

# Double Click Synthesis and Second-Order Nonlinearities of Polystyrenes Bearing Donor–Acceptor Chromophores

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ABSTRACT: Donor-acceptor chromophores were almost quantitatively introduced into the side chains of a polystyrene derivative by sequential "click chemistry"-type addition reactions as an efficient postfunctionalization method. The first click reaction is the conventional Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC), and the second one is the atom-economic addition of strong acceptor molecules, such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), to the aniline-substituted electron-rich alkynes. Steric hindrance was found to be an important factor in determining the reactivity of alkyne-acceptor addition reactions. All obtained polymers showed good solubility in common organic solvents, and they were fully characterized by GPC, <sup>1</sup>H NMR and IR spectroscopy, and elemental analysis. After the acceptor addition, the polymers showed an intense charge-transfer (CT) band centered at ca. 480 nm for the TCNE adducts and ca. 710 nm for the TCNQ adducts. Electrochemical measurements of these polymers also revealed well-defined oxidation and reduction potentials, offering consistency between the electrochemical and optical band gaps. The second harmonic generation (SHG) coefficients ( $d_{33}$  and  $d_{15}$ ) of the polymer thin films were evaluated by SHG measurements before and after corona poling at 150 °C, a temperature that was determined on the basis of thermal analyses. The results show that the TCNE adducted polymers possess better SHG properties than the corresponding TCNQ adducted polymers, probably reflecting the superior chromophore mobility within the polymers.

## Introduction

Click chemistry became one of the most important techniques to prepare functional polymers with well-defined chemical structures.<sup>1</sup> In particular, when click chemistry is applied as a postfunctionalization method, desired functional moieties can be introduced into polymer side chains and the polymer properties are greatly improved.<sup>2</sup> One of the most powerful and well-studied click chemistry reactions is probably the Cu(I)-catalyzed azidealkyne cycloaddition (CuAAC) reaction, originated by Sharpless and co-workers, which is capable of selectively combining two components in terms of covalent bonds in excellent yields.<sup>3</sup> However, this reaction has several limitations, such as the need for a metal catalyst for the control of high yield and regioselectivity, the explosive nature of some azide substances, and the poor optoelectronic properties of the 1,4-triazole ring. In order to solve these problems, metal-free azide-alkyne click chemistry has been developed.<sup>4</sup> Moreover, thiol-ene/thiol-yne reactions and Diels-Alder reactions were recently applied as a metal- and azide-free click chemistry to preparation of a series of macro-molecular architectures.<sup>5–7</sup> Nevertheless, there are few reports that can solve the last limitation of the poor optoelectronic properties.

Tuning of the electronic HOMO and LUMO levels is crucial in improving the optoelectronic properties of organic materials. Design of new donor-acceptor type  $\pi$ -conjugated molecules is one solution because through-bond interactions between donor and acceptor moieties result in narrow band gaps originating from the elevated HOMO and lowered LUMO levels. We recently focused on the highly efficient addition reactions between electron-rich alkynes and strong acceptor molecules, such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), forming nonplanar donor-acceptor chromophores via the thermal [2 + 2] cycloaddition followed by the ring-opening (Scheme 1).<sup>8</sup> The reactivity largely depends on the electron-donating groups substituted by the alkyne moiety, and dialkylanilino donors were found to afford the desired donor-acceptor structures in a quantitative yield at room temperature.9 No special purification process is necessary because of the absence of byproducts. Therefore, this reaction satisfies most of the requirements of click chemistry suggested in the original review,<sup>3a</sup> and it can be classified as a new metal-free click chemistry that further improves optoelectronic properties of organic materials. Some small nonplanar donor-acceptor molecules prepared by these reactions were demonstrated to show excellent second-order<sup>10</sup> and third-order<sup>11</sup> nonlinear optical effects.

We have already succeeded in introducing these donor– acceptor chromophores in aromatic polymers by the high-yielding postfunctionalization method using TCNE as an acceptor molecule.<sup>12</sup> Note that the postfunctional preparation of donor–acceptor structures within polymers has previously been reported using the tricyanovinylation of electron-rich aromatic rings with TCNE, but this reaction requires harsh conditions and produces hydrogen cyanide (HCN) as a byproduct.<sup>13</sup> Therefore, the efficiency is much less than that of our approach. However, we have not yet attempted double postfunctionalization using this reaction. Double postfunctionalization is a convenient methodology to prepare more complex functional polymers from a readily available precursor polymer in a controlled manner.

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Scheme 1. Thermal Addition Reaction between Alkynes Activated by Electron-Donating Groups (EDGs) and Strong Acceptor Molecules



The key requirements for achieving desired polymers are for quantitative yield and orthogonality to occur in both reactions. There is in fact increasing interest in the development of double click postfunctionalization, and many complex macromolecular architectures have successfully been synthesized.<sup>14</sup>

In this paper, we report for the first time the combination of the conventional CuAAC and alkyne-acceptor click reaction for establishment of the new double click postfunctionalization.<sup>15</sup> We selected the azide-functionalized polystyrene as a readily available and universally applicable precursor polymer, which was applied to the sequential click chemistry reactions. This report also demonstrates the applicability of the alkyne–TCNQ reaction to the postfunctional modification of polymers. The final polymer products contain densely attached donor–acceptor chromophores, featuring strong charge-transfer (CT) bands in the visible and near-IR region as well as redox activities in both anodic and cathodic directions. Therefore, the nonlinear optical properties of the polymers were evaluated by second-harmonic generation (SHG) measurements, and the structure–property relationship was summarized.

# **Experimental Section**

**Materials.** All reagents were purchased from Kanto, Tokyo Kasei, Wako, and Aldrich and used as received. [(4-Ethynylphenyl)ethynyl](triisopropyl)silane,<sup>16</sup> [(3-ethynylphenyl)ethynyl](triisopropyl)silane,<sup>16</sup> and poly(4-azidomethylstyrene) (4)<sup>17</sup> were synthesized according to the reported methods.

General Measurements. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a JEOL model AL300 spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from SiMe<sub>4</sub>, using the solvent's residual signal as an internal reference. The resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), and m (multiplet). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. 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<sup>-1</sup>. Relative molecular weights were determined by comparison with the calibrated standard polystyrenes. Absolute molecular weights were determined by using the detector miniDAWN Tristar. UV-vis spectra were recorded on a JASCO V-550 spectrophotometer. Elemental analysis was performed on a PerkinElmer 2400-Series II CHNS/O analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out on a Seiko SII TG 6220 and a Seiko SII DSC 6200, respectively, under nitrogen flow at a scanning rate of 10 °C min<sup>-1</sup>. Thickness of films was measured on a Dektak3ST surface profiler. Electrochemical measurements were carried out at 20 °C in dehydrated CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M (nC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>-NClO<sub>4</sub> in a classical three-electrode cell. The working and auxiliary electrodes were a glassy carbon disk electrode (2 mm in diameter) and a platinum wire, respectively. The reference electrode was Ag/AgCl/CH<sub>3</sub>CN/(nC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub>. All potentials are referenced to the ferricinium/ferrocene (Fc<sup>+</sup>/Fc) couple used as an internal standard.

Film Fabrication. Polymers were dissolved in dehydrated toluene at a concentration of  $\sim 3$  wt % and then filtered through a 0.2  $\mu$ m syringe filter. Polymer solutions were spin-coated on a glass slide, which has sequentially been cleaned by detergent, pure water, and acetone in an ultrasonic bath, followed by the

treatment with hexamethyldisilazane before use.<sup>18</sup> Residual solvents were removed by heating the films in vacuum at 70 °C.

NLO Measurements. Second-order optical nonlinearity of the polymers was determined by second harmonic generation (SHG).<sup>18</sup> The poling of polymer films was performed in a wire-to-plane geometry under in situ conditions. The discharging wire to plane distance was 10 mm. As the temperature gradually increased to a point 15–20 °C higher than  $T_{g}$ , 9.0 kV of corona voltage was applied and kept for 30 min. The films were cooled to 20 °C in the presence of the electric field, after which the SHG measurements were carried out with a Nd:YAG laser LOTIS TII LS-2132UTF operating at the 15 Hz repetition rate and 5-6 ns pulse duration at 1064 nm. The electric field vector of the incident beam was either parallel (p-polarization) or perpendicular (s-polarization) to the plane of incidence. SHG signals are corrected with a photomulitiplier after through a couple of blocking filters. The electric field of vector of SHG signals was selected with a polarizer to be either p- or s-polarization. A Y-cut crystal served as the reference.

