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PAPER

# Six-branched chromophores with isolation groups: synthesis and enhanced optical nonlinearity<sup>†</sup>

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Three new six-branched chromophores with different isolation groups were designed and synthesized by incorporating azo chromophores onto phenyl glycerol ester *via* an esterification reaction. The chemical structures were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR spectroscopy, mass spectrometry, element analysis and UV-visible absorption spectra. The six-branched dendritic chromophores can form thin films directly without adding any polymer matrix and show a quite high chromophore loading density. After electric poling, the nonlinear optical coefficients ( $d_{33}$ ) of the dendrimer films were determined to be around 113, 142 and 136 pm V<sup>-1</sup>, which are almost 3 times the maximum  $d_{33}$  value of the azo-chromophore doped polymer films. The further improvement in optical nonlinearity was successfully realized by mixing the six-branched chromophores containing different isolation groups.

# Introduction

Investigations of second-order nonlinear optical (NLO) materials are of current interest because of their wide applications in all-optical switching, fast optical communications, and electrooptic modulation.<sup>1-4</sup> Organic NLO materials offer a number of advantages over the traditional inorganic crystalline NLO materials, such as large nonlinear optical coefficients, low dielectric constants and excellent processing.5-18 For most developmental work on NLO polymers, the guest-host system is routinely employed because of wide selection and easy control of the material compositions through doping chromophores in the host matrix. However, the poled guest-host NLO materials usually suffer from phase separation problem. Although incorporating the chromophores via covalent bonds onto polymer chains can effectively alleviate this problem, it is difficult to precisely control the compositions and properties (e.g., molecular weight) of the NLO polymers from batch to batch. In addition, how to efficiently translate the large  $\beta$  values of the organic chromophores into high macroscopic NLO activities of polymers is still a major challenge. The strong dipole-dipole interactions among the chromophores in the guest-host polymer systems make the chromophores tend to align in an antiparallel fashion, diminishing the macroscopic NLO effect.<sup>19</sup> Therefore, the guest-host NLO polymers often display a saturated trend in

macroscopic optical nonlinearity with the increase of chromophore concentration.  $^{\rm 20}$ 

In the past few years, Dalton and Jen have pioneered the dendritic structure to decrease the dipole–dipole interactions and increase the poling efficiency by applying the site isolation principle,<sup>21–23</sup> in which the dipolar chromophores were incorporated into dendritic structures or functionalized with dendrons in order to create a pseudospherical structure isolating the dipolar unit from its surroundings. Compared to the small chromophore molecules, the dendrimers display better overall mechanical stability and film-forming properties, and offer unique characteristics such as globular shape, large internal free-volume, and an outer periphery capable of providing physical isolation of the contents within. It has been demonstrated that the dendritic architecture is a very promising molecular topology for the next generation of highly efficient NLO materials.<sup>24–27</sup>

Up to now, three-branched dendritic chromophores were mostly reported due to their convenient synthetic method. According to the molecular theoretical studies, multichromophores with more branches may exhibit larger chromophore loading density and higher NLO activity.28 Our recent work on the six-branched NLO multichromophore, prepared via incorporating FTC-type chromophores onto phenyl glycerol ester core, has shown excellent film-forming properties and dramatically enhanced NLO activity.29 Considering that the isolation groups could further benefit the optical nonlinearity of the six-branched multichromophore, thus we introduce the different isolation groups on to the arm of the six-branched multichromophore and try to study the relationship between the isolation group and properties. In this work, three six-branched chromophores with different isolation groups (Fig. 1) were synthesized and the films were fabricated directly using the sixbranched multichromophores without any addition of polymer

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Fig. 1 The chemical structures of six-branched chromophores S1, S2 and S3.

matrix. Then, the NLO properties of these films were discussed in detail.

