

Electronic Supplementary Information:

Novel Global-like Second-Order Nonlinear Optical (NLO) Dendrimers: Convenient Synthesis by Click Chemistry and Large NLO Effects

Wenbo Wu, Lijin Huang, Changfei Song, Gui Yu, Cheng Ye, Yunqi Liu, Jingui Qin and Zhen Li*

Chart S1.

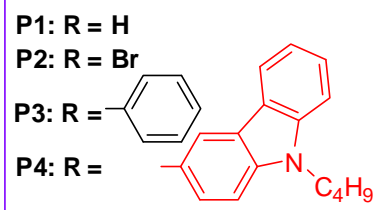
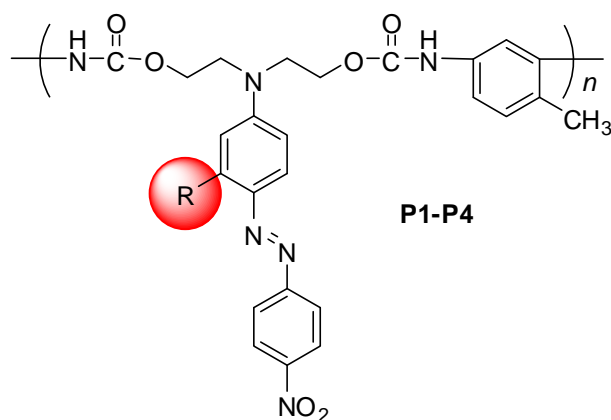


Chart S2.

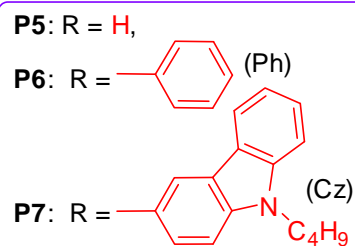
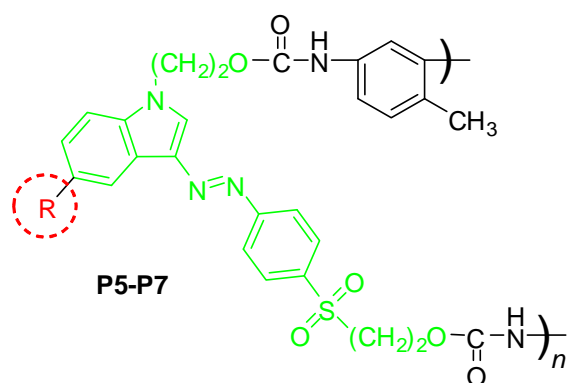


Chart S3.

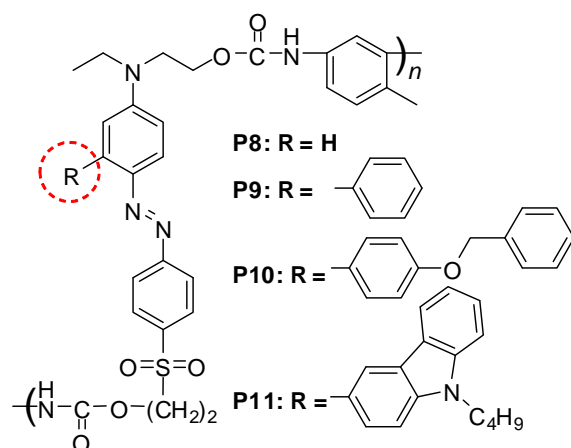


Chart S4.

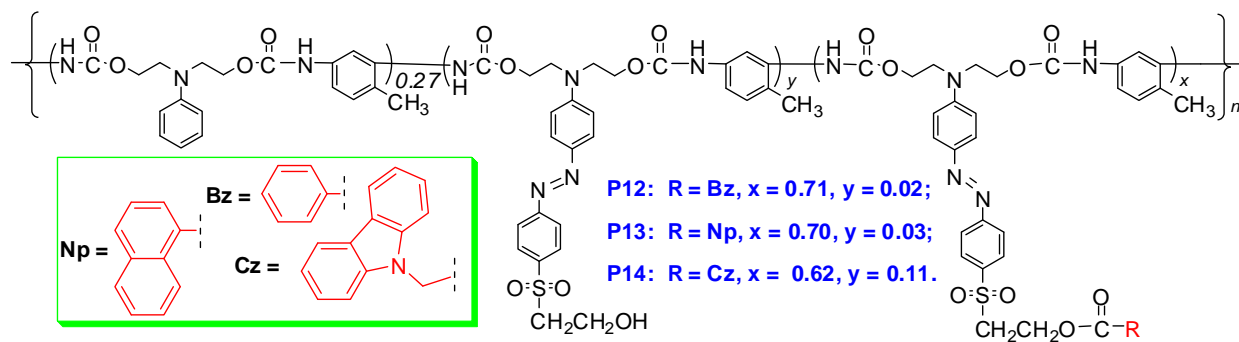


Chart S5.

