Electronic Supplementary Information for:

Using Orthogonal Approach and One-Pot Method to Simplify the Synthesis of Nonlinear Optical (NLO) Dendrimers

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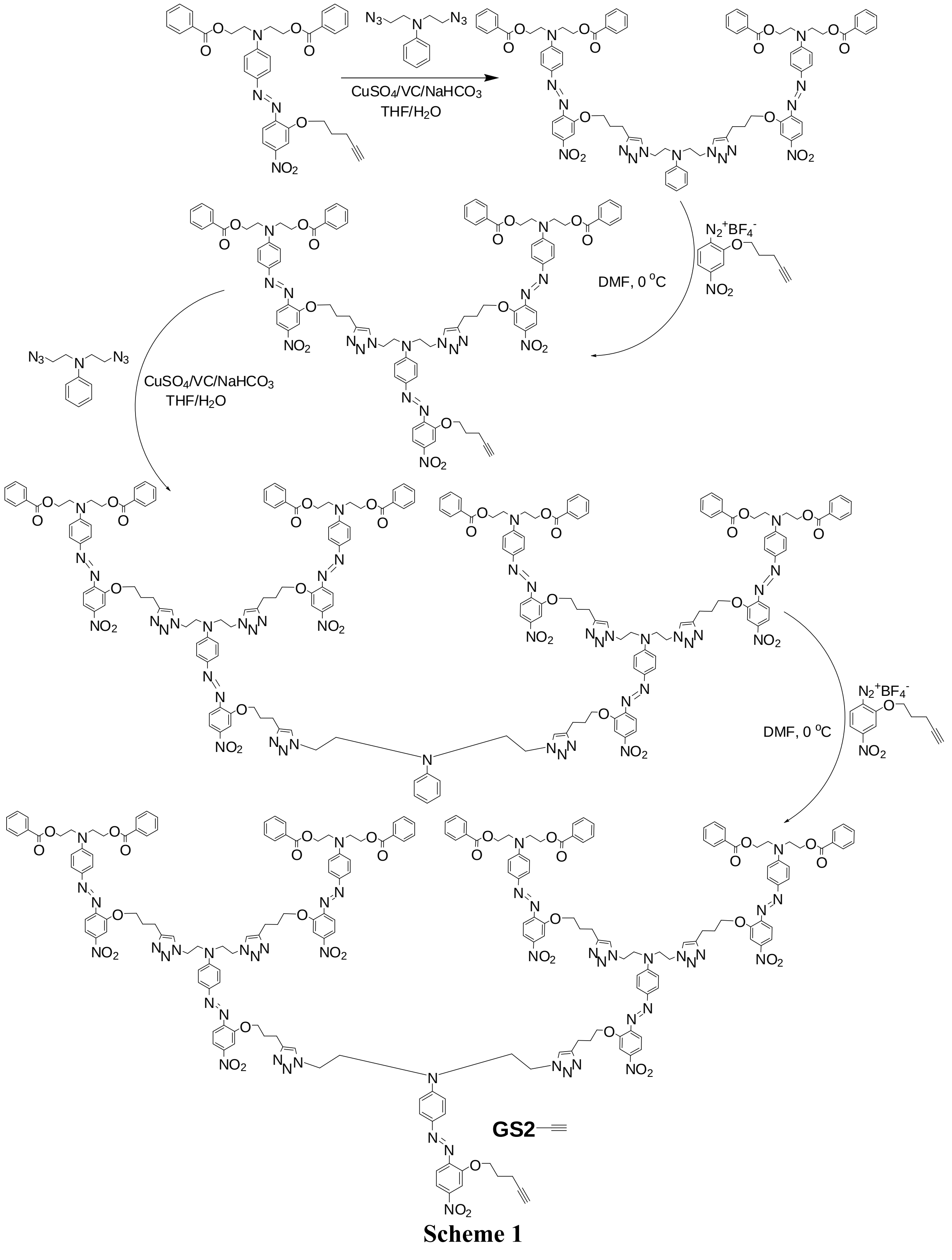
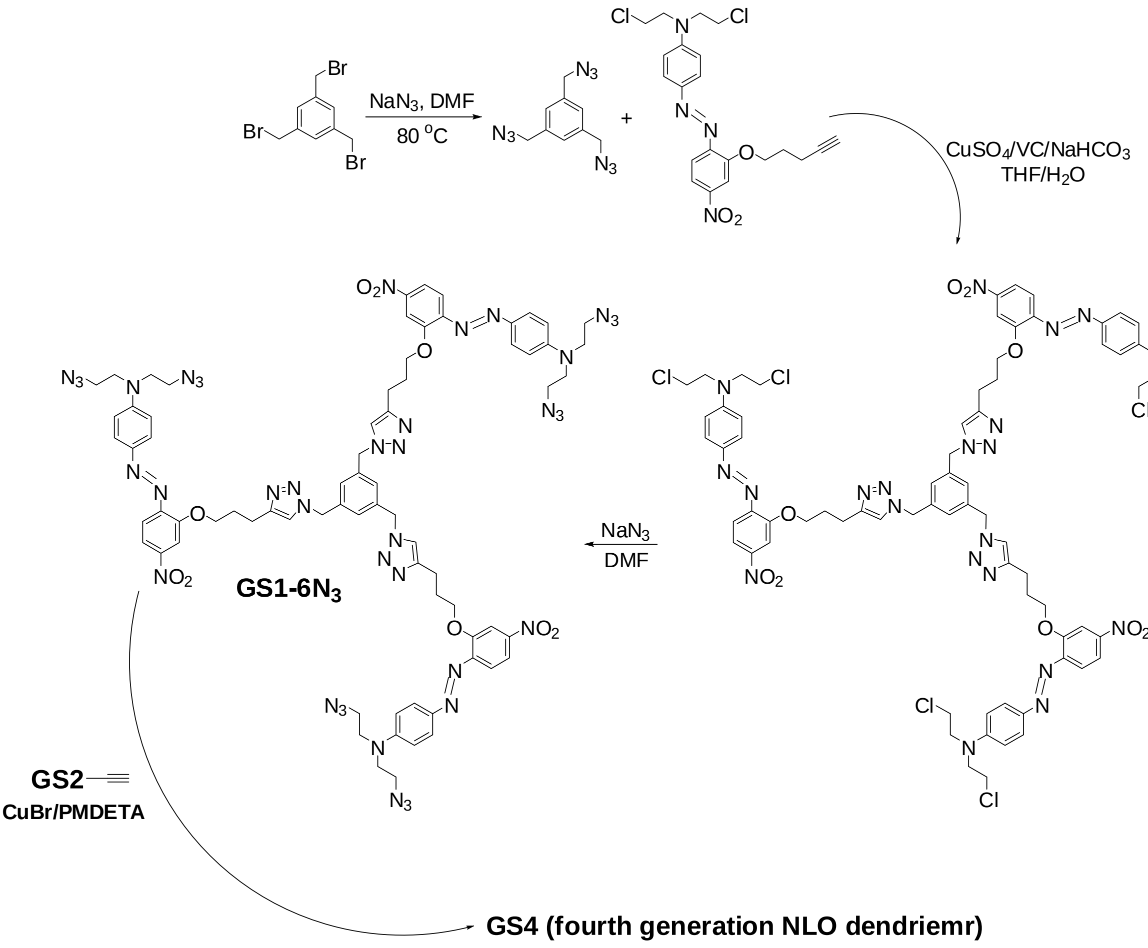


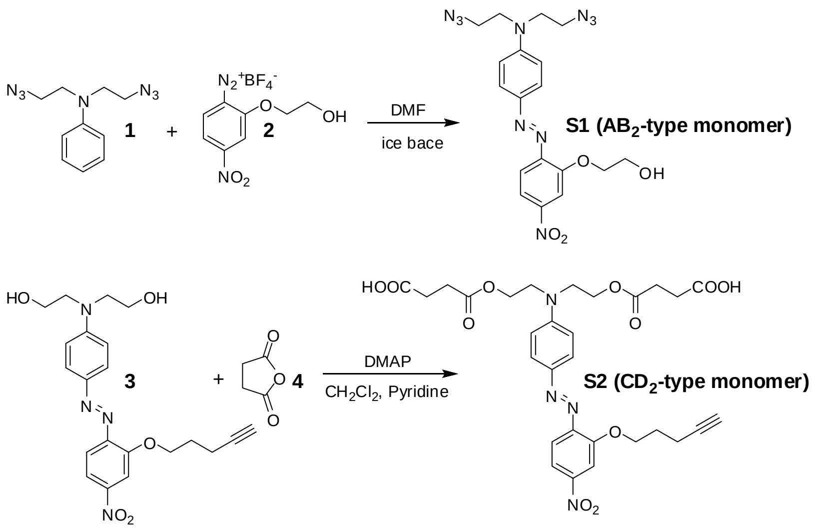
Scheme 1



Scheme 2

Experimental Section

Materials and Instrumentation. Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. *N,N*-Dimethylform amide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Dichloromethane was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Compound **1**,[1] **2**,[2] and **3**,[3] were prepared in our previous work. $Cu(PPh_3)_3Br$ was prepared according to the literature.[4] PMDETA was purchased from Alfa Aesar. All other reagents were used as received. ^1H and ^{13}C NMR spectra were measured on a Varian Mercury300 or Bruker ARX 400 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 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 (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 was used as an eluent, and the flow rate was 1.0 mL/min. The absolute molecular weights of polymers were tested by laser light scattering (DOWN-EOS, Wyatt, US). Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 ^{o}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 surface profilometer (FTS2-S4C-3D, Taylor Hobson, UK).