*N*,*N*-**Dihexadecyl-4-iodoaniline (1).** To a solution of 4-iodoaniline (5.30 g, 24.2 mmol) in dehydrated DMF (50 mL), 1-iodohexadecane (28.0 g, 79.5 mmol) and sodium carbonate (4.50 g, 42.5 mmol) were added under nitrogen. The mixture was stirred at 95 °C for 20 h. After cooling to 20 °C, the mixture was washed with water (200 mL) and extracted by dichloromethane (200 mL). The organic phase was collected and dried over sodium sulfate. Evaporation and column chromatography (SiO<sub>2</sub>, hexane) afforded the desired product (13.0 g, 78%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.88 (m, 6 H), 1.26 (s, 52 H), 1.52 (m, 4 H), 3.18 (m, 4 H), 6.38 (d, *J* = 9.0 Hz, 2 H), 7.39 (d, *J* = 9.0 Hz, 2 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.13, 22.70, 27.02, 27.11, 28.56, 29.37, 29.43, 29.51, 29.56, 29.61, 29.67, 29.70, 30.52, 31.94, 33.58, 50.99, 75.29, 113.95, 137.60, 147.56.

N,N-Dihexadecyl-4-({4-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)aniline (2p). To a degassed solution of [(4-ethynylphenyl)ethynyl](triisopropyl)silane (1.00 g, 3.54 mmol) and 1 (2.36 g, 3.53 mmol) in diisopropylamine (40 mL), bis(triphenylphosphine)palladium(II) dichloride (50 mg, 0.070 mmol) and cuprous iodide (25 mg, 0.13 mmol) were added under argon. The mixture was stirred at 20 °C for 18 h. After removal of the precipitated salt by filtration, evaporation and column chromatography (SiO<sub>2</sub>, hexane) afforded the desired product (2.16 g, 74%)as a viscous liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.89 (m, 6 H), 1.14 (s, 18 H), 1.27 (m, 52 H), 1.58 (m, 7 H), 3.27 (m, 4 H), 6.57 (d, J = 8.7 Hz, 2 H), 7.36 (d, J = 8.7 Hz, 2 H), 7.41 (s, 4 H).<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 11.33, 14.12, 18.67, 22.68, 27.17, 29.54, 31.95, 50.95, 87.00, 91.98, 92.99, 107.01, 108.35, 111.17, 122.16, 124.33, 130.89, 131.85, 132.93, 148.07. IR (KBr): 2923, 2853, 2208, 2152, 1610, 1596, 1521, 1465, 1401, 1368, 1195, 1134, 882, 835, 812 cm<sup>-1</sup>. MALDI-TOF MS (dithranol): *m/z*: calcd for  $C_{57}H_{95}NSi^+$ : 821.72 g mol<sup>-1</sup>; found: 823.5 g mol<sup>-1</sup> [M + H]<sup>+</sup>. N,N-Dihexadecyl-4-({3-[(triisopropylsilyl)ethynyl]phenyl}-

ethynyl)aniline (2m). To a degassed solution of [(3-ethynylphenyl)ethynyl](triisopropyl)silane (1.00 g, 3.54 mmol) and 1 (2.36 g, 3.53 mmol) in diisopropylamine (40 mL), bis(triphenylphosphine)palladium(II) dichloride (50 mg, 0.070 mmol) and cuprous iodide (25 mg, 0.13 mmol) were added under argon. The mixture was stirred at 20 °C for 18 h. After removal of the precipitated salt by filtration, evaporation and column chromatography (SiO<sub>2</sub>, hexane) afforded the desired product (1.98 g, 68%)as a viscous liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.81 (m, 6 H), 1.07 (s, 18 H), 1.22 (m, 52 H), 1.51 (m, 7 H), 3.19 (m, 4 H), 6.49 (d, J = 7.2 Hz, 2 H), 7.17 (m, 1 H), 7.28 (m, 3 H), 7.34 (m, 1 H), 7.53 (s, 1 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 11.31, 14.13, 18.67, 22.70, 22.17, 29.54, 31.94, 50.96, 86.30, 90.86, 91.56, 106.49, 108.38, 111.15, 123.65, 124.55, 128.13, 130.74, 131.00, 132.92, 134.62, 148.03. IR (KBr): 2924, 2853, 2203, 2150, 1608, 1590, 1519, 1465, 1399, 1368, 1221, 1189, 1125, 1074, 883, 811, 790 cm<sup>-1</sup>. MALDI-TOF MS (dithranol): m/z: calcd for C<sub>57</sub>H<sub>95</sub>NSi<sup>+</sup>: 821.72 g mol<sup>-1</sup>; found: 823.5 g mol<sup>-1</sup> [M + H]<sup>+</sup>.

**4-[(4-Ethynylphenyl)ethynyl]**-*N*,*N*-dihexadecylaniline (3p). To a solution of **2p** (1.00 g, 1.21 mmol) in tetrahydrofuran (12 mL), tetrabutylammonium fluoride (1 M in tetrahydrofuran) (2.4 mL) was added under air. The mixture was stirred at 0 °C for 20 min. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) afforded the desired product (786 mg, 95%) as a yellow solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.90 (m, 6 H), 1.31 (m, 52 H), 1.55 (m, 4 H), 3.15 (s, 1 H), 3.34 (m, 4 H), 6.58 (d, *J* = 9 Hz, 2 H), 7.37 (d, *J* = 9 Hz, 2 H), 7.44 (s, 4 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.11, 22.69, 27.17, 29.61, 31.93, 50.94, 78.32, 83.57, 86.76, 93.24, 108.26, 111.17, 120.67, 124.97, 120.67, 124.97, 130.99, 131.92, 132.94, 148.11. IR (KBr): 3308, 2919, 2850, 2206, 2098, 1611, 1595, 1524, 1467, 1398, 1352, 1132, 842, 820 cm<sup>-1</sup>. MALDI-TOF MS (dithranol): *m/z*: calcd for C<sub>48</sub>H<sub>75</sub>N<sup>+</sup>: 665.59 g mol<sup>-1</sup>; found: 667.1 g mol<sup>-1</sup> [*M* + H]<sup>+</sup>.

**4-**[(**3-Ethynylphenyl)ethynyl]-***N***,***N***-dihexadecylaniline (<b>3m**). To a solution of **2m** (650 mg, 0.790 mmol) in tetrahydrofuran (8 mL), tetrabutylammonium fluoride (1 M in tetrahydrofuran) (2.4 mL) was added under air. The mixture was stirred at 0 °C for 20 min. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) afforded the desired product (520 mg, 99%) as a yellow solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.88 (m, 6 H), 1.29 (m, 52 H), 1.56 (s, 4 H), 3.07 (s, 1 H), 3.27 (m, 4 H), 6.56 (d, *J* = 9 Hz, 2 H), 7.29 (m, 1 H), 7.36 (m, 3 H), 7.46 (d, *J* = 7.5 Hz, 1 H), 7.52 (s, 1 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.13, 22.70, 27.15, 29.62, 31.94, 50.93, 83.04, 86.10, 91.75, 108.19, 111.10, 122.21, 124.70, 128.24, 130.76, 131.45, 132.92, 134.68, 148.01. IR (KBr): 3309, 2923, 2852, 2200, 1611, 1591, 1419, 1466, 1398, 1369, 1122, 811, 791 cm<sup>-1</sup>. MALDI-TOF MS (dithranol): *m/z*: calcd for C<sub>48</sub>H<sub>75</sub>N<sup>+</sup>: 665.59 g mol<sup>-1</sup>; found: 667.1 g mol<sup>-1</sup> [*M* + H]<sup>+</sup>.