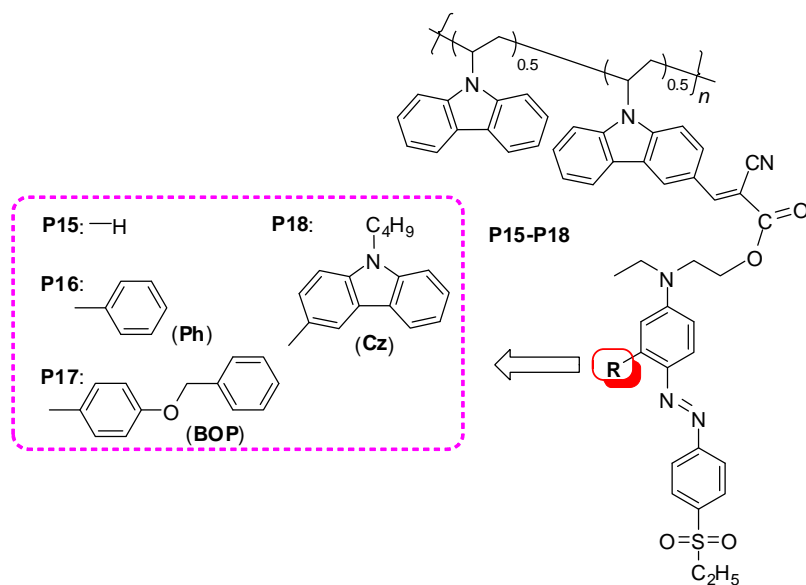
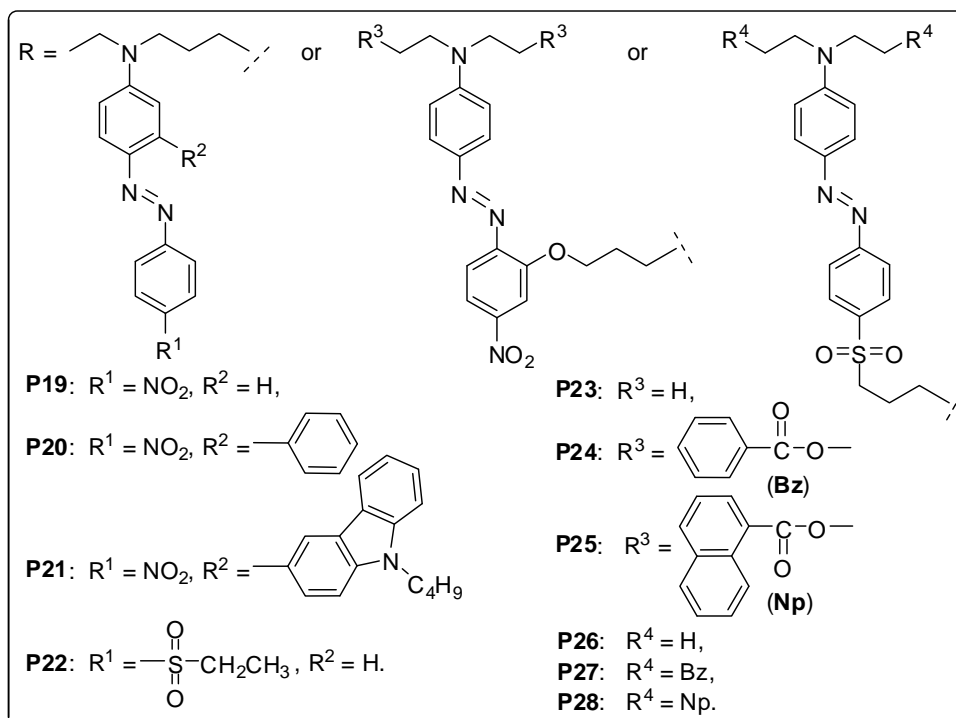
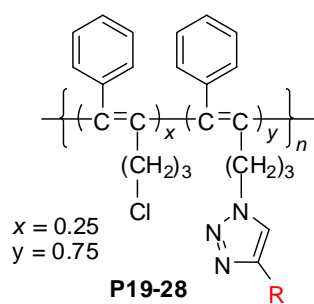
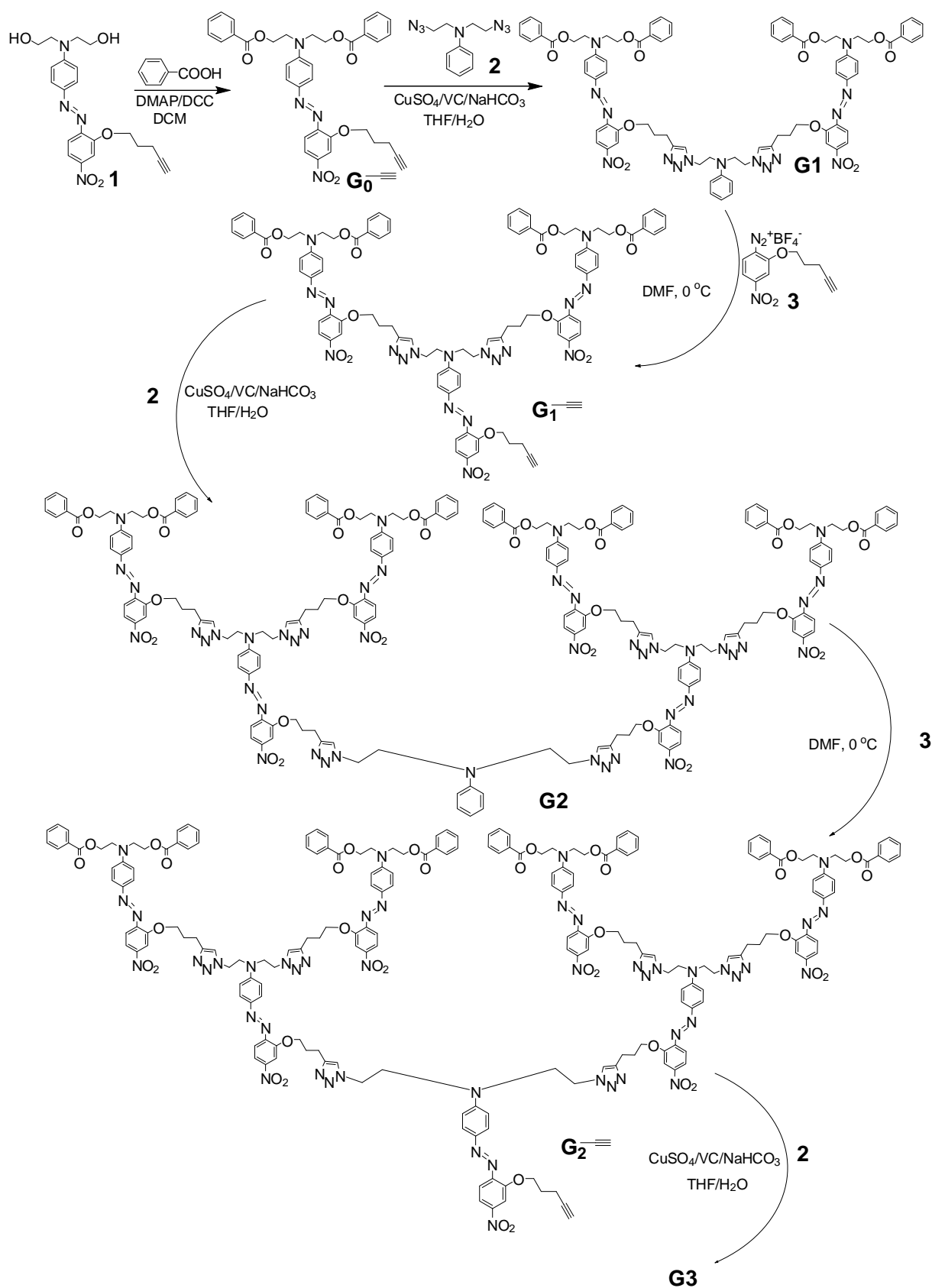


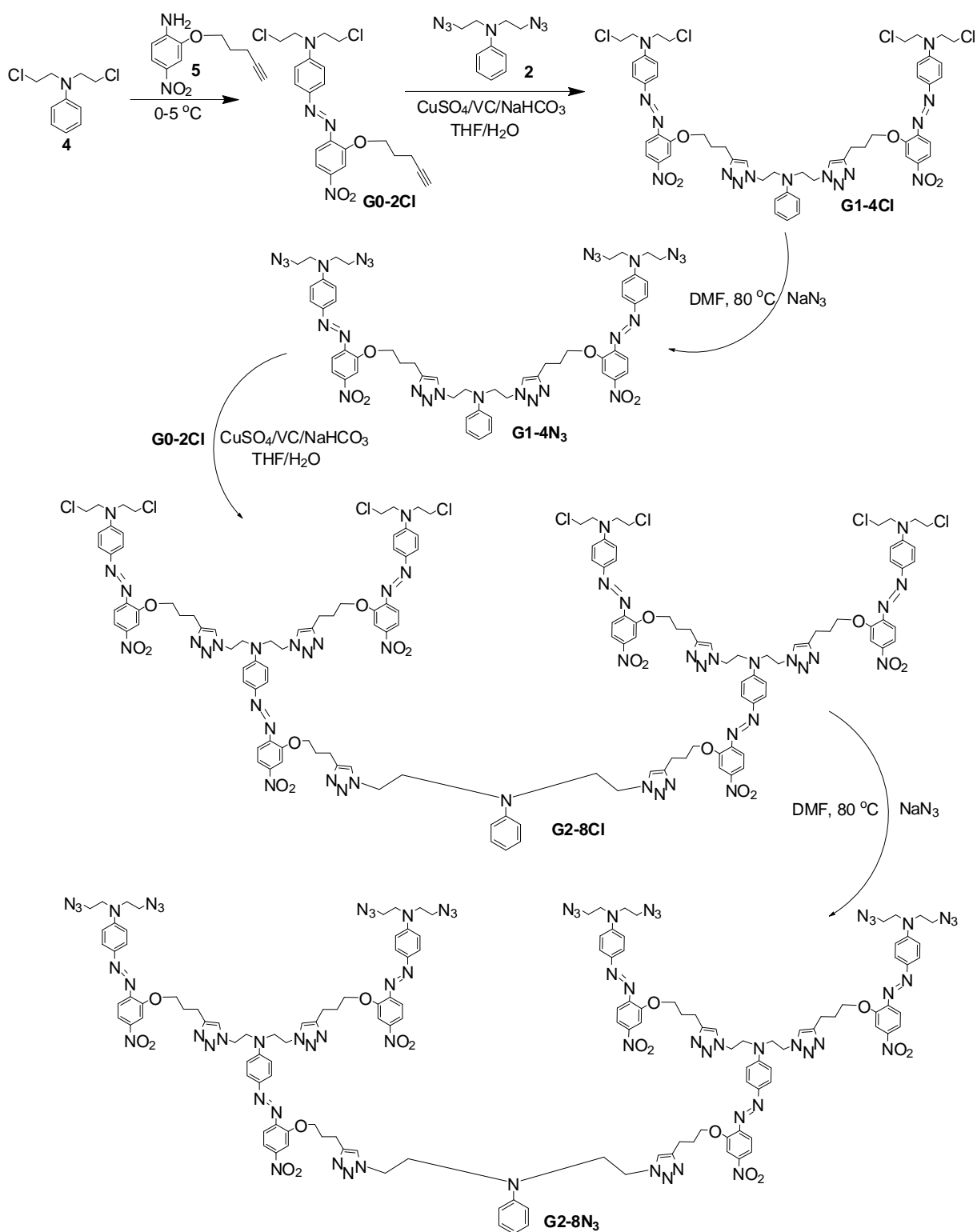
Chart S6.



