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Dendronized Polyfluorenes with High Azo-Chromophore Loading Density: Convenient Synthesis and Enhanced Second-Order Nonlinear Optical Effects

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ABSTRACT: Two new dendronized nonlinear optical (NLO) polyfluorenes were synthesized with high azo-chromophore loading density by the introduction of high generation chromophore dendrons on the side chains. Thanks to the advantages of Sharpless' click chemistry reaction, the dendrons were conveniently bonded to the backbone of polyfluorene with the conversion of 100%, although they were really very bulky. The new-formed triazole rings in the dendrons acted as suitable isolation groups to minimize the strong dipole–dipole interactions among the polar chromophore moieties to improve NLO effects, according to the results obtained from UV–vis spectra and order parameters. All the polymers were well characterized and exhibited good solubility, high thermal ability, wide optical window, and large NLO effects (up to 106.0 pm/V). In addition, the tested NLO results of these dendronzied polymers demonstrated a deviation from the dipolar frustration that typically limits the NLO effect in conventional chromophore/polymer composite materials, indicating that the frequently observed asymptotic dependence of electro-optic activity on chromophore density may be overcome through rational design.

Introduction

Since 1987, in pursuit of much larger size, well-defined macromolecular objects, chemistry researchers have designed a new architecture, termed as "dendronized polymers", by the attachment of the dendrimers to the linear polymeric backbone.[1−3] Dendronized polymers merge the concepts of dendrimers and linear polymers, and their most particular feature is that all of the side chains of polymers are dendrons, which make their shape like a "cylinder".[4] According to the literatures, the strategies for the preparation of dendronized polymers could be summarized into three categories—the graft-to, the graft-from, and the macromonomer approach—while the major challenges for these approaches are the difficulty in achieving complete dendron coverage of backbone in the graft-to and graft-from strategies and sometimes low polymerization degree in the macromonomer strategy.[5,6] Fortunately, as reported in the literature,[6] by the utilization of the 1,3-dipolar cycloaddition reactions between azides and alkynes (click chemistry),[7] a widely used synthetic tool in the preparation of dendrimers,[8] the converting efficiency via graft-to approach, could be perfect, even for the introduction of high generation dendrons.

On the other hand, the development of organic second-order nonlinear optical (NLO) materials is motivated by the promising of performance and cost improvements related to telecommunications, computing, embedded network sensing, terahertz wave generation and detection, and many other applications.[9,10] For the further development of NLO materials, one of the major problems encountered is how to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers, since the strong intermolecular dipole–dipole interactions among the chromophore moieties in the polymeric system make the poling-induced noncentrosymmetric alignment of chromophores a daunting task.[11] According to the site-isolation principle, the introduction of some isolation groups to the chromophore moieties is an effective approach to decrease the interactions and improve the poling efficiency.[11] Dalton and Jen et al. have prepared various series of NLO dendrimers and dendronized polymers, and their work confirmed that the dendritic structure is a very promising molecular topology for the next generation of highly efficient NLO materials.[12,13] Other groups also have synthesized some NLO dendrimers with good performance succsessfully.[14,15] On the basis of their excellent job, since 2006, with the attempt to partially solve the above problem, we prepared different kinds of NLO polymers, in which the size of the isolation groups in NLO chromophore moieties was changed from small to very larger, and the obtained experimental results demonstrated that the macroscopic nonlinearity of NLO polymers could be boosted several times higher by bonding "suitable isolation groups" to the NLO chromophore moieties.[16,17] Recently, our work on NLO hyperbranched polymers and dendrimers, prepared through click chemistry, showed that the triazole rings formed in the click chemistry reaction could act as suitable isolation groups to boost the NLO effects of the resultant polymer as high as possible, if carefully designed.[18] And very excitingly, in the case of NLO dendrimers, accompanied by the increasing of the loading density of the chromophore moieties, the tested NLO effects were going higher, indicating that the frequently observed asymptotic dependence of electro-optical activity on chromophore number density may be overcome through rational design,[18b] in accordance with the results and prediction of Sullivan, Robinson, and Dalton.[19]

To further confirm the abnormal but very important phenomenon, also considering that the "cylinder" structure of NLO dendronized polymers could benefit their NLO effects as proved

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by Jen et al.[20] and the relatively easy syntheses of dendronized polymers in comparison with those of dendrimers, we would like to introduce NLO dendrons with different generations and concentrations of chromophore moieties to linear polymeric backbone and try to study the relationship between the structure and properties. As discussed above, to achieve complete dendron coverage of the backbone, we prepared three dendronized polyfluorenes (**PG0**−**PG2**) by the usage of sharpless "click" reaction (Scheme 1). Although the bulky of **G2-≡** was very large, it could still be bonded to the backbone conveniently and completely, confirming the power of the click chemistry. To the best of our knowledge, this is the first report of high generation dendron-containing NLO dendronized polymers from the Sharpless "click" reaction. Compared to **PG0**, the chromophore loading density of **PG2** increased nearly 2 times (from 0.238 to 0.461); correspondingly, the macroscopic nonlinearity was also enhanced as high as 2.8 times (from 38.1 to 106.0 pm/V), repeating the interesting results obtained in the case of NLO dendrimers.[18b] In addition, from the UV−vis spectra, the isolation effect in **PG1**and **PG2** could be observed more clearly than that in **PG0**, indicating that the triazole moieties surrounded the azo chromophore moieties acted as suitable isolation groups and played a key role to shield them from the solvatochromic effect, further confirming our previous work.[18] Herein, we would like to report the syntheses, characterization, and NLO properties of these polymers.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried over and distilled from K−Na alloy under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Dichloromethane (CH_2Cl_2) was dried over anhydrous $CaCl_2$ and fresh distilled before use. *N,N*-Bis(2-azidoethyl)aniline (**2**) was synthesized through two steps according to the literature methods.[21] Compound **3**, chromophore **1**, and polymers (**P-N$_3$** and **PG0**) were prepared in our previous work.[17b,18] *N,N,N,N,N*-Pentamethyldiethylenetriamine (PMDETA) was purchased from Alfa Aesar. All other reagents were used as received.