**5p.** To a solution of **4** (31 mg, 0.20 mmol repeat  $unit^{-1}$ ) in DMF (8 mL), 3p (130 mg, 0.20 mmol), sodium ascorbate (3.9 mg, 0.012 mmol), and copper(II) sulfate pentahydrate (2.3 mg, 0.0098 mmol) were added under argon. The mixture was stirred at 20 °C for 24 h, yielding a yellow precipitate. The precipitate was filtered and washed with DMF, followed by methanol and water to afford the yellow solid (135 mg, 87%). The filtrate was poured into methanol to yield the residual desired polymer (total: 152 mg, 98%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.86 (m, 6n H), 1.25 (s, 52n H), 1.57 (m, 7n H), 3.19 (br s, 4n H), 5.47 (s, 2n H), 6.48 (br s, 2n H), 6.75 (br s, 2n H), 7.30 (d, J = 12.6 Hz, 4n H), 7.74 (br s, 5n H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 14.13, 22.69, 26.01, 27.15, 29.73, 31.92, 50.88, 87.13, 92.04, 108.51, 111.09, 123.98, 125.38, 127.55, 129.41, 131.66, 132.93, 147.27, 147.85. IR (KBr): 2923, 2852, 2207, 1603, 1524, 1458, 1368, 1190, 1136, 842, 812 cm<sup>-</sup>

**5m.** To a solution of **4** (47.7 mg, 0.300 mmol repeat unit<sup>-1</sup>) in DMF (12 mL), **3m** (200 mg, 0.300 mmol), sodium ascorbate (6.0 mg, 0.030 mmol), and copper(II) sulfate pentahydrate (3.7 mg, 0.0015 mmol) were added under argon. The mixture was stirred at 20 °C for 24 h, yielding a yellow precipitate. The precipitate was filtered and washed with DMF, followed by methanol and water to afford the yellow solid (209 mg, 87%). The filtrate was poured into methanol to yield the residual desired polymer (total: 235 mg, 98%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.86 (m, 6n H), 1.24 (s, 52n H), 1.50 (m, 7n H), 3.18 (br s, 4n H), 5.30 (s, 2n H), 6.19 (br s, 2n H), 6.49 (br s, 4n H), 6.72 (br s, 3n H), 7.68 (br s, 2n H), 7.96 (br s, 2n H). IR (KBr): 2923, 2852, 2210, 1603, 1579, 1519, 1458, 1368, 1198, 1130, 1045, 812, 791 cm<sup>-1</sup>.

**6p.** To a solution of **5p** (24.5 mg, 0.0295 mmol repeat unit<sup>-1</sup>) in chloroform (0.3 mL), a TCNE solution in 1,2-dichloroethane (0.163 M, 0.18 mL) was added under air. The mixture was stirred at 20 °C for 1 h. The solution was evaporated to afford **6p** (28.2 mg, 100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.86 (m, 6n H), 1.24 (s, 52n H), 1.59 (s, 7n H), 3.34 (m, 4n H), 5.48 (s, 2n H), 6.68 (br s, 4n H), 7.69 (br s, 8n H), 7.98 (s, n H). IR (KBr): 2923, 2852, 2214, 1604, 1489, 1418, 1346, 1212, 1182, 971, 820 cm<sup>-1</sup>. Elemental analysis calcd for (C<sub>63</sub>H<sub>84</sub>N<sub>8</sub>)<sub>n</sub>: C 79.37, H 8.88, N 11.75; found: C 79.56, H 9.27, N 11.17%.

(8.6 mM, 3.2 mL) was added under air. The mixture was stirred at 20 °C for 1 h. The solution was evaporated to afford **6m** (26.2 mg, 100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.86 (m, 6n H), 1.24 (s, 52n H), 1.59 (s, 7n H), 3.34 (br s, 4n H), 5.36 (br s, 2n H), 6.63 (s, 7n H), 7.46 (br s, 2n H), 7.76 (br s, 2n H), 8.00 (br s, n H), 8.44 (br s, n H). IR (KBr): 2923, 2852, 2214, 1603, 1490, 1417, 1342, 1211, 1183, 819, 701 cm<sup>-1</sup>. Elemental analysis calcd for (C<sub>63</sub>H<sub>84</sub>-N<sub>8</sub>)<sub>n</sub>: C 79.37, H 8.88, N 11.75; found: C 79.44, H 8.99, N 11.57%.

**7p.** To a solution of **5p** (21.0 mg, 0.0254 mmol repeat unit<sup>-1</sup>) in *o*-dichlorobenzene, a TCNQ solution in 1,2-dichloroethane (7.0 mM, 3.6 mL) was added under nitrogen. The mixture was stirred at 160 °C for 24 h. The solution was evaporated to afford **7p** (26.1 mg, 100%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.87 (m, 6n H), 1.26 (s, 52n H), 1.60 (s, 7n H), 3.33 (m, 4n H), 5.15–5.50 (br s, 2n H), 6.42–6.70 (br s, 6n H), 6.72–7.07 (br s, 4n H), 7.37–7.50 (br s, 4n H), 7.70–8.00 (s, n H). IR (KBr): 2922, 2852, 2202, 1581, 1522, 1458, 1401, 1348, 1178, 826, 715 cm<sup>-1</sup>. Elemental analysis calcd for (C<sub>69</sub>H<sub>88</sub>N<sub>8</sub>)<sub>n</sub>: C 80.50, H 8.62, N 10.88; found: C 81.07, H 8.93, N 10.00%.

**7m.** To a solution of **5m** (23.4 mg, 0.0284 mmol repeat unit<sup>-1</sup>) in *o*-dichlorobenzene, a TCNQ solution in 1,2-dichloroethane (7.0 mM, 4.0 mL) was added under nitrogen. The mixture was stirred at 160 °C for 24 h. The solution was evaporated to afford **7m** (29.0 mg, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.86 (m, 6n H), 1.24 (s, 52n H), 1.60 (s, 7n H), 3.33 (m, 4n H), 5.15–5.50 (br s, 2n H), 6.47–6.75 (br s, 6n H), 6.80–7.05 (br s, 4n H), 7.37–7.90 (br s, 7n H). IR (KBr): 2920, 2851, 2203, 1581, 1521, 1465, 1400, 1347, 1176, 822 cm<sup>-1</sup>. Elemental analysis calcd for (C<sub>69</sub>H<sub>88</sub>N<sub>8</sub>)<sub>n</sub>: C 80.50, H 8.62, N 10.88; found: 81.02, H 8.67, N 10.11%.

#### **Results and Discussion**

Monomer Synthesis. For the sequential and double click reactions, orthogonality in each reaction is important. We designed new molecules **3p** and **3m** having two kinds of alkyne groups: one a terminal alkyne and the other an internal electron-rich alkyne. The terminal alkynes will selectively react with azide substances under the CuAAC conditions, whereas the internal alkynes will be inert under those conditions. On the other hand, only the internal alkynes will display sufficient reactivity toward acceptors because of the activation by the dialkylanilino groups. In order to enhance the solubility of the final polymers, long alkyl chains of hexadecyl groups were introduced.

Starting from *N*,*N*-dihexadecyl-4-iodoaniline (1), prepared from 4-iodoaniline and 1-iodohexadecane, Sonogashira coupling with HC=CPhC=CSi(*i*Pr)<sub>3</sub> followed by silyl deprotection with  $(nC_4H_9)_4NF$  afforded the desired key molecules **3p** and **3m** in moderate yields (67–70% in two steps) (Scheme 2). The terminal alkynes of **3p** and **3m** were stable under ambient conditions, which were verified by the <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> with a sharp peak at 3.19 ppm for **3a** and 3.15 ppm for **3m**.

**Polymer Synthesis.** Poly(4-azidomethylstyrene) (4) was prepared as a precursor polymer by radical polymerization of 4-chloromethlystyrene with azobis(isobutyronitrile), followed by substitution of chlorine atoms with azide groups.<sup>17</sup> The molecular weight  $(M_n)$  and the polydispersity  $(M_w/M_n)$  determined by GPC relative to standard polystyrenes were 11 500 and 1.75, respectively. The azide group was confirmed by IR spectra with a strong vibrational peak at 2095 cm<sup>-1</sup> (Figure 1), and the content was determined to be 96% by elemental analysis.