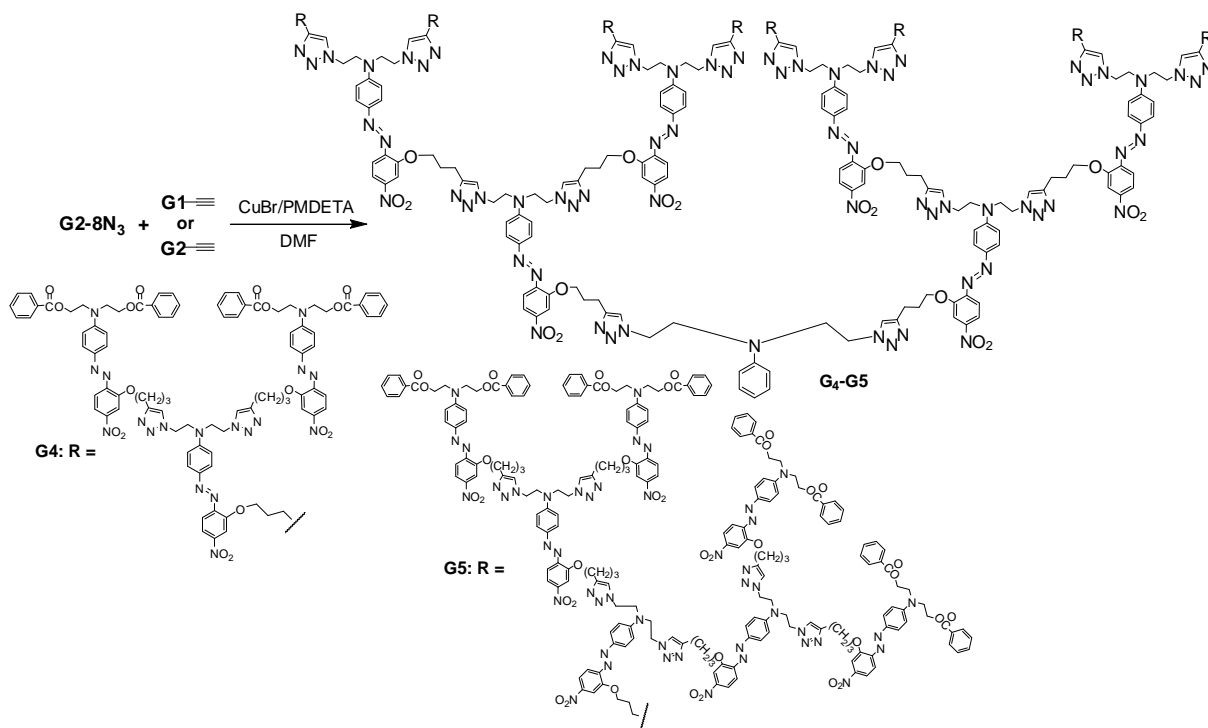
Scheme S1.



Scheme S2.



Scheme S3



Experimental Section

Materials and Instrumentation.

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Triethylamine (Et₃N) was distilled under normal pressure and kept over potassium hydroxide. *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH₂ under an atmosphere of dry nitrogen. Aryl triiodide (**S1**), chromophore **G0-2Cl**, end-capped dendrons **G0**-≡, **G1**-≡ and **G2**-≡ were prepared in our previous work. Chromophore **C1** was prepared with the normal reactions of azo-coupling and esterification by two steps according to our previous work. *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) was purchased from Alfa Aesar. All other reagents were used as received.

¹H NMR and ¹³C NMR 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. UV-visible spectra were obtained using a Shimadzu 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 (EA) were performed by a CARLOERBA-1106 micro-elemental 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. THF or DMF was used as an eluent, and the flow rate was 1.0 mL/min. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in nitrogen at a flow rate of 50 cm³/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 G0-6Cl-TPA

A mixture of chromophore **G0-2Cl** (1.12 g, 2.50 mmol), **S1** (470 mg, 0.755 mmol), triphenylphosphine and tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) (3 mol-%), copper iodide (CuI) (5 mol-%), triphenylphosphine (PPh₃) (5 mol-%) was carefully degassed and charged with argon. THF (22.5 mL) / Et₃N (7.5 mL) was then added. The reaction was stirred for 2 days at room temperature, then treated with H₂O and extracted with CHCl₃, 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 (1/40) as eluent, and recrystallized from chloroform/methanol to afford red solid **G0-6Cl-TPA** (350 mg, 29.2 %). $M_w = 2159$, $M_w/M_n = 1.04$ (GPC, polystyrene calibration). IR (KBr), ν (cm⁻¹): 1510, 1338 (-NO₂). ¹H NMR (300MHz, CDCl₃, 298 K), δ (TMS, ppm): 2.21 (t, $J = 6.0$ Hz, 6H, -CH₂-), 2.71 (m, 6H, -CH₂C-), 3.71 (t, $J = 6.3$ Hz, 12H, -NCH₂-), 3.85 (t, $J = 6.3$ Hz, 12H, -CH₂Cl), 4.39 (t, $J = 5.7$ Hz, 6H, -OCH₂-), 6.78 (d, $J = 8.7$

Hz, 6H, ArH), 6.93 (d, $J = 8.1$ Hz, 6H, ArH), 7.24 (d, $J = 8.1$ Hz, 6H, ArH), 7.68 (d, $J = 8.4$ Hz, 3H, ArH), 7.92 (m, 12H, ArH). MALDI-TOF MS: calcd for ($C_{81}H_{75}N_{13}O_9Cl_6$): m/z $[M+H]^+$: 1588.26; found: m/z 1588.42.

Synthesis of G0-6N₃-TPA

A Schlenk flask was charged with compound **G0-6Cl-TPA** (206 mg, 0.13 mmol), NaN_3 (102 mg, 1.56 mmol) and DMF (2.5 mL). The reaction was allowed to stir in 80 °C for 12 h and then the solution was poured into a lot of water. The precipitate was collected and washed several times with water and methanol/water (1/1) and then dried under vacuum to afford orange solid (65.0 mg, 30.8 %). $M_w = 3063$, $M_w/M_n = 1.18$ (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 2098 ($-N_3$), 1511, 1339 ($-NO_2$). 1H NMR (300MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 2.21 (br, s, 6H, $-CH_2-$), 2.71 (br, s, 6H, $-CH_2C-$), 3.59 (br, s, 12H, $-CH_2N_3$), 3.71 (br, s, 12H, $-NCH_2-$), 4.39 (br, s, 6H, $-OCH_2-$), 6.81 (d, $J = 7.2$ Hz, 6H, ArH), 6.93 (d, $J = 7.2$ Hz, 6H, ArH), 7.24 (br, s, 6H, ArH), 7.69 (br, s, 3H, ArH), 7.94 (br, s, 12H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 16.14, 28.35, 29.64, 48.70, 50.74, 68.35, 81.09, 88.30, 109.21, 111.80, 116.47, 117.41, 118.03, 123.77, 126.15, 132.59, 145.09, 146.27, 146.74, 148.42, 149.59, 155.24. MALDI-TOF MS: calcd for ($C_{81}H_{75}N_{31}O_9$): m/z $[M]^+$: 1625; found: m/z 1623. $C_{52}H_{59}N_{25}O_4S_2$ (EA) (%), found/calcd): C, 60.67/59.81; H, 4.88/4.65; N, 25.74/26.69.