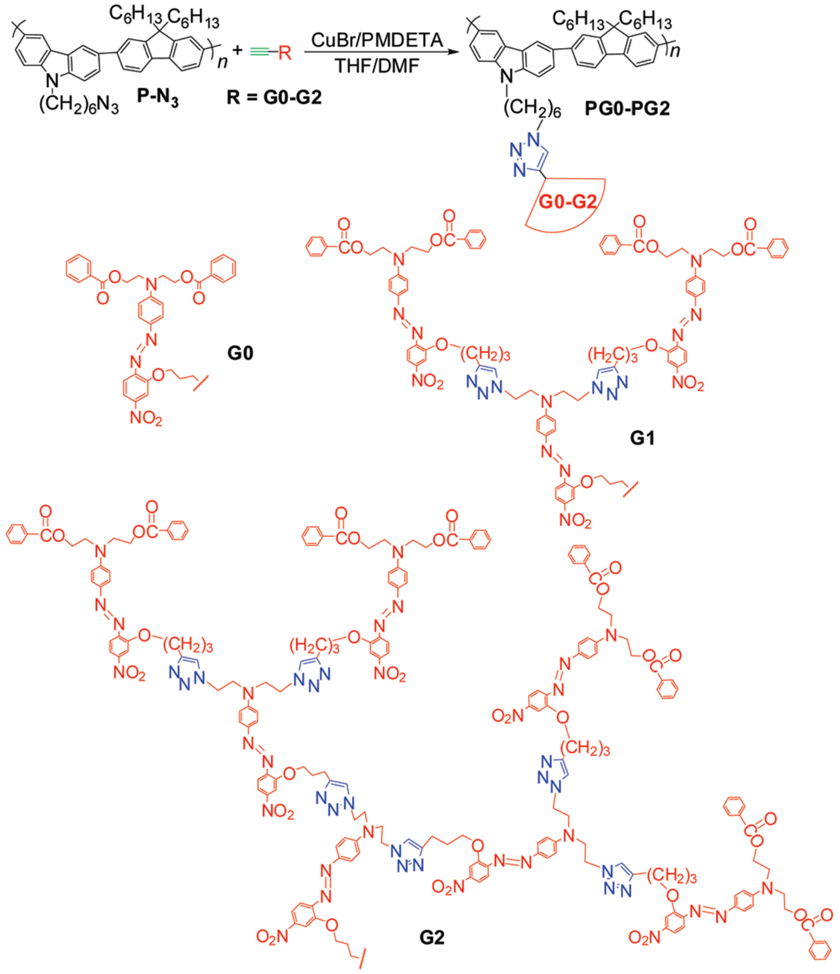
Instrumentation. ^1H and ^{13}C NMR and spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000−400 cm^{-1} on NaCl pellets. UV−vis spectra were obtained using a Schimadzu UV-2550 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectra were measured on a Voyager-DE-STR MALDI-TOF mass spectrometer (MALDI-TOF MS; ABI, American) equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive ion mode. Elemental analyses were performed by a CARLOERBA-1106 microelemental analyzer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. DMF was used as an eluent, and the flow rate was 1.0 mL/min. Thermal analysis was performed on a NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in nitrogen at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e under nitrogen at a scanning rate of 10 °C/min. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

Synthesis of G0-≡. Chromophore **1** (521 mg, 1.26 mmol), benzoic acid (463 mg, 3.80 mmol), dicyclohexylcarbodiimide (DCC) (900 mg, 4.36 mmol), and 4-(*N,N*-dimethyl)aminopyridine (DMAP) (55 mg, 0.45 mmol) were dissolved in dry CH_2Cl_2 (50 mL) and stirred at room temperature for 24 h. The precipitate was filtered, and the crude product was purified by column chromatography using ethyl acetate/chloroform (1/20) as eluent to afford red solid **G0-≡** (750 mg, 95.9%); mp = 130−132 °C. IR (thin film), υ (cm^{-1}): 1718 ($C{=}O$), 1516, 1342 ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 2.00 (s, 1H, $C{\equiv}CH$), 2.15 (m, 2H, $-CH_2-$), 2.50 (t, J = 6.6 Hz, 2H, $-CH_2C-$), 3.95 (t, J = 6.0 Hz, 4H, $-NCH_2-$), 4.34 (t, J = 5.7 Hz, 2H, $-OCHH_2-$), 4.58 (t, J = 5.7 Hz, 4H, $-OCHH_2-$), 6.97 (d, J = 8.7 Hz, 2H, ArH), 7.44 (t, J = 7.2 Hz, 4H, ArH), 7.56 (t, = 7.2 Hz, 2H, ArH), 7.67 (d, J = 8.7 Hz, 1H, ArH), 7.91 (m, 4H, ArH), 8.01 (d, J = 7.5 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 15.40, 28.26, 50.08, 61.97, 68.36, 69.51, 83.40, 109.52, 112.12, 116.85, 117.74, 126.44, 128.74, 129.87, 133.54, 145.27, 147.21, 148.64, 151.01, 155.42, 166.72. MS (EI), m/z [M^+]: 620.6, calcd: 620.2. $C_{35}H_{32}N_4O_7$ (EA) (%, found/calcd): C, 67.90/67.73; H, 5.17/5.20; N, 8.88/9.03.

Synthesis of Dendrimer G1. Chromophore **G0-≡** (732 mg, 1.18 mmol), *N,N*-bis(2-azidoethyl)aniline (**2**) (130 mg, 0.56), $CuSO_4\cdot 5H_2O$ (10 mol %), $NaHCO_3$ (20 mol %), and ascorbic acid (20 mol %) were dissolved in THF (15 mL)/H_2O (3 mL) under nitrogen in a Schlenk flask. The mixture was stirred at room temperature for 24 h, then extracted with chloroform, and washed with 1 N HCl, 1 N NH_4OH, and water subsequently. The organic layer was dried over anhydrous magnesium sulfate and purified by column chromatography using ethyl acetate/chloroform (2/1) as eluent to afford red solid **G1** (800 mg, 97.5%). IR (thin film), υ (cm^{-1}): 1723 ($C{=}O$), 1511, 1341 ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 2.23 (m, 4H, $-CH_2-$), 2.94 (t, J = 6.6 Hz, 4H, $-CH_2C-$), 3.60 (t, J = 5.1 Hz, 4H, $-NCH_2-$), 3.94 (t, J = 5.1 Hz, 8H, $-NCH_2-$), 4.14 (t, J = 5.7 Hz, 4H, $-NCH_2-$), 4.29 (t, J = 6.0 Hz, 4H, $-OCHH_2-$), 4.57 (t, J = 6.0 Hz, 8H, $-COOCH_2-$), 6.49 (d, J = 8.1 Hz, 2H, ArH), 6.69 (t, J = 7.2 Hz, 1H, ArH), 6.94 (d, J = 8.7 Hz, 4H, ArH), 7.15 (m, 4H, ArH and $C{=}CH$), 7.41 (t, J = 7.5 Hz, 8H, ArH), 7.55 (t, J = 7.2 Hz, 4H, ArH), 7.63 (d, J = 8.7 Hz, 2H, ArH), 7.79−7.86 (m, 4H, ArH), 7.92 (d, J = 8.7 Hz, 4H, ArH), 8.00 (d, J = 7.2 Hz, 8H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 22.02, 28.71, 47.58, 50.09, 51.75, 61.94, 68.70, 109.37, 112.13, 112.96, 116.72, 117.71, 118.68, 122.45, 126.44, 128.74, 129.85, 130.02, 133.54, 145.22, 145.99, 147.13, 148.56, 151.02, 155.36, 166.71. MALDI-TOF MS: calcd for ($C_{80}H_{77}N_{15}O_{14}$): m/z $[M + H]^+$: 1472.6; found: m/z 1472.6. $C_{80}H_{77}N_{15}O_{14}$ (EA) (%, found/calcd): C, 65.62/65.25; H, 4.95/5.27; N, 14.07/14.27.