Scheme 3. The synthesis of AB$_2$-type monomer **S1** and CD$_2$-type monomer **S2**.

Synthesis of AB_2-type monomer S1. Diazonium salt **2** (817 mg, 4.0 mmol) and compound **1** (1.78 g, 6.0 mmol) were dissolved in DMF (4 mL) at 0 °C. The reaction mixture was stirred for 12 h at 0 °C, then treated with H_2O and extracted with $CHCl_3$, 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 petroleum ether/ethyl acetate (1/1,v/v) as eluent to afford red solid (1.45 g, 82.1 %). ^1H NMR (300 MHz, $CDCl_3$, 298 K), δ(ppm): 3.21 (s, 1H, -OH), 3.60 (t, J = 5.7 Hz, 4H, $-CH_2N_3$), 3.70 (t, J = 5.7 Hz, 4H, $-NCH_2-$), 4.02 (s, br, 2H, $-OCH_2-$), 4.36 (t, J = 4.2 Hz, 4H, $-OCH_2-$), 6.81 (d, J = 9.0 Hz, 2H, ArH), 7.70 (d, J = 9.0 Hz, 1H, ArH), 7.88-7.94 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ(ppm): 48.4, 50.3, 60.5, 109.7, 114.4, 116.6, 117.4, 126.0, 144.3, 146.2, 147.8, 149.8, 154.5. $C_{18}H_{20}N_{10}O_4$ (EA) (%, found/calcd): C, 49.08/49.09; H, 4.66/4.58; N, 31.22/31.80.

Synthesis of CD_2-type monomer S2. Chromophore **3** (619 mg, 1.5 mmol), compound **4** (3.0 g, 30.0 mmol), and 4-(*N,N*-dimethyl)aminopyridine (DMAP) (548 mg, 4.5 mmol) were dissolved in dry dichloromethane (7.5 mL). And then, pyridine (1 mL) was added into the reaction mixture. The reaction mixture was stirred stirred at room temperature for 3 h, then treated with H_2O and extracted with $CHCl_3$, 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 chloroform/methanol (20/1,v/v) as eluent to afford red solid (687 mg, 74.8 %). ^1H NMR (300 MHz, $CDCl_3$, 298 K), δ(TMS, ppm): 2.02 (s, 1H, $-C\equiv CH$), 2.16 (m, 2H, $-CH_2-$), 2.51 (t, J = 4.2 Hz, 2H, $-CH_2-$), 2.70 (s, br, 8H, $-CH_2COO-$), 3.72 (t, J = 5.4 Hz, 4H, $-NCH_2-$), 4.56(m, 6H, $-OCH_2-$), 6.82 (d, J = 9.0 Hz, 2H, ArH), 7.68 (d, J = 8.4 Hz, 1H, ArH), 7.89-7.94 (m, 4H, ArH). ^{13}C NMR (100 MHz, CD_3OD, 298 K), δ(ppm): 15.9, 29.9, 31.0, 50.7, 63.0, 69.7, 70.6, 84.2, 110.3, 113.2, 117.5, 118.7, 127.3, 146.1, 149.9, 152.8, 156.9, 174.4, 176.2. $C_{29}H_{32}N_4O_{11}$ (EA) (%, found/calcd): C, 56.54/56.86; H, 4.92/5.27; N, 9.31/9.15.

Synthesis of dendrimer G1-OH. Chromophore **G0-≡** (682.7 mg, 1.1 mmol), **S1** (220.2 mg, 0.5 mmol), $CuSO_4 \cdot 5H_2O$ (10 mol %), $NaHCO_3$ (20 mol %), and ascorbic acid (20 mol %) were dissolved in THF (15 mL)/H_2O (1.5 mL) under nitrogen in a Schlenk flask. The mixture was stirred at room temperature for 8 h, then extracted with chloroform, and washed with brine. The organic layer was dried over anhydrous magnesium sulfate and purified by column chromatography using pure ethyl acetate as eluent to afford red solid (774.5 mg, 92.1 %). IR (thin film), υ (cm^{-1}): 1716 (C=O), 1513, 1338 ($-NO_2$). ^1H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 2.24 (m, 4H, $-CH_2-$), 2.94 (t, J = 6.3 Hz, 4H, $-CH_2C-$), 3.75 (s, br, 4H, $-NCH_2-$), 3.93 (t, 8H, $-NCH_2-$), 4.00 (s, br, 2H, $-OCH_2-$), 4.11 (t, J = 6.0 Hz, 4H, $-NCH_2-$), 4.30 (s, br, 2H, $-OCH_2-$), 4.37 (s, br, 4H, $-OCH_2-$), 4.55 (t, J = 5.7 Hz, 8H, $-COOCH_2-$), 6.47 (d, J = 8.7 Hz, 2H, ArH), 6.94 (d, J = 9.0 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 (75 MHz, $CDCl_3$, 298 K), δ (ppm): 21.4, 25.2, 28.0, 46.7, 49.4, 61.4, 67.5, 107.9, 108.7, 111.5, 115.9, 116.8, 122.2, 125.8, 128.1, 129.2, 132.9, 144.3, 146.1, 146.7, 147.7, 150.5, 154.7, 166.0. MALDI-TOF MS: calcd for ($C_{88}H_{84}N_{18}O_{18}$): m/z $[M+Na]^+$: 1703.6; found: m/z 1704.4. $C_{88}H_{84}N_{18}O_{18}$ (EA) (%, found/calcd): C, 63.19/62.85; H, 4.93/5.03; N, 14.94/14.99.

Synthesis of dendrimer G2-≡. Dendrimer **G1-OH** (630.6 mg, 0.375 mmol), **S2** (91.9 mg, 0.15 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (143.8 mg, 0.75 mmol), and DMAP (3.6 mg, 0.03 mmol) were dissolved in dry CH_2Cl_2 (2mL)/THF (2mL) and stirred at room temperature for 24 h, and then treated with saturated solution of citric acid and extracted with CH_2Cl_2, washed with saturated solution of citric acid and brine. After the removal of the solvent, the crude product was purified by column chromatography on silica gel using chloroform/THF (2/1, v/v) as eluent to afford red solid (410 mg, 69.4%). IR (thin film), υ (cm^{-1}): 1718 (C=O), 1514, 1335 (-NO$_2$). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K), δ (ppm): 1.86 (s, br, -CH$_2$-), 2.05 (s, -C≡CH), 2.23 (s, br, -CH$_2$-), 2.62 (m, -CH$_2$C-), 2.70 (s, br, -CH$_2$COO-), 2.93 (t, J = 6.3 Hz, -CH$_2$C-), 3.69-3.75 (m, -NCH$_2$-), 3.92 (s, br, -NCH$_2$-), 4.13 (s, br, -NCH$_2$-), 4.26 (m, -OCH$_2$-), 4.37 (s, br, -OCH$_2$-), 4.54 (t, J = 6.0 Hz, -COOCH$_2$-), 6.56 (d, J = 9.0 Hz, ArH), 6.76 (d, J = 8.7 Hz, ArH), 6.94 (d, J = 8.4 Hz, ArH), 7.32 (s, C=CH), 7.42 (t, J = 7.8 Hz, ArH), 7.5-7.9 (m, ArH), 7.98 (d, J = 7.2 Hz, ArH). ^{13}C NMR (75 MHz, CDCl$_3$, 298 K), δ (ppm): 21.5, 23.1, 25.2, 28.1, 29.3, 32.9, 34.0, 46.8, 49.4, 61.4, 67.1, 67.5, 68.2, 97.9, 108.7, 111.5, 116.0, 116.9, 122.2, 125.8, 128.1, 129.2, 132.9, 134.5, 144.4, 146.2, 146.7, 147.8, 149.1, 150.5, 154.7, 166.0, 171.8. MALDI-TOF MS: calcd for ($C_{205}H_{196}N_{40}O_{45}$): m/z [M+Na]$^+$: 3963.0; found: m/z 3966.0. $C_{205}H_{196}N_{40}O_{45}$ (EA) (%, found/calcd): C, 62.83/62.49; H, 5.13/5.01; N, 14.34/14.22.