General procedure of the synthesis of G1-TPA, G2-TPA and G3-TPA

A mixture of **G0-6N₃-TPA** (1.00 equiv), **G0**-≡ or **G1**-≡ or **G2**-≡(7.00 equiv), and CuBr (1.00 equiv) were dissolved in DMF (0.02 M- N_3) under nitrogen in a Schlenk flask, then *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) (1.00 equiv) was added. After the mixture was stirred at 30 °C for 3 hours, the reaction was stopped by addition of water. The precipitate was purified by repeating precipitations of their THF solutions into methanol/acetone (**G1-TPA**) or acetone (**G2-TPA** and **G3-TPA**), dried in vacuum at 40 °C to a constant weight.

G1-TPA: G0-6N₃-TPA (24.4 mg, 0.015 mmol), **G0**≡ (65.2 mg, 0.105 mmol). **G1-TPA** was obtained as red powder (56.0 mg, 69.7 %). $M_w = 5410$, $M_w/M_n = 1.05$ (GPC, polystyrene calibration). IR (KBr), ν (cm⁻¹): 2099 (-C≡C), 1717 (C=O), 1515, 1339 (-NO₂). ¹H NMR (300MHz, CDCl₃, 298 K), δ (TMS, ppm): 2.23 (m, 18H, -CH₂-), 2.68 (br, s, 6H, -CH₂C-), 2.94 (br, s, 12H, -CH₂C-), 3.71 (br, s, 12H, -NCH₂-), 3.92 (br, s, 24H, -NCH₂-), 4.13 (br, s, 12H, -NCH₂-), 4.36 (br, s, 6H, -OCH₂-), 4.55 (br, s, 24H, -COOCH₂-), 6.56 (d, $J = 7.5$ Hz, 4H, ArH), 6.66 (d, $J = 8.7$ Hz, 2H, ArH), 6.94 (d, $J = 9.0$ Hz, 12H, ArH), 7.23 (s, 6H, C=CH), 7.43 (t, $J = 7.5$ Hz, 24H, ArH), 7.53-7.63 (m, 21H, ArH), 7.75-7.89 (m, 36H, ArH), 7.98 (d, $J = 6.9$ Hz, 24H, ArH). ¹³C NMR (75 MHz, CDCl₃, 298 K), δ (ppm): 16.08, 21.76, 28.33, 47.14, 49.79, 51.16, 61.60, 68.54, 81.16, 88.28, 109.20, 111.82, 116.41, 117.38, 122.26, 123.72, 126.09, 128.41, 129.51, 132.56, 133.22, 144.88, 146.79, 147.07, 148.20, 148.48, 150.73, 155.03, 166.35. MALDI-TOF MS: calcd for (C₂₉₁H₂₆₇N₅₅O₅₁): m/z [M+H]⁺: 5377; found: m/z 5377. C₂₉₁H₂₆₇N₅₅O₅₁ (EA) (% found/calcd): C, 64.93/65.32; H, 5.40/5.03; N, 14.94/14.40.

G2-TPA: G0-6N₃-TPA (11.4 mg, 0.0070 mmol), **G1**≡ (85.2 mg, 0.050 mmol). **G2-TPA** was obtained as red powder (75.0 mg, 90.5 %). $M_w = 9637$, $M_w/M_n = 1.05$ (GPC, polystyrene calibration). IR (KBr), ν (cm⁻¹): 1717 (C=O), 1515, 1338 (-NO₂). ¹H NMR (300MHz, CDCl₃, 298 K), δ (TMS, ppm): 2.18 (br, s, 46H, -CH₂-), 2.90 (br, s, 36H, -CH₂C-), 3.70 (br, s, 36H, -NCH₂-), 3.90 (br, s, 48H, -NCH₂-), 4.08 (br, s, 36H, -NCH₂-), 4.36 (br, s, 42H, -OCH₂-), 4.55 (br, s, 48H, -COOCH₂-), 6.50 (br, s, 12H, ArH), 6.58 (br, s, 6H, ArH), 6.92 (br, s, 24H, ArH), 7.20-8.00 (m, 225H, ArH and C=CH). ¹³C NMR (75 MHz, CDCl₃, 298 K), δ (ppm): 21.68, 28.31, 47.11, 49.72, 51.16, 61.59, 68.49, 109.16, 111.78, 116.29, 117.24, 122.34, 126.02, 128.35, 129.44, 133.14, 144.77, 147.01, 148.03, 150.74, 154.96, 166.29. MALDI-TOF MS: calcd for (C₆₂₇H₅₉₁N₁₃₉O₁₁₁): m/z [M]⁺: 11864; found: m/z 11861. C₆₂₇H₅₉₁N₁₃₉O₁₁₁ (EA) (% found/calcd): C, 63.15/63.55; H, 5.04/5.03; N, 16.76/16.43.

G3-TPA: G0-6N₃-TPA (5.7 mg, 0.0035 mmol), **G2**≡ (94.8 mg, 0.025 mmol). **G3-TPA** was obtained as red powder (60.2 mg, 69.3 %). $M_w = 14850$, $M_w/M_n = 1.09$ (GPC, polystyrene

calibration). 1716 (C=O), 1515, 1338 (-NO₂). ¹H NMR (300MHz, CDCl₃, 298 K), δ (TMS, ppm): 2.00-2.30 (-CH₂-), 2.80-3.00 (-CH₂C-), 3.60-4.20 (-NCH₂-), 4.30-4.60 (-OCH₂- and -COOCH₂-), 6.40-6.60 (ArH), 6.80-7.00 (ArH), 7.20-8.00 (ArH and C=CH). ¹³C NMR (75 MHz, CDCl₃, 298 K), δ (ppm): 21.81, 28.36, 47.22, 49.85, 61.67, 68.67, 109.24, 111.91, 116.33, 126.12, 128.42, 129.52, 133.22, 144.89, 146.73, 148.11, 150.82, 155.09, 166.40. C₁₂₉₉H₁₂₃₉N₃₀₇O₂₃₁ (EA) (% found/calcd): C, 62.81/62.79; H, 4.96/5.03; N, 16.80/17.31.

Preparation of Polymer Thin Films. The dendrimers **G1-TPA**, **G2-TPA** and **G3-TPA** were dissolved in THF (concentration ~3 wt %) and the solutions were filtered through syringe filters, and the 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 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 dendrimers was determined by in-situ second harmonic generation (SHG) experiment using a closed temperaturecontrolled 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 dendrimer (Table 1); voltage: 7.0 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 rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

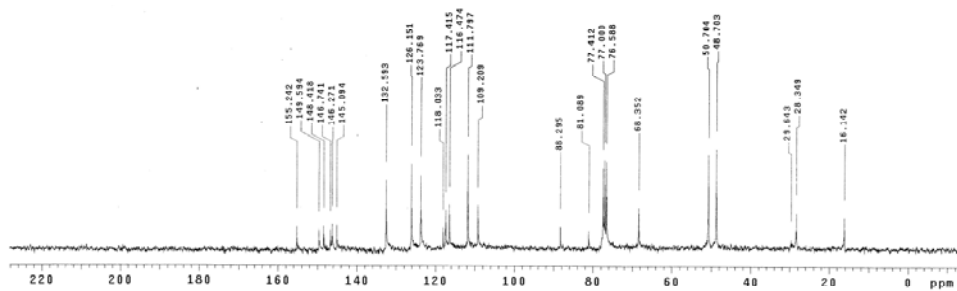


Figure S3. ^{13}C NMR spectrum of **G0-TPA-6N₃** in chloroform-*d*.

