

Dendronized Polymers with High FTC-chromophore Loading Density: Large Second-order Nonlinear Optical Effects, Good Temporal and Thermal Stability

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Electronic Supplementary Information

Abstract In this study, two new dendronized nonlinear optical (NLO) polymers were synthesized with high FTC chromophore loading density by introduction of high generation chromophore dendrons on the side chains. Due to their suitable molecular weights, both of them possessed good solubility in common solvents. They also inherited the advantages of dendrimers (large NLO coefficient), especially for **PG2** whose NLO coefficient d_{33} value was as high as 282 pm·V⁻¹. Also, **PG2** had a good temporal stability with 80% of its maximum value being retained at the temperature as high as 129 °C.

Keywords Second-order nonlinear optics; Dendronized polymers; Chromophore

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INTRODUCTION

Organic polymeric nonlinear optical (NLO) materials have attracted much research interest due to their potential applications in photonic devices, such as frequency doublers, ultrafast optical switches, optical storage devices, and optical modulators. Compared to inorganic NLO materials, for example, lithium niobate, polymeric NLO materials possess lots of advantages including large NLO effect, good processability, chemical resistance, and ultrafast response.^[1–6] Our group has conducted systematic study on organic polymeric NLO materials, such as linear polymers, hyperbranched polymers, dendronized polymers, and dendronized hyperbranched polymers.^[7–12] As for dendronized polymers, they possess some interesting properties from both dendritic macromolecules and linear polymers, especially large NLO effect and good solubility. In 2009, two dendronized polymers were synthesized with high azo chromophore loading density by the introduction of high generation chromophore dendrons on the side chains, which exhibited good solubility, high thermostability (up to 295 °C), and large NLO coefficient (up to 106.0 pm·V⁻¹).^[13–18] However, a higher macroscopic NLO coefficient was limited by the lower intrinsic

microscopic $\mu\beta$ value of azo chromophore. We realized that the FTC chromophore (Fang's thermally-stable chromophores) with a higher $\mu\beta$ value should be employed to achieve better integrated properties (Fig. 1).

On the other hand, a major problem must be solved for the realization of higher macroscopic NLO effects, that is, how to efficiently translate large β values of organic chromophores into high macroscopic NLO activities.^[14,15] Because chromophores have strong intermolecular dipole-dipole interactions, the required electric poling could not be so efficient to convert the natural centrosymmetric alignment of chromophore moieties into the badly needed noncentrosymmetric alignment. As a result, the macroscopic NLO activities could not be boosted as high as possible but somehow depressed. Fortunately, based on the excellent works of other scientists, our group found that the intermolecular dipole-dipole interactions among chromophore moieties can be reduced largely by introducing suitable isolation groups.^[16–22] Even for FTC chromophores, the triazole group could be a suitable isolation group for reserving its high NLO activities and high thermal stability.^[23–26] Thus, the click reaction to get triazole under mild conditions was chosen for the synthesis of dendronized polymers **PG1** and **PG2** (Fig. 1), in which two FTC and three FTC were linked to the polymeric backbone by the click chemistry reaction. This is the first time that FTC dendrons were introduced into linear polymers for the construction of dendronized polymers, to the best of our knowledge. Herein,

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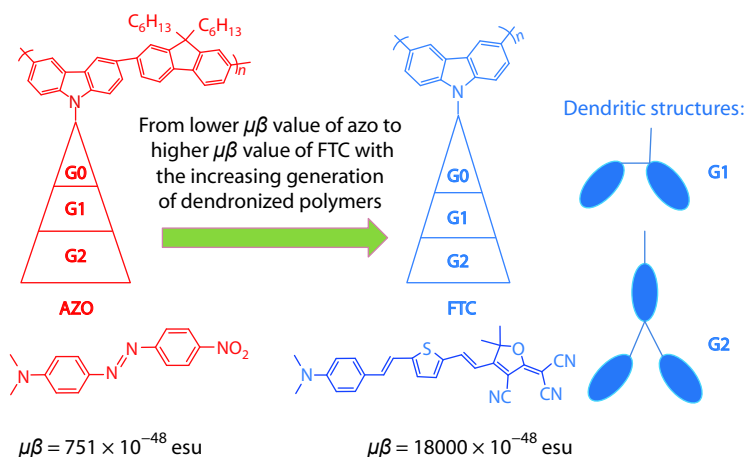


Fig. 1 Concept of molecular design.

we would like to present the synthesis, characterization, thermal stability, and optical and NLO properties of the dendronized polymers **PG1**, **PG2**, and linear polymer **PG0** in detail.

EXPERIMENTAL

Materials and Instrumentation

Dichloromethane and *N,N*-dimethylformamide (DMF) were dried over and distilled from calcium hydride. Anhydrous ethanol was dried over and distilled from metallic sodium. Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Compound **5**, compound **7**, and **G0** have been previously reported by our group (molecular structures of the compounds are given in Figs. S1–S4 in the electronic supplementary information, ESI). All other reagents were used as received.