The terminal alkynes of **3p** or **3m** were selectively reacted with azide groups of **4** in the presence of Cu(I) catalysts, yielding the tolane-appended polymers **5p** and **5m** (Scheme 3). We found that when the reaction is performed in DMF, the resulting high molecular weight polymers are deposited from



<sup>*a*</sup> Reagents and conditions: (a) HC=CPhC=CSi(*i*Pr)<sub>3</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, *i*Pr<sub>2</sub>NH, N<sub>2</sub>, 18 h; (b) (*n*C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NF, THF, 0 °C, 20 min.



Figure 1. IR spectra of polymers (a) 4, (b) 5p, (c) 6p, and (d) 7p.

the solutions. Thus, a simple filtration of the deposited precipitates after the reaction for 24 h provided the desired polymers **5p** and **5m** in a fairly good yield of 87%. Evaporation of the filtrate and subsequent precipitation into a water/ methanol (4:1) mixture afforded the residual desired polymers in a combined yield of 98%. The GPC measurements revealed a reasonable molecular weight increase. The  $M_{\rm n}$  and  $M_{\rm w}/M_{\rm n}$ values determined by GPC relative to standard polystyrenes are 52300 and 1.55 for 5p and 49000 and 1.85 for 5m (Table 1). The slightly lower molecular weight and higher polydispersity of the *m*-phenylene-linked 5m than the *p*-phenylene-linked **5p** seem to reflect the different hydrodynamic volumes in the GPC measurements. The absence of the terminal alkynes and the presence of the internal alkynes were confirmed by the <sup>1</sup>H NMR and IR spectra of 5p and 5m. In the IR spectra, both the strong azide vibrational peak at 2095 cm<sup>-1</sup> and the vibrational peak at  $3308 \text{ cm}^{-1}$  ascribed to the terminal alkynes of **3p** and **3m** disappeared, whereas the vibrational peak at 2207  $\text{cm}^{-1}$ originating from the internal alkynes of 3p and 3m remained (Figure 1). In the <sup>1</sup>H NMR spectra, the benzyl proton peak of **4** at 4.60 ppm completely shifted to 5.47 ppm for **5p** and 5.30 ppm for **5m** (Figure 2). Moreover, the terminal alkyne proton peak for **3m** centered at 3.07 ppm disappeared and the dialkylaniline peaks appeared after the CuAAC click modification. The <sup>13</sup>C NMR spectrum of **5p** also revealed the presence of the internal alkynes (Figure 1SI).

Subsequently, the second postfunctionalization was performed by adding acceptor molecules to **5p** and **5m** in chlorinated solvents. Because the resulting donor-acceptor chromophores usually feature well-defined CT bands in the visible region, the reactions were initially investigated by UV-vis spectroscopic titration experiments. When TCNE was selected as a compact acceptor molecule, the reaction immediately proceeded at room temperature, suggesting the occurrence of click postfunctionalization. Thus, the absorption intensities of the precursor polymers started to decrease, and a new CT band with the most intense peak at 481 nm for  $5p \rightarrow 6p$  and 483 nm for  $5m \rightarrow 6m$  appeared (Figure 3). The peak positions of the CT bands were unchanged, while the intensities almost linearly increased with the increasing amount of added TCNE, finally leading to completely red solutions. The presence of the isosbestic points at 308 and 382 nm for 5p and at 306 and 377 nm for 5m indicates no side reactions.

The same titration experiments were carried out for **5p** and 5m by using TCNQ as an expanded acceptor. Although the TCNQ addition to the monomeric electron-rich alkyne molecules proceeded at room temperature,<sup>19</sup> the polymeric reaction required heating. After a TCNQ solution was added to the precursor polymer solutions in o-dichlorobenzene, the mixtures were heated to 160 °C. The reaction temperature was carefully determined on the basis of thermal analyses of both precursor and produced polymers (vide infra). The solution color was gradually changed from yellow to green, and the UV-vis spectral changes suggested reaction completion in 40 min in the case of  $5p \rightarrow 7p$  and 90 min in the case of  $5m \rightarrow 7m$ . Stepwise addition of TCNQ to the precursor polymers 5p and 5m followed by heating to 160 °C for 40 and 90 min, respectively, provided clear spectral changes with the isosbestic points at 335 and 383 nm for 5p and at 310 and 372 nm for 5m, implying the absence of any undesired side reactions (Figure 4). The generated CT bands bathochromically shifted compared to the TCNE adducts, and the end absorptions reached the near-IR region. Thus, the most intense CT band was centered at 712 nm for 7p and 715 nm for **7m**, resulting in the green color.

The acceptor titration experiments revealed that TCNQ showed lower reactivity than TCNE, despite the similar first reduction potential of TCNQ ( $E_{red,1} = -0.25$  V vs Fc<sup>+/</sup>Fc) to that of TCNE ( $E_{red,1} = -0.32$  V vs Fc<sup>+/</sup>Fc).<sup>8c</sup> Furthermore, the *m*-phenylene-linked bent side chain needed a longer reaction time than the *p*-phenylene-linked straight side chain. These results indicate that the reactivity of the alkyne-acceptor addition is governed not only by the electron density of the alkyne moieties but also by steric factors. The larger molecular size of TCNQ compared to TCNE made the reactions more difficult on the confined polymer side chains, and this effect was more significant for the *m*-phenylene-linked **5m** than for the *p*-phenylene-linked **5p**.

The UV-vis titration experiments enabled us to prepare the full TCNE and TCNQ adducted polymers without any special purification processes. Addition of a stoichiometric amount of TCNE at room temperature and TCNQ at 160 °C to **5p** and **5m**, followed by evaporation of the solvents, quantitatively furnished the desired polymers, **6p**, **6m**, **7p**, and **7m** (Scheme 3). GPC measurements revealed a slight increase in the relative  $M_n$  values and a greater increase in the relative  $M_w$  values compared with the corresponding precursor polymer values (Table 1). These molecular weight

#### Scheme 3. Sequential Double Click Postfunctionalization of Polystyrene Derivative 4<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) CuSO<sub>4</sub>·5H<sub>2</sub>O, sodium ascorbate, DMF, 24 h; (b) TCNE, CHCl<sub>3</sub>, 1 h; (c) TCNQ, o-dichlorobenzene, 160 °C, 24 h.

 
 Table 1. Summary of Molecular Weights and Thermal Properties of the Polymers

polymer	$M_n^a$	$M_{ m w}/M_{ m n}{}^a$	$M_n^{\ b}$	$M_{ m w}/M_{ m n}^{\ b}$	$T_{\rm g}/^{\rm o}{\rm C}^c$	$T_{5\%}/^{\circ}\mathbf{C}^{d}$
4	11 500	1.75				
5p	52 300	1.55	217 000	1.64		361
5m	49 000	1.85	215 000	1.72		371
6р	58 500	1.80	306 000	1.33	130	313
6m	51 000	1.99	222 000	1.42	134	321
7p	53 200	2.55	131 000	1.16	127	315
7m	42 200	2.39	181 000	2.10	129	318

<sup>*a*</sup> Molecular weights determined by GPC (eluent: THF, calibrated by standard polystyrenes). <sup>*b*</sup> Molecular weights determined by GPC-MALS (multiangle light scattering). <sup>*c*</sup> Glass transition temperatures determined by DSC at the scanning rate of 10 °C min<sup>-1</sup>. <sup>*d*</sup> The 5% weight loss temperatures determined by TGA at the heating rate of 10 °C min<sup>-1</sup>.

increases are consistent with the definition of  $M_n$  and  $M_w$ . Accordingly, the polydispersities became larger after the acceptor additions, and this tendency is more significant when TCNQ was employed as an acceptor. The absolute molecular weights were also measured for the clicked polymers. They were ~4 times larger than the corresponding relative molecular weights, except for 7p (Table 1). The apparent decrease in the absolute  $M_n$  after TCNQ addition is probably ascribed to the low solubility of the products in the GPC eluent, THF.