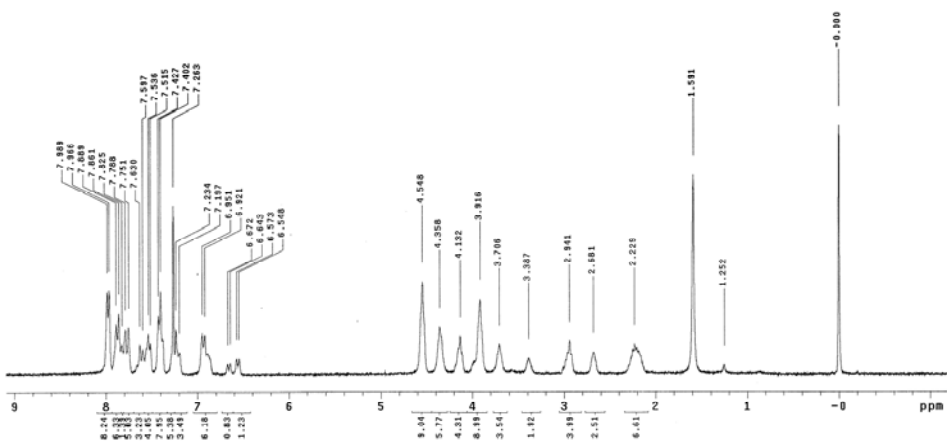


Figure S4. ^1H NMR spectrum of **G1-TPA** in chloroform-*d*.

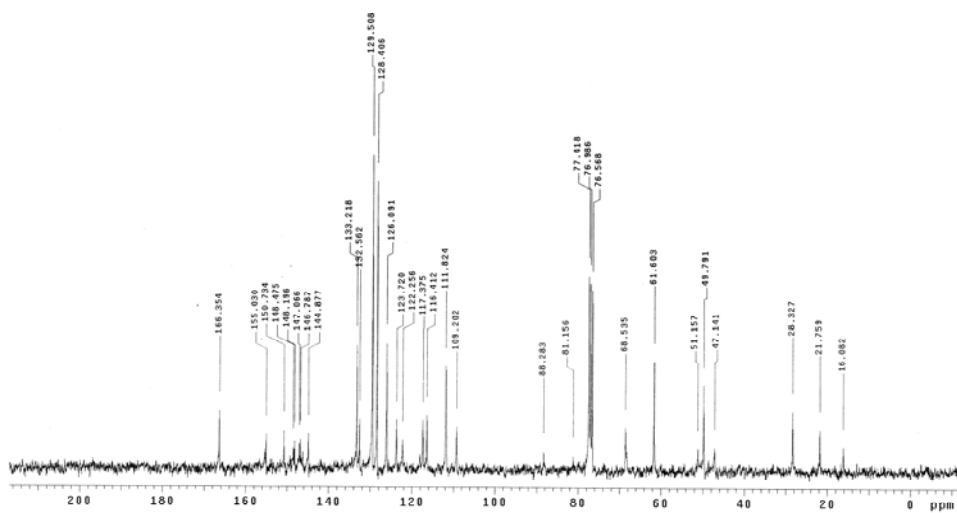


Figure S5. ^{13}C NMR spectrum of G1-TPA in chloroform-*d*.

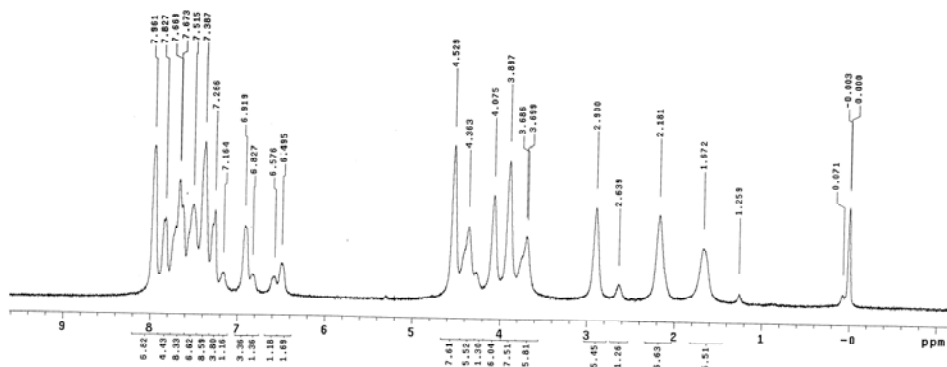


Figure S6. ^1H NMR spectrum of G2-TPA in chloroform-*d*.

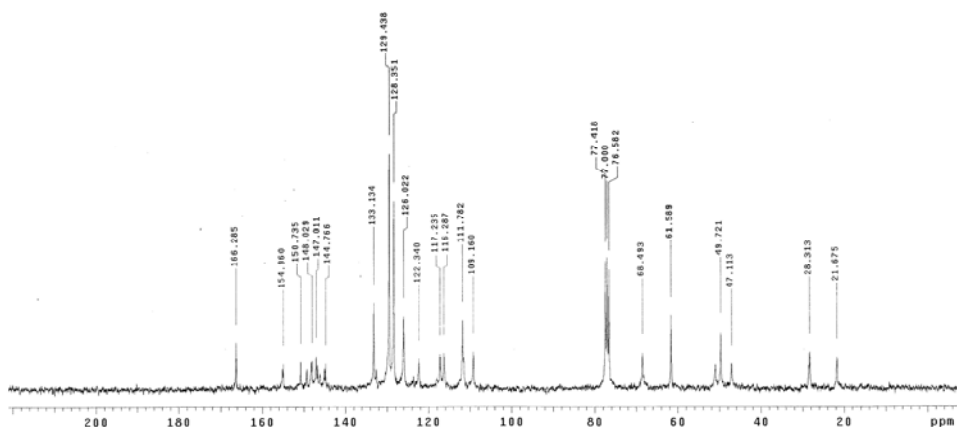


Figure S7. ^{13}C NMR spectrum of G2-TPA in chloroform-*d*.

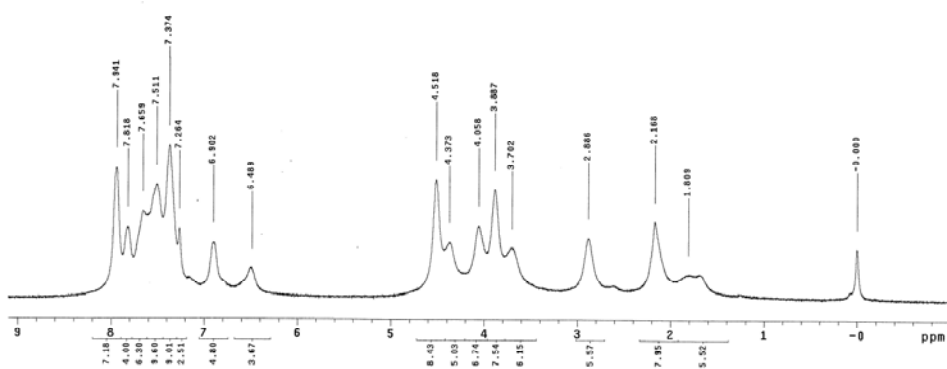


Figure S8. ^1H NMR spectrum of G3-TPA in chloroform-*d*.