G1. Under an atmosphere of dry nitrogen, a solution of compound **6** (Fig. S2 in ESI, 146 mg, 0.11 mmol), 1,4-diethynylbenzene (53 mg, 0.33 mmol), copper sulfate pentahydrate (10% mmol), sodium bicarbonate (20% mmol), and sodium L-ascorbate (20% mmol) in 6 mL of THF/H₂O (5/1, V/V) was stirred at 30 °C for 3 h. Then, the reaction mixture was poured into water and extracted with CH₂Cl₂ for three times (50 mL × 3). The combined organic solution was dried over anhydrous sodium sulfate and condensed *via* rotary evaporation. The residue was purified by column chromatography on silica gel using CH₂Cl₂/ethyl acetate (15/1, V/V) as eluent to give blue solid (124 mg, 80.2%). ¹H-NMR (400 MHz, CD₂Cl₂, δ , ppm): 9.08 (d, *J* = 15.7 Hz, 1H, —CH=), 7.97 (s, 1H, —CH=), 7.90–7.71 (m, 4H, —CH= and ArH), 7.62–7.54 (m, 2H, ArH), 7.46–7.32 (m, 5H, —CH= and ArH), 7.29 (s, 1H, —CH=), 7.18–6.96 (m, 5H, —CH= and ArH), 6.75–6.57 (m, 6H, —CH= and ArH), 4.44 (dt, *J* = 14.1, 7.1 Hz, 4H, —CH₂—), 3.34 (q, *J* = 7.5 Hz, 8H, —CH₂—), 3.23 (s, 1H, —C≡H), 2.03–1.94 (m, 4H, —CH₂—), 1.83 (s, 6H, —CH₃), 1.78 (s, 6H, —CH₃), 1.63 (d, *J* = 9.9 Hz, 6H, —CH₂—), 1.48–1.33 (m, 22H, —CH₂—), 0.98–0.91 (m, 6H, —CH₃). ¹³C-NMR (100 MHz, CD₂Cl₂, δ , ppm): 174.35, 173.32, 154.26, 152.95, 149.27, 148.93, 146.58, 142.68, 140.50, 139.33, 138.93, 137.71, 135.42, 134.52, 132.58, 132.24, 131.33, 129.04, 128.88, 126.92, 125.82, 125.34, 122.83, 122.69, 122.33, 121.45, 120.11, 115.43, 114.64, 112.58, 112.15, 112.05, 111.96, 111.84,

111.70, 111.58, 111.16, 97.65, 97.28, 83.26, 77.85, 53.96, 53.69, 53.41, 51.00, 50.77, 50.55, 50.34, 31.71, 30.22, 30.07, 27.23, 27.05, 26.73, 26.41, 26.38, 26.34, 22.71, 13.85. C₈₃H₈₆N₁₄O₂S₂ (EA) (Found/Calcd., %): C, 72.42/72.59; H, 6.34/6.38; N, 14.19/14.11; MALDI-TOF MS: Calcd. for (C₈₃H₈₆N₁₄O₂S₂): *m/z* [M + Na]⁺ 1411.57; Found: *m/z* 1410.85.

G2. Under an atmosphere of dry nitrogen, a solution of compound **9** (175 mg, 0.12 mmol), 1,4-diethynylbenzene (59 mg, 0.48 mmol), copper sulfate pentahydrate (10% mmol), sodium bicarbonate (20% mmol), and sodium L-ascorbate (20% mmol) in 6 mL of THF/H₂O (5/1, V/V) was stirred at 30 °C for 3 h. Then, the reaction mixture was poured into water and extracted with CH₂Cl₂ for three times (50 mL × 3). The combined organic solution was dried over anhydrous sodium sulfate and condensed *via* rotary evaporation. The residue was purified by column chromatography on silica gel using CH₂Cl₂/ethyl acetate (5/1, V/V) as eluent to give blue powder (126 mg, 68.2%). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 8.95 (dd, *J* = 28.4, 15.6 Hz, 2H, —CH=), 7.93 (d, *J* = 8.9 Hz, 2H, —CH=), 7.79 (d, *J* = 8.6 Hz, 3H, —CH= and ArH), 7.71 (d, *J* = 15.5 Hz, 1H, —CH=), 7.58–7.50 (m, 2H, ArH), 7.40–7.28 (m, 8H, —CH= and ArH), 7.24 (s, 1H, —CH=), 7.11–6.85 (m, 7H, —CH= and ArH), 6.67–6.44 (m, 9H, —CH= and ArH), 4.42 (q, *J* = 7.5 Hz, 6H, —CH₂—), 3.45–3.23 (m, 12H, —CH₂—), 3.13 (s, 1H, —C≡H), 1.99 (s, 6H, —CH₂—), 1.79 (s, 6H, —CH₃), 1.74 (s, 6H, —CH₃), 1.71 (s, 6H, —CH₃), 1.47–1.24 (m, 34H, —CH₂—), 1.18 (t, *J* = 7.0 Hz, 3H, —CH₃), 0.90 (d, *J* = 6.8 Hz, 6H, —CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 175.89, 174.21, 174.09, 154.56, 153.30, 152.67, 149.27, 148.91, 148.84, 146.94, 142.74, 142.56, 140.34, 140.22, 139.33, 139.14, 137.83, 137.36, 135.71, 135.14, 134.80, 132.64, 132.36, 132.18, 131.01, 129.21, 129.09, 126.88, 126.04, 125.97, 125.44, 122.73, 122.70, 122.67, 122.26, 121.65, 120.00, 115.39, 115.07, 114.69, 112.66, 112.38, 111.70, 111.62, 111.48, 111.25, 97.54, 97.49, 97.01, 95.51, 94.85, 83.43, 78.06, 77.23, 55.01, 51.08, 50.78, 50.55, 50.31, 50.10, 45.10, 31.68, 30.21, 29.99, 27.29, 27.06, 26.78, 26.64, 26.56, 26.48, 26.41, 26.33, 22.69, 14.07, 12.39. C₁₁₈H₁₂₁N₂₁O₃S₃ (EA) (Found/Calcd., %): C, 71.83/71.67; H, 6.13/6.17; N, 14.80/14.87; MALDI-TOF MS: Calcd. for (C₁₁₈H₁₂₁N₂₁O₃S₃): *m/z* [M + Na]⁺ 1998.81; Found: *m/z* 1997.77.