Synthesis of dendrimer G1-6N$_3$. Chromophore **S1** (145.3 mg, 0.33 mmol), compound **S3** (26.5 mg, 0.10 mmol), and DMAP (40.3 mg, 0.23 mmol) were dissolved in dry THF (2 mL). The mixture was stirred at 0 °C for 3 h, at 30 °C for 12 h, respectively. And then, the reaction was stopped by addition of water, and extracted with CH$_2$Cl$_2$, washed with brine. After the removal of the solvent, the crude product was purified by column chromatography on silica gel using pure chloroform as eluent to afford red solid (94.2 mg, 63.1%). IR (thin film), υ (cm^{-1}): 2100 (-N$_3$), 1732 (C=O), 1517, 1336 (-NO$_2$). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K), δ (TMS, ppm): 3.55 (t, J = 4.8 Hz, 12H, -CH$_2$N$_3$-), 3.64 (t, J = 5.7 Hz, 12H, -NCH$_2$-), 4.52 (s, br, 6H, -OCH$_2$-), 4.78 (s, br, 6H, -COOCH$_2$-), 6.70 (d, J = 9.0 Hz, 6H, ArH), 7.63 (d, J = 8.4 Hz, 3H, ArH), 7.80-7.87 (m, 12H, ArH), 8.87 (s, 3H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K), δ (ppm): 29.9, 48.9, 50.7, 50.8, 63.8, 68.3, 110.5, 111.9, 112.1, 117.4, 117.6, 126.4, 131.2, 135.1, 145.1, 147.0, 148.4, 150.1, 155.0, 164.7. MALDI-TOF MS: calcd for

($C_{63}H_{60}N_{30}O_{15}$): *m/z* $[M+H]^+$: 1478.3; found: *m/z* 1449.4([M+H-N_2]). $C_{63}H_{60}N_{30}O_{15}$ (EA) (%, found/calcd): C, 52.61/51.22; H, 4.17/4.09; N, 27.92/28.44.

Synthesis of dendrimer G4. A mixture of **G1-6N$_3$** (6.0 mg, 0.04 mmol), **G2-≡** (110.3 mg, 0.028 mmol), and CuBr (4 mg) were dissolved in DMF (4 mL) under nitrogen in a Schlenk flask, then PMDETA (12 μL) 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 acetone, and then filtered and washed with lots of acetone, dried in vacuum at 40 °C to a constant weight. **G4** was obtained as red solid (84.1 mg, 83.7 %). IR (thin film), *υ* (cm^{-1}): 1771 (C=O), 1721 (C=O), 1517, 1336 (-NO_2). ^1H NMR (300 MHz, $CDCl_3$, 298 K), δ (ppm): 2.1-2.3 (-CH_2-), 2.5-2.7 (-CH_2-), 2.8-3.0 (-CH_2C-), 3.6-3.8 (-NCH_2-), 3.8-4.0 (-NCH_2-), 4.0-4.2 (-NCH_2-), 4.1-4.4 (-OCH_2-), 4.4-4.6 (-$COOCH_2$-), 6.5 (s, br, ArH), 6.7 (s, br, ArH), 6.8-7.0 (ArH), 7.3-8.0 (ArH and C=CH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 22.0, 28.6, 29.0, 47.3, 50.0, 61.9, 62.8, 68.2, 68.7, 108.8, 111.8, 112.0, 116.6, 117.5, 122.4, 126.3, 128.6, 129.7, 133.5, 145.0, 146.9, 147.3, 148.3, 149.8, 151.0, 155.2, 166.6, 172.3. $C_{1293}H_{1236}N_{270}O_{285}$ (EA) (%, found/calcd): C, 61.23/61.83; H, 4.57/4.96; N, 15.33/15.06.

Synthesis of dendrimer G2-≡ by one-pot method: Chromophore **G0-≡** (75.7 mg, 0.122 mmol), AB$_2$-type monomer **S1** (26.4 mg, 0.060 mmol), and $Cu(PPh_3)_3Br$ (113.5 mg, 0.122 mmol), were dissolved in THF (2 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 60 °C under nitrogen atmosphere for 4 h, and then cooled to room temperature, stirred at room temperature with exposure to dry air for another 1 h. CD$_2$-type monomer **S2** (12.3 mg, 0.020 mmol), EDC (38.8 mg, 0.20 mmol), DMAP (2.4 mg, 0.02 mmol), cyclen (34.5 mg,0.2 mmol), and dichloromethane (2 mL) were added to the reaction system. After stirred at 20 °C for 4 h, the reaction was terminated by the addition of water, and then extracted with chloroform, and washed with brine. The organic layer was combined, dried over anhydrous sodium sulfate and purified by column chromatography using ethyl THF/chloroform (1/2, v/v) as eluent to afford red solid (53.7 mg, 68.2%). IR (thin film), *υ* (cm^{-1}): 1718 (C=O), 1514, 1335 ($-NO_2$). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.86 (s, br, $-CH_2-$), 2.05 (s, -C≡CH), 2.23 (s, br, $-CH_2-$), 2.62 (m, $-CH_2C-$), 2.70 (s, br, $-CH_2COO-$), 2.93 (t, *J* = 6.3 Hz, $-CH_2C-$), 3.69-3.75 (m, $-NCH_2-$), 3.92 (s, br, $-NCH_2-$), 4.13 (s, br, $-NCH_2-$), 4.26 (m, $-OCH_2-$), 4.37 (s, br, $-OCH_2-$), 4.54 (t, *J* = 6.0 Hz, $-COOCH_2-$), 6.56 (d, *J* = 9.0 Hz, ArH), 6.76 (d, *J* = 8.7 Hz, ArH), 6.94 (d, *J* = 8.4 Hz, ArH), 7.32 (s, C=CH), 7.42 (t, *J* = 7.8 Hz, ArH), 7.5-7.9 (m, ArH), 7.98 (d, *J* = 7.2 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 21.5, 23.1, 25.2, 28.1, 29.3, 32.9, 34.0, 46.8, 49.4, 61.4, 67.1, 67.5, 68.2, 97.9, 108.7, 111.5, 116.0, 116.9, 122.2, 125.8, 128.1, 129.2, 132.9, 134.5, 144.4, 146.2, 146.7, 147.8, 149.1, 150.5, 154.7, 166.0, 171.8. MALDI-TOF MS: calcd for ($C_{205}H_{196}N_{40}O_{45}$): *m*/*z* $[M+Na]^+$: 3963.0; found: *m*/*z* 3966.0. $C_{205}H_{196}N_{40}O_{45}$ (EA) (%, found/calcd): C, 62.89/62.49; H, 4.89/5.01; N, 14.41/14.22.

Synthesis of dendrimer G4 by one-pot method: Dendrimer **G2-≡** (55.2 mg, 0.014 mmol), AB_2-type monomer **S1** (2.64 mg, 0.0060 mmol), $Cu(PPh_3)_3Br$ (13.0 mg, 0.014 mmol), DMAP (2 mg), and the THF solution of core **S3** (2 mL, 0.001 mmol/mL) were added in a Schlenk flask. The mixture was stirred at 0 °C under and atmosphere of nitrogen for 0.5 h, at 30 °C for 3h, and at 60 °C for 3h, respectively. And then, the reaction was stopped by the addition of water. The precipitate was purified by repeating precipitations of their THF solutions into acetone, and then filtered and washed with lots of acetone, dried in vacuum at 40 °C to a constant weight. **G4** was obtained as red solid (36.1 mg, 72.1 %). IR (thin film), *υ* (cm^{-1}): 1771 (C=O), 1721 (C=O), 1517, 1336 ($-NO_2$). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 2.1-2.3 ($-CH_2-$), 2.5-2.7 ($-CH_2-$), 2.8-3.0 ($-CH_2C-$), 3.6-3.8 ($-NCH_2-$), 3.8-4.0 ($-NCH_2-$), 4.0-4.2 ($-NCH_2-$), 4.1-4.4 ($-OCH_2-$), 4.4-4.6 ($-COOCH_2-$), 6.5 (s, br, ArH), 6.7 (s, br, ArH), 6.8-7.0 (ArH), 7.3-8.0 (ArH and C=CH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm):

22.0, 28.6, 29.0, 47.3, 50.0, 61.9, 62.8, 68.2, 68.7, 108.8, 111.8, 112.0, 116.6, 117.5, 122.4, 126.3, 128.6, 129.7, 133.5, 145.0, 146.9, 147.3, 148.3, 149.8, 151.0, 155.2, 166.6, 172.3. $C_{1293}H_{1236}N_{270}O_{285}$ (EA) (%, found/calcd): C, 61.44/61.83; H, 5.34/4.96; N, 14.73/15.06.