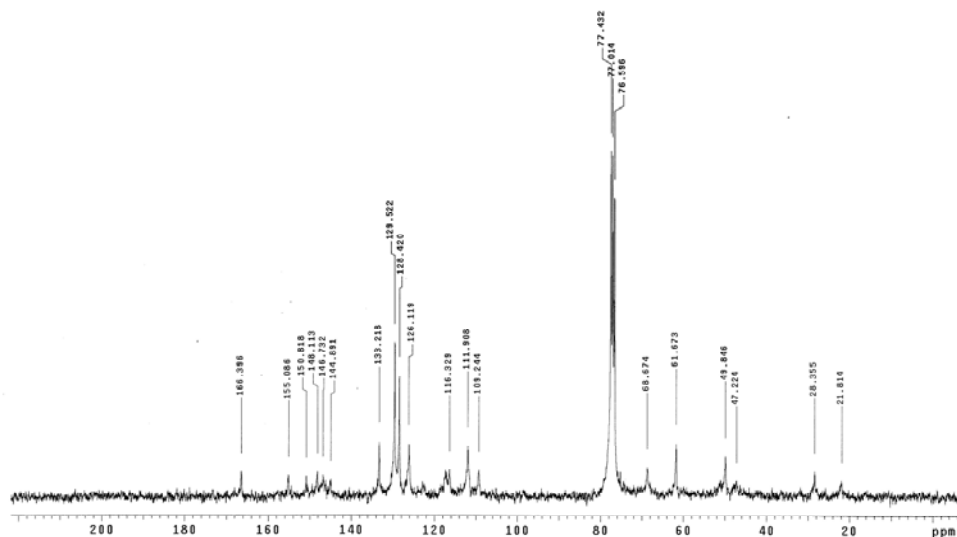


Figure S9. ^{13}C NMR spectrum of G3-TPA in chloroform-*d*.

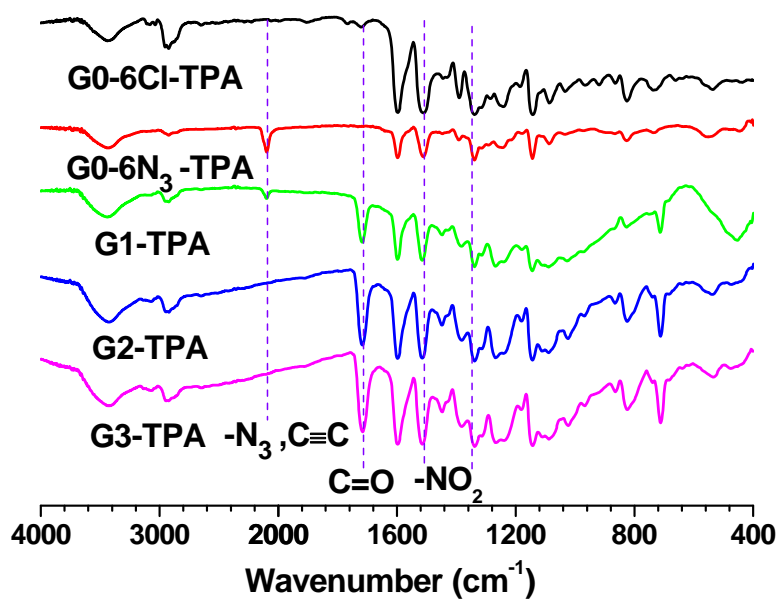


Figure S10. The FT-IR spectra of dendrimers.

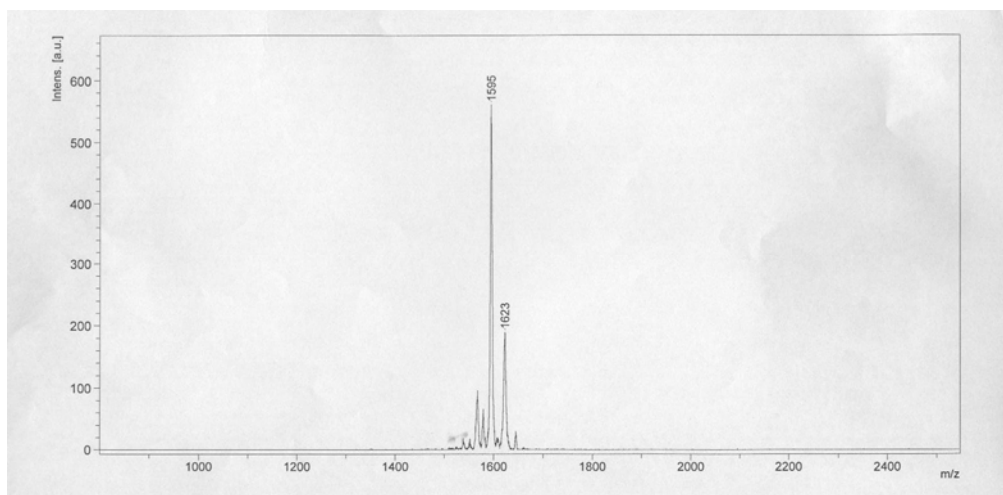


Figure S11. The MALDI-TOF mass spectrum of **G0-6N₃-TPA**.

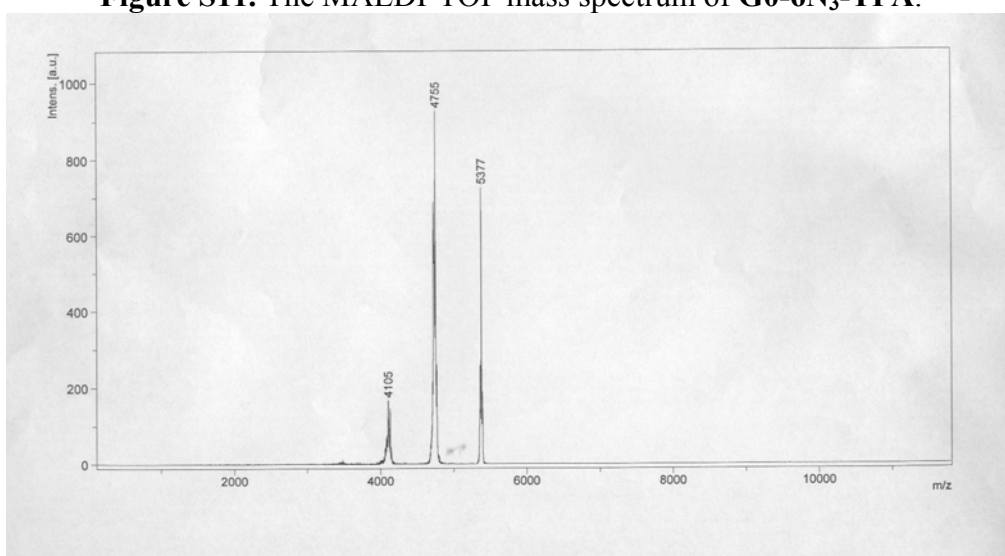


Figure S12. The MALDI-TOF mass spectrum of **G1-TPA**.

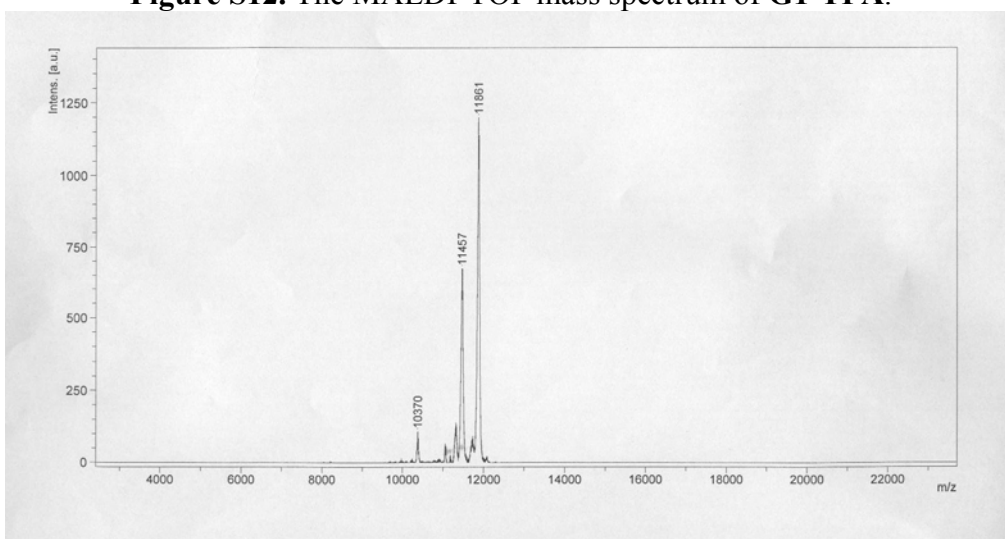


Figure S13. The MALDI-TOF mass spectrum of **G2-TPA**.