PG0. Under an atmosphere of dry nitrogen, a solution of **P0**

(30 mg, 0.1 mmol), **G0** (123 mg, 0.2 mmol), copper sulfate pentahydrate (10% mmol), sodium bicarbonate (20% mmol), and sodium L-ascorbate (20% mmol) in 6 mL of THF/H₂O (5/1, V/V) was stirred at 30 °C for 3 h. Then, the reaction mixture was poured into water and extracted with CH₂Cl₂ for three times (50 mL × 3). Next, the solid residue was washed by Soxhlet extraction in methanol and acetone; CHCl₃ was added and the products were condensed *via* rotary evaporation to get blue powder (68 mg, 74.5%). $M_w = 8.15 \times 10^3$ g·mol⁻¹, $M_w/M_n = 1.08$ (GPC, polystyrene calibration). ¹H-NMR (400 MHz, CD₂Cl₂, δ , ppm): 8.9–8.7 (—CH=), 8.5–8.2 (—CH=), 7.9–7.5 (ArH and —CH=), 7.5–7.1 (ArH and —CH=), 7.1–6.6 (ArH and —CH=), 6.6–6.3 (ArH), 4.4–3.8 (—CH₂—), 3.3–3.0 (—CH₂—), 2.0–0.9 (—CH₂—), 0.9–0.7 (—CH₃).

PG1. Under an atmosphere of dry nitrogen, a solution of **P0** (30 mg, 0.1 mmol), **G1** (278 mg, 0.2 mmol), copper sulfate pentahydrate (10% mmol), sodium bicarbonate (20% mmol), and sodium L-ascorbate (20% mmol) in 6 mL of THF/H₂O (5/1, V/V) was stirred at 30 °C for 12 h. Then, the reaction mixture was poured into water and extracted with CH₂Cl₂ for three times (50 mL × 3). Next, the solid residue was washed by Soxhlet extraction in methanol and acetone; CHCl₃ was added and the products were condensed *via* rotary evaporation to get blue powder (86 mg, 50.8%). $M_w = 8.83 \times 10^3$ g·mol⁻¹, $M_w/M_n = 1.28$ (GPC, polystyrene calibration). ¹H-NMR (400 MHz, CD₂Cl₂, δ , ppm): 9.0–8.8 (—CH=), 7.9–7.5 (ArH and —CH=), 7.5–7.0 (ArH and —CH=), 7.0–6.6 (ArH and —CH=), 6.6–6.2 (ArH), 4.4–4.0 (—CH₂—), 3.3–3.0 (—CH₂—), 2.0–1.4 (—CH₂—), 1.4–1.0 (—CH₂—), 0.9–0.7 (—CH₃).