Preparation of thin films. The dendrimer **G4** were dissolved in THF (concentration ~4 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*-dimethyformamide, 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 ^{o}C. And the thickness of three thin films was tested to be 210, 220, and 190 nm, respectively, by surface profilometer.

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^{o} to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature: 110 ^{o}C; voltage: 7.5 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.

Reference.

[1] Z. Li, G. Yu, W. Wu, Y. Liu, C. Ye, J. Qin, Z. Li, *Macromolecules*, 2009, **42**, 3864-3868.

[2] Z. Zhu, Q. Li, Q. Zeng, Z. Li, Z. Li, C. Ye, J. Qin, *Dyes Pigm.*, 2008, **78**, 199-206.

[3] Z. Li, Q. Zeng, G. Yu, Z. Li, C. Ye Y. Liu, J. Qin, *Macromol. Rapid Commun.*, 2008, 29, 136-141.

[4] R. Gujadhur, D. Venkataraman, J. T. Kintigh, *Tetrahedron Lett.*, 2001, **42**, 4791-4793.

Table 1. Characterization data of dendrimers.

No.	$M_w{}^a$	$M_w/M_n{}^a$	$M_w{}^b$	m/z^c	m/z(cal)
G1-OH	1860	1.07	2950	1704.4	1703.6[d]
G2-≡	3970	1.04	4300	3966.0	3963.0[d]
G1-6N$_3$	1590	1.08	2740	1449.4	1477.3
G4	13200	1.05	34360	(-)[e]	25117
G4 (one-pot)	13500	1.04	33890	(-)[e]	25117

[a] Determined by GPC in THF on the basis of a polystyrene calibration. [b] Determined by LLS technology. [c] Measured by MALDI-TOF mass spectroscopy. [d] Calculated for $[M+Na]^+$ [e] Not obtained.

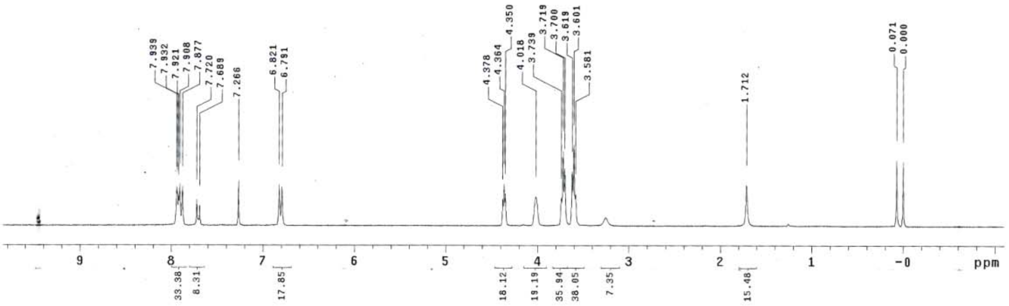


Fig. S1. ^{1}H NMR spectrum of AB$_2$-type monomer **S1** in chloroform-*d*.

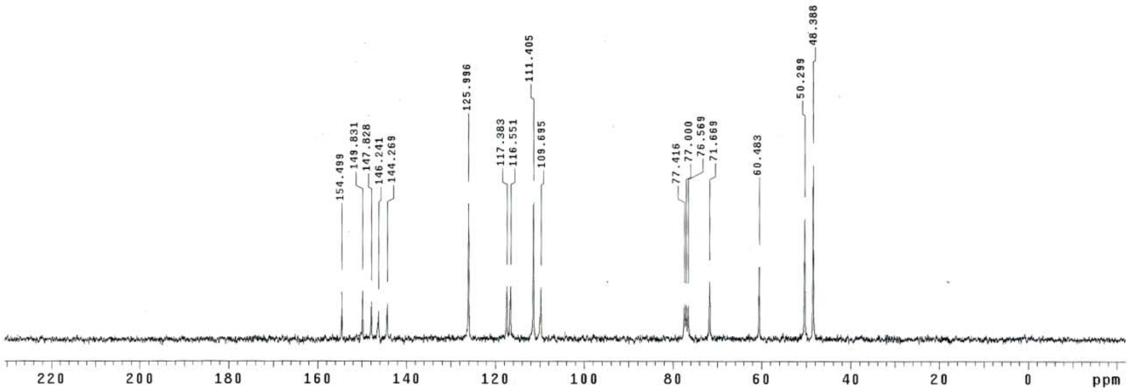


Fig. S2. ^{13}C NMR spectrum of AB$_2$-type monomer **S1** in chloroform-*d*.

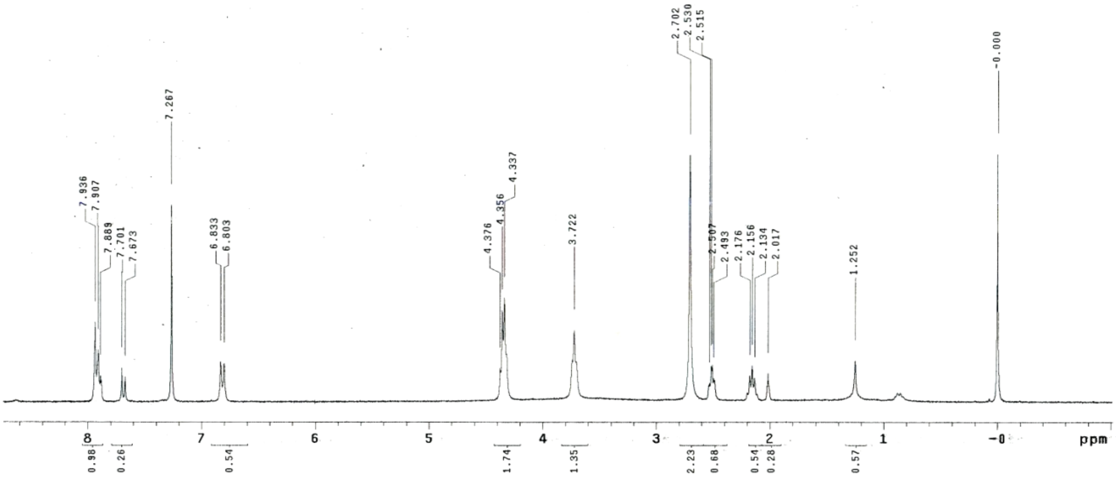


Fig. S3. ^{1}H NMR spectrum of CD$_2$-type monomer **S2** in chloroform-*d*.

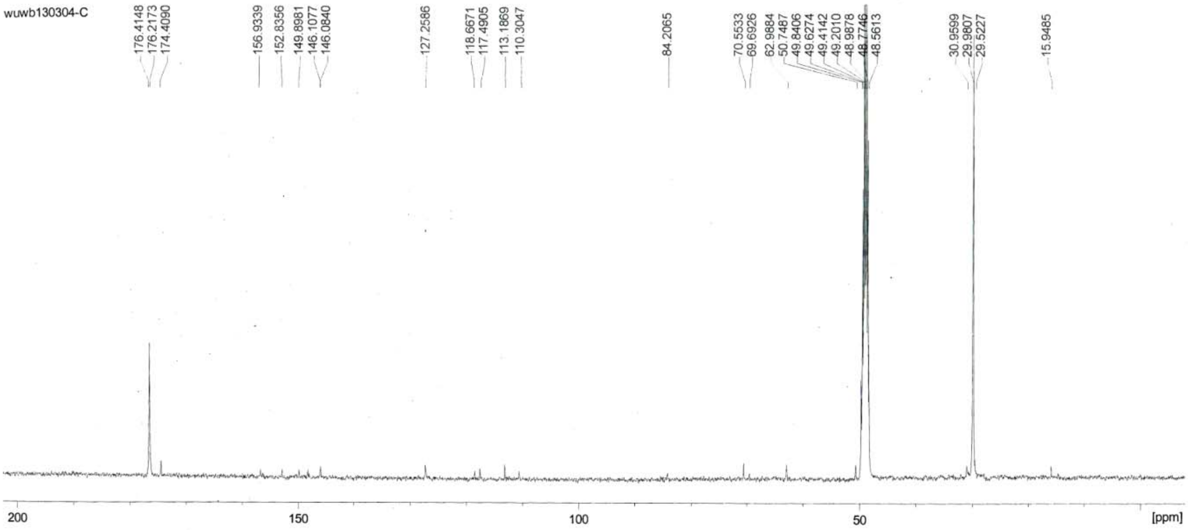


Fig. S4. ^{13}C NMR spectrum of CD$_2$-type monomer **S2** in CD$_3$OD.

