



A 3-phenoxypropane-1, 2-diol based bichromophore for enhanced nonlinear optical properties

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ABSTRACT

The structure of a novel bichromophore that comprised a readily hyperpolarisable chromophore with 3-phenoxypropane-1, 2-diol via esterification, was confirmed by elemental analysis, UV–visible absorption spectra and ^1H NMR. Nonlinear optical polymer films were fabricated by doping the bichromophore and the corresponding monochromophore into poly(4-vinylphenol). *In situ* second harmonic generation measurements revealed that the bichromophore imparted a 2.2-fold enhancement in the second harmonic generation coefficients of the films, indicating that the novel 3-phenoxypropane-1, 2-diol derivative could be used in the design and synthesis of multi-chromophoric dendrimers with large macroscopic optical nonlinearity.

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1. Introduction

Organic second-order nonlinear optical (NLO) materials have attracted great interest owing to their potential application in electro-optic (EO) modulation, optical switching and optical information processing [1–5]. Compared with inorganic materials, organic NLO materials display many advantages such as high EO coefficient, low dielectric constant, ease of processing and device integration [6,7]. To generate macroscopic optical nonlinearity, readily hyperpolarisable chromophores have been incorporated in a nonlinear optically inactive polymeric host matrix and poled using an electrical field so as to obtain a noncentrosymmetric arrangement [8,9]. However, a major challenge for this approach is to convert the high hyperpolarisability (β) of the chromophore to large macroscopic optical nonlinearity in the polymer, because of strong inter-chromophore dipole–dipole interactions which are detrimental to the realisation of large nonlinear susceptibility [10–13].

In recent years, multi-chromophoric dendritic NLO materials have been introduced as an efficient means of reducing such inter-chromophore electrostatic interactions and achieving large EO coefficients [14–18]. Generally, multichromophores are synthesized by incorporating chromophores with tether groups and

tether cores. Multichromophores using different tether groups have been widely studied, such as bichromophore and trichromophore bundles, three-armed multi-chromophoric dendrimers, 9,10-dihydroanthracene based azo-type bichromophores, calix[4]arene linked multichromophores and tris(allyl) silane based trichromophores [19–23]. Multichromophores display larger EO coefficients than monochromophores [1,24].

This paper describes a simple approach for the design and synthesis of bichromophores that show enhanced bulk nonlinearity due to their supramolecular morphology. The bichromophore **B1** comprises 1,3-phenoxypropane-1, 2-diol as the tether group; a typical TCF-type chromophore **1** with large β was chosen as the monochromophore [25] (Fig. 1). The bichromophore was synthesized by connecting the carboxylic acid functionalized monochromophore with 3-phenoxypropane-1, 2-diol via esterification.

2. Experimental

2.1. Materials and measurements

All chemicals were purchased from Aldrich and Alfa Aesar and used as received. Dichloromethane and DMF were distilled over drying agents before use; all other solvents were commercially available and were used without further purification.

UV–visible absorption spectra were obtained using a Perkin–Elmer Lambda 20 spectrophotometer, mass spectrometry

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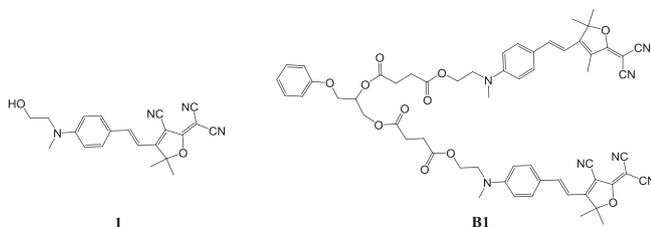


Fig. 1. Structure of compound **1** and **B1**.

performed on a Bruker Daltonics esquire3000^{plus} mass spectrometer. High resolution mass analysis was obtained using a Bruker Apex III (7.0 T) FTICR mass spectrometer. ¹H NMR and ¹³C NMR spectra were taken on a Bruker Avance DMX500 spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analyses were obtained from a Thermo Finnigan Flash EA1112 microelemental analyzer. Differential scanning calorimetry (DSC) was performed using a Netzsch Instruments 200 F3 with a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Film thicknesses were measured using a Tencor alpha-step 200 surface profilometer. The second harmonic generation (SHG) coefficient (*d*₃₃) of the poled film was measured using a Q-switched Nd:YAG laser at 1064 nm and a Y-cut quartz crystal (*d*₁₁ = 0.5 pm V⁻¹) was used as the reference [26–29].