PG2. Under an atmosphere of dry nitrogen, a solution of **P0** (30 mg, 0.1 mmol), **G2** (395 mg, 0.2 mmol), copper sulfate pentahydrate (10% mmol), sodium bicarbonate (20% mmol), and sodium L-ascorbate (20% mmol) in 6 mL of THF/H₂O (5/1, V/V) was stirred at 30 °C for 24 h. Then, the reaction mixture was poured into water and extracted with CH₂Cl₂ for three times (50 mL × 3). Next, the solid residue was washed by Soxhlet extraction in methanol and acetone; CHCl₃ was added and the products were condensed *via* rotary evaporation to get blue powder (88 mg, 38.5%). $M_w = 1.02 \times 10^4$ g·mol⁻¹, $M_w/M_n = 1.15$ (GPC, polystyrene calibration). ¹H-NMR (400 MHz, CD₂Cl₂, δ , ppm): 9.0–8.8 (—CH=), 7.9–7.7 (ArH and —CH=), 7.7–7.4 (ArH and —CH=), 7.3–7.0 (ArH and —CH=), 7.0–6.7 (ArH and —CH=), 6.6–6.3 (ArH), 4.4–4.1 (—CH₂—), 3.4–3.0 (—CH₂—), 2.0–1.4 (—CH₂—), 1.4–1.0 (—CH₂—), 0.9–0.7 (—CH₃).

Preparation of Thin Films

The three polymers were dissolved in THF (concentration, 4 wt%) and the solutions were filtered using syringe filters. Then, the solutions were spin-coated onto indium-tin-oxide (ITO)-coated glass substrates and the ITO glasses were cleaned by DMF, acetone, distilled water, and THF sequentially in an ultrasonic bath before use. The residual solvent was removed by heating the films in a vacuum oven at 40 °C for 8 h.

NLO Measurements of Poled Films

The second-order nonlinear optical (NLO) efficiencies of the compounds were measured 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 conducting planes faced the laser. Then, the laser was lighted and the SHG intensity was monitored simultaneously. The poling temperatures of the five kinds of films were different. They shared the same other poling conditions: gap distance of 0.8 cm and voltage of 7.0 kV at the needle point. The 1950 nm laser irradiation was used for investigating the NLO efficiencies. The double frequency signals, which were 975 nm, were detected using an Andor's DU420A-BR-DD CCD after the mixed signals passed through the monochromator and a customized Y-cut quartz crystal served as the reference.

RESULTS AND DISCUSSION

Synthesis

The overall pathway of the polymer synthesis is presented in Fig. 2 and Figs. S1–S4 (in ESI). **P0** containing carbazole and azide group was synthesized by 5 steps. The first step was the bromination of carbazole using *N*-bromosuccinimide. Next, the substitution reaction of proton on the nitrogen atom yielded compound **2**, and because the acidity of the proton on the nitrogen atom is weak, the strong base of potassium hydroxide was needed. Then, the substitution reaction of bromine was conducted by using sodium azide to give compound **3**, and the borate substitution reaction with bis(pinacolato)diboron went on to yield compound **4**. In the last step, the Suzuki coupling reaction between compound **3** and compound **4** produced the reactive polymer intermediate of **P0**, which is the linear polymer containing azide groups in the side chain for the following click chemistry reaction. The polymerization procedure proceeded smoothly through the Suzuki coupling reaction using Pd(PPh₃)₄ as a catalyst, K₂CO₃ as a base, and a mixture of THF/H₂O (5/1, V/V) as the solvent. To ensure the solubility of **P0**, the polymerization reaction should be controlled.

G0 containing one terminal alkyne group and compound **5** containing two azide group were synthesized according to our previous work.^[27–30] Compound **6** was prepared through a powerful click reaction between azide and terminal alkyne group. **G1** was obtained in the same way as compound **6**. Compound **9** containing 3 FTC and a azide group was synthesized by adding another FTC to it through powerful click reaction. It is worth pointing out that the TCF acceptor must be added after the click chemistry reaction for compound **7**, as it was not so stable if FTC chromophore contained azide and terminal alkyne group simultaneously. **PG0**, **PG1**, and **PG2** were synthesized by using **P0** with **G0**, **G1**, and **G2**, respectively, through click reaction.

Characterization

The molecular weights of **PG0**, **PG1**, and **PG2** determined by gel permeation chromatography (GPC) with THF as the eluent and polystyrenes as the calibration standards were about 10⁴ g·mol⁻¹, with polydispersity indexes (PDI) of 1.08, 1.28, and 1.15, respectively, which confirmed the successful polymerization. As shown in Table 1, the molecular weights of **PG0** were lower than those of **PG1**, while the molecular weights of **PG1** were lower than those of **PG2**. This was understandable since the molecular weights of single **G0**, **G1**, and **G2** gradually increased and the steric hindrance also increased. The reaction time was monitored before the appearance of insoluble gel,

which gradually increased with the increased steric hindrance.

Spectroscopic techniques were employed to characterize the structures of the products and all of them gave satisfactory analysis data corresponding to their expected structures (Figs. S5–S12, in ESI). Fig. S5 (in ESI) shows the FTIR spectra of

PG0, **PG1**, and **PG2**. Obviously, the band appearing at 2222 cm^{-1} for all of them confirmed that the cyano group was unbroken during the post-functionalization reaction.