Synthesis of Dendrimer G1-≡. Diazonium salt (**3**) (177 mg, 0.55 mmol) and dendrimer **G1** (741 mg, 0.50 mmol) were dissolved in DMF (6 mL) at 0 °C. The reaction mixture was stirred for 40 h at 0 °C, then treated with H_2O and extracted with CH_2Cl_2 (DCM), and washed with brine. The organic layer was dried over anhydrous sodium sulfate. After removal the organic solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate/chloroform (2/1) as eluent to afford red solid **G1-≡** (650 mg, 76.5%). IR (thin film), υ (cm^{-1}): 1719 ($C{=}O$), 1518, 1342 ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 2.04 (s, 1H, $C{\equiv}CH$), 2.11 (m, 2H, $-CH_2-$), 2.24 (m, 4H, $-CH_2-$), 2.48 (m, 2H, $-CH_2C-$), 2.94 (t, J = 6.6 Hz, 4H, $-CH_2C-$), 3.71 (br, s, 4H, $-NCH_2-$), 3.93 (t, J = 6.0 Hz, 8H, $-NCH_2-$), 4.14 (t, J = 5.7 Hz, 4H, $-NCH_2-$), 4.37 (m, 6H, $-OCHH_2-$), 4.56 (t, J = 5.7 Hz, 8H, $-COOCH_2-$), 6.54 (d, J = 9.0 Hz, 2H, ArH), 6.93 (d, J = 8.7 Hz, 4H, ArH), 7.23 (s, 2H, $C{=}CH$), 7.41 (t, J = 8.1 Hz, 8H, ArH), 7.52−7.65 (m, 7H, ArH), 7.75−7.90 (m, 12H, ArH), 7.98 (d, J = 7.5 Hz, 8H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 15.65, 22.37, 28.54, 28.93, 47.77, 50.42, 51.79, 62.22, 68.62, 69.14, 69.84, 83.66, 109.84, 112.27, 112.45, 116.96, 117.05, 117.93, 118.03, 122.83, 126.63, 126.72, 129.03, 130.14, 133.83, 145.52, 145.93, 147.00, 147.45, 147.70, 148.86, 149.17, 149.67, 151.34, 155.64, 155.89, 166.98. MALDI-TOF MS: calcd for ($C_{91}H_{86}N_{18}O_{17}$): m/z $[M + H]^+$: 1703.6; found:

Scheme 1



m/z 1703.4. $C_{91}H_{86}N_{18}O_{17}$ (EA) (%, found/calcd): C, 64.56/64.15; H, 4.62/5.09; N, 14.73/14.80.