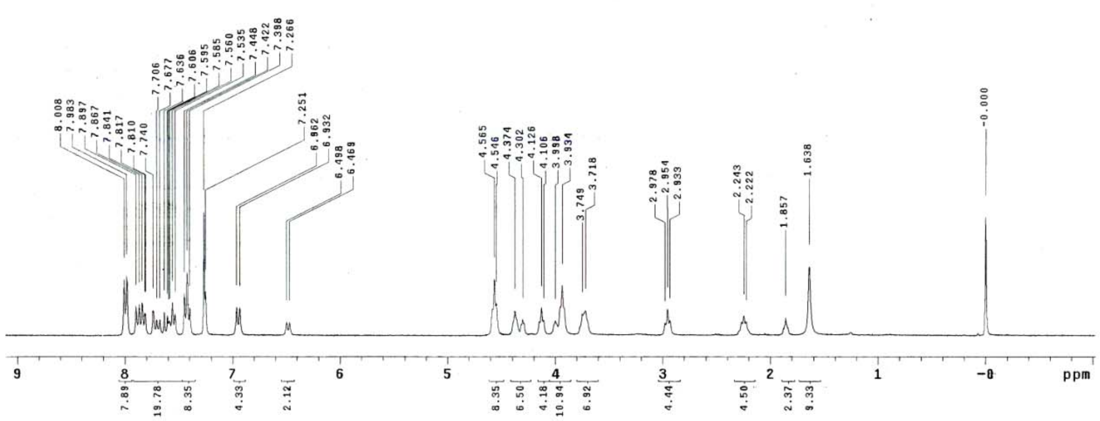


Fig. S5. ^{1}H NMR spectrum of **G1-OH** in chloroform-*d*.

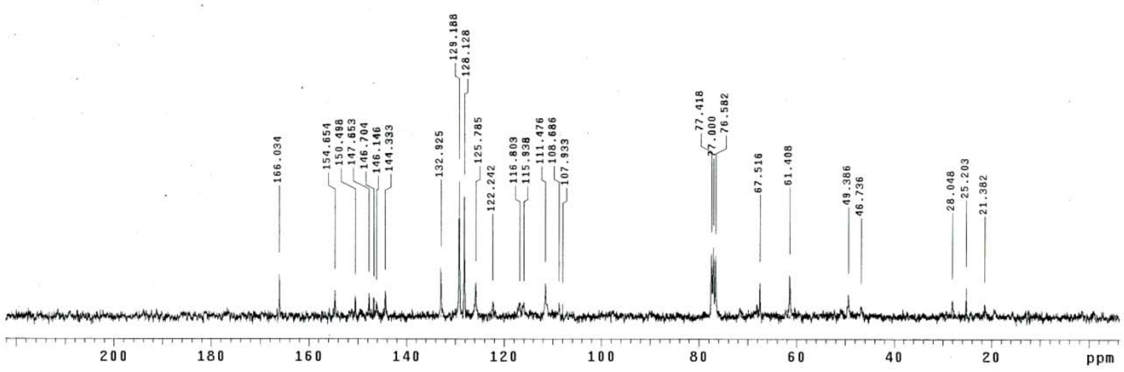


Fig. S6. ^{13}C NMR spectrum of **G1-OH** in chloroform-*d*.

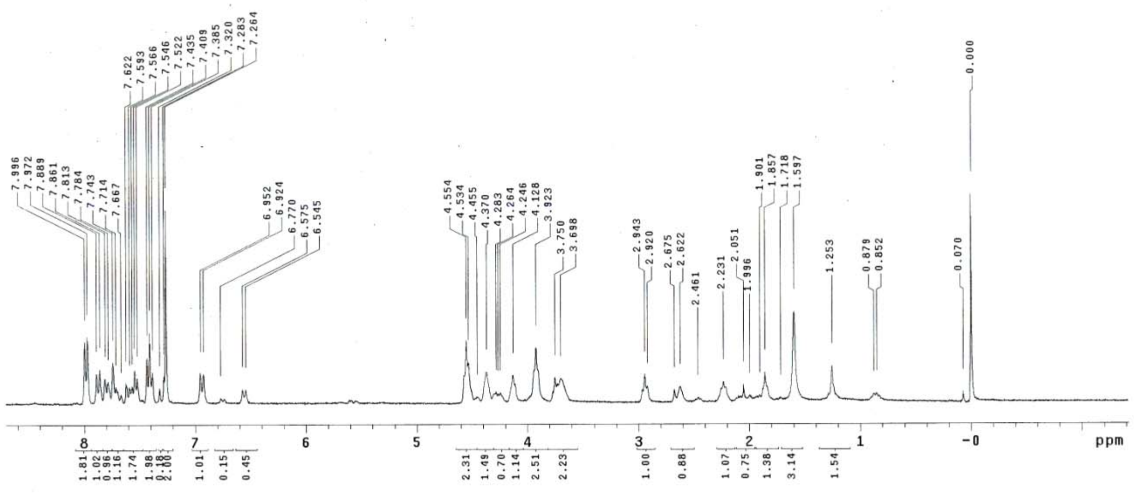


Fig. S7. ^{1}H NMR spectrum of **G2-≡** in chloroform-*d*.

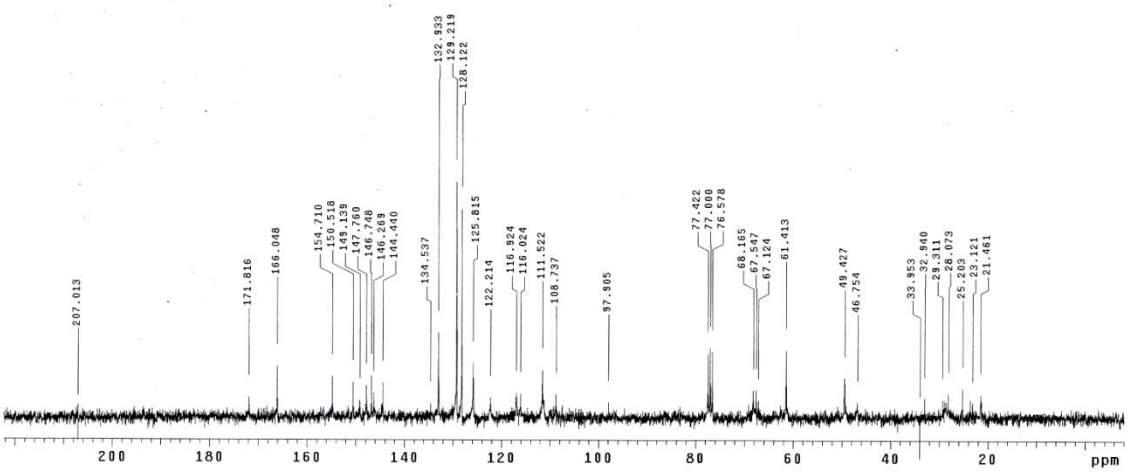


Fig. S8. ^{13}C NMR spectrum of **G2-≡** in chloroform-*d*.