Fig. 3(a) shows the partial ^1H -NMR spectra of **G1** and **G2**, and Figs. S8–S10 (in ESI) shows the ^1H -NMR spectra of **G1**, **G2**,

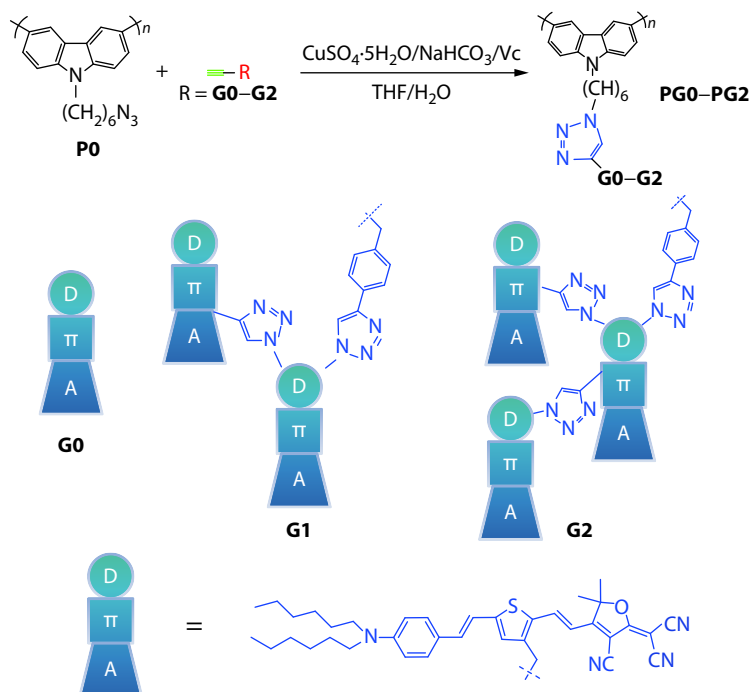


Fig. 2 Synthetic routes to **PG0**, **PG1**, and **PG2**.

Table 1 Characterization data of polymers **PG0**, **PG1**, and **PG2**.

Sample	Reaction time (h)	Yield (%)	$M_w^a \times 10^{-3}$	PDI	T_g^b (°C)	T_d^c (°C)	T_e^d (°C)	I_s^e (nm)	d_{33}^f (pm·V $^{-1}$)	$T_{80\%}^g$ (°C)
PG0	3	74.5	8.15	1.08	183	262	158	130	186	136
PG1	12	50.8	8.83	1.28	181	288	153	95	242	132
PG2	24	38.5	10.21	1.15	177	301	150	90	282	129

^a Determined by GPC in THF on the basis of a polystyrene calibration; ^b Glass transition temperature (T_g) of polymers detected by DSC under argon at a heating rate of 10 °C·min $^{-1}$; ^c The 5% weight loss temperature (T_d) of polymers detected by TGA under nitrogen at a heating rate of 10 °C·min $^{-1}$; ^d The best poling temperature; ^e Film thickness; ^f Second harmonic generation (SHG) coefficient; ^g The temperature at which d_{33} values decreased to its 80%.

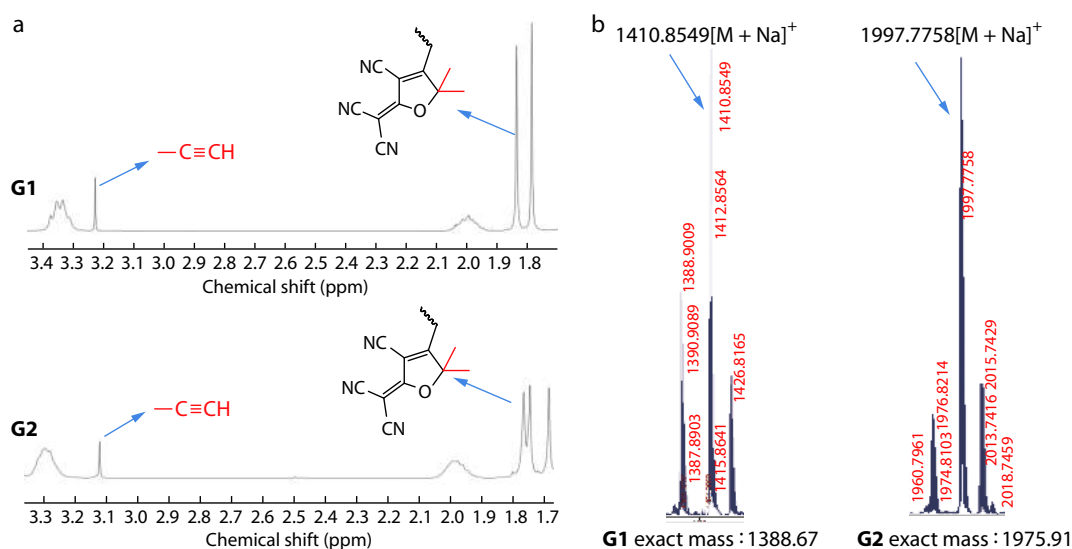


Fig. 3 (a) Partial ^1H -NMR spectra of **G1** and **G2**; (b) TOF spectra of **G1** and **G2**.