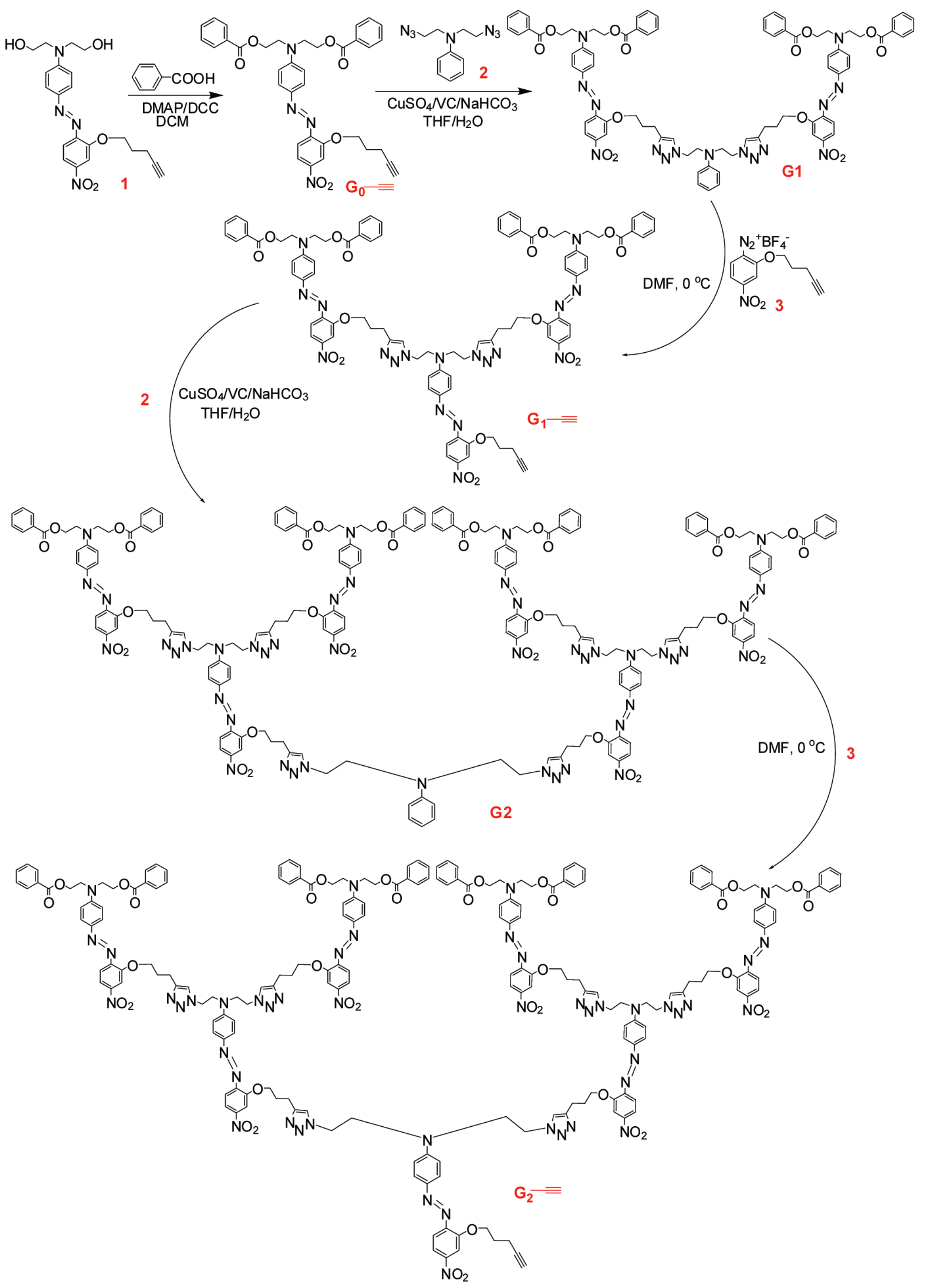
Synthesis of Dendrimer G2. The procedure was similar as the synthesis of dendrimer **G1**. Dendrimer **G1-≡** (468 mg, 0.275 mmol), *N,N*-bis(2-azidoethyl)aniline (**2**) (29 mg, 0.125 mmol). The crude product was purified by column chromatography on silica gel using THF/chloroform (1/2) as eluent to afford red solid **G2** (330 mg, 72.6%). IR (thin film), υ (cm^{-1}): 1719 (C=O), 1518, 1339 ($-NO_2$). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.20 (br, s, 12H, $-CH_2-$), 2.94 (br, s, 12H, $-CH_2C-$), 3.75 (m, 12H, $-NCH_2-$), 3.92 (br, s, 16H, $-NCH_2-$), 4.08 (br, s, 12H, $-NCH_2-$), 4.44 (br, s, 12H, $-OCHH_2-$), 4.55 (br, s, 16H, $-COOCH_2-$), 6.51 (d, J = 9.6 Hz, 4H, ArH), 6.57 (d, J = 7.5 Hz, 2H, ArH), 6.73 (t, J = 7.2 Hz, 1H, ArH), 6.93 (d, J = 8.1 Hz, 8H, ArH), 7.13 (t, J = 7.5 Hz, 2H, ArH), 7.37 (t, J = 7.5 Hz, 16H, ArH), 7.45−7.80 (m, 36 H, ArH and C=CH), 7.85 (d, J = 8.1 Hz, 8H, ArH), 7.96 (d, J = 8.1 Hz, 16H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.96, 25.83, 28.58, 28.85, 47.64, 47.89, 50.12, 51.37, 51.81, 61.93, 68.21, 68.72, 109.41, 111.86, 112.13, 113.36, 116.58, 116.71, 117.64, 122.96, 126.24, 126.47, 128.73, 129.74, 129.82, 129.99, 133.54, 145.08, 145.43, 146.36, 146.80, 146.95, 147.20, 148.42, 148.64, 149.56, 151.08, 155.26, 155.48, 166.69. MALDI-TOF MS: calcd for ($C_{192}H_{185}N_{43}O_{34}$): m/z $[M + Na]^+$: 3661.8; found: m/z 3661.9. $C_{192}H_{185}N_{43}O_{34}$ (EA) (%, found/calcd): C, 63.49/63.37; H, 5.29/5.12; N, 16.45/16.55.

Synthesis of Dendrimer G2-≡. The procedure was similar as the synthesis of dendrimer **G1-≡**. Dendrimer **G2** (255 mg, 0.070 mmol), diazonium salt (**3**) (50 mg, 0.157 mmol). The crude product was purified by column chromatography on silica gel using THF/chloroform (1/2) as eluent to afford red solid **G2-≡** (150 mg, 62.8%). IR (thin film), υ (cm^{-1}): 1719 (C=O), 1518, 1342 ($-NO_2$). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.10−2.26 (br, s, 15H, $-CH_2-$ and $C\equiv CH$), 2.44 (t, 2H, $-CH_2C-$), 2.93 (br, s, 12H, $-CH_2C-$), 3.75−3.92 (m, 28H, $-NCH_2-$), 4.07 (m, 12H, $-NCH_2-$), 4.26 (t, J = 6.9 Hz, 2H, $-OCHH_2-$), 4.42 (br, s, 12H, $-OCHH_2-$), 4.55 (m, 16H, $-COOCH_2-$), 6.48 (d, J = 7.8 Hz, 4H, ArH), 6.60 (d, J = 9.6 Hz, 2H, ArH), 6.95 (d, J = 7.8 Hz, 8H, ArH), 7.37−7.46 (m, 16H, ArH), 7.49−7.80 (m, 41 H, ArH and C=CH), 7.83 (d, J = 8.7 Hz, 8H, ArH), 7.96 (d, J = 7.8 Hz, 16H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 15.65, 22.00, 28.63, 29.92, 30.90, 47.66, 50.15, 51.45, 61.94, 68.74, 68.80, 83.39, 109.44, 112.14, 116.70, 117.64, 122.92, 126.43, 128.72, 129.82, 133.53, 145.18, 147.29, 128.41, 149.60, 151.08, 155.28, 155.51, 166.65. MALDI-TOF MS: calcd for ($C_{203}H_{194}N_{46}O_{37}$): m/z $[M + Na]^+$: 3893.0; found: m/z 3893.2. $C_{203}H_{194}N_{46}O_{37}$ (EA) (%, found/calcd): C, 63.16/63.00; H, 5.07/5.05; N, 16.83/16.65.

General Procedure for the Synthesis of PG1 and PG2. A mixture of polymer **P-N$_3$** (1.00 equiv), dendrimers **G1-≡** or **G2-≡** (1.10 equiv), and CuBr (1.00 equiv) were dissolved in THF/DMF (2/1 in volume) (0.1 M **N$_3$** in THF) under nitrogen in a Schlenk flask, and then *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) (1.00 equiv) was added. The mixture was stirred at room temperature for 3 h and then dropped into a large amount of methanol. The obtained polymer was filtered and washed with a lot of acetone.