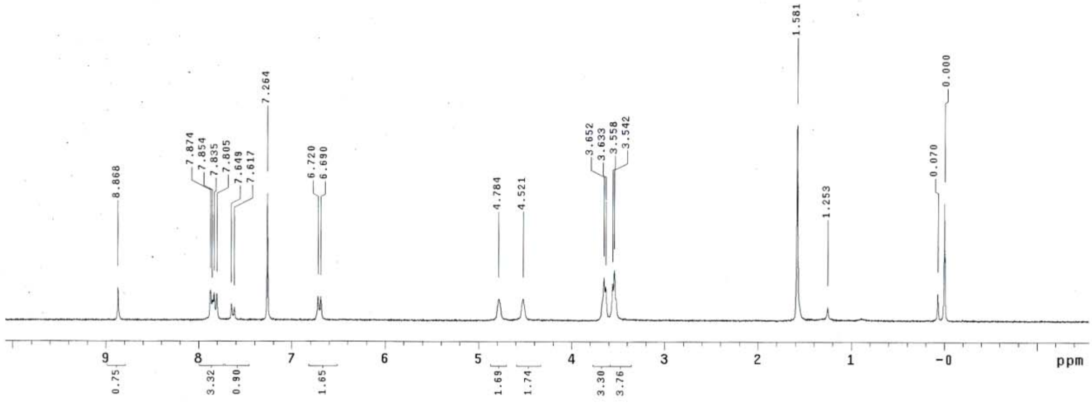


Fig. S9. ^{13}H NMR spectrum of **G1-6N$_3$** in chloroform-*d*.

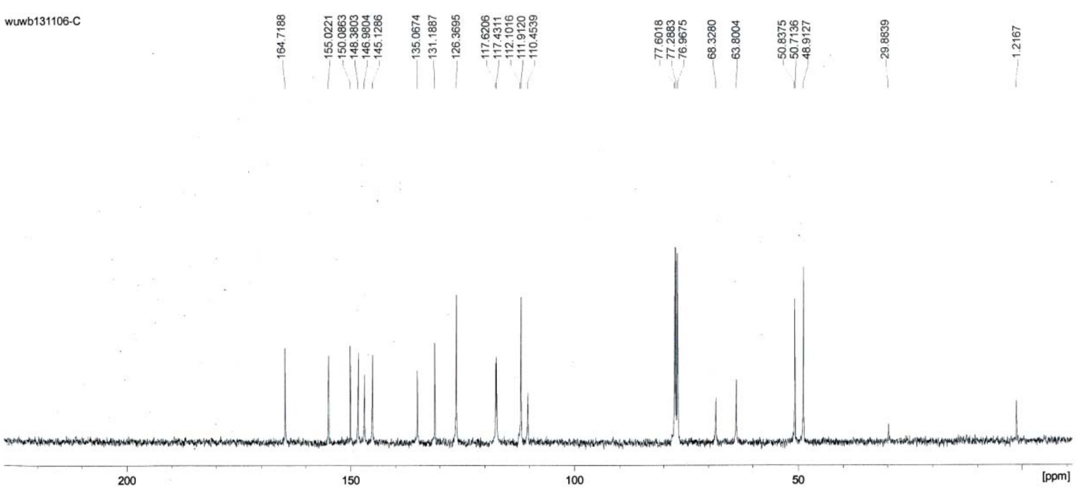


Fig. S10. ^{13}C NMR spectrum of **G1-6N$_3$** in chloroform-*d*.

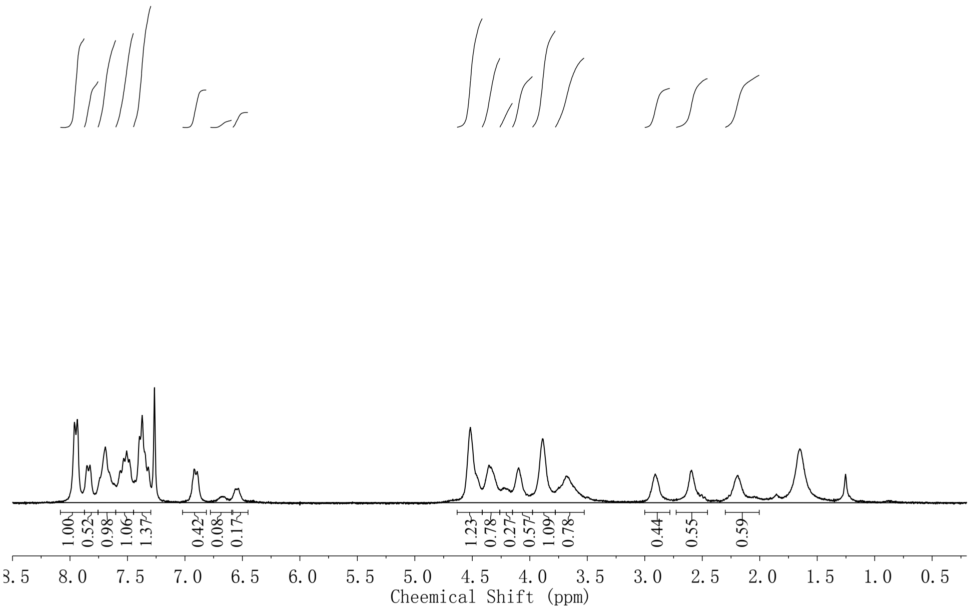


Fig. S11. ^{1}H NMR spectrum of **G4** (prepared by orthogonal approach) in chloroform-*d*.

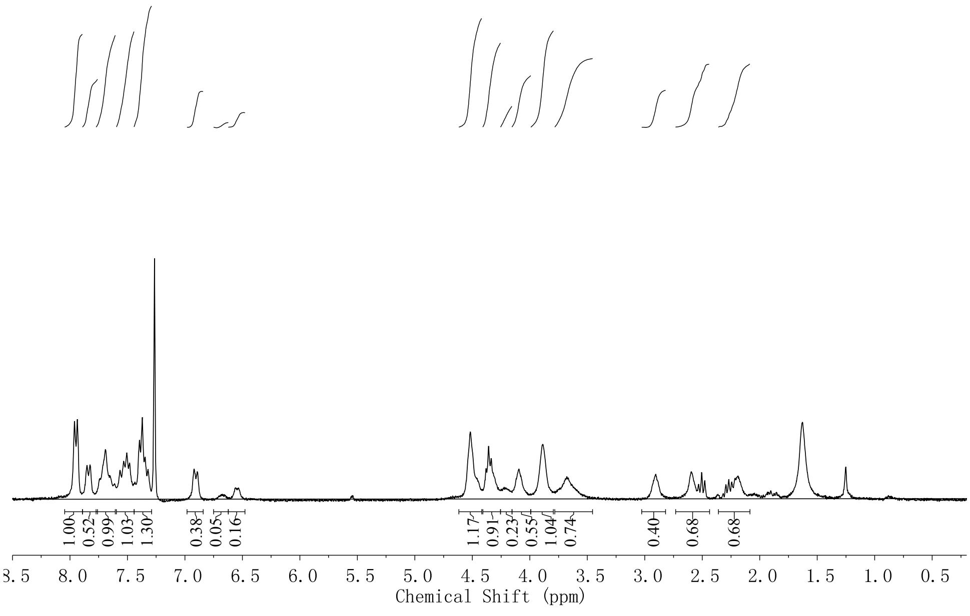


Fig. S12. ^{1}H NMR spectrum of **G4** (prepared by two “one-pot” steps) in chloroform-*d*.

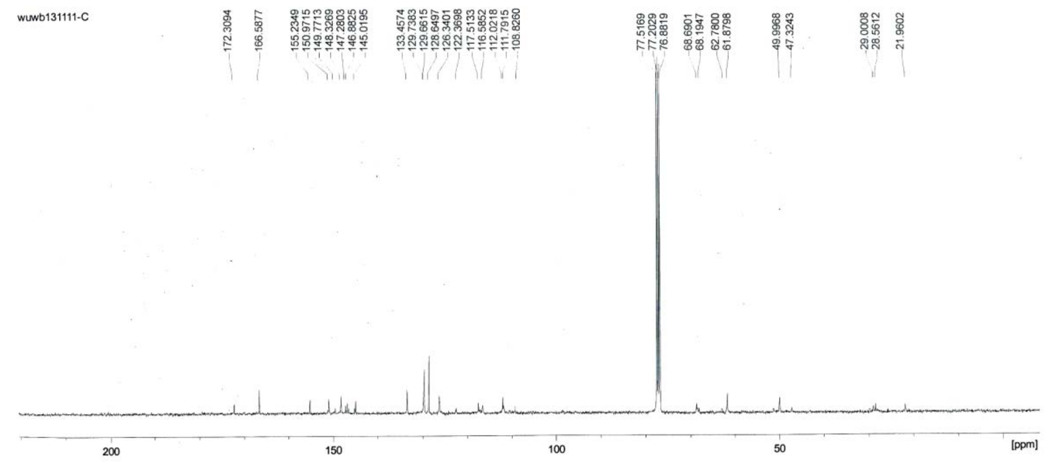


Fig. S13. ^{13}C NMR spectrum of **G4** (prepared by orthogonal approach) in chloroform-*d*.