PG0, PG1, and PG2. Clearly, no unexpected resonance signal was observed, and the chemical shifts were consistent with the target molecules. The single signals at 1.79 and 1.84 ppm belonged to 12 hydrogen atoms in TCF acceptors for **G1**, and the multiplet at 3.35 and 4.5 ppm were the chemical shifts for 8 hydrogen atoms near the nitrogen atoms and 4 hydrogen atoms near the triazole group, respectively. The single signals at 1.69, 1.75, and 1.77 ppm belonged to 18 hydrogen atoms in TCF acceptors for **G2**. The single signals at 3.23 and 3.12 ppm could be found for **G1** and **G2**, respectively, indicating the presence of terminal alkyne groups. However, in comparison with those of monomers, the resonance signals in the ^1H -NMR spectra of polymers were in consistency with their proposed structure but showed an inclination of signal broadening due to polymerization. Also, compared to the spectra of **G1** and **G2**, it is easily seen that there were some new signals at 7.8–8.0 ppm (signal of triazole group) for **PG1** and **PG2**, indicating the success of the post-functionalization of **P0**.

Fig. 3(b) shows the MALDI-TOF-MS results of **G1** and **G2**, with sodium ionization and potassium ionization adopted for the characterization of exact molecular weights. The peaks at 1410.8549 and 1426.8165 belonged to $[\text{M} + \text{Na}]^+$ and $[\text{M} + \text{K}]^+$ of **G1**, and the peaks at 1997.7758 and 2013.7416 should be ascribed to $[\text{M} + \text{Na}]^+$ and $[\text{M} + \text{K}]^+$ of **G2**, which could undoubtedly confirm the successful synthesis of **G1** and **G2**.

Thermal Properties

The TGA curves of **PG0**, **PG1**, and **PG2** are shown in Fig. 4. All of them possessed very good thermal stability, with decomposition temperatures (temperature for 5% weight loss) of 262, 288, and 301 °C, respectively. Relatively, it is obvious that the decomposition temperatures gradually increased from **PG0** to **PG2**, indicating that this kind of dendronized polymers had better thermal stability than linear polymers. Fig. S6 (in ESI) shows DSC curves of **PG0**, **PG1**, and **PG2**, and the glass transition temperatures (T_g) were 183, 181, and 177 °C for **PG0**, **PG1**, and **PG2**, respectively. According to literature, the poling process means that under the external electric field of high voltage, the chromophores would be oriented to orderly alignment at the glass transition temperature or above it. And gradually decreasing glass transition temperature means that the poling process would become easier from **PG0** to **PG2**.

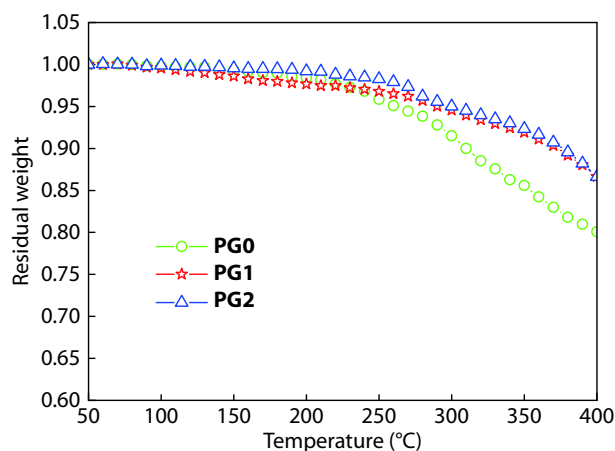


Fig. 4 TGA thermograms of **PG0**, **PG1** and **PG2**.

Optical Properties

The UV-Vis absorption spectra of **PG0**, **PG1**, and **PG2** in different solvents are shown in Fig. 5, and their maximum absorption wavelengths (λ_{max}) are summarized in Table 2, which were all about 660 nm and red-shifted with the improvement of solvent polarity. There was a typical maximum absorption wavelength for FTC chromophore.^[27–32] Because the FTC moieties were linked by triazole group and the conjugation of the chromophore was unchanged, all of the polymers showed similar maximum absorption peaks in the same solvent.^[33–35] In this research, the Δ value, the difference between the maximum absorption wavelengths in 1,4-dioxane and DMSO, was introduced