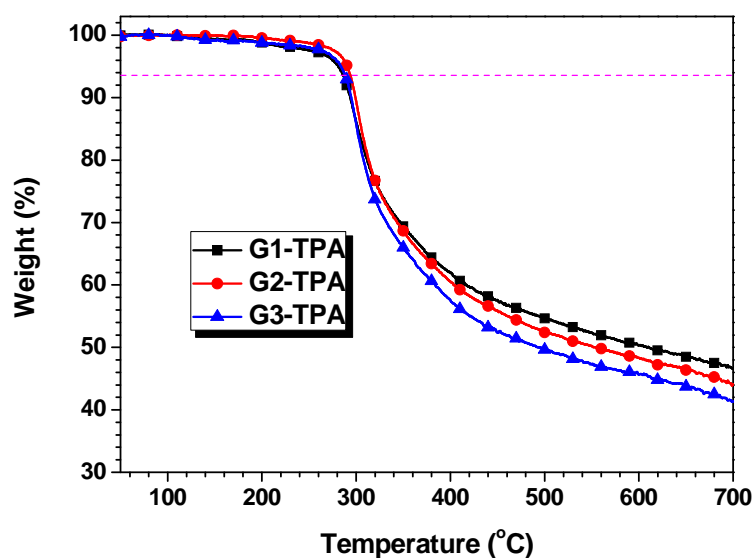


Figure S14. TGA thermograms of dendrimers, measured in nitrogen at a heating rate of 10 °C/min.

Table S1. The maximum absorption of dendrimers (0.02 mg/mL, λ_{\max} , nm).

	THF	1,4-dioxane	chloroform	dichloromethane	DMF	DMSO	film
G1-TPA	461	456	457	458	473	483	470
G2-TPA	458	456	455	458	472	482	470
G3-TPA	458	457	457	457	470	476	470

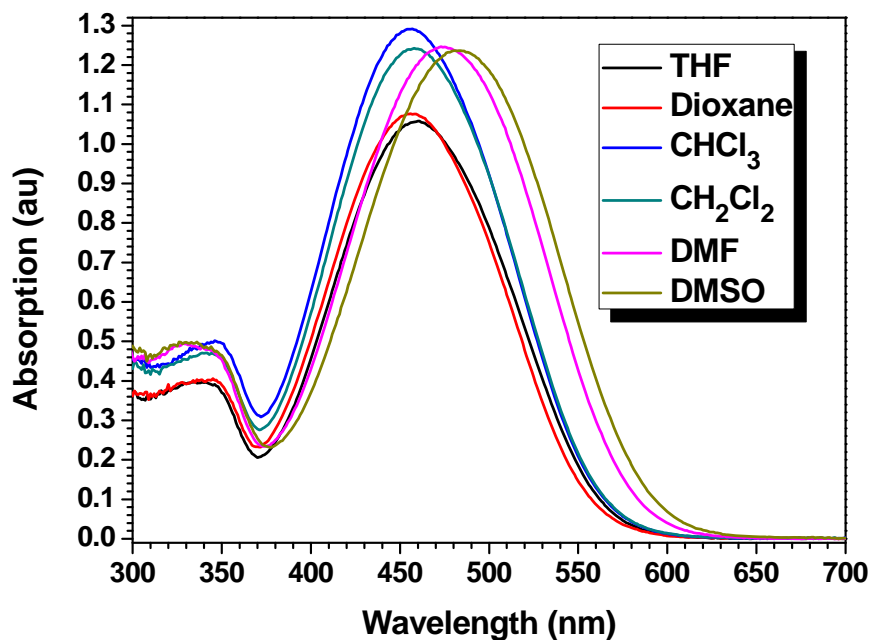


Figure S15. UV-Vis spectra of G1-TPA in different solutions (0.02 mg/mL).

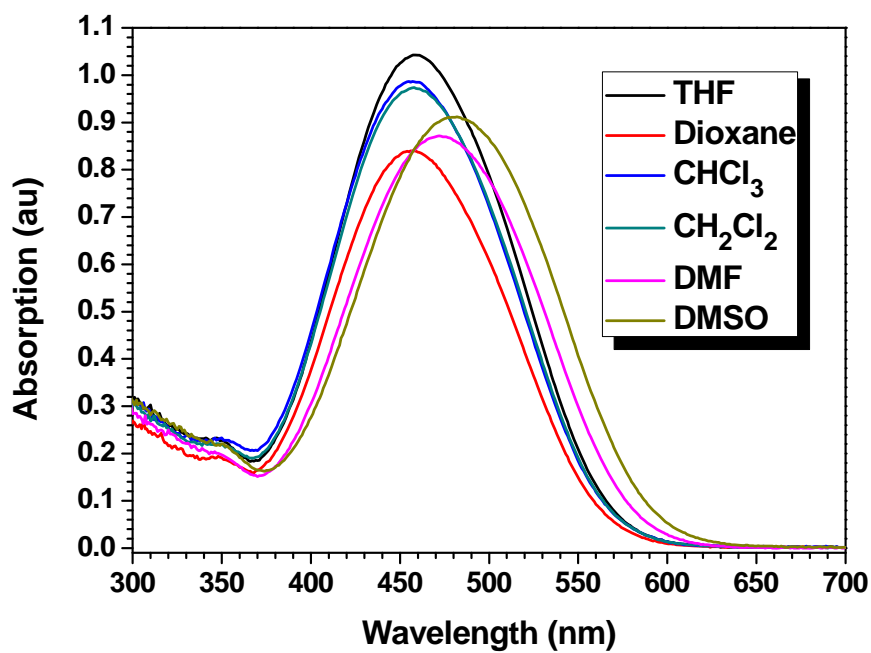


Figure S16. UV-Vis spectra of G2-TPA in different solutions (0.02 mg/mL).

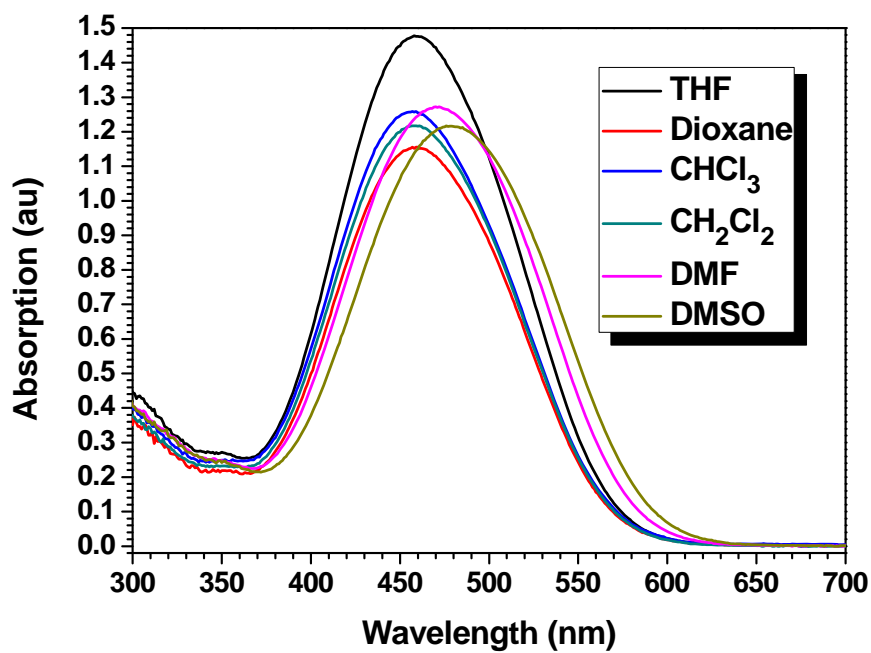


Figure S17. UV-Vis spectra of G3-TPA in different solutions (0.02 mg/mL).