PG1. **P-N$_3$** (20 mg), **G1-≡** (60 mg, 0.035 mmol). **PG1** was obtained as red powder (72 mg, 97.3%). M_w = 15 570, M_w/M_n = 2.56 (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1723 (C=O), 1516, 1342 ($-NO_2$). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.5−0.9 ($-CH_3$), 0.9−1.4 ($-CH_2-$and $-CH_3$), 1.6−1.9 ($-CH_2-$), 1.9−2.3 ($-CH_2-$), 2.7−3.0 ($-CH_2-$), 3.5−4.6

Scheme 2



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(−NCH$_2$− and −OCHH$_2$−), 6.3−6.5 (ArH), 6.7−7.0 (ArH), 7.0−8.0 (ArH), 8.4 (ArH).

PG2. **P-N$_3$** (8 mg), **G2-≡** (55 mg, 0.014 mmol). **PG2** was obtained as red powder (52 mg, 91.5%). M_w = 18 440, M_w/M_n = 2.38 (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1719 (C=O), 1519, 1339 (−NO$_2$). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.6−0.9 (−CH$_3$), 0.9−1.4 (−CH$_2$−and −CH$_3$), 1.5−2.0 (−CH$_2$−), 2.0−2.4 (−CH$_2$−), 2.8−3.0 (−CH$_2$−), 3.6−4.6 (−NCH$_2$− and −OCHH$_2$−), 6.4−6.6 (ArH), 6.8−7.0 (ArH), 7.2−8.1 (ArH), 8.5 (ArH).

Preparation of Polymer Thin Films. The polymers were dissolved in THF (concentration ~3 wt %), and the solutions were filtered through syringe filters. Polymer films were spin-coated onto indium−tin oxide (ITO)-coated glass substrates, which were cleaned by *N*,*N*-dimethylformamide, acetone, distilled water, and THF sequentially in an ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

NLO Measurement of Poled Films. The second-order optical nonlinearity of the polymers was determined by in situ second harmonic generation (SHG) experiment using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature: different for each polymer (Table 2); voltage: 7.7 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a 10 Hz repetition

Table 1. Polymerization Results and Characterization Data of Polymers

no.	yield (%)	M_w[a]	M_w/M_n[a]	T_g[b] (°C)	T_d[c] (°C)	T_e[d] (°C)	l_s[e] (μm)	d_{33}[f] (pm/V)	$d_{33(\infty)}$[g] (pm/V)	Φ[h]	N[i]
PG0	78.5	14 600	1.39	86	290	70	0.42	38.1	7.7	0.10	0.238
PG1	97.3	15 570	2.56	90	290	86	0.37	91.0	16.9	0.14	0.382
PG2	91.5	18 440	2.38	96	295	106	0.39	106.0	19.9	0.15	0.461

[a] Determined by GPC in THF on the basis of a polystyrene calibration. [b] Glass transition temperature (T_g) of polymers detected by the DSC analyses under argon at a heating rate of 10 °C/min. [c] The 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 10 °C/min. [d] The best poling temperature. [e] Film thickness. [f] Second harmonic generation (SHG) coefficient. [g] The nonresonant d_{33} values calculated by using the approximate two-level model. [h] Order parameter $\Phi = 1 - A_1/A_0$; A_1 and A_0 are the absorbance of the polymer film after and before corona poling, respectively. [i] The loading density of the effective chromophore moieties.

rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

Table 2. Maximum Absorption of Polymers (0.01 mg/mL) (λ_{max}, nm)

	THF	1,4-dioxane	$CHCl_3$	CH_2Cl_2	DMF	DMSO	film
PG0	464	463	464	464	481	487	474
PG1	461	460	455	455	474	481	467
PG2	461	458	455	456	472	480	466

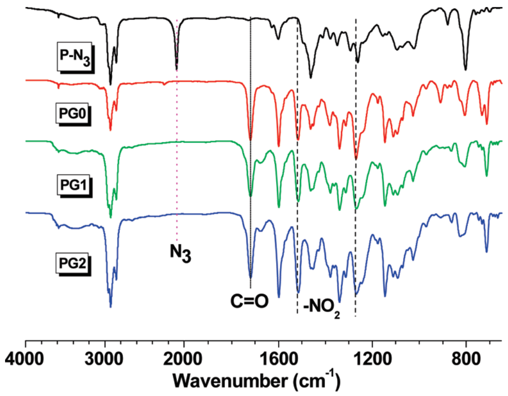


Figure 1. IR spectra of polymer **P0** and dendronized polymers **PG0**−**PG2**.

Results and Discussion

Synthesis. As shown in Scheme 2, the dendrons (**G1-≡** and **G2-≡**), containing a reactive terminal alkyne group for the further functionalization, were successfully synthesized using the convergent methodology through the combination of Cu^I-catalyzed alkyne−azide "click chemistry" and azo coupling reaction. The formed triazole heterocycles in each layer acted as good isolation groups, of which the function was often ignored. Moreover, the dendrimers constructed through convergent approach by click chemistry are still rare, and most were obtained using divergent approach.[8,22] This is possibly due to the difficulty in finding a suitable reaction route. Here, we took advantage of the combination of click chemistry and azo coupling reaction, making all the involved reactions being conducted under very mild conditions, and the efficiency of this synthetic approach was very high, with no need to protect/deprotect some functional groups or include the converting process from one reactive group to another.

P-N$_3$ and **PG0** were prepared as reported previously,[17b] and here, **P-N$_3$** was used as important mother polymer, while **PG0** for comparison. Following similar synthetic procedure as **PG0**, dendronized polymers **PG1** and **PG2** were prepared conveniently through the click reaction between azido-containing conjugated polymer **P-N$_3$** and the predesigned NLO dendritic chromophores (**G1-≡** and **G2-≡**). The reaction progress was monitored by FT-IR spectrum as the azido groups absorb strongly at about 2096 cm^{-1}. Thanks to the powerful "click chemistry", all the reactions proceeded quickly and completely in about 3 h, although the bulky of the introduced dendrons was very large.

Structural Characterization. The dendritic chromophores and dendronized polymers were characterized by spectroscopic methods, and all gave satisfactory spectral data corresponding to their expected molecular structures (see Experimental Section and Tables 1 and 2 for detailed analysis data). Figure 1 showed the IR spectra of **P-N$_3$** and dendronized polymers **PG0**−**PG2**; it was easily seen that after the click reaction not only the absorption bands of the azido groups of **P-N$_3$** centered at 2096 cm^{-1} but also the ≡C−H stretching vibrations of chromophores at about 3296 cm^{-1} disappeared completely in **PG0**−**PG2**, indicating the complete conversion of the dendrons. In addition, the new absorption bands associated with the nitro groups (1340 and 1519 cm^{-1}) and the carbonyl groups (1723 cm^{-1}) appeared in the IR spectra in **PG0**−**PG2**, further confirming the successful attachment of the NLO dendritic chromophore moieties to the conjugated backbone.