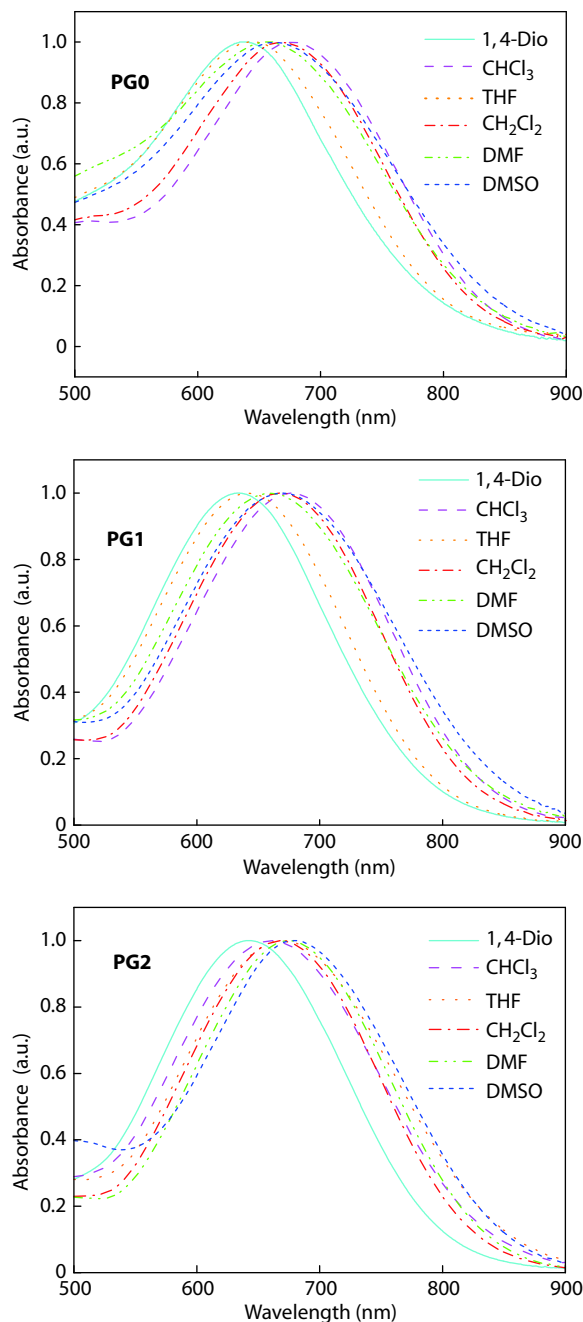


Fig. 5 Solvatochromism spectra of **PG0**, **PG1**, and **PG2**.

Table 2 The maximum absorption wavelengths of polymers **PG0**, **PG1**, and **PG2** ($\lambda_{\max}$, nm).^a

Sample	1,4-Dioxane	CHCl ₃	THF	CH ₂ Cl ₂	DMF	DMSO	Δ
PG0	629	673	643	647	655	668	39
PG1	633	677	641	670	660	671	38
PG2	640	661	669	667	675	681	41

^a The maximum absorption wavelength in different solvents (0.02 mg·mL⁻¹), $\Delta = \lambda_{\max}(\text{in DMSO}) - \lambda_{\max}(\text{in 1,4-dioxane})$; dielectric constant of solvents: 1,4-dioxane = 2.2; CHCl₃ = 4.8; THF = 7.5; CH₂Cl₂ = 8.9; DMF = 37.6; DMSO = 46.7.

ced to evaluate the shielding effect of solvents on the molecular structures. It has been confirmed that solvent polarity has a significantly effect on the solvatochromism phenomena of polymers.^[36–39] In low polarity solvents, the interactions between NLO chromophore moieties and solvent molecules are very weak and the solvatochromism will be significantly related to the molecular structures. By contrast, in the high polarity solvents such as DMSO, the interactions are too strong to be ignored. For example, in the low polarity solvent of 1,4-dioxane, the maximum absorption showed the red-shifts from **PG0** to **PG2**, indicating that the intramolecular charge transfer became stronger. The Δ values of the three polymers were 39, 38, and 41 nm, and the small difference means that the shielding effect of solvents on the molecular structures was almost the same.