# Experimental

# Materials and measurements

All chemical reagents were purchased from Aldrich and Alfa Aesar, and used without further purification. Dichloromethane  $(CH_2Cl_2)$  and tetrahydrofuran (THF) were refluxed and distilled before use, while *N*,*N*-dimethylformamide (DMF) was dried by rotary evaporation before reaction. Other solvents, of analytical-grade quality, were used as received.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were performed on a Bruker Avance DMX500 spectrometer using tetramethylsilane (TMS) as an internal standard. Fourier-transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm<sup>-1</sup> by a Thermo Scientific Nicolet iS10 in KBr disks. Mass spectrometry was carried out on a Bruker Daltonics esquire3000<sup>plus</sup> mass spectrometer. Element analysis was done on a Thermo Finnigan Flash EA 1112 element analyzer. UV-visible absorption spectra were studied with a Hitachi spectrometer U-4100. Thermogravimetric analysis (TGA) was investigated at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere on a TA Instruments SDT Q600. The thicknesses of films were determined by a Tencor alfa-step 200 surface profiler (Lencoi). The second harmonic generation coefficients ( $d_{33}$ ) of the poled films were studied according to the Maker fringe technique.

# Second harmonic generation (SHG) measurement

The second-order optical nonlinearity of hybrid films was determined by *in situ* SHG measurement. The laser source is a Q-switched Nd:YAG pulse laser with a 1064 nm P-polarized fundamental beam (500 mJ maximum energy, 3–5 ns pulse width, and 10 Hz repeating rate). The generated second harmonic signal

was detected by a photomultiplier monitored by a monochromator to eliminate all traces of the fundamental light and processed by a Stanford Research Systems (SRS) model SR-250 gated integrator.<sup>30-33</sup>

Synthesis of compound 3,3',3"-((ethane-1,1,1-triyltris(benzene-4,1-diyl))tris (oxy))tris(propane-1,2-diol) (1). Compound 4,4',4"-(ethane-1,1,1-triyl)triphenol (3.00 g, 10 mmol) was dissolved in ethanol (6 mL). A solution of NaOH (1.50 g, 37.5 mmol) in water (5 mL) was added and the ensuing mixture was refluxed for 30 min with stirring. A solution of 3-chloropropane-1,2-diol (3.96 g, 36 mmol) in ethanol (5 mL) was added and the resulting blend was stirred and heated at reflux for 4 h before cooled to room temperature. Then the resulting solution was poured into water (100 mL) and was extracted with ethyl acetate, the organic layers were dried over MgSO<sub>4</sub>. After the solvent was evaporated under reduced pressure, the residue was purified by silica column chromatography using a mixture of ethanol/ethyl acetate (v : v =1:5) as the eluent to give white solid 1. Yield: 81%. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ (ppm)): 2.03 (s, 3H, C*H*<sub>3</sub>), 3.43 (d, 6H, OCH<sub>2</sub>), 3.80 (m, 6H, OH), 3.95 (m, 3H, CH), 4.67(d, 3H, higher field branch of AB quartet, CH<sub>2</sub>OH), 4.95 (d, 3H, lower field branch of AB quartet, CH<sub>2</sub>OH), 6.82 (d, 6H, ArH), 6.91 (d, 6H, Ar*H*). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ (ppm)): 157.2, 141.8, 129.7, 114.1, 70.5, 69.9, 63.2, 50.6, 30.9. Elemental analysis calcd (%) for C<sub>29</sub>H<sub>36</sub>O<sub>9</sub>: C, 65.89; H, 6.86; Found: C, 65.52, H, 7.06. MS (ESI): exact mass calcd for  $C_{29}H_{36}O_9$  [M + H]<sup>+</sup>, 527.20. Found: 527.90.

Synthesis of 4-nitro-2-((perfluorophenyl)methoxy)aniline (2). 2-Amino-5-nitrophenol (1.54 g, 10 mmol) and 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene (1.51 mL, 10 mmol) were dissolved in absolute DMF, and potassium carbonate (1.66 g, 12 mmol) was added. After it was refluxed for 12 h with stirring at 80 °C, the resulting solution was diluted with  $CH_2Cl_2$  and washed with brine and deionized water. Then the organic phase was dried over MgSO<sub>4</sub> and concentrated by rotary evaporation, the residue was purified *via* flash chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as the eluent to yield yellow powder **2**. Yield: 57.2%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 4.49 (s, 2H, OCH<sub>2</sub>), 5.24 (s, 2H, NH<sub>2</sub>), 6.66–6.68 (d, 1H, ArH), 7.86–7.88 (d, 2H, ArH). MS (ESI): exact mass calcd for C<sub>13</sub>H<sub>7</sub>F<sub>5</sub>N<sub>2</sub>O<sub>3</sub> [M + Na]<sup>+</sup>, 357.20. Found: 357.00.