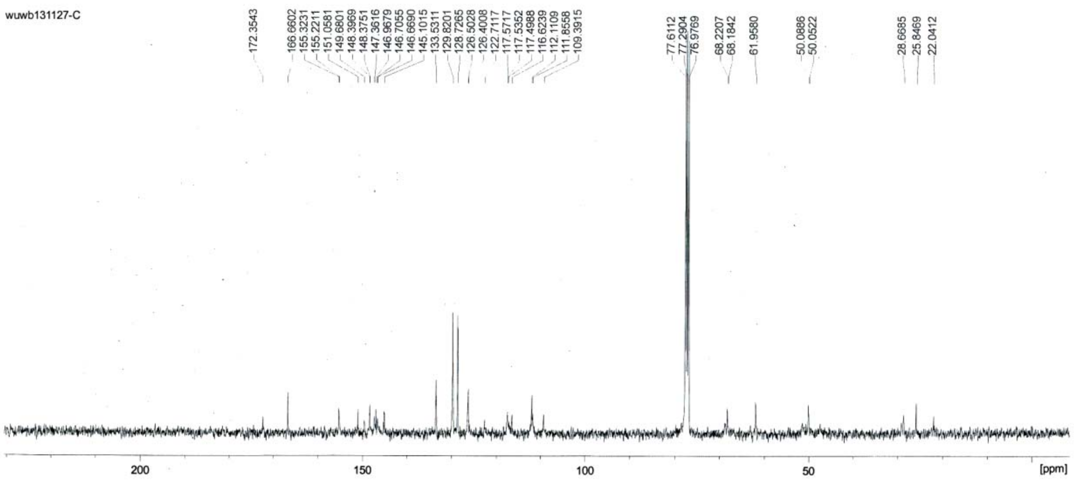


Fig. S14. ^{13}C NMR spectrum of **G4** (prepared by two "one-pot" steps) in chloroform-*d*.

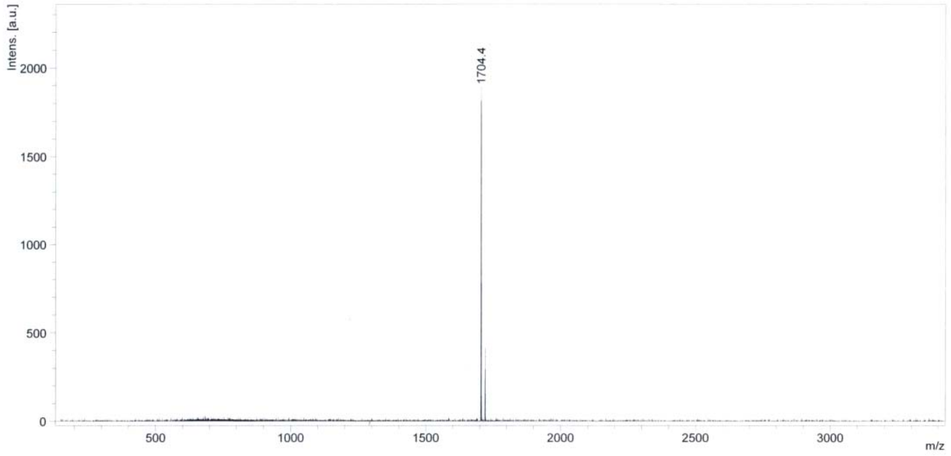


Fig. S15. The MALDI-TOF Mass spectrum of **G1-OH**.

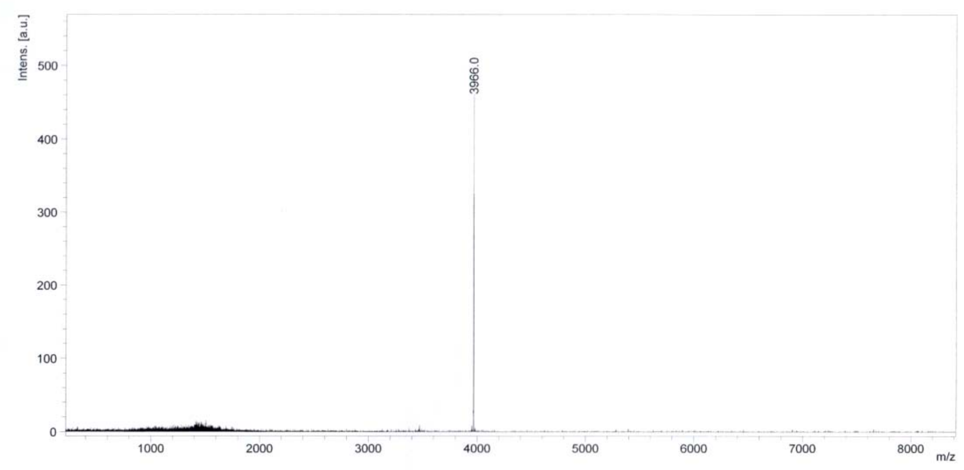


Fig. S16. The MALDI-TOF Mass spectrum of **G2-≡**.

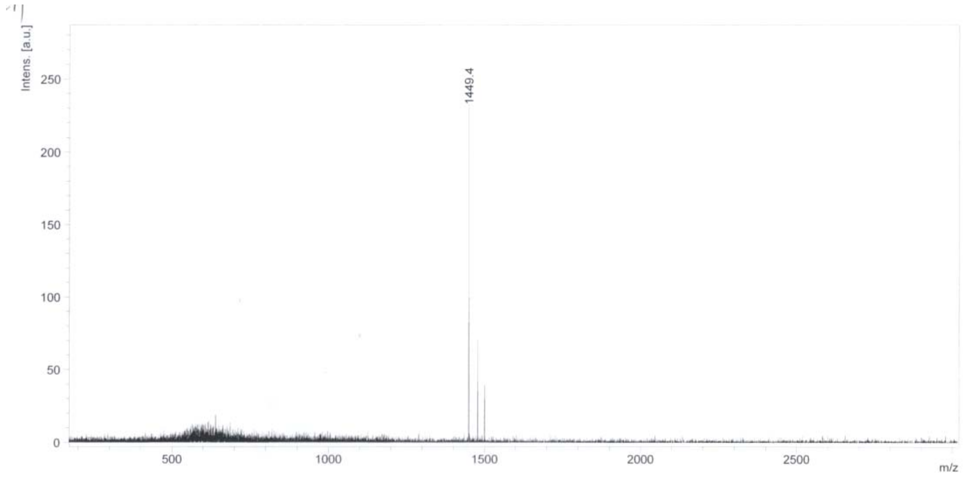


Fig. S17. The MALDI-TOF Mass spectrum of **G1-6N$_3$**.

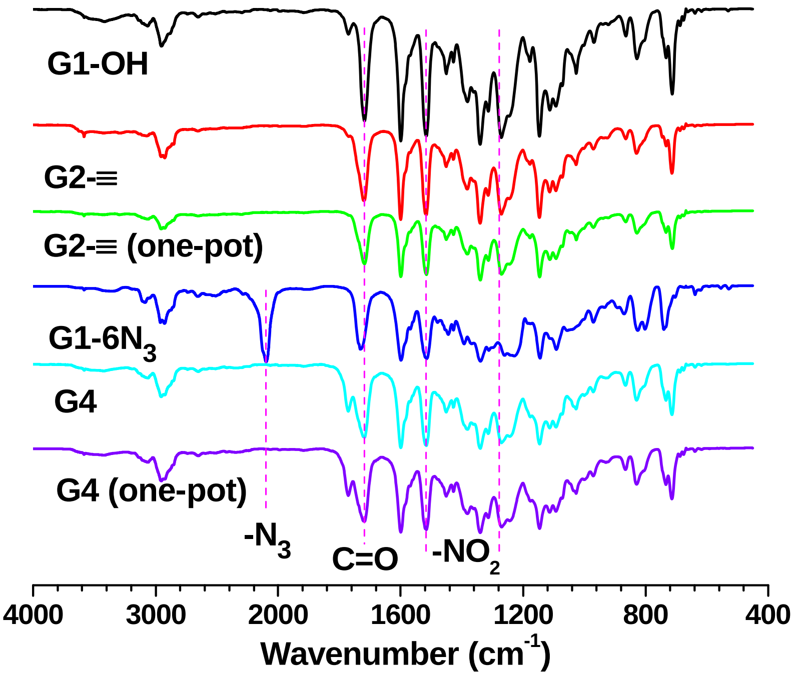


Fig. S18. The FT-IR spectra of dendrimers.