Spatial Geometry

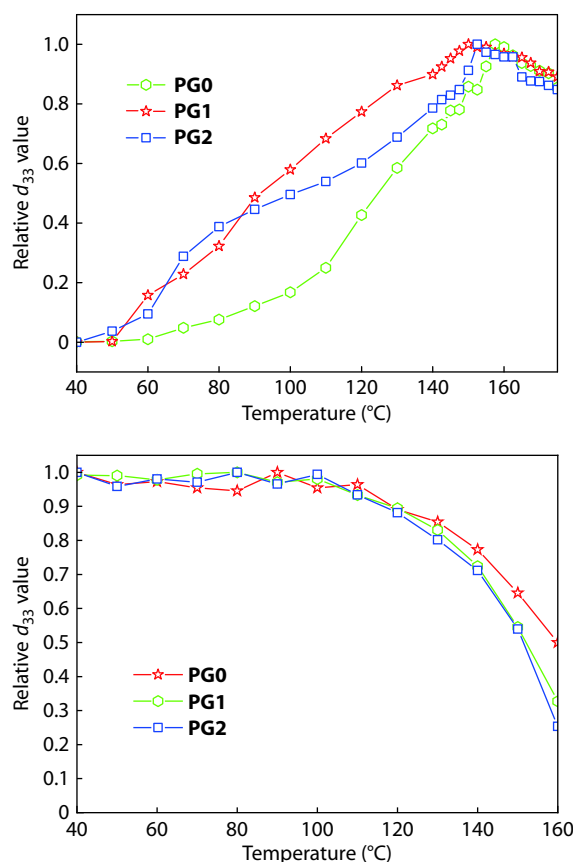
To obtain deep understanding of the topological structure and optical properties, especially the distribution of FTC chromophores in the dendronized structure, the spatial conformation of **G1** and **G2** was calculated by the semi-empirical quantum chemistry method (Fig. S13, in ESI). Theoretically, in **G1**, the two FTC moieties were perpendicular to each other but with a twisted angle to a certain degree due to the strong intermolecular dipole-dipole interactions. In **G2**, the three FTC moieties were almost perpendicular to each other in space and the benzene alkynyl group tended to other orientation for steric hindrance. Besides, they were far away from each other and none of them overlapped, so the shielding effect of solvents on the molecular structures would be small. This might be the reason why the solvatochromism phenomena of **PG1** and **PG2** were similar. Although the spatial distribution of FTC parts would change a little in the dendronized polymers, it was still a useful strategy to analyze the topological structure, and the theoretical prediction was in accordance with the experiment results.

NLO Properties

To evaluate the NLO activity of the polymers, their poled thin films were fabricated. The most convenient technique to study the second-order NLO activity is to investigate the second harmonic generation (SHG) processes characterized by d_{33} , an SHG coefficient. The method for calculating d_{33} for the poled films has been reported in our previous papers.^[40–44] From the experimental data, the d_{33} values of **PG0**, **PG1**, and **PG2** were calculated to be 186, 242, and 282 pm·V⁻¹, respectively, at a 1950 nm fundamental wavelength (Table 1). To check the reproducibility, we repeated the measurements three times and got similar results. And as far as we know, the d_{33} values of other linear polymers containing FTC chromophore moieties were rarely higher than 200 pm·V⁻¹, which demonstrated the advantages of dendronized polymers. Obviously, the d_{33} values of

these polymers gradually increased from **PG0** to **PG2**, showing that the dendronized structure was beneficial to getting higher NLO properties. This should be ascribed to the high loading density of FTC moieties and perfect configuration of dendronized polymers. Another reason should be that all of the FTC moieties were linked by suitable isolation group of triazole. The isolation group could weaken the intermolecular dipole-dipole interactions, thus facilitating the conversion of its centrosymmetric alignment into noncentrosymmetric one during the poling process under an electric field. Besides, in comparison with dendronized polymers containing azo chromophores, these results proved our guess that the macroscopic NLO activities could be improved by using better chromophores with higher $\mu\beta$ values.

The poling and decaying curves of **PG0**, **PG1**, and **PG2** are given in Fig. 6. Under the best poling temperature, the chromophore moieties would be in accordance with the poling electric field, and the NLO properties reached the maximum d_{33} values. Thus, the best poling temperature of NLO polymers was useful to estimate the difficulty of the poling process. Under the depoling temperature, with the increase of temperature, the non-centrosymmetric arrangement of the chromophore moieties in poled films would change to their original centrosymmetric arrangement due to the thermal motion of chromophore moieties, and the d_{33} values would decline gradually. The temperature at which d_{33} values decreased to 80% of the maximum values was used to evaluate the temporal stability and named as $T_{80\%}$. From the experimental data, the best poling temperature of **PG0**, **PG1**, and

**Fig. 6** Poling and decay curves of **PG0**, **PG1**, and **PG2**.

PG2 was 158, 153, and 150 °C, respectively, indicating that the poling process was not so difficult for them to reach the maximum d_{33} values. $T_{80\%}$ of **PG0**, **PG1**, and **PG2** was 136, 132, and 129 °C, respectively, showing their good temporal stabilities. Comparing **PG0** and **PG2**, it could be concluded that the best poling temperature of **PG2** was lower while temporal stability was better, which demonstrated the superior properties of dendronized polymers.

CONCLUSIONS

In this work, different generations of NLO dendrons containing FTC chromophore moieties were introduced into conjugated polymers through the powerful click chemistry reaction. With the increase of loading density of the chromophore moieties, the NLO coefficient d_{33} values were enhanced and reached 282 pm·V⁻¹. In comparison with similar dendronized polymers containing azo chromophores, **PG1** and **PG2** possessed higher macroscopic NLO activities as well as good thermal stability. Thus, this study demonstrated that the macroscopic NLO coefficient and thermal stability of NLO materials could be improved by using FTC chromophore with higher $\mu\beta$ value.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2307-z>.

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