2.2. Synthesis of compound **1**

Chromophore **1** was prepared according to the literature [30]. To a solution of 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde (1.78 g, 10 mmol) and 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (2.3 g, 11 mmol) in absolute ethanol (60 mL), 12 drops of piperidine were added. The reaction mixture was refluxed for 6 h with stirring and then cooled to room temperature. The blue solid was filtered and recrystallized from ethanol. Yield: 69%. 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). Elemental analysis calcd (%) for C₂₁H₂₀N₄O₂: C, 69.98; H, 5.59; N, 15.55. Found: C, 69.76; H, 5.55; N, 15.43.

2.3. Synthesis of compound **2**

To a solution of **1** (0.29 g, 0.84 mmol) and succinic anhydride (0.09 g, 0.9 mmol) in anhydrous dichloromethane (30 mL),

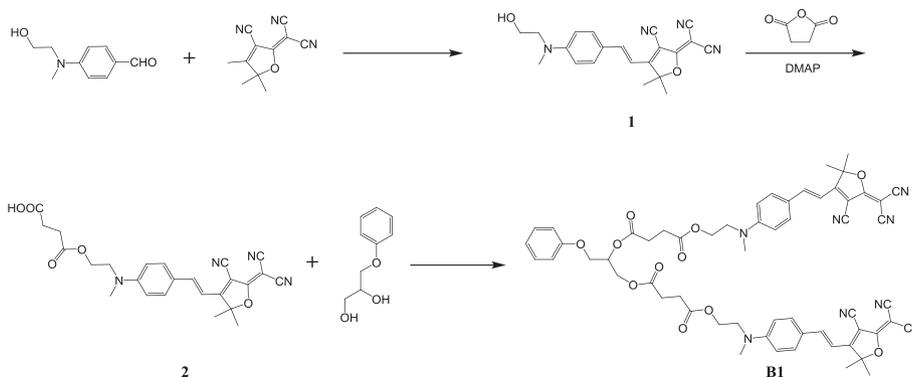
4-dimethylaminopyridine (DMAP; 0.90 g) and pyridine (0.3 mL) were added. The reaction mixture was stirred at room temperature overnight and then washed with brine and water. The organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by silica column chromatography using 5% ethanol in CH₂Cl₂ as the eluent. Yield: 78%. 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). MS (ESI): exact mass calcd for C₂₅H₂₄N₄O₅ [M – H]⁻, 459.1. Found: 459.1.

2.4. Synthesis of compound **B1**

3-phenoxypropane-1,2-diol (1 mmol, 0.168 g) and compound **2** (2.2 mmol, 1.01 g) were dissolved in CH₂Cl₂ (80 mL). Dicyclohexylcarbodiimide (DCC; 2.2 mmol, 0.45 g) and DMAP (1 mmol, 0.12 g) were added and the ensuing mixture was stirred at room temperature for 24 h. The resulting solution was diluted with CH₂Cl₂ (100 mL) and washed with brine and water. The organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure. The product was obtained by silica column chromatography using 10% ethyl acetate in CH₂Cl₂ as the eluent. Yield: 71%. ¹H NMR (500 MHz, DMSO-*d*₆, δ ppm): 1.75 (s, 12H, C(CH₃)₂), 2.59 (m, 8H, COCH₂), 3.13 (s, 6H, NCH₃), 3.72 (t, 4H, NCH₂), 4.10 (d, 2H, CCH₂O), 4.30 (s, 4H, OCH₂), 4.33 (d, 1H, higher field branch of AB quartet, ArOCH₂), 4.41 (d, 1H, lower field branch of AB quartet, Ar–O–CH₂), 5.37 (s, 1H, CHCH₂), 6.76 (d, 4H, ArH; CH=CH, *J* = 16 Hz), 6.88 (d, 2H, ArH), 6.97 (s, 1H, ArH), 7.28 (d, 2H, ArH), 7.54 (d, 4H, ArH), 7.60 (d, 2H, CH=CH, *J* = 16 Hz). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 177.855, 176.075, 172.363, 172.276, 172.155, 171.940, 158.491, 153.482, 149.763, 133.293, 130.060, 122.774, 121.616, 115.084, 113.947, 113.117, 112.842, 112.424, 109.279, 98.818, 93.179, 70.179, 66.429, 62.663, 61.998, 51.795, 50.549, 39.200, 29.060, 28.896, 26.134. Elemental analysis calcd (%) for C₅₉H₅₆N₈O₁₁: C, 67.290; H, 5.36; N, 10.64. Found: C, 67.66; H, 5.60; N, 10.36. MS (ESI): exact mass calcd for C₅₉H₅₆N₈O₁₁ [M], 1052.4. Found: 1051.9. HRMS (ESI): exact mass calcd for C₅₉H₅₆N₈O₁₁ [M + K]⁺, 1091.3700. Found: 1091.3645.

2.5. Thin film fabrication

Each compound was mixed with solid PVPh. The solid components were then dissolved into cyclopentanone (8