In all the ^{1}H NMR spectra of the polymers (Figure 2 and Figure S1), the chemical shifts were consistent with the proposed polymer structure as demonstrated in Scheme 1. For example, as shown in Figure 2, the peak attributed to the methylene groups linked with the azido groups ($-CH_2N_3$) of **P-N$_3$** at about 3.3 ppm could not be found; this further confirmed the complete conversion of the dendrons. In addition, in comparison with the ^{1}H NMR spectrum of **P-N$_3$**, it was clearly seen that the appeared new peaks were in good agreement with the chemical shifts of the protons of the dendritic chromophore (**G2-≡**), for example, the peaks at about 6.4−6.6 and 6.8−7.0 ppm, which were attributed to the signal of the phenyl proton at the ortho position to the amino group in two types of aniline moieties.

The molecular weights of polymers were determined by gel permeation chromatography (GPC) with THF as an eluent and polystyrene standards as calibration standards. As shown in Table 1 and the Experimental Section, after the dendritic chromophores introduced, the weight-average molecular weights (M_w) of dendronized polymers (**PG0**−**PG2**) increased, and with the growth of dendrons, the increased extent of M_w was much higher. The polymers were thermolytically resistant, with their TGA thermograms shown in Figure 3, and the 5% weight loss temperature of polymers are listed in Table 1. The results showed that all the polymers exhibited good thermal stability and nearly no apparent weight loss observed blow 215 °C. The growth of the NLO dendrimers introduced into the polymer also caused the increasing of the glass transition temperature (T_g), as observed by DSC measurement (Table 1). The T_g increased from **PG0**, 86 °C, to **PG1**, 90 °C, and then further increased to **PG2**, 96 °C.

UV−vis Spectra and Site-Isolation Effects. All the dendronized polymers exhibited good solubility, and they were easily soluble in common polar organic solvents such as $CHCl_3$, CH_2Cl_2, THF, 1,4-dioxane, DMF, and DMSO. The UV−vis absorption spectra of the polymers in different

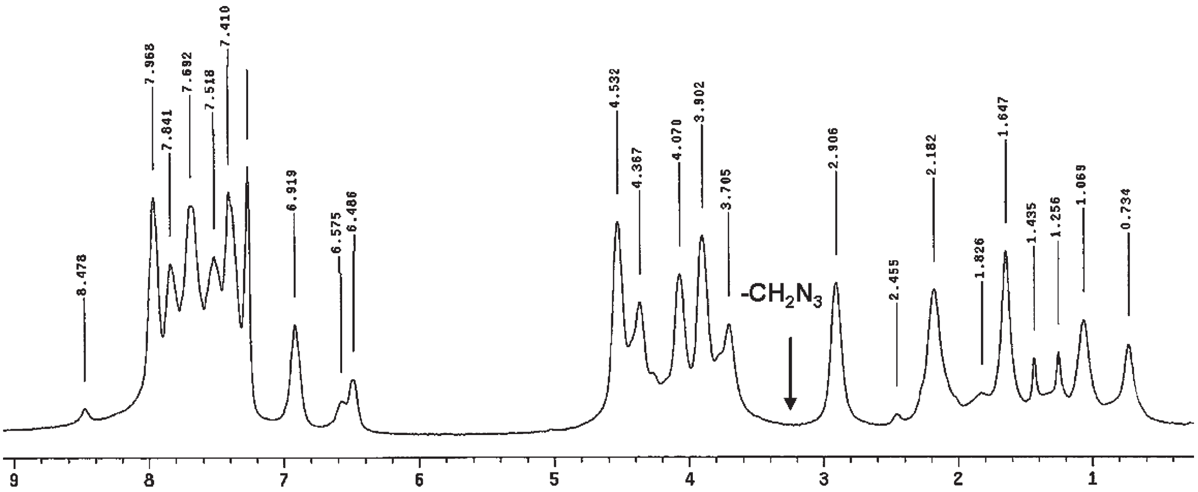


Figure 2. ^{1}H NMR spectrum of **PG2** in chloroform-*d*.

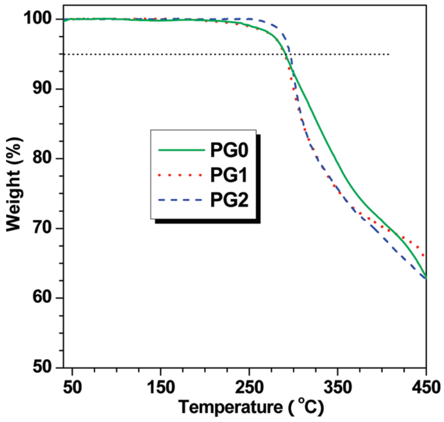
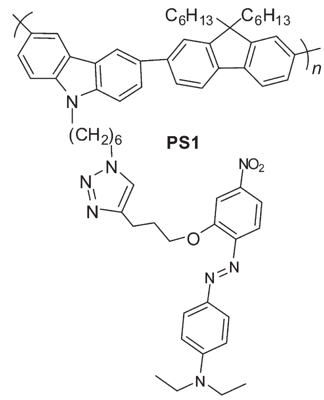


Figure 3. TGA thermograms of **PG0**−**PG2**, measured in nitrogen at a heating rate of 10 °C/min.

Chart 1



solvents are demonstrated in Figures 4 and Figures S2−S5, and the maximum absorption wavelengths for the π−π* transition of the azo moieties in them are listed in the Experimental Section and Table 2. As shown in Figure 4, from the spectrum of **PG0** to **PG2**, the peak at 350 nm attributed to the absorption of conjugated backbone weakened, while the peak at 460−480 nm enhanced, indicating the increase of the chromophore loading density with the growth of the introduced NLO dendrons.

It was easily seen that from **PG0** to **PG2**, the maximum absorption wavelength was blue-shifted up to 9 nm (in CHCl$_3$, Figure 4) in different organic solvents. And the difference of the same dendronized polymer in different solvents was also different, for example, the maximum absorption of **PG0** was 464 nm in THF, but 481 nm in DMF (17 nm red-shifted), while those of **PG2** are 461 and 472 nm (only 11 nm red-shifted), respectively. The phenomena should be ascribed to the site-isolation effect, revealing the fact that the isolation moieties surrounded the azo chromophore moieties shielded them from the solvatochromic effect upon the growth of the NLO dendrons introduced.