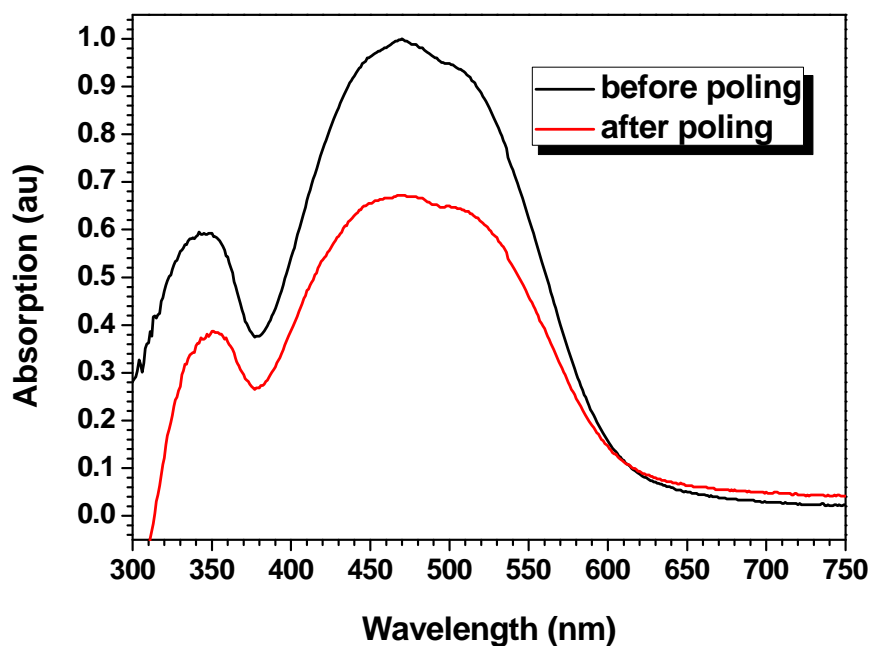


Figure S18. Absorption spectra of the film of G1-TPA before and after poling.

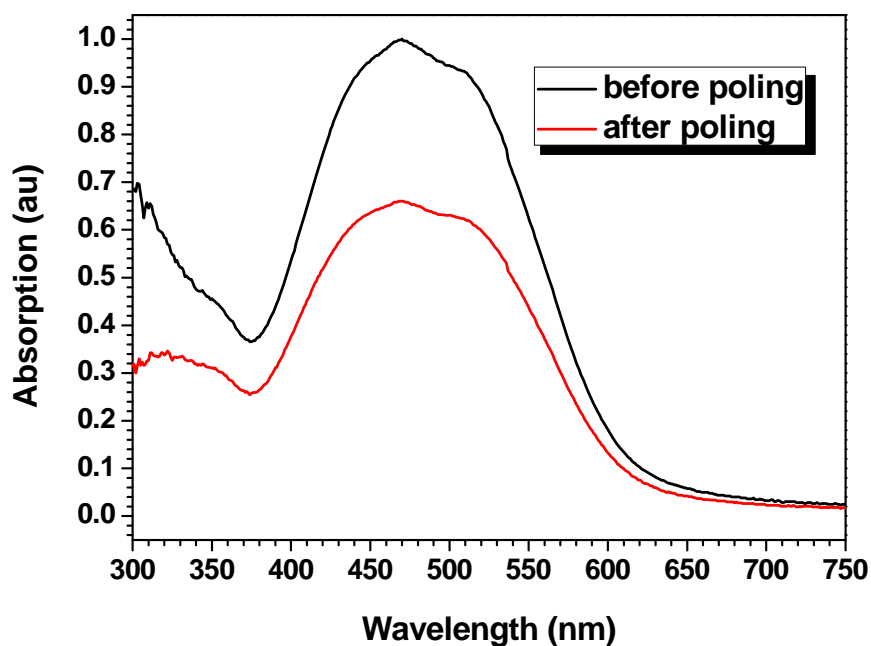


Figure S19. Absorption spectra of the film of G2-TPA before and after poling.

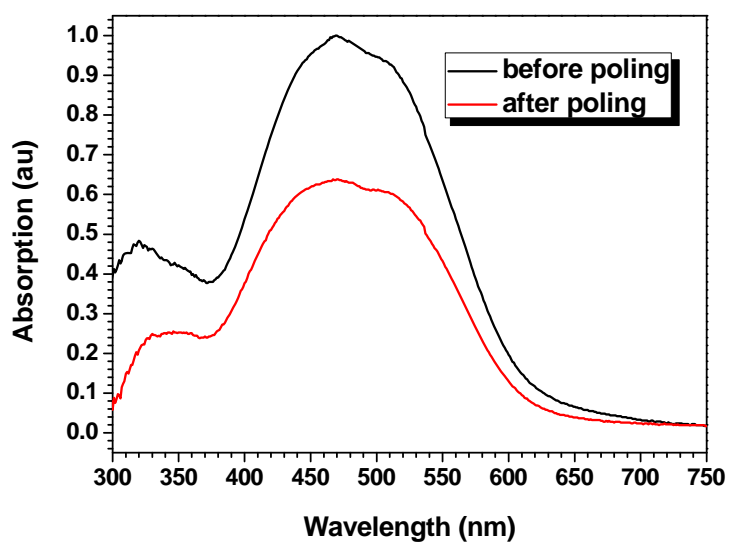


Figure S20. Absorption spectra of the film of G3-TPA before and after poling.

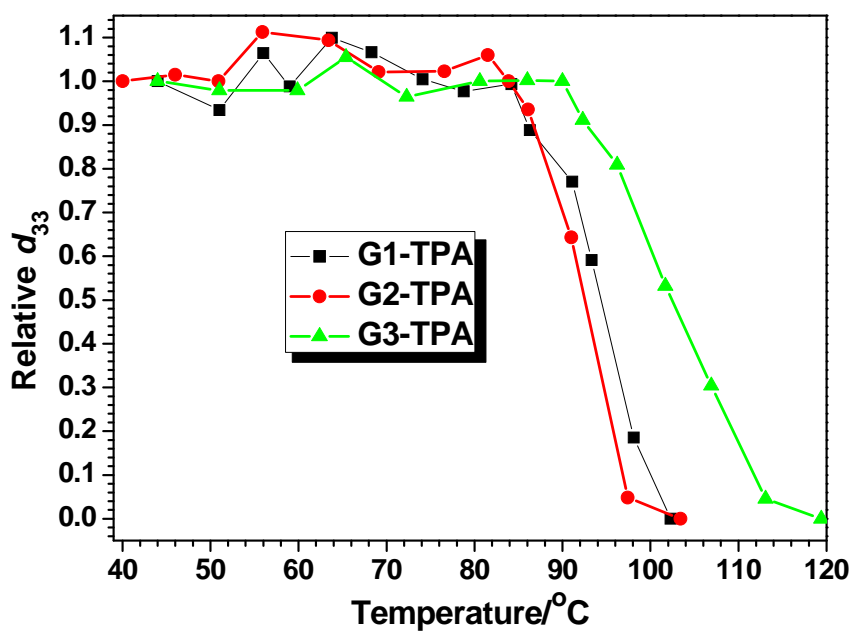


Figure S21. Decay curves of the SHG coefficients of dendrimers as a function of the temperature.