible reduction steps at the first reduction potential ($E_{\text{red},1}$) of -0.46 and the second reduction potential ($E_{\text{red},2}$) of -0.93 V (vs Fc^+/Fc) for **1** and at $E_{\text{red},1}$ of -0.47 and $E_{\text{red},2}$ of -0.96 V for **P1**, ascribed to the TCNQ moieties (Figures 6a and c). After the addition reaction with the electron-rich alkyne molecule, the reduction potentials cathodically shifted, and the current intensity of $E_{\text{red},2}$ significantly decreased. In addition, a new irreversible oxidation peak ($E_{\text{ox},1}$) ascribed to the dimethylanilino groups appeared at 0.34 V for **2** and at 0.19 V for **P2**. Different peak top values of $E_{\text{ox},1}$ might reflect the stronger adsorption features of **P2** to the working electrode. The calculated electrochemical band gaps ($\Delta|E_{\text{ox},1}-E_{\text{red},1}|$) of **2** and **P2** were 1.24 and 1.11 V, respectively, which are consistent with the optical band gaps determined by the end absorption in CH_2Cl_2 . The energy levels estimated from the redox potentials and optical band gaps indicated that both HOMO and LUMO levels were elevated after the addition reaction. In contrast to the acceptor addition to the p-type precursor polymers resulting in a marked decrease in the LUMO levels,^{11,25} the addition of electron-rich alkyne molecules to the n-type precursor polymers leads to a more significant elevation of HOMO levels than LUMO levels.

CONCLUSION

The post-functional preparation of persistent intramolecular CT interactions in the n-type precursor polymer was achieved using the addition reaction between the electron-rich alkynes and TCNQ moiety. The quantitative conversion ensures a facilitated preparation protocol without special purification, such as column chromatography. The conventional analytical methods and a comparison with the model reaction of the monomer moiety demonstrated the high purity of the post-functionalized polymer. A sufficiently high thermal stability with the onset decomposition temperature of ~ 200 °C was retained even after post-functionalization. The electrochemical and optical measurements clearly revealed the formation of intramolecular CT bands, accompanying the marked change in energy levels. With designable electron-rich alkyne molecules, the TCNQ polymers can serve as a reactive functional polymer for preparing various CT energies.

ACKNOWLEDGEMENTS

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

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