Actually, the effective isolation effect was achieved in **PG0** to some degree, in comparison with **PS1** (Chart 1),[17b] in which no isolation groups was introduced. The maximum absorption of **PS1** was 494 nm in THF, but 505 nm in dichloromethane (11 nm red-shifted), while those of **PG0** were nearly the same in these two different solvents. However, **PG1** and **PG2** were even blue-shifted 6 nm, while the solvents changed from THF to dichloromethane. The enhanced isolation effects in **PG1** and **PG2** should be attributed to the new-formed [1,2,3]-triazole rings in each layer of the NLO dendritic chromophore moieties, which possibly acted as suitable isolation groups, similar as observed in our previous work.[18] The maximum absorption wavelengths of **PG1** and **PG2** in solid films were also blue-shifted (about 6 nm) in comparison with that of **PG0** and further confirmed the above conclusion. Generally, the enhanced effective site isolation achieved no matter whether in solution or solid state of **PG1** and **PG2** would directly reduce the strong intermolecular dipole−dipole interactions between chromophore moieties and benefit the ordered noncentrosymmetric alignment during the poling process. In addition, the blue-shifted maximum absorption of dendronized polymers would surely result in their wide optical transparency window and contribute to the practical application.

NLO Properties. To evaluate the NLO activity of the polymers, their poled thin films were prepared. The most convenient technique to study the second-order NLO activity was to investigate the second harmonic generation (SHG) processes characterized by d_{33}, an SHG coefficient.[23] Calculation of the SHG coefficients (d_{33}) for the poled films was based on the eq 1:[24]

$$\frac{d_{33,\mathrm{s}}}{d_{11,\mathrm{q}}} = \sqrt{\frac{I_\mathrm{s}}{I_\mathrm{q}}\frac{l_{\mathrm{c,q}}}{l_\mathrm{s}}}F \qquad (1)$$

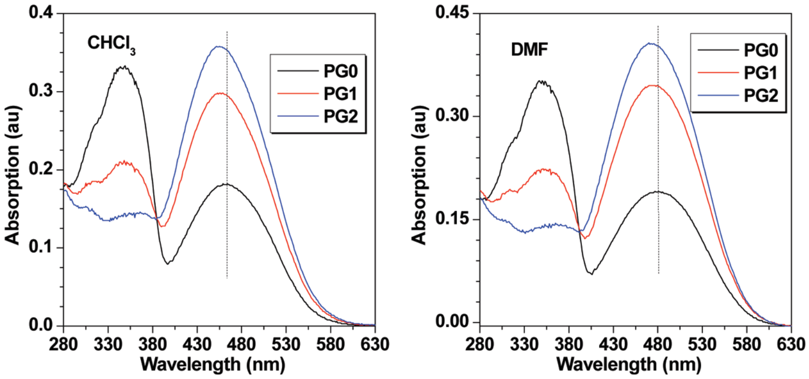


Figure 4. UV−vis spectra of CHCl$_3$ and DMF solutions of polymers **PG0**−**PG2** (0.01 mg/mL).

where $d_{11,q}$ is d_{11} of the quartz crystals, which is equal to 0.45 pm/V. I_s and I_q are the SHG intensities of the sample and the quartz, respectively, $l_{c,q}$ is the coherent length of the quartz, l_s is the thickness of the polymer film, and F is the correction factors of the apparatus and equals 1.2 when $l_c \gg l_s$. The poling conditions and measured d_{33} values of these polymers were similar as used previously,[16−18] and from the experimental data, the d_{33} values of **PG1** and **PG2** were calculated at 1064 nm fundamental wavelength (Table 1). As the dendronized polymers were derived from the same starting reactive polyfluorene **P-N$_3$**, their NLO properties could be compared nearly on the same level.

Here, as shown in Table 1, the obtained NLO results were encouraging, and the dendronized polymers demonstrated relatively larger d_{33} values (up to 106.0 pm/V) than our other linear NLO side-chain polymers carrying the similar azobenzene chromophores such as **PS1** (21.7 pm/V) and those with suitable isolation groups. This should be ascribed to their good "cylinder" structure, which could decrease the dipole−dipole interaction of chromophore moieties effectively. As there might be some resonant enhancement due to the absorption of the chromophore moieties at 532 nm, the NLO properties of dendronized polymers should be smaller as shown in Table 1 ($d_{33}(\infty)$), which were calculated by using the approximate two-level model. Because of their high d_{33} values and wide optical transparency window, the $d_{33}(\infty)$ value of **PG2** was still as high as 19.9 pm/V, much higher than those of the reported NLO polymers with nitro as acceptor.

According to the one-dimensional rigid orientation gas model[25]

$$d_{33} = \frac{1}{2} N\beta f^{2\omega}(f^{\omega})^2\langle\cos^3\theta\rangle \qquad (2)$$

where N is the number density of the chromophore, β is its first hyperpolarizability, f is the local field factor, 2ω is the double frequency of the laser, ω is its fundamental frequency, and $\langle\cos^3\theta\rangle$ is the average orientation factor of the poled film; under identical experimental conditions, we could consider d_{33} was proportional to the density of the chromophore moieties. However, the relationship between the chromophore density and the NLO effect was not linear any longer, especially at high chromophore loading density, due to the strong chromophores dipole−dipole electrostatic interaction. So there would be a maximum value of NLO effect at a special concentration of the chromophore moieties, and further increasing the loading level of chromophore moieties would only decrease the NLO effect. Fortunately, the introduction of isolation groups could restrain the interaction to enhance the poling efficiency, according to the site-isolation principle. However, they also caused the decrease of chromophore density. Thus, there was still a critical point and the relationship was not linear. Here, the results observed from these dendronzied polymers demonstrated a deviation from the dipolar frustration that typically limited the NLO effect in conventional chromophore/polymer composite materials. Figure 5A displayed the comparison of the d_{33} values at different effective chromphore density (N) in the polymers. It was seen that the chromophores loading density increased upon the growth of NLO dendrons; correspondingly, the tested NLO effect also became larger. In comparison with that of **PG0** (38.1 pm/V), the d_{33} value of **PG1** enhanced 2.39 times (91.0 pm/V), while their chromophores loading density was raised from 0.238 to 0.382. When the loading density further increased to 0.461, the d_{33} values of **PG2** enhanced even higher (106.0 pm/V) accordingly.