**Synthesis of 2-((2-ethylhexyl)oxy)-4-nitroaniline (3).** Compound **3** was synthesized using a similar procedure to that for compound **2** as orange oil. Yield: 63.34%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 0.87–0.93 (m, 6H, CH<sub>2</sub>CH<sub>3</sub>), 1.29–1.31 (m, 4H, CH(CH<sub>2</sub>)<sub>2</sub>), 1.38–1.49 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.74–1.76 (t, 1H, CH(CH<sub>2</sub>)<sub>2</sub>), 3.91–3.93 (m, 2H, OCH<sub>2</sub>), 4.74 (s, 2H, NH<sub>2</sub>), 6.62–6.64 (d, 1H, ArH), 7.61–7.62 (d, 1H, ArH), 7.75–7.77 (m, 1H, ArH). MS (ESI): exact mass calcd for C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> [M + H]<sup>+</sup>, 267.34. Found: 267.00. [M – H]<sup>-</sup>, 265.34. Found: 265.10.

Synthesis of (E)-2-(ethyl(4-((4-nitrophenyl)diazenyl)phenyl) amino)ethanol (E1). The chromophore E1 was prepared as reported previously.<sup>34</sup> Compound 4-nitroaniline (2.76 g, 20 mmol) was dissolved in a solution of 35% hydrochloric acid and the mixture was stirred in an ice bath at 0–5 °C. Subsequently, a water solution of sodium nitrite (1.38 g, 20 mmol) was added slowly and the resulting solution was stirred in the ice bath for 30 min, a solution of 2-(ethyl(phenyl)amino)ethanol (3.96 g, 24 mmol) in distilled ethanol was added dropwise and stirred for 1 h at 5 °C. After pH of the resulting solution was stirred for another 30 min. The red solution was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine and deionized water. The crude product was purified by recrystallization. E1 was obtained as red powder. Yield: 72.7%.

Synthesis of (E)-2-(ethyl(4-((4-nitro-2-((perfluorophenyl) methoxy)phenyl) diazenyl)phenyl)amino)ethanol (E2). The chromophore E2 was synthesized using a similar procedure to that for E1. Yield: 40.39%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 1.24–1.27 (t, 3H, CH<sub>3</sub>), 3.56–3.57 (d, 2H, CH<sub>2</sub>OH), 3.61–3.64 (t, 2H, CH<sub>2</sub>CH<sub>3</sub>), 3.89–3.90 (d, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 5.40 (s, 2H, OCH<sub>2</sub>), 6.79–6.81 (d, 2H, ArH), 7.73–7.75 (d, 1H, ArH), 7.84–7.86 (d, 2H, ArH), 7.97–8.00 (t, 1H, ArH), 8.04 (d, 1H, ArH). Elemental analysis calcd (%) for C<sub>12</sub>H<sub>19</sub>F<sub>5</sub>N<sub>4</sub>O<sub>2</sub>: C, 54.12; H, 3.75; N, 10.98. Found: C, 54.40; H, 3.80; N, 10.54. MS (ESI): exact mass calcd for C<sub>12</sub>H<sub>19</sub>F<sub>5</sub>N<sub>4</sub>O<sub>2</sub> [M + H]<sup>+</sup>, 511.41. Found: 511.30. [M – H]<sup>-</sup>, 509.41. Found: 509.30.

Synthesis of (E)-2-(ethyl(4-((2-((2-ethylhexyl)oxy)-4-nitrophenyl)diazenyl) phenyl)amino)ethanol (E3). The chromophore E3 was synthesized in a similar procedure to that for E1. Yield: 69.21%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 0.88–0.91 (t, 3H, CH<sub>3</sub>), 0.96–0.99 (t, 3H, CH<sub>3</sub>), 1.20–1.22 (d, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 1.22–1.27 (t, 4H, CH(CH<sub>2</sub>)<sub>2</sub>), 1.33–1.38 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.89 (s, 1H, CH(CH<sub>2</sub>)<sub>2</sub>), 3.55–3.59 (t, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 3.61–3.63 (t, 2H, CH<sub>2</sub>OH), 3.89–3.90 (d, 2H, OCH<sub>2</sub>), 4.09–4.10 (d, 2H, NCH<sub>2</sub>), 6.80–6.81 (d, 2H, ArH), 7.66–7.68 (d, 1H, ArH), 7.86–7.90 (m, 4H, ArH). Elemental analysis calcd (%) for C<sub>24</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>: C, 65.14; H, 7.74; N, 12.66. Found: C, 65.11; H, 7.72; N, 12.51. MS (ESI): exact mass calcd for C<sub>24</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>

 $[M + H]^+$ , 443.55. Found: 443.30.  $[M - H]^-$ , 441.55. Found: 441.50.

Synthesis of (E)-4-(2-(ethyl(4-((4-nitrophenyl)diazenyl) phenyl) amino)ethoxy)-4-oxobutanoic acid (4). A mixture of chromophore E1 (0.628 g, 2 mmol), succinic anhydride (0.24 g, 2.4 mmol), 4-dimethylaminopyridine (DMAP) (0.24 g, 2.4 mmol), pyridine (0.3 mL) and anhydrous CH<sub>2</sub>Cl<sub>2</sub> was stirred at room temperature overnight. The resulting solution was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine and deionized water. The organic layer was dried over MgSO<sub>4</sub>, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (v : v = 25 : 1) as the eluent and compound 4 was gained as red powder. Yield: 68.11%. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$  (ppm)): 1.15–1.18 (t, 3H, CH<sub>3</sub>), 2.36–2.46 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>COOH), 3.54–3.55 (d, 2H, NCH<sub>2</sub>), 3.70–3.72 (t, 2H, NCH2CH2), 4.23-4.25 (t, 2H, NCH2CH2), 6.92-6.93 (d, 2H, ArH), 7.84-7.86 (d, 2H, ArH), 7.93-7.95 (d, 2H, ArH), 8.36-8.37 (d, 2H, ArH).

Synthesis of (E)-4-(2-(ethyl(4-((4-nitro-2-((perfluorophenyl) methoxy)phenyl)diazenyl)phenyl)amino)ethoxy)-4-oxobutanoic acid (5). Compound 5 was synthesized using a similar procedure to that for 4 as red powder. Yield: 80.33%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 1.24–1.27 (t, 3H, CH<sub>3</sub>), 2.64–2.68 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>COOH), 3.53–3.54 (d, 2H, NCH<sub>2</sub>), 3.69 (s, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 4.32–4.33 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 5.41 (s, 2H, OCH<sub>2</sub>), 6.78–6.79 (d, 2H, ArH), 7.73–7.75 (d, 1H, ArH), 7.84–7.86 (d, 2H, ArH), 7.99 (s, 1H, ArH), 8.04–8.05 (d, 1H, ArH).

Synthesis of (E)-4-(2-(ethyl(4-((2-((2-ethylhexyl)oxy)-4-nitrophenyl)diazenyl)phenyl)amino)ethoxy)-4-oxobutanoic acid (6). Compound 6 was synthesized using a similar procedure to that for 4 as red powder. Yield: 60.92%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 0.88–0.91 (t, 3H, CH<sub>3</sub>), 0.96–0.99 (t, 3H, CH<sub>3</sub>), 1.23– 1.26 (t, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 1.32–1.37 (m, 8H, (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>3</sub>), 1.88–1.90 (t, 1H, CH(CH<sub>2</sub>)<sub>3</sub>), 2.62–2.67 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>COOH), 3.49–3.54 (m, 2H, NCH<sub>2</sub>), 3.66–3.69 (t, 2H, OCH<sub>2</sub>), 4.09–4.10 (d, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 4.31–4.34 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 6.77–6.79 (d, 2H, ArH), 7.65–7.67 (d, 1H, ArH), 7.85–7.89 (m, 4H, ArH).

#### Synthesis of six-branched chromophore S1

Compound 1 (0.52 g, 1 mmol), 4 (3.31 g, 8 mmol), EDC·HCl (2.09 g, 11 mmol) and DMAP (0.24 g, 2 mmol) were dissolved in mixed solvent of CH<sub>2</sub>Cl<sub>2</sub> and THF (v : v = 3 : 1). The mixture was stirred at room temperature for 72 h. The resulting solution was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine and water and the organic phase was dried over MgSO<sub>4</sub>. After the solvent was evaporated under reduced pressure, the residue was purified by silica column chromatography on silica gel using a mixture of CH<sub>2</sub>Cl<sub>2</sub>/THF (v : v = 40 : 1) as the eluent to yield the red powder S1. Yield: 46.21%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 1.21–1.25 (m, 18H, CH<sub>2</sub>CH<sub>3</sub>), 2.01 (s, 3H, CCH<sub>3</sub>), 2.61–2.63 (m, 24H, (OCCH<sub>2</sub>)<sub>2</sub>), 3.48–3.65 (m, 24H, NCH<sub>2</sub>), 4.04–4.05 (d, 6H, CHCH<sub>2</sub>O), 4.28–4.44 (m, 18H, OCH<sub>2</sub>, CHCH<sub>2</sub>O), 5.35–5.37 (t, 3H, CHCH<sub>2</sub>), 6.73–6.93(m, 24H, ArH), 7.86–7.90 (m, 24H,

Ar*H*), 8.28–8.29 (d, 12H, Ar*H*). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 172.3, 172.2, 172.0, 171.8, 156.9, 156.4, 151.4, 147.6, 144.0, 142.5, 129.8, 126.4, 124.8, 122.8, 113.9, 111.6, 70.2, 66.1, 62.9, 61.8, 48.9, 45.8, 30.5, 29.1, 29.0, 28.9, 12.5. Elemental analysis calcd (%) for C<sub>149</sub>H<sub>156</sub>N<sub>24</sub>O<sub>39</sub>: C, 61.56; H, 5.41; N, 11.56. Found: C, 61.31; H, 5.58; N, 11.38. MALDI-TOF MS: exact mass calcd for C<sub>149</sub>H<sub>156</sub>N<sub>24</sub>O<sub>39</sub> [M], 2906.97. Found: 2905.00.

#### Synthesis of six-branched chromophore S2

A similar procedure to that for S1 was used to afford the sixbranched chromophore S2 as red powder. Yield: 48.72%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ (ppm)): 1.21–1.24 (m, 18H, CH<sub>2</sub>CH<sub>3</sub>), 2.01 (s, 3H, CCH<sub>3</sub>), 2.60–2.64 (m, 24H, (OCCH<sub>2</sub>)<sub>2</sub>), 3.49-3.50 (d, 12H, NCH<sub>2</sub>), 3.64-3.66 (m, 12H, NCH<sub>2</sub>CH<sub>2</sub>), 4.04-4.05 (d, 6H, CHCH<sub>2</sub>O), 4.27–4.29 (m, 18H, OCH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>O), 5.38 (d, 15H, CHCH<sub>2</sub>, CH<sub>2</sub>ArF), 6.72–6.76 (t, 18H, ArH), 6.91– 6.93 (d, 6H, ArH), 7.69-7.71 (m, 6H, ArH), 7.81-7.83 (m, 12H, ArH), 7.94–7.96 (m, 6H, ArH), 8.01–8.02 (d, 6H, ArH). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>, δ (ppm)): 172.3, 172.2, 172.0, 171.8, 156.5, 154.5, 151.5, 148.6, 148.1, 147.0, 145.0, 144.6, 142.5, 129.8, 126.6, 118.8, 118.1, 113.9, 113.2, 111.6, 109.9, 70.3, 66.1, 62.9, 61.8, 61.2, 48.9, 45.9, 29.1, 29.0, 28.9, 28.7, 12.5. Elemental analysis calcd (%) for C<sub>191</sub>H<sub>162</sub>F<sub>30</sub>N<sub>24</sub>O<sub>45</sub>: C, 56.18; H, 4.00; N, 8.23. Found: C, 55.87; H, 4.04; N, 7.82. MALDI-TOF MS: exact mass calcd for C<sub>191</sub>H<sub>162</sub>F<sub>30</sub>N<sub>24</sub>O<sub>45</sub>[M], 4083.42. Found: 4082.80.

#### Synthesis of six-branched chromophore S3

The red powder chromophore S3 was synthesized using a similar procedure to that for S1. Yield: 45.34%. <sup>1</sup>H NMR (500 MHz,  $CDCl_3, \delta$  (ppm)): 0.87–0.90 (t, 18H,  $CH_2CH_3$ ), 0.95–0.98 (t, 18H, CH<sub>2</sub>CH<sub>3</sub>), 1.21-1.24 (m, 18H, CH<sub>2</sub>CH<sub>3</sub>), 1.31-1.59 (m, 48H, CH<sub>2</sub>CH<sub>3</sub>, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.87–1.88 (d, 6H, CH(CH<sub>2</sub>)<sub>3</sub>), 2.03 (s, 3H, CCH<sub>3</sub>), 2.62–2.66 (m, 24H, (OCCH<sub>2</sub>)<sub>2</sub>), 3.48–3.52 (m, 12H, NCH<sub>2</sub>), 3.64-3.66 (t, 12H, OCH<sub>2</sub>), 4.05-4.09 (m, 18H, CHCH<sub>2</sub>O, NCH<sub>2</sub>CH<sub>2</sub>), 4.28–4.30 (t, 18H, OCH<sub>2</sub>, CHCH<sub>2</sub>O), 5.37 (s, 3H, CHCH<sub>2</sub>), 6.75–6.77(m, 18H, ArH), 6.93–6.95 (d, 6H, ArH), 7.64–7.66 (m, 6H, ArH), 7.83–7.89 (m, 24H, ArH). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>, δ (ppm)): 172.3, 172.2, 172.0, 171.8, 156.4, 155.8, 151.0, 148.5, 147.3, 144.8, 142.5, 129.8, 126.4, 117.4, 116.4, 113.9, 111.6, 109.3, 72.9, 70.2, 66.1, 62.9, 61.9, 48.9, 45.9, 39.6, 30.8, 29.3, 29.1, 29.0, 28.9, 24.3, 23.2, 14.3, 12.5, 11.4. Elemental analysis calcd (%) for C<sub>197</sub>H<sub>252</sub>N<sub>24</sub>O<sub>45</sub>: C, 64.36; H, 6.91; N, 9.14. Found: C, 63.96; H, 6.93; N, 9.04. MALDI-TOF MS: exact mass calcd for C<sub>197</sub>H<sub>252</sub>N<sub>24</sub>O<sub>45</sub> [M], 3676.24. Found: 3675.40.

#### Thin films fabrication

The six-branched chromophore S1, S2 and S3 were dissolved in cyclopentanone (8% of total solid weight). After filtered by 0.22  $\mu$ m Teflon membrane filters, the resulting solutions were spin-coated on the indium-tin oxide (ITO) glass substrates to fabricate films. The films were dried in a vacuum oven at 60 °C for 12 h to remove the residual solvent. The azo chromophore E1, E2 and E3 doped polymer films using the poly(4-vinylphenol) (PVPh) as matrix were also prepared through a similar procedure as a reference.

#### **Results and discussion**

#### Synthesis and characterization

The detailed synthetic routes to the azo chromophores **E1–3** and six-branched chromophores **S1–3** are shown in Scheme 1. Three kinds of azo chromophores **E1–3** with different functional groups on the acceptor were prepared *via* a direct diazo coupling reaction between 2-(ethyl(phenyl)amino)ethanol and the different nitroaniline derivatives. The phenyl glycerol ester core 1 was produced by the Williamson ester reaction between Frechettype tri-phenol core 4,4',4''-(ethane-1,1,1-triyl)triphenol and 3-chloropropane-1,2-diols. The esterification reaction between azo chromophores **E1–3** and succinic anhydride yielded the compounds **4–6** with carboxylic acid. Then the six-branched chromophores **S1–3** were synthesized *via* esterification between compounds **4–6** and tether core **1**.

The structures of chromophores **E1–3** and six-branched chromophores **S1–3** were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR spectroscopy, elemental analysis and mass spectrometry. The details of the characterizations are described in the Experimental Section. In the <sup>1</sup>H NMR spectra of the chromophores, the chemical shifts were consistent with the proposed molecular structure as demonstrated in Scheme 1. The FTIR spectra of chromophore **E2**, compound **6** and six-branched chromophore **S2** were illustrated in Fig. 2 as an example. For chromophore **E2**, the absorption of the hydroxy group was observed around 3500– 3200 cm<sup>-1</sup>. In the spectra of compound **6**, the peak at 1734 cm<sup>-1</sup> and 1708 cm<sup>-1</sup> attributed to the carboxyl group emerged obviously. In the spectra of **S2**, the band at 3500–3200 cm<sup>-1</sup> vanished, while the peak at 1734 cm<sup>-1</sup> remained, indicating that the sixbranched chromophore has been successfully synthesized.

Thermal properties of azo chromophores E1-3 and sixbranched chromophores S1-3 were analyzed by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The decomposition temperatures  $(T_d)$  of chromophore E1-3 are determined to be 286 °C, 268 °C and 273 °C, respectively. As shown in Fig. 3, all the six-branched chromophores show the higher decomposition temperatures than that of the corresponding azo chromophores. The six-branched chromophore S1 displays the highest decomposition temperature ( $T_d$ ) of 317 °C, while S2 exhibits the lowest decomposition temperature of 283 °C. The results indicate that molecular thermal stability could be efficiently improved when chromophores were combined into phenyl glycerol ester core to yield multichromophores, which increased the rigidity of the chromophores. The high thermal stability of the six-branched chromophores make them could be widely applied in photonic device fabrications.

#### Linear and nonlinear optical properties

The linear optical properties of the chromophores were observed from UV-visible absorption spectra. As shown in Fig. 4, all the chromophores exhibited strong absorption bands in the visible region. The maximum absorption wavelengths ( $\lambda_{max}$ ) of chromophores **E1–3** and **S1–3** were at about 475–495 nm and 470–485 nm in CHCl<sub>3</sub>, respectively. Compared with **S1**, the small red-shift of **S2** and **S3** (about 9–12 and 2 nm) was observed due to the introduction of isolation substituents. The interesting phenomena were primarily associated with the isolation groups



Scheme 1 Synthesis of chromophores E1–3 and six-branched chromophores S1–3.



Fig. 2 FTIR spectra of chromophore E2, compound 6 and six-branched chromophore S2.

being anchored on the acceptor-end of the chromophores which caused a decrease of electron-release ability. Meanwhile, sixbranched chromophores S1–3 blue shift about 10–20 nm in their intrinsic absorptions compared to E1–3. This may be ascribed to the interactions of the sub-chromophores in multichromophores and the generation of new group (–COO–) in six-branched chromophores S1–3. The same phenomena were also observed in THF and DMF.

To investigate the NLO properties of the six-branched chromophores, the thin films (Film-S1, Film-S2, Film-S3) were prepared, and the chromophore E1, E2 and E3 doped polymer films were also fabricated by doping the chromophores into



Fig. 3 TGA traces for chromophores E1, E2, E3, S1, S2 and S3.

polymer matrix PVPh, and the largest loading densities were up to 40 wt%. The second-order NLO properties of the thin films were studied by SHG measurement and the poling processes were carried out with a 5.0 kV dc voltage. Then the applied voltage was removed after the films were cooled to room temperature. Calculation of the SHG coefficients ( $d_{33}$ ) for the films was based on the following equation:<sup>33</sup>

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s}{I_q}} \frac{L_{qc}}{L_s} F \tag{1}$$

where  $d_{33,s}$  is the SHG coefficient of the poled films and  $d_{11,q}$  is  $d_{11}$  of the quartz crystals, which is equal to 0.5 pm V<sup>-1</sup>.  $I_s$  and  $I_q$  are the SHG intensities of the film and quartz, respectively.  $L_{qc}$  is



Fig. 4 UV-visible absorption spectra of chormophores E1, E2, E3, S1, S2 and S3 in CHCl<sub>3</sub>.

the coherent length of quartz crystals, which is equal to 20.6  $\mu$ m, and  $L_s$  is the thickness of the poled films. *F* is the correction factor of the apparatus and equals 1.2 when  $I_c \gg I_s$ .

As shown in Fig. 5, the  $d_{33}$  value of the chromophore E1 doped polymer film increased with the increase of chromophore loading density and displayed a maximum of 56 pm  $V^{-1}$  at 30 wt%, then the  $d_{33}$  value decreased at around 40 wt% due to the strong interchromophore electrostatic interactions. The similar behaviour was observed in the chromophore E2 and E3 doped polymer films. It was reported in the literature that the chromophore loading densities of guest-host doped NLO polymers typically have to be kept below 25 wt%, which was guite consistent with our results. The  $d_{33}$  values of the E1, E2 and E3 doped films at the chromophore concentration of 40 wt% were calculated to be 49, 45 and 42 pm V<sup>-1</sup>, respectively. The active chromophore loading density in the films containing six-branched chromophores (Film-S1, Film-S2, Film-S3) were about 65, 75 and 72 wt%, respectively, which was much higher than the usual loading level of guest-host doped polymer NLO materials as shown in the chromophore E1, E2 and E3 doped polymer films. In contrast to the chromophore doped polymer films, the films containing six-branched chromophores exhibited the larger  $d_{33}$  values. As shown in Table 1, the  $d_{33}$  value of Film-S1 was determined to be



Fig. 5  $d_{33}$  values of polymer films as a function of molecule loading densities of chromophore E1, E2 and E3.

**Table 1** The wavelength of maximum absorption  $(\lambda_{max})$  in chloroform and second harmonic coefficients of the films

Films	$\lambda_{\max}$ (nm)	$d_{33} ({ m pm}  { m V}^{-1})$
E1-doped film (40 wt%)	478	49
E2-doped film (40 wt%)	491	45
E3-doped film (40 wt%)	482	42
Film-S1	472	113
Film-S2	484	142
Film-S3	474	136
Film-M1	476	153
Film-M2	468	133
Film-M3	475	168

113 pm V<sup>-1</sup>, which is almost 3 times the maximum  $d_{33}$  value of the E1 doped polymer film. The above results demonstrated that the six-branched structure can efficiently reduce the interchromophore electrostatic interactions, thus improving the active chromophore loading density and enhancing the macroscopic optical nonlinearities.<sup>29</sup>

Interestingly, the **Film-S2** and **Film-S3** showed the higher optical nonlinearity than that of the **Film-S1**. The  $d_{33}$  values of **Film-S2** and **Film-S3** were calculated to be 142 and 136 pm V<sup>-1</sup>, respectively. This behaviour may be rationalized by considering the introduction of isolation groups. In six-branched chromophores **S2** and **S3**, the isolation groups could further isolated the chromophore branch from each other and then restrain the interchromophore electrostatic interactions. It needs to be mentioned that **Film-S3** showed lower  $d_{33}$  values than **Film-S2** due to the flexible substituents being too flexible to work efficiently as the rigid groups. Therefore, the introduction of the isolation groups in six-branched chromophores can further improve the macroscopic NLO properties; furthermore, the rigid isolation group exhibited a better effect on enhancing the  $d_{33}$  values than the flexible group.

To further explored the influence on NLO properties of the isolation groups in the six-branched chromophore, we also fabricated mixed thin films **Film M1**, **Film-M2** and **Film-M3** by mixing the six-branched chromophores at the equally quantity. The  $d_{33}$  values of the mixed films were determined to be 153 pm V<sup>-1</sup>, 133 pm V<sup>-1</sup> and 168 pm V<sup>-1</sup>, respectively, suggesting that the  $d_{33}$  values could be further enhanced by mix the six-branched chromophores with different isolation groups. This should be attributed to the synergetic effect of the different isolation groups, thus minimizing the strong intermolecular dipole–dipole interactions. Thus, the successful examples might open up a new avenue to achieve further good NLO polymers by mixing the NLO dendrimers with different isolation groups.

The thermal stability of optical nonlinearity was also investigated by a depoling experiment, in which the SHG signal was monitored as the poled film was heated at a rate of 10 °C min<sup>-1</sup> from 45 to 100 °C. As shown in Fig. 6, the  $d_{33}$  value of Film-S1 and Film-S2 maintained half of the original signals around 70 °C, indicating that the thermal stability of optical nonlinearity were rarely influenced by the isolation groups. A further study will aim to introduce a rigid dendritic core, which may produce the excellent dendrimers with high thermal stability of nonlinearity.



**Fig. 6** Decay of the normalized  $d_{33}$  values as a function of temperature for **Film-S1** and **Film-S2**.

#### Conclusions

In summary, three six-branched chromophores S1-3 were designed and synthesized via incorporating azo chromophores onto a phenyl glycerol ester core. The molecular structures were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR spectroscopy, elemental analysis and mass spectrometry. Compared with the azo chromophores E1, E2 and E3, the six-branched chromophores S1, S2 and S3 showed higher thermal decomposition temperatures up to about 300 °C. The six-branched chromophores can form thin films directly without any added polymer matrix and show a quite high chromophore loading density. The poled films containing six-branched chromophores display 2-3 times enhancement in nonlinear optical coefficient in comparison with the azo chromophores-doped films, in which, the rigid isolation group exhibits better enhanced effect than the flexible group. The further improving in optical nonlinearity are successfully realized by mix the six-branched chromophores containing different isolation groups, which might open up a new avenue to achieve further good NLO polymers.

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