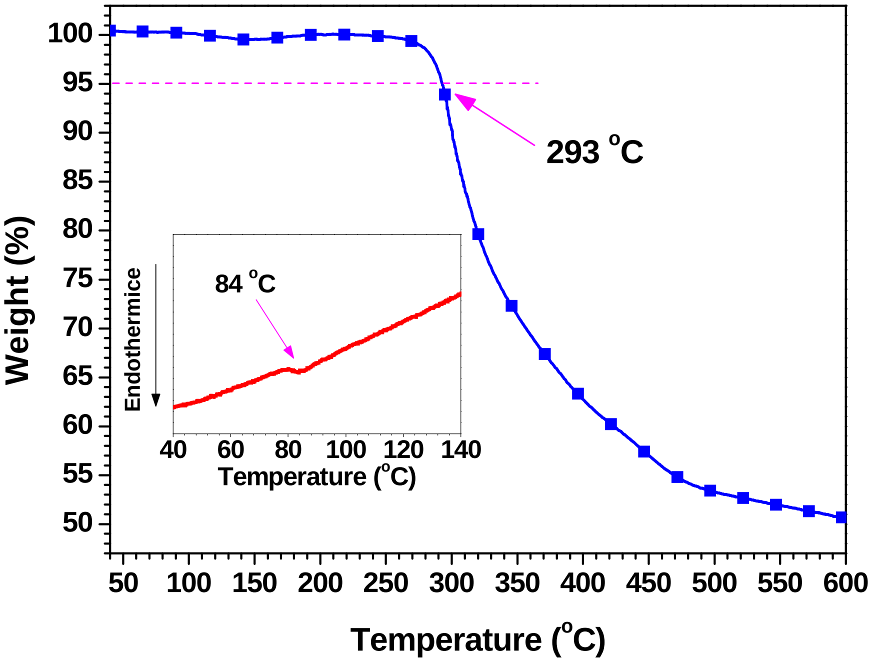


Fig. S19. TGA and DSC (insert) thermograms of **G4**, measured in nitrogen at a heating rate of 10 °C/min.

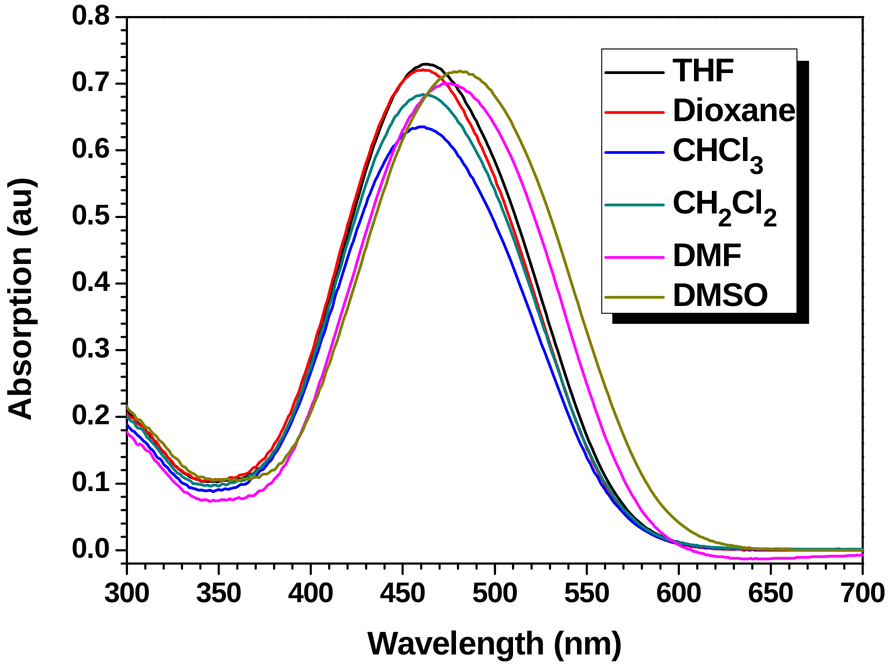


Fig. S20. UV-Vis spectra of G4 in different solutions. (0.02 mg/mL).

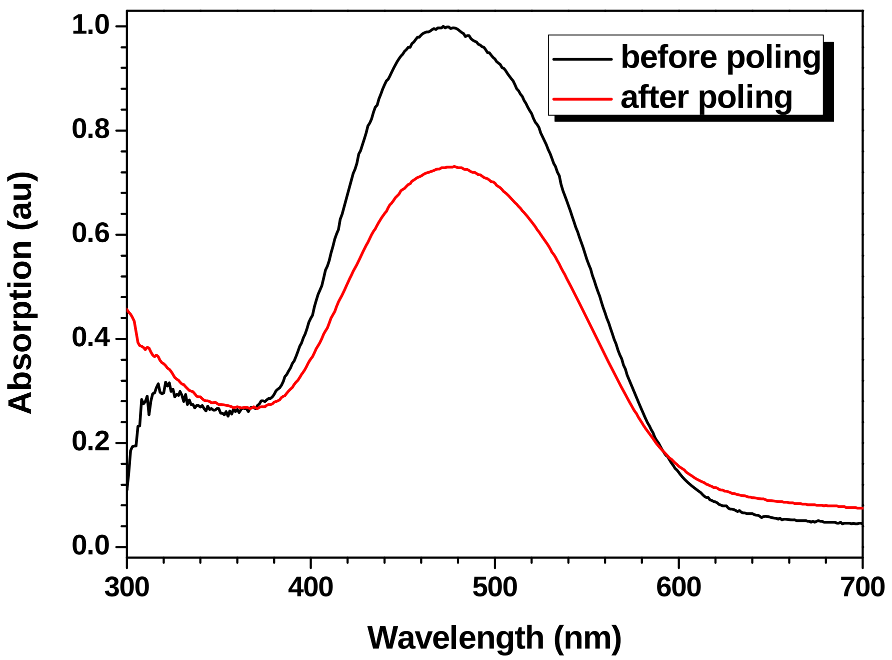


Fig. S21. Absorption spectra of the film of **G4** before and after poling.

From Fig. S21, we can calculate the order parameter (Φ), which could express the alignment of the chromophore moieties in poled thin films, of **G4**. By using the equation of $\Phi = 1\text{-}A_1/A_0$, (where A_1 and A_0 are the absorbance of the polymer film after and before poling), its Φ value was determined as 0.28, confirming that the alignment of the chromophore moieties in **G4** was good.

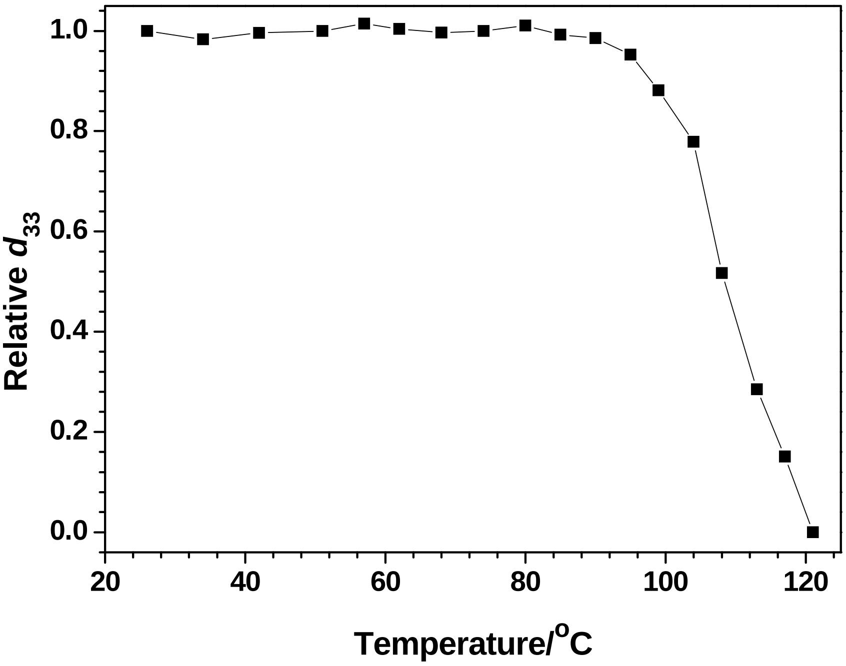


Fig. S22. Decay curves of the SHG coefficients of **G4** as a function of the temperature.