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Preparation of polymer films containing multi-branched chromophores for enhanced nonlinear optical activity



PIGMENTS

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ABSTRACT

Two new multi-branched chromophores were synthesized via esterification from monochromophores to achieve ideal macroscopic nonlinear optical activities. Molecular chemical structures of chromophores were confirmed by ¹H NMR, FT-IR spectroscopy, elemental analysis, mass spectrometry and UV–visible absorption spectra. Monochromophore **N1** and bichromophore **DN** were doped into poly (4-vinylphenol) to fabricate guest-host polymer films **Film-N1** and **Film-DN** with high molecular loading density (up to 30 wt%). And the maximum second harmonic generation coefficients (d_{33}) of polymer films **Film-N1** and **Film-DN** reached to 25 pm V⁻¹ and 39 pm V⁻¹, respectively. In contrast, six-branched dendritic chromophore **SN** was utilized directly to prepare thin film **Film-SN** without any polymer matrix due to its large molecular weight (about 3183 Da) and the d_{33} value of **Film-SN** was up to 208 pm V⁻¹. Compared with **Film-N1**, films containing multi-branched chromophores **Film-DN** and **Film-SN** exhibited about 1.6-fold and 8.3-fold enhancement in the d_{33} value indicating the multi-branched chromophore could significantly promote the macroscopic optical nonlinearity through the site-isolation effect.

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1. Introduction

Nonlinear optical (NLO) materials are widely investigated by researchers after the mid 1980s [1–5]. Compared with inorganic materials, organic ones are paid more attention for their large nonlinear optical coefficients, low dielectric constants, and excellent of processing [6,7]. The organic second-order nonlinear optical materials could be used as optical switching, optical information processing, and electro-optic modulation based on these advantages [8–10].

A number of organic chromophores with high hyperpolarizabilities ((β)) values have been synthesized up to now [11–14]. However, a problem emerged in achieving ideal nonlinearity is converting the large β values of organic chromophores to the macroscopic nonlinearity of NLO materials in effect. The electro-optic (EO) coefficient often decreases with the increase of chromophore number density due to the strong inter-chromophore electrostatic interactions. Generally, the strong dipole-dipole interactions between readily hyperpolarisable chromophores

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induced head-to-tail interactions, and the noncentrosymmetric arrangement is hard to be gained in NLO material efficiently. Therefore, the macroscopic nonlinear optical activities do not come up to the expectation [15–17].

Multi-chromophoric dendritic chromophores, such as bichromophore, trichromophore bundles, three-armed multi-chromophoric dendrimers, and star-shaped dipolar chromophores, have been reported to resolve the issue these years [18–24]. The dendritic structures could reduce the inter-chromophore electrostatic interactions through the site-isolation effect and obtain large EO coefficients and favorable stability in multiple-dendron-modified NLO chromophores [25–28]. Multichromophores are prepared by monochromophores with tether groups or tether cores, and they show larger EO coefficients and more stable than monochromophores [18,21,22,26,28–34].

In this paper we report a handy and efficient method for the preparation of multi-branched chromophores which show enhanced nonlinear activities due to their tree-like morphology. The bichromophore **DN** and six-branched chromophore **SN** are synthesized from monochromophore **N1** via esterification [18,35]. (Fig. 1). To gain macroscopic optical nonlinearity, hyperpolarisable bichromophore **DN** is doped as a gust in a polymeric host matrix poly (vinyl phenol) (PVPh) and six-branched chromophores **SN** are prepared as films directly, following by poled via an electrical field



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[25,36,37]. The linear properties of chromophores and nonlinear optical properties of films are discussed in detail.

2. Experimental

2.1. Materials and measurements

All chemical reagents were gained from Aldrich and Alfa Aesar, and used without further purification. Dichloromethane (CH₂Cl₂) 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.

¹H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer (500 MHZ) using tetramethylsilane (TMS) as an internal standard. Fourier-transform infrared (FT-IR) spectra were obtained via Thermo Scientific Nicolet iS10. A Bruker Daltonics esquire 3000^{plus} mass spectrometer and a Bruker Dalton Microflex MALDI-TOF mass spectrometer were used for mass spectrometry and MALDI-TOF analysis, respectively. Element analysis was carried out on a Thermo Finnigan Flash EA 1112 element analyzer. Differential scanning calorimetry (DSC) and Thermalgravimetric analysis (TGA) were studied on a Netzsch Instruments 200 F3 and a TA Instruments SDT Q600 under nitrogen atmosphere. UV-visible absorption spectra were performed by a Hitachi spectrometer U-4100. The second harmonic generation coefficients (d_{33}) of the films were investigated according to the Maker fringe technique [38,39]. The films were measured by SHG measurement with a Q-switched Nd:YAG laser at 1064 nm, which a Y-cut quartz crystal $(d_{11} = 0.5 \text{ pm V}^{-1})$ was used as reference [40–43].

2.2. Synthesis of N1

Chromophore **N1** was synthesized via a direct Knoevenagel condensation on the basis of the literature [18]. Yield: 74%. ¹H NMR (500 MHz, DMSO- d_6 , δ ppm): 1.75 (s, 6H, C(CH₃)₂), 3.12 (s, 3H, N(CH₃)), 3.58–3.59 (d, 4H, NCH₂CH₂), 4.78 (s, 1H, OH), 6.85–6.87 (d, 3H, ArH, CH=CH), 7.75–7.77 (d, 2H, ArH), 7.90–7.94 (d, 1H, CH=CH). FT-IR (KBr, cm⁻¹): 3473 (s), 2874 (w), 2227 (s), 1525 (s), 1463 (m), 1373 (s), 1278 (s), 1161 (s), 1108 (w), 1048 (s), 959 (m), 871 (w), 832 (m), 750 (m), 658 (m), 560 (m), 486 (m). Elemental analysis calcd (%) for C₂₁H₂₀N₄O₂: C, 69.98; H, 5.59; N, 15.55. Found: C, 69.94; H, 5.60; N, 15.28.

2.3. Synthesis of compound 1

Compound **1** was gained according to the literature [44]. Yield: 90%. ¹H NMR (500 MHz, CDCl₃, δ ppm): 0.23 (s, 6H, Si(CH₃)₂), 0.38 (t, 12H, Si(CH₃)₂), 0.99 (s, 9H, C(CH₃)₃), 1.04 (s, 18H, C(CH₃)₃), 7.71 (d, 2H, ArH), 8.28 (s, 1H, ArH).

2.4. Synthesis of compound 2

Compound **2** was synthesized on the basis of the literature [44]. Yield: 72%. ¹H NMR (500 MHz, DMSO- d_6 , δ ppm): 0.27 (s, 6H, Si(CH₃)₂), 1.01 (s, 9H, C(CH₃)₃), 7.61 (d, 2H, ArH), 8.15 (t, 1H, ArH), 13.37 (s, 2H, COOH). Elemental analysis calcd (%) for C₁₄H₂₀O₅Si: C, 56.73; H, 6.80. Found: C, 56.72; H, 6.89.

2.5. Synthesis of bichromophore DN

Compound N1 (1.08 g, 3 mmol) and 2 (0.45 g, 1.5 mmol) were dissolved in CH₂Cl₂ (180 mL). EDC•HCl (0.68 g, 3.6 mmol) and 4dimethylaminopyridine (DMAP; 0.42 g, 3.6 mmol) were added and stirring was continued at room temperature for 24 h. The resulting solution was diluted with CH₂Cl₂ (200 mL) and washed with brine and water. After the organic phase was dried over Na₂SO₄ and concentrated by rotary evaporation, the residue was purified via flash chromatography on silica gel using a mixture of CH_2Cl_2 /ethyl acetate (v:v = 20:1) as the eluent to yield solid products. Yield: 45%. ¹H NMR (500 MHz, CDCl₃, δ ppm): 0.20 (s, 6H, Si(CH₃)₂), 1.0 (s, 9H, C(CH₃)₃), 1.75 (s, 12H, C(CH₃)₂), 3.20 (s, 6H, N(CH₃)), 3.88-3.90 (t, 4H, NCH₂), 4.55-4.57 (t, 4H, NCH₂CH₂), 6.75-6.78 (d, 2H, CH=CH), 6.82-6.84 (d, 4H, ArH), 7.55-7.60 (m, 8H, ArH, CH=CH), 8.14 (s, 1H, ArH). FT-IR (KBr, cm⁻¹): 2934 (w), 2227 (s), 1730 (s), 1521 (m), 1445 (w), 1380 (s), 1276 (m), 1167 (m), 1113 (m), 997 (w), 966 (w), 819 (w). Elemental analysis calcd (%) for C₅₆H₅₆N₈O₇Si: C, 68.55; H, 5.75; N, 11.42. Found: C, 68.32; H, 5.98; N, 11.40. MS (ESI): exact mass calcd for C₅₆H₅₆N₈O₇Si [M+H]⁺, 981.40. Found: 981.5.

2.6. Synthesis of compound DH

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 MgSO₄. 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 **DH**. Yield: 81%. ¹H NMR (500 MHz, DMSO-*d*₆, d (ppm)): 2.03 (s, 3H, C**H**₃), 3.43 (d, 6H, OCH₂), 3.80 (m, 6H, OH), 3.95 (m, 3H, CH), 4.67 (d, 3H, higher field branch of AB quartet, CH₂OH), 4.95 (d, 3H, lower field branch of AB quartet, CH₂OH), 6.82 (d, 6H, ArH), 6.91 (d, 6H, ArH). ¹³C NMR (125 MHz, DMSO-d₆, d (ppm)): 157.2, 141.8, 129.7, 114.1, 70.5, 69.9, 63.2, 50.6, 30.9. Elemental analysis calcd (%) for C₂₉H₃₆O₉: C, 65.89; H, 6.86; Found: C, 65.52, H, 7.06. MS (ESI): exact mass calcd for C₂₉H₃₆O₉ [M+H]⁺, 527.20. Found: 527.90.

2.7. Synthesis of compound 3

The chromophore **N1** (0.36 g, 1 mmol), succinic anhydride (0.15 g, 1.5 mmol), 4-dimethylaminopyridine (DMAP) (0.13 g, 1 mmol) and pyridine (2 mL) were dissolved in anhydrous CH₂Cl₂ and stirring was continued at room temperature overnight. Then the resulting solution was washed with brine and deionized water. The organic layer was extracted by CH₂Cl₂ and dried over MgSO₄. After the solvent was evaporated under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture of CH₂Cl₂/ethyl acetate (v: v = 10: 1) as the eluent and compound **3** was gained. Yield: 74%. ¹H NMR (500 MHz, DMSO-*d*₆, δ ppm): 1.76 (s, 6H, C(CH₃)₂), 2.34 (d, 2H, COCH₂), 2.41 (m, 2H, CH₂COOH), 3.10 (m, 3H, NCH₃), 3.77 (d, 2H, NCH₂), 4.23 (d, 2H, CH₂O), 6.87–6.91 (d, 3H, ArH, CH=CH), 7.78 (d, 2H, ArH), 7.91 (d, 1H, CH=CH, *J* = 15.8 Hz). MS (ESI): exact mass calcd for C₂₅H₂₄N₄O₅ [M–H]⁻: 459.1.

2.8. Synthesis of six-branched chromophore SN

Compound 3 (0.49 g, 1.05 mmol) and DH (0.079 g, 0.15 mmol) were dissolved in mixed solution THF/CH₂Cl₂ (25 mL/75 mL). The mixture was stirred at room temperature for 48 h after the addition of EDC•HCl (0.30 g, 1.58 mmol) and 4-dimethylaminopyridine (DMAP; 0.037 g, 0.3 mmol). The reacting solution was evaporated and the residue was dissolved in CH₂Cl₂ (150 mL). Then the organic phase was washed with brine and water. After the resulting solution was dried over MgSO₄ and concentrated, the products were obtained via flash chromatography on silica gel using a mixture of CH_2Cl_2/THF (v:v = 25:1) as the eluent. Yield: 82%. ¹H NMR (500 MHz, CDCl₃, δ ppm): 1.74 (s, 36H, C(CH₃)₂), 2.04 (d, 3H, CCH₃), 2.59 (m, 24H, COCH₂), 3.13 (s, 18H, NCH₃), 3.74 (t, 12H, NCH₂), 4.05 (d, 6H, CCH₂O), 4.30 (s, 15H, OCH₂; higher field branch of AB quartet, ArOCH₂), 4.41 (d, 3H, lower field branch of AB quartet, Ar- $O-CH_2$), 5.37 (s, 3H, CHCH₂), 6.76 (m, 24H, ArH; CH=CH, I = 16 Hz), 6.93 (d, 6H, ArH), 7.55 (d, 12H, ArH), 7.61 (d, 6H, CH=CH, J = 16 Hz). ¹³C NMR (125 MHz, CDCl₃, δ ppm): 176.5, 174.7, 172.3, 156.5, 153.2, 148.6, 142.5, 132.5, 129.9, 122.6, 114.0, 112.9, 112.7, 112.2, 111.7, 109.5, 97.3, 94.9, 70.3, 66.2, 62.9, 61.7, 54.9, 50.9, 39.2, 30.6, 29.1, 28.9, 26.9. FT-IR (KBr, cm⁻¹): 2223 (s), 1734 (s), 1521 (m), 1377 (s), 1279 (m), 1167 (m), 962 (w), 816 (w), 730 (w), 653 (w). Elemental analysis calcd (%) for C₁₇₉H₁₆₈N₂₄O₃₃ (%): C, 67.54; H, 5.32; N, 10.56. Found: C, 67.41; H, 5.92; N, 9.78. MS (ESI): exact mass calcd for C179H168N24O33 [M]:3183.39. Found: 3182.93.

2.9. Preparation of films

Monochromophore N1 and bichromophore DN were doped into

the polymeric host matrix PVPh, and then the solid mixtures were dissolved into cyclopentanone (8% of total solid weight). Meanwhile, six-branched chromophore **SN** was dissolved into cyclopentanone directly at same ratio without polymeric host matrix for large molecular weight of **SN**. The mixed solutions were stirred for 1 h and filtered by 0.22 μ m Teflon membrane filters. After that, the resulting solutions were spin-coated on the indium-tin oxide (ITO) glass substrates to fabricate **Film-N1**, **Film-DN** and **Film-SN**.

3. Results and discussion

3.1. Synthesis and characterization

For the strong inter-chromophore dipole-dipole interactions, high hyperpolarisability (β) is hard to convert to large macroscopic optical nonlinearity. To reduce the inter-chromophore dipole-dipole electrostatic interactions through the site-isolation effect from dendritic structures, bichromophore **DN** and six-branched chromophore **SN** are synthesized from monochromophore **DN** and six-branched chromophore **SN** are shown in Scheme 1.

The Knoevenagel reaction between 4-((2-hydroxyethyl) (methyl)amino)benzaldehyde and TCF acceptor 2-(3-cyano-4,5,5trimethylfuran-2 (5H)-ylidene)malononitrile afforded chromophore N1. Besides, 5-hydroxyisophthalic acid and tert-butylchlorodimethylsilane produced compound 1, then it was reacted with AcOH to create compound **2** with a functional terminal group. Under EDC•HCl coupling conditions, bichromophore DN was prepared by chromophore N1 attaching to the compound 2 via esterification reaction in which 4-(dimethylamino)-pyridine (DMAP) acted as a catalyst. As for six-branched chromophore **SN**, the tether core DH was produced by Williamson ester reaction of 4,4',4"-(ethane-1,1,1-triyl)triphenol and 3-chloropropane-1,2-diol. Then, carboxylic acid functionalized chromophore 3, which synthesized from monochromophore and succinic anhydride, attached to tether core **DH** through esterification to obtain six-branched chromophore **SN**. The structures of **N1**, **DN** and **SN** were confirmed by ¹H NMR, FT-IR spectroscopy, elemental analysis and mass spectrometry. The details of the synthesis and characterizations were described in the Experimental Section.

Thermal properties of chromophore N1, DN and SN were studied by differential scanning calorimetry (DSC) and thermalgravimetric analysis (TGA). The melting point (T_m) of chromophore N1 was 276 °C, while bichromophore DN and six-branched SN showed glass transition temperatures (T_g) at about 115 °C and 129 °C without melting point. Compared with **DN**, **SN** exhibited higher T_{g} for its larger molecular weight and more rigid structure resulting in bigger limitation of movement. The decomposition temperatures (T_d) of chromophore N1 and DN were 281 °C and 313 °C respectively (Fig. 2) indicating connecting two chromophores could improve thermal stability. However, the *T*_d of **SN** dropped to 265 °C due to the star-shaped structure and two adjacent ester groups which connected monochromophores and DH to form SN. The starshaped structure was influenced greatly by temperature and the bonds of two adjacent ester groups were destroyed easily resulting in low T_d of **SN**.

3.2. Linear and nonlinear optical properties

The linear optical properties of **N1**, **DN** and **SN** were performed by UV–visible absorption spectra. The maximum absorption wavelengths (λ_{max}) of chromophore **N1**, **DN** and **SN** were 586 nm, 574 nm and 568 nm in DMF, indicating the absorption of chromophore shifted bluely with the increase of chromophoric branch (Fig. 3). Compared with chromophore **N1**, multichromophore

Synthesis of monochromophore N1



Synthesis of bichromophore DN



Synthesis of six-branched chromophore SN



Scheme 1. Synthesis of chromophore N1, DN and SN.

showed blue shifts in λ_{max} due to the π - π^* electronic transition. Take **DN** for an example, the variation of the **DN** structure, a new chemical group (–COO–) was synthesized from **N1** via esterification, induced the reduction of electron-release behavior of the donor resulting in the λ_{max} of bichromophore **DN** blue shifts [45–47]. The same phenomena occurred in **SN**. As for the small blue-shift of 6 nm for **SN**, comparing with biochromophore **DN**,

resulted from spatial interactions between monochromophores in multichromophore. Besides, no significant absorption broadening in multichromophores compared with monochromophore **N1**, reveal there was no influence in charge-transfer band after chromophores were connected to form multi-branched chromophores.

NLO polymer films (**Film-N1** and **Film-DN**) were fabricated by doping the chromophores into polymer matrix PVPh and the



Fig. 2. TGA traces for chromophore N1, DN and SN.



Fig. 3. UV-visible absorption spectra of compound N1, DN and SN in DMF.

molecule loading densities were up to 30 wt% without phase separation. Six-branched chromophore **SN** was adopted to fabricate film **Film-SN** directly. The second-order NLO properties of the films were investigated by SHG measurement.



Fig. 4. *d*₃₃ values of polymer films as a function of molecule loading densities of compound **N1** and **DN**: black, **Film-N1**; red, **Film-DN**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The d_{33} values of polymer films, which were poled by a 5.5 kV dc voltage, were displayed in Fig. 4. The d_{33} values of gust-host films improved with the increase of chromophore loading density and reached to the highest values (**Film-DN** was 39 pm V^{-1} and **Film-N1** was 25 pm V^{-1}) when the loading concentration was 30 wt%. Compared with Film-N1, the Film-DN was about 1.6 times in the second harmonic coefficient, indicating that the bichromophore could promote the macroscopic optical nonlinearities because of the site-isolation effect from their tree-like structures. For large molecular weight of SN, Film-SN was prepared directly without any polymer matrix. The active chromophore density of Film-SN reached to 68 wt% and the d_{33} value up to 208 pm V^{-1} which was 8.3 times in that of Film-N1, revealing six-branched chromophore could further improve nonlinear optical properties and loading content simultaneously (Fig. 5). Introducing dendritic multichromophores into films could decrease the inter-chromophore electrostatic interactions and improve the macroscopic optical nonlinearity effectively.

3.3. Stability of nonlinear activity

Besides, temperature-dependent decay of d_{33} was used to evaluate the long-time stability of molecular orientation in films. The temperature-dependent decays of **Film-N1**, **Film-DN** and **Film-SN** were illustrated in Fig. 6. The d_{33} of **Film-DN** decayed obviously after 100 °C, and remained 50% of original d_{33} at 119 °C. Meanwhile,



Fig. 5. Illustration of maximum d₃₃ values of polymer films and pure film.



Fig. 6. Temperature-dependence decays of NLO coefficients for Film-N1, Film-DN and Film-SN.

the second harmonic coefficient of **Film-N1** decayed rapidly after 80 °C and maintained half of the original signals at 111 °C. These phenomena revealed that the site-isolation effect from the tree-like architectures could improve the stability of polymer films markedly. However, the d_{33} of **Film-SN** maintained half of the original signals at 92 °C showing less stable than polymer films. It could be attributed to the absence of polymer matrix and the flexibility of tether core.

4. Conclusions

New multi-chromophores **DN** and **SN** were synthesized from monochromophore **N1** via esterification. The d_{33} values of **Film-DN** enhanced with the increase of loading densities, and the highest value reached to 39 pm V⁻¹ when the chromophore concentration was 30 wt%. Furthermore, the second harmonic coefficient of **Film-SN** was up to 208 pm V⁻¹ and the active chromophore density was 68 wt%. Compared with **Film-N1**, the films containing multibranched chromophores **Film-DN** and **Film-SN** were about 1.6fold and 8.3-fold enhancement in the d_{33} values, indicating the dendritic architecture could reduced dipole-dipole interactions between chromophores significantly and improved the macroscopic nonlinear optical activities markedly. The easy and practicable strategy of the preparation of multi-branched chromophores provided broader potential application in design and synthesis of multichromophore dendrimers with excellent nonlinear activity.

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