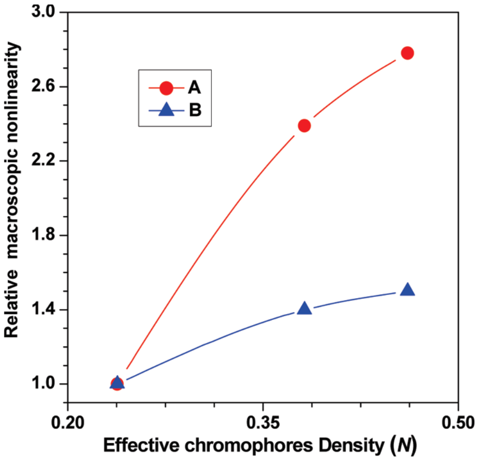


Figure 5. (A) Comparison of the d_{33} values at different effective chromphore density (N) of the polymers. (B) Comparison of the Φ values at different effective chromphore density (N) of the polymers.

This exciting phenomenon was reasonable. Here, through carefully design, we synthesized different generation of NLO dendrons and then introduced them into polymer backbone to form dendronized polymers. With the growth of the NLO dendrons, the shape of polymers would be adjusted from a flattened sphere to cylinder, which was the best shape requested by the site-isolation principle. In addition, the peripheral phenyl rings and the triazole rings in each layer could act as "suitable isolation groups" based on our previous work[16−18] and the results from their UV−vis spectra as discussed above. Therefore, the strong chromophore dipole−dipole interactions could be effectively restrained, and the unwanted attenuation of nonlinear optical activity would minimize at high chromophore loading density due to

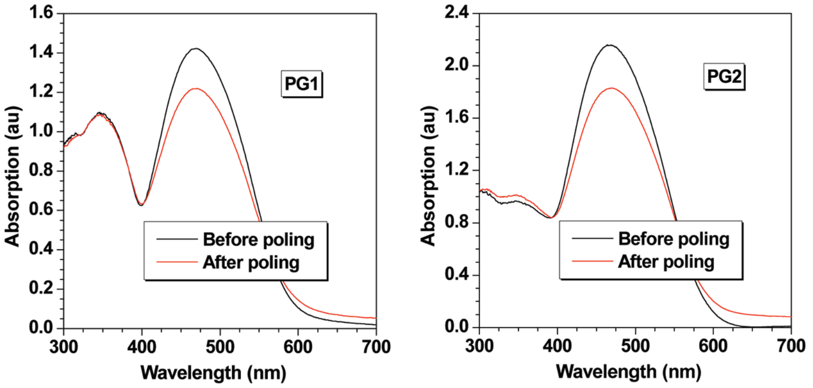


Figure 6. Absorption spectra of the films of **PG1** and **PG2** before and after poling.

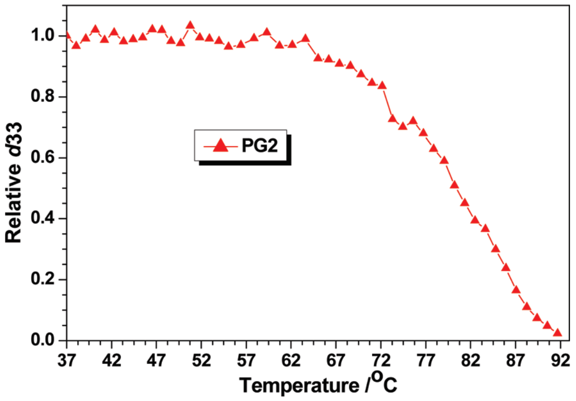


Figure 7. Decay curve of SHG coefficient of **PG2** as a function of temperature.

the well-designed molecular architectures (cylinder shape and the linked suitable isolation groups). Combined with the recent work of Sullivan, Robinson, and Dalton and their prediction,[19] our obtained results disclosed that by choosing suitable isolation spacers and through rational design, it is possible to experimentally realize the linear relationship between the loading density of chromophore moieties and the electro-optical activity.

To further explore the alignment of the chromophore moieties in these dendronized polymers, we measured their order parameter (Φ), and the results are listed in Table 1. Figure 6 demonstrated the UV−vis spectrum of the films of **PG1** and **PG2** before and after corona poling, and in order to observe the results more directly, Figure 5B displayed the comparison of the Φ values at different effective chromophore density (N) of the polymers. Similar to the trend of the d_{33} values, the Φ values also increased accompanying with the increase of the chromophore loading density, indicating that the alignment of the chromophore moieties under electric field poling became much easier, with the growth of the generation number of dendrons introduced into the polymer backbone. This should be attributed to the triazole rings, which played a key role to minimize the strong intermolecular dipole−dipole interactions as good isolation groups. And upon the growth of dendrons, their effects gradually enhanced, realizing our original idea of the utilization of triazole rings as suitable isolation spacers.

The dynamic thermal stabilities of the NLO activity of **PG2** were investigated by depoling experiments, in which the real time decays of their SHG signals were monitored as the poled films were heated from 35 to 100 °C in air at a rate of 4 °C/min. Figure 7 showed the decay of the SHG coefficient of **PG2** as a function of temperature; the onset temperature for decay was found to be 70 °C. Although not high enough for practical application, it would be a relatively good result, considering that the T_g of **PG2** was only 96 °C. In the next step, we would like to introduce these dendrons into high-T_g polymeric backbone, which might produce better NLO dedronized polymers with very exciting long-term stability of the NLO effect. Further study is still in progress in our laboratory.

Conclusion

For the first time, different generation NLO dendrons were introduced into conjugated polymers (polyfluorene) through powerful Sharpless' click chemistry. Upon the growth of the generation number, the bulk of dendrons became much larger, but the dendron conversion efficiency still remained about 100%, confirming the remarkable features of click chemistry. The experimental results of UV−vis spectra and order parameters confirmed that the triazole rings act as suitable isolation groups. And accompanying with the increasing of the loading density of the chromophore moieties, the NLO test demonstrated that for well-designed dendritic materials the NLO effects became much higher, partially proving the prediction of Dalton et al. and indicated that the frequently observed asymptotic dependence of electro-optic activity on chromophore number density may be overcome through rational design.

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Supporting Information Available: ^{1}H NMR spectra of **PG1** and UV−vis spectra of **PG1** and **PG2** in different solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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