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

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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 ^{1}H 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.

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 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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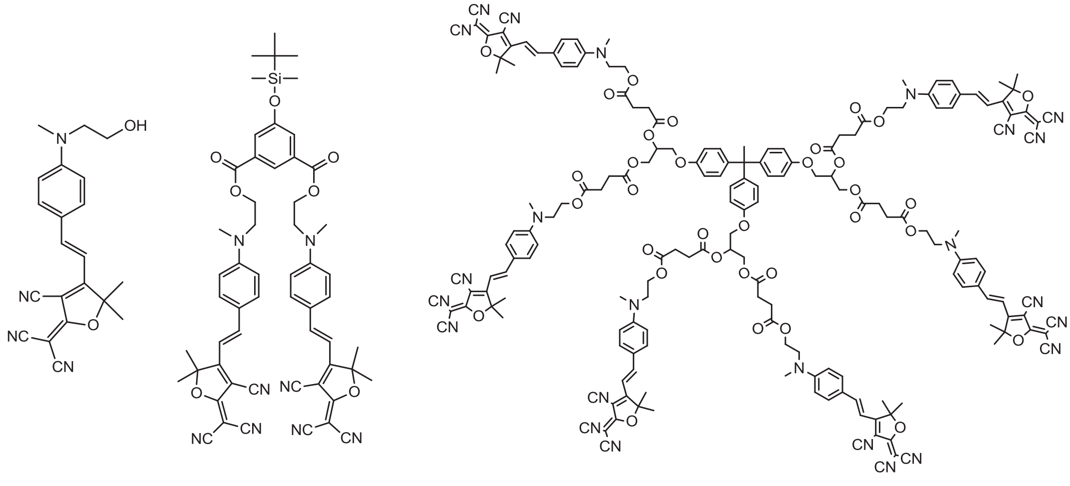

Fig. 1. Structure of compound **N1**, **DN** and **SN**.

[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 (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.

^{1}H 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 ($d_{11} = 0.5$ 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%. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 1.75 (s, 6H, $C(C\mathbf{H}_3)_2$), 3.12 (s, 3H, $N(C\mathbf{H}_3)$), 3.58–3.59 (d, 4H, $NC\mathbf{H}_2C\mathbf{H}_2$), 4.78 (s, 1H, O**H**), 6.85–6.87 (d, 3H, Ar**H**, C**H**=CH), 7.75–7.77 (d, 2H, Ar**H**), 7.90–7.94 (d, 1H, CH=C**H**). 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 $C_{21}H_{20}N_4O_2$: 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%. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 0.23 (s, 6H, $Si(C\mathbf{H}_3)_2$), 0.38 (t, 12H, $Si(C\mathbf{H}_3)_2$), 0.99 (s, 9H, $C(C\mathbf{H}_3)_3$), 1.04 (s, 18H, $C(C\mathbf{H}_3)_3$), 7.71 (d, 2H, Ar**H**), 8.28 (s, 1H, Ar**H**).

2.4. Synthesis of compound 2

Compound **2** was synthesized on the basis of the literature [44]. Yield: 72%. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 0.27 (s, 6H, $Si(C\mathbf{H}_3)_2$), 1.01 (s, 9H, $C(C\mathbf{H}_3)_3$), 7.61 (d, 2H, Ar**H**), 8.15 (t, 1H, Ar**H**), 13.37 (s, 2H, COO**H**). Elemental analysis calcd (%) for $C_{14}H_{20}O_5Si$: 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 CH_2Cl_2 (180 mL). EDC•HCl (0.68 g, 3.6 mmol) and 4-dimethylaminopyridine (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 CH_2Cl_2 (200 mL) and washed with brine and water. After the organic phase was dried over Na_2SO_4 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%. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 0.20 (s, 6H, $Si(C\mathbf{H}_3)_2$), 1.0 (s, 9H, $C(C\mathbf{H}_3)_3$), 1.75 (s, 12H, $C(C\mathbf{H}_3)_2$), 3.20 (s, 6H, $N(C\mathbf{H}_3)$), 3.88–3.90 (t, 4H, $NC\mathbf{H}_2$), 4.55–4.57 (t, 4H, $NCH_2C\mathbf{H}_2$), 6.75–6.78 (d, 2H, C**H**=CH), 6.82–6.84 (d, 4H, Ar**H**), 7.55–7.60 (m, 8H, Ar**H**, CH=C**H**), 8.14 (s, 1H, Ar**H**). 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 $C_{56}H_{56}N_8O_7Si$: 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 $C_{56}H_{56}N_8O_7Si$ $[M+H]^+$, 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-