The chemical structures of the chromophore-appended polymers were further characterized. The <sup>1</sup>H NMR and IR spectral changes of *p*-phenylene-linked and *m*-phenylenelinked derivatives were similar, so the representative spectra are shown in Figures 1 and 2. In the <sup>1</sup>H NMR spectra, some peaks such as the benzyl and aromatic protons became broader after the acceptor additions, implying the increased rotational barriers of parts of the single bonds due to the bulky and nonplanar acceptor moieties (Figure 2). This broadening was more significant in the case of the TCNQ adducted polymers, probably reflecting the larger chromophore size. The same tendency was observed for the <sup>13</sup>C NMR spectra (Figure 1SI). In the IR spectra, a weak alkyne vibrational peak ascribed to the tolane moieties of the precursor polymer **5p** was replaced by a strong cyano peak at 2214 cm<sup>-1</sup> for **6p** and 2202 cm<sup>-1</sup> for **7p** (Figure 1). The elemental analyses of all polymers **6p**, **6m**, **7p**, and **7m** showed good agreement with the calculated values. All of these results support the perfect postfunctionalization by the alkyne-acceptor addition reactions.

UV-vis absorption spectra of the chromophore-appended polymers were investigated in various solvents. Addition of trifluoroacetic acid (TFA) to the polymer solutions provided evidence of the CT bands. Because protonation of the dihexadecylaniline moieties results in a dramatic decrease in the electron-donating power, it is concluded that the decreased low-energy bands in the presence of TFA are derived from the CT bands (Figure 2SI). These bands were almost fully regenerated when the solutions were neutralized with triethylamine, suggesting good reversibility under the employed acid-base conditions.

Absorption and emission spectra of **6p** and **6m** were measured in various organic solvents, and the data were summarized as a function of solvent polarity  $E_{\rm T}(30)$  (Figure 3SI and Table 1SI).<sup>20</sup> Similarly to the small donor-substituted 1,1,4, 4-tetracyanobutadienes (TCBDs), both polymers displayed positive solvatochromism in the absorption spectra (Figure 4SI). Emission spectra were very weak and were composed of two peaks. The longer wavelength emission at ~670 nm is assumed to originate from the excimers, and these excimers tended to be predominantly formed in less polar solvents

such as cyclohexane and diethyl ether. This tendency is remarkable in the case of **6m**, probably representing the confined polymer environments.

**Electrochemistry.** One of the most important features of donor-acceptor chromophores is the redox activities. The obtained polymers were soluble in common organic solvents, such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and THF. Thus, cyclic voltammograms (CVs) were measured in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M  $(nC_4H_9)_4$ NClO<sub>4</sub> at 20 °C.



Figure 2.  ${}^{1}H$  NMR spectra of (a) 4, (b) 5m, (c) 6m, and (d) 7m in CDCl<sub>3</sub> at 20 °C.

Figure 5 shows the typical CV curves of the polymers. The tolane-appended polymers 5p and 5m displayed the only aniline-centered quasi-reversible oxidation waves at 0.28 and 0.22 V (vs Fc<sup>+</sup>/Fc), respectively (Table 2). On the other hand, the TCNE adducted polymers 6p and 6m showed anodically shifted first oxidation potentials  $(E_{\text{ox},1})$  at 0.84 and 0.79 V, respectively, as well as the TCBD-centered reversible first reduction potentials ( $E_{red,1}$ ) at -0.91 and -0.95 V, respectively. In contrast to the small donor-substituted TCBD molecules showing two well-resolved reduction steps,<sup>21</sup> the polymers displayed only single reduction waves. This is because the polymers tended to adsorb on the electrode surface during the voltage sweep. The anodic shift of  $E_{ox,1}$ can be explained by the efficient interaction of the dihexadecylanilino moiety with the TCBD acceptor, which makes the oxidation more difficult. The TCNQ adducted polymers **7p** and **7m** exhibited easier oxidations ( $E_{\text{ox},1}$  at 0.42 and 0.47 V, respectively) and reductions ( $E_{\text{red},1}$  at -0.68 and -0.76 V, respectively) than the corresponding TCNE adducted polymers, probably caused by the expanded  $\pi$ -conjugation of the acceptor moieties. This result means that the acceptor moieties of 7p and 7m more weakly interact with the dihexadecylanilino donors than the TCBD moieties of 6p and 6m. Consequently, the electrochemical band gaps  $\Delta(E_{\text{ox},1} E_{\rm red,1}$ ) of the TCNQ adducted polymers were much smaller than those of the TCNE adducted polymers, as summarized in Table 2. These electrochemical band gaps were in good agreement with the optical band gaps determined by the end absorptions in chlorinated solvents.

Thermal Properties. Thermal stability is very important for application of functional polymers in organic devices. To reveal the thermal properties of the postfunctionalized polymers in this work, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed at a scanning rate of 10 °C min<sup>-1</sup> under flowing nitrogen. In contrast to the previous report that demonstrated the thermal improvements in aromatic polyamine by the TCNE addition,<sup>12a</sup> the 5% decomposition temperatures  $(T_{5\%})$  of the TCNE adducted polymers **6p** and **6m** were lower than those of the corresponding precursor polymers 5p and **5m** (Table 1 and Figure 6). A similar decrease in  $T_{5\%}$  was also observed for the TCNQ adducted polymers 7p and 7m. These results may be derived from the intrinsic electron-accepting nature of the triazole ring. The  $T_{5\%}$ s of the *p*-phenylenelinked 6p and 7p are slightly lower than those of the corresponding *m*-phenylene-linked 6m and 7m due to the efficient through-bond communication between the triazole ring and the acceptor moieties. However, it was also shown that all the obtained polymers are thermally stable without any decomposition at least up to 200 °C.

DSC measurements of the chromophore-appended polymers were performed to estimate the glass transition temperatures



Figure 3. UV-vis spectral changes of (a) 5p and (b) 5m upon titration with TCNE (0-1.0 equiv) in chloroform at 20 °C.



Figure 4. UV-vis spectral changes of (a) 5p and (b) 5m upon titration with TCNQ (0-1.0 equiv) in o-dichlorobenzene at 160 °C.



Figure 5. Cyclic voltammograms of (a) 5p, (b) 6p, (c) 7p, (d) 5m, (e) 6m, and (f) 7m in CH<sub>2</sub>Cl<sub>2</sub> (+0.1 M (*n*C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub>) at 20 °C.

Table 2. Summary of the Electrochemistry Data of the Postfunctionalized Polymers in  $CH_2Cl_2 (+ 0.1 \text{ M} (nC_4H_9)_4\text{NCIO}_4)^a$ 

polymer	$E_{\rm ox,1}/{\rm V}$	$E_{\rm red,1}/{\rm V}$	$\Delta(E_{\rm ox,1}-E_{\rm red,1})/{\rm V}$	$\lambda_{end}/nm~(eV)$
5p	0.28			
5m	0.22			
6р	0.84	-0.91	1.75	750(1.65)
6m	0.79	-0.95	1.74	760 (1.63)
7p	0.42	-0.68	1.10	1150 (1.08)
7m	0.47	-0.76	1.23	1130 (1.15)

<sup>*a*</sup>Potentials vs Fc<sup>+</sup>/Fc. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl.

 $(T_{\rm g}s)$ , but they did not show any well-defined transitions in the range from -50 to 200 °C. Therefore, the synthesized polymers with unknown  $T_{\rm g}$  values were homogeneously mixed with poly(methyl methacrylate) (PMMA;  $M_{\rm w} =$ 250 000,  $M_{\rm n} = 178$  000) at various ratios, and the mixtures were subjected to the DSC measurements. PMMA displayed a  $T_{\rm g}$  of 115 °C, and this value gradually increased with the increasing synthesized polymer content (see Figure 5SI as an example of **6m**). Plots of the synthesized polymer content vs  $T_{\rm g}$  values were analyzed according to the Fox equation  $(T_{\rm g}^{-1} = w_1/T_{\rm g1} + w_2/T_{\rm g2}$ , where w is the weight



Figure 6. TGA curves of polymers (a) 5p, 6p, and 7p and (b) 5m, 6m, and 7m at the heating rate of 10 °C min<sup>-1</sup> under flowing nitrogen.

Table 3. Summary of SHG Measurements									
polymer	$\lambda_{\rm max}/{\rm nm}~({\rm eV})^a$	$\Phi^b$	film thickness/nm <sup>c</sup>	poling <sup>d</sup>	$d_{15}/\mathrm{pm}~\mathrm{V}^{-1}$	$d_{33}/\mathrm{pm}~\mathrm{V}^{-1}$	$d_{33}/d_{15}$		
6р	480 (2.58)	0.10	110	before poling	1.1	1.9	1.6		
				after poling	1.6	5.3	3.2		
<b>6m</b> 482	482 (2.57)	0.04	150	before poling	0.40	0.63	1.6		
				after poling	0.97	1.8	1.9		
<b>7</b> p 71	712.5(1.74)	0.51	165	before poling	0.40	0.27	0.69		
	× /			after poling	0.40	0.32	0.81		
<b>7m</b> 711.5	711.5 (1.74)	0.17	140	before poling	0.95	2.3	2.4		
				after poling	1.2	2.8	2.4		

<sup>*a*</sup> Measured as a thin film state on a glass slide. <sup>*b*</sup> Order parameter  $\Phi = 1 - A_1/A_0$ , where  $A_0$  and  $A_1$  are the absorbance of the polymer films before and after corona poling, respectively. <sup>*c*</sup> Measured by a Dektak3ST. <sup>*d*</sup> At 9.0 kV and 150 °C for 30 min.



**Figure 7.** SHG response from film of **6p** after poling. (a) Angular dependence of SHG signals. (b, c) Polarization dependence of p-polar and s-polar SHG signal measured at incident angle of  $45^{\circ}$ , respectively. In (b) and (c) polarization angle  $0^{\circ}$  corresponds to s-polarization of incident fundamental field.

fraction and  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of each polymer), which enabled estimation of the unknown  $T_{gs}$  of the chromophore-appended polymers. The estimated  $T_{g}$  values ranged from 127 to 134 °C (Table 1).

**NLO Properties.** To evaluate the second-order NLO activities of the obtained polymers bearing donor-acceptor chromophores, their thin films were prepared by spin-coating of the toluene solutions on a hydrophobically treated glass

substrate with hexamethyldisilazane. The film thicknesses were controlled in the range of 110-165 nm. The most efficient technique for studying the second-order NLO activities was to investigate the second harmonic generation (SHG) processes characterized by SHG coefficients ( $d_{15}$  and  $d_{33}$ ).<sup>2</sup> The noncentrosymmetric alignment of the donor-acceptor chromophores is essential for high SHG, and this is usually achieved by corona poling. Taking into account the thermal properties of the polymers, the corona poling was performed at 9.0 kV and 150 °C, slightly above  $T_g$ , for 30 min. Figure 6SI shows the UV–vis spectra of **6p**, **6m**, **7p**, and **7m** before and after the poling. The  $\lambda_{\rm max}$  values of the polymer thin films were almost the same as those in chlorinated solvents (Table 3). The solvatochromic investigations of 6p and 6m suggest that the solid state environment of these polymers corresponds to an  $E_{\rm T}(30)$  of ca. 40 kcal mol<sup>-1</sup>. Although the absorption wavelengths or the CT bands were unchanged, the intensities explicitly decreased after the poling. The absorbance decrease in the *p*-phenylene-linked side chain polymers **6p** and **7p** was more significant than that in the corresponding m-phenylenelinked side chain polymers 6m and 7m. The order parameters  $(\Phi)$  are summarized in Table 3.

The SHG measurements were performed at a fundamental wavelength of 1064 nm using a Nd: YAG laser at 20 °C. From the angular dependence of the SHG signals, the SHG coefficients ( $d_{15}$  and  $d_{33}$ ) were calculated with respect to the  $d_{11}$  of the quartz crystals (0.50 pm V<sup>-1</sup>).<sup>23</sup> Figure 7 shows an example of the measured data for the film of **6p** after poling. The specific symmetric shapes of the plots in Figure 7b,c suggest  $C_{\infty \nu}$  symmetry in chromophore ordering, where only  $d_{15}$  and  $d_{33}$  contribute to the SHG response. The  $d_{33}$  value of **6p** after the poling was the largest  $(5.3 \text{ pm V}^{-1})$  among the measured polymer samples (Table 3). After the corona poling of the **6p** thin film, the ratio of  $d_{33}/d_{15}$  was almost doubled and was slightly larger than the theoretical value of 3.<sup>24</sup> Although the  $d_{33}$  of **6m** and **7m** also increased due to the corona poling, their  $d_{33}/d_{15}$  values were almost unchanged. This result means that the number of the poled chromophores increased after the poling, but the chromophores were assumed to obliquely align due to the restricted movements. This effect was most remarkable in the case of 7p. The  $d_{15}$  is larger than  $d_{33}$  both before and after the poling, implying the difficulty of the chromophore alignment even by the poling above the estimated  $T_{\rm g}$ . All of these results indicate the importance of the isolated space for chromophore alignment. Thus, 6p with the small sized and less hindered compact donor-acceptor chromophores displayed the best SHG result. The reasons why the SHG activities were observed before poling and that the ratio of  $d_{33}/d_{15}$  was above 3 for **6p** are probably attributable to the specific interfacial interactions between the hydrophobically treated glass surface and the polymer peripheral substituents, such as aliphatic chains.

## Conclusion

A highly efficient sequential double click postfunctionalization method to introduce nonplanar donor-acceptor chromophores into polystyrene side chains was developed. In the first click postfunctionalization using CuAAC, selection of the appropriate reaction media such as DMF enabled us to isolate the desired polymers by simple filtration in good yields (up to 87%). The alkyne-acceptor addition reactions that we recently focused on as a metal-free click reaction were found to have compatibility with the conventional CuAAC click chemistry. When TCNE was employed as an acceptor, the reaction proceeded at 20 °C in a click chemistry fashion, while heating was necessary for reaction completion in the case of the TCNQ addition. This difference mainly reflects the steric factors in the congested polymer environments. The final polymers bearing donor-acceptor chromophores displayed intense CT bands at ca. 480 nm for the TCNE adducts and ca. 710 nm for the TCNQ adducts. Thus, the polymer colors are tunable from yellow (precursor) to red (TCNE adducts) and green (TCNQ adducts). The UV-vis absorption spectra were substantiated by the electrochemical measurements. The electrochemical band gaps were consistent with the corresponding optical band gaps determined by the end absorptions. There were no noticeable differences in the linear absorption and electrochemical properties between the straight *p*-phenylene spacer and the bent *m*-phenylene spacer in the side chain structure, namely 6p vs 6m or 7p vs 7m. However, when we further advanced into the SHG measurements with sufficient thermal stability in mind, a great difference resulted. Polymer 6p with the straight *p*-phenylene spacer and the compact TCBD acceptor moiety in the side chains displayed a much larger  $d_{33}$ value than those of **6m** with the bent *m*-phenylene spacer as well as 7p and 7m with bulky TCNQ adducted acceptor moieties. This result clearly indicates the importance of sufficient space for chromophore movement upon poling. The recent trend in designing organic electrooptic materials is directed toward dendritic structures utilizing the inner nanospaces.<sup>25</sup> Application of the double click postfunctionalization to the synthesis of dendritic donor-acceptor molecules and polymers will be worthwhile for future projects.

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**Supporting Information Available:** <sup>13</sup>C NMR spectra of **5p**, **6p**, and **7p**, and UV–vis and fluorescence spectral behavior of **6p**, **6m**, **7p**, and **7m** in various solvents and glass transition temperatures of **6m**/PMMA mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **References and Notes**

- (a) Fournier, D.; Hoogenboom, R.; Schubert, U. S. Chem. Soc. Rev. 2007, 36, 1369–1380. (b) Meldal, M.; Tornøe, C. W. Chem. Rev. 2008, 108, 2952–3015. (c) Tang, B. Z. Macromol. Chem. Phys. 2008, 209, 1303–1307. (d) Franc, G.; Kakkar, A. Chem. Commun. 2008, 5267–5276. (e) Binder, W. H.; Sachsenhofer, R. Macromol. Rapid Commun. 2008, 29, 952–981. (f) Lundberg, P.; Hawker, C. J.; Hult, A.; Malkoch, M. Macromol. Rapid Commun. 2008, 29, 998–1015. (g) Meldal, M. Macromol. Rapid Commun. 2008, 29, 1016–1051. (h) Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. Macromol. Rapid Commun. 2008, 29, 1052–1072. (i) Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. Chem. Rev. 2009, 109, 5620–5686. (j) Liu, J.; Lam, J. W. Y.; Tang, B. Z. Chem. Rev. 2009, 109, 5799–5867. (k) Carlmark, A.; Hawker, C. J.; Hult, A.; Malkoch, M. Chem. Soc. Rev. 2009, 38, 352–362.
- (2) (a) Gauthier, M. A.; Gibson, M. I.; Klok, H.-A. Angew. Chem., Int. Ed. 2009, 48, 48–58. (b) Sumerlin, B. S.; Vogt, A. P. Macromolecules 2010, 43, 1–13.
- (3) (a) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Angew. Chem., Int. Ed. 2001, 40, 2004–2021. (b) Tornøe, C. W.; Christensen, C.; Meldal, M. J. Org. Chem. 2002, 67, 3057–3064.
- (4) Baskin, J. M.; Prescher, J. A.; Laughlin, S. T.; Agard, N. J.; Chang, P. V.; Miller, I. A.; Lo, A.; Codelli, J. A.; Bertozzi, C. R. Proc. Natl. Acad. Sci. U.S.A. 2007, 104, 16793–16797.
- (5) For thiol-ene click chemistry, see: (a) Gress, A.; Völkel, A.; Schlaad, H. *Macromolecules* 2007, 40, 7928–7933. (b) Killops, K. L.; Campos, L. M.; Hawker, C. J. J. Am. Chem. Soc. 2008, 130, 5062–5064. (c) Shin, J.; Nazarenko, S.; Hoyle, C. E. *Macromolecules* 2008, 41, 6741–6746. (d) Campos, L. M.; Killops, K. L.; Sakai, R.; Paulusse, J. M. J.; Damiron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. J. *Macromolecules* 2008, 41, 7063–7070. (e) Chan, J. W.; Hoyle, C. E.; Lowe, A. B. J. Am. Chem. Soc. 2009, 131, 5751–5753. (f) Ma, X.; Tang, J.; Shen, Y.; Fan, M.; Tang, H.; Radosz, M. J. Am. Chem. Soc. 2009, 131, 14795–14803. (g) Hoyle, C. E.; Bowman, C. N.

*Angew. Chem., Int. Ed.* **2009**, *49*, 1540–1573. (h) Jones, M. W.; Mantovani, G.; Ryan, S. M.; Wang, X.; Brayden, D. J.; Haddleton, D. M. *Chem. Commun.* **2009**, 5272–5274. (i) Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. *Chem. Soc. Rev.* **2010**, *39*, 1355–1387. (j) Jim, C. K. W.; Qin, A.; Lam, J. W. Y.; Mahtab, F.; Yu, Y.; Tang, B. Z. Adv. *Funct. Mater.* **2010**, *20*, 1319–1328. (k) Lowe, A. B. *Polym. Chem.* **2010**, *1*, 17–36. (l) Koo, S. P. S.; Stamenović, M. M.; Prasath, R. A.; Inglis, A. J.; Du Prez, F. E.; Barner-Kowollik, C.; Camp, W. V.; Junkers, T. J. Polym. Sci., Part A: Polym. Chem. **2010**, *48*, 1699–1713. (m) Bardts, M.; Ritter, H. *Macromol. Chem. Phys.* **2010**, *211*, 778–781.

- (6) For Diels-Alder click chemistry, see: (a) Gacal, B.; Tasdelen, M. A.; Hizal, G.; Tunca, U.; Yagci, Y.; Demirel, A. L. Macromolecules 2006, 39, 5330-5336. (b) Ishida, K.; Yoshie, N. Macromol. Biosci. 2008, 8, 916-922. (c) Dag, A.; Durmaz, H.; Tunca, U.; Hizal, G. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 178-187. (d) Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. Macromolecules 2010, 43, 2643-2653. (e) Kavitha, A. A.; Singha, N. K. Macromolecules 2010, 43, 3193-3205. (f) Syrett, J. A.; Mantovani, G.; Barton, W. R. S.; Price, D.; Haddleton, D. M. Polym. Chem. 2010, 1, 102-106. (g) Akat, H.; Gacal, B.; Balta, D. K.; Arsu, N.; Yagci, Y. J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 2109-2114.
- (7) For other metal- and azide-free click chemistry, see: (a) Koyama, Y.; Yonekawa, M.; Takata, T. *Chem. Lett.* **2008**, *37*, 918–919. (b) Singh, I.; Zarafshani, Z.; Lutz, J.-F.; Heaney, F. *Macromolecules* **2009**, *42*, 5411–5413. (c) Lee, Y.-G.; Koyama, Y.; Yonekawa, M.; Takata, T. *Macromolecules* **2009**, *42*, 7709–7717. (d) Gutsmiedl, K.; Wirges, C.; Ehmke, V.; Carell, T. *Org. Lett.* **2009**, *11*, 2405–2408. (e) Lee, Y.-G.; Yonekawa, M.; Koyama, Y.; Takata, T. *Chem. Lett.* **2010**, *39*, 420–421.
- (8) (a) Bruce, M. I.; Rodgers, J. R.; Snow, M. R.; Swincer, A. G. J. Chem. Soc., Chem. Commun. 1981, 271–272. (b) Milan, K.; Diederich, F. Acc. Chem. Res. 2009, 42, 235–248. (c) Kato, S.-i.; Diederich, F. Chem. Commun. 2010, 46, 1994–2006.
- (9) Michinobu, T.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Frank,
   B.; Moonen, N. N. P.; Gross, M.; Diederich, F. *Chem.*—*Eur. J.* 2006, *12*, 1889–1905.
- (10) (a) Wu, X.; Wu, J.; Liu, Y.; Jen, A. K.-Y. J. Am. Chem. Soc. 1999, 121, 472–473. (b) Cai, C.; Liakatas, I.; Wong, M.-S.; Bösch, M.; Bosshard, C.; Günter, P.; Concilio, S.; Tirelli, N.; Suter, U. W. Org. Lett. 1999, 1, 1847–1849. (c) Ma, H.; Jen, A. K.-Y.; Wu, J.; Wu, X.; Liu, S.; Shu, C.-F.; Dalton, L. R.; Marder, S. R.; Thayumanavan, S. Chem. Mater. 1999, 11, 2218–2225. (d) Ma, H.; Chen, B.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. J. Am. Chem. Soc. 2001, 123, 986–987. (e) Ma, H.; Liu, S.; Luo, J.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. Adv. Funct. Mater. 2002, 12, 565–574. (f) Luo, J.; Ma, H.; Haller, M.; Jen, A. K.-Y.; Barto, R. R. Chem. Commun. 2002, 888–889. (g) Pereverzev, Y. V.; Prezhdo, O. V.; Dalton, L. R. Chem. Phys. Lett. 2003, 373, 207–212. (h) Luo, J.; Haller, M.; Ma, H.; Liu, S.; Kim, T.-D.; Tian, Y.; Chen, B.; Jang, S.-H.; Dalton, L. R.; Jen, A. K.-T. J. Phys. Chem. B 2004, 108, 8523–8530.
- (11) (a) Michinobu, T.; May, J. C.; Lim, J. H.; Boudon, C.; Gisselbrecht, J.-M.; Seiler, P.; Gross, M.; Biaggio, I.; Diederich, F. *Chem. Commun.* 2005, 737–739. (b) May, J. C.; LaPorta, P. R.; Esembeson, B.; Biaggio, I.; Michinobu, T.; Bures, F.; Diederich, F. *Proc. SPIE* 2006, 6331, 633101–1–14. (c) Esembeson, B.; Scimeca, M. L.; Michinobu, T.; Diederich, F.; Biaggio, I. *Adv. Mater.* 2008, 20, 4584–4587. (d) Koos, C.; Vorreau, P.; Vallaitis, T.; Dumon, P.; Bogaerts, W.; Baets, R.; Esembeson, B.; Biaggio, I.; Michinobu, T.; Diederich, F.; Freude, W.; Leuthold, J. *Nat. Photonics* 2009, *3*, 216–219.
- (12) (a) Michinobu, T. J. Am. Chem. Soc. 2008, 130, 14074–14075.
   (b) Michinobu, T.; Kumazawa, H.; Noguchi, K.; Shigehara, K. Macromolecules 2009, 42, 5903–5905.
- (13) (a) Wang, X.; Chen, J.-I.; Marturunkakul, S.; Li, L.; Kumar, J.; Tripathy, S. K. *Chem. Mater.* **1997**, *9*, 45–50. (b) Faccini, M.; Balakrishnan, M.; Diemeer, M. B. J.; Torosantucci, R.; Driessen, A.; Reinhoudt, D. N.; Verboom, W. *J. Mater. Chem.* **2008**, *18*, 5293–5300.
  (c) No, H. J.; Jang, H.-N.; Cho, Y. J.; Lee, J.-Y. J. Polym. Sci., Part A: Polym. Chem. **2010**, *48*, 1166–1172.
- (14) (a) Gacal, B.; Akat, H.; Balta, D. K.; Arsu, N.; Yagci, Y. Macromolecules 2008, 41, 2401–2405. (b) Dag, A.; Durmaz, H.; Demir, E.; Hizal, G.; Tunca, U. J. Polym. Sci., Part A: Polym. Chem. 2008, 46,

6969–6977. (c) Durmaz, H.; Dag, A.; Hizal, A.; Hizal, G.; Tunca, U. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 7091–7100.
(d) DeForest, C. A.; Polizzotti, B. D.; Anseth, K. S. Nat. Mater. 2009, 8, 659–664. (e) Shin, J.; Matsuhima, H.; Chan, J. W.; Hoyle, C. E. Macromolecules 2009, 42, 3294–3301. (f) Nurmi, L.; Lindqvist, J.; Randev, R.; Syrett, J.; Haddleton, D. M. Chem. Commun. 2009, 2727–2729. (g) Gupta, N.; Lin, B. F.; Campos, L. M.; Dimitriou, M. D.; Hikita, S. T.; Treat, N. D.; Tirrell, M. V.; Clegg, D. O.; Kramer, E. J.; Hawker, C. J. Nat. Chem. 2010, 2, 138–145. (x) Polaske, N. W.; McGrath, D. V.; McElhanon, J. R. Macromolecules 2010, 43, 1270–1276. (h) Stadermann, J.; Erber, M.; Komber, H. Macromolecules 2010, 43, 3136–3140. (i) Vieyres, A.; Lam, T.; Gillet, R.; Franc, G.; Castonguay, A.; Kakkar, A. Chem. Commun. 2010, 46, 1875–1877. (j) Durmaz, H.; Dag, A.; Gursoy, D.; Demirel, A. L.; Hizal, G.; Tunca, U. J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 1557–1564.

- (15) For a preliminary communication of this work, see: Li, Y.; Michinobu, T. *Polym. Chem.* **2010**, *1*, 72–74.
- (16) (a) Godt, A. J. Org. Chem. 1997, 62, 7471–7474. (b) Wang, F.; Kaafarani, B. R.; Neckers, D. C. Macromolecules 2003, 36, 8225– 8230.
- (17) (a) Urbani, C. N.; Bell, C. A.; Lonsdale, D. E.; Whittaker, M. R.; Monteiro, M. J. *Macromolecules* 2007, 40, 7056–7059. (b) Ornelas, C.; Mery, D.; Cloutet, E.; Aranzaes, J. R.; Astruc, D. J. Am. Chem. Soc. 2008, 130, 1495–1506.
- (18) (a) Lu, Z.; Shao, P.; Li, J.; Hua, J.; Qin, J.; Qin, A.; Ye, C. *Macromolecules* 2004, *37*, 7089–7096. (b) Raimundo, J.-M.; Lecomte, S.; Edelmann, M. J.; Concilio, S.; Biaggio, I.; Bosshard, C.; Günter, P.; Diederich, F. J. Mater. Chem. 2004, *14*, 292–295. (c) Li, Z.; Yu, G.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. Macromolecules 2009, *42*, 6463–6472.
- (19) (a) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* 2007, 4731–4733. (b) Kato, S.-i.; Kivala, M.; Schweizer, W. B.; Boudon, C.; Gisselbrecht, J.-P.; Diederich, F. *Chem.—Eur. J.* 2009, *15*, 8687–8691.
- (20) Reichard, C. Chem. Rev. 1994, 94, 2319-2358.
- (21) (a) Mochida, T.; Yamazaki, S. Dalton Trans. 2002, 3559–3564.
  (b) Morioka, Y.; Yoshizawa, N.; Nishida, J.-i.; Yamashita, Y. Chem. Lett. 2004, 33, 1190–1191. (c) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. Angew. Chem., Int. Ed. 2007, 46, 6357–6360. (d) Reutenauer, P.; Kivala, M.; Jarowski, P. D.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Diederich, F. Chem. Commun. 2007, 4898–4900. (e) Kivala, M.; Stanoeva, T.; Michinobu, T.; Frank, B.; Gescheidt, G.; Diederich, F. Chem.—Eur. J. 2008, 14, 7638–7647.
  (f) Shoji, T.; Ito, S.; Toyota, K.; Yasunami, M.; Morita, N. Chem.— Eur. J. 2008, 14, 8398–8408. (g) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Enko, B.; Seiler, P.; Müller, I. B.; Langer, N.; Jarowski, P. D.; Gescheidt, G.; Diederich, F. Chem.—Eur. J. 2009, 15, 4111–4123. (h) Frank, B. B.; Blanco, B. C.; Jakob, S.; Ferroni, F.; Pieraccini, S.; Ferrarini, A.; Boudon, C.; Gisselbrecht, J.-P.; Sieselbrecht, F. Chem.—Eur. J. 2009, 15, 4111–4123. (h) Frank, B. B.; Blanco, B. C.; Jakob, S.; Ferroni, F.; Pieraccini, S.; Ferrarini, A.; Boudon, C.; Gisselbrecht, J.-P.; Spida, G. P.; Diederich, F. Chem.—Eur. J. 2009, 15, 9005–9016.
- (22) (a) Dalton, L. R.; Harper, A. W.; Chosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K.-Y. *Chem. Mater.* 1995, 7, 1060–1081. (b) Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. J. *Mater. Chem.* 1997, 7, 2175–2189. (c) Ma, H.; Jen, A. K.-Y.; Dalton, L. R. *Adv. Mater.* 2002, *14*, 1339–1365. (d) Asselberghs, I.; Clays, K.; Persoons, A.; Ward, M. D.; McCleverty, J. J. *Mater. Chem.* 2004, *14*, 2831–2839. (e) Cho, M. J.; Choi, D. H.; Sullivan, P. A.; Akelaitis, A. J. P.; Dalton, L. R. *Prog. Polym. Sci.* 2008, *33*, 1013–1058.
- (23) Jerphagnon, J.; Kurtz, S. K. Phys. Rev. B 1970, 1, 1739-1744.
- (24) (a) Williams, D. J. In Nonlinear Optical Properties of Organic Molecules and Crystals; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987.(b) Eich, M.; Sen, A.; Looser, H.; Bjorklund, G. C.; Swalen, J. D.; Twieg, R.; Yoon, D. Y. J. Appl. Phys. 1989, 66, 2559–2567.
- (25) (a) Li, Z.; Qin, A.; Lam, J. W. Y.; Dong, Y.; Dong, Y.; Ye, C.; Williams, I. D.; Tang, B. Z. *Macromolecules* 2006, *39*, 1436–1442.
  (b) Dalton, L. R.; Sullivan, P. A.; Bale, D. H. *Chem. Rev.* 2010, *110*, 25–55.
  (c) Sullivan, P. A.; Dalton, L. R. *Acc. Chem. Res.* 2010, *43*, 10–18.
  (d) Li, Z.; Wu, W.; Li, Q.; Yu, G.; Xiao, L.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. Angew. Chem., Int. Ed. 2010, *49*, 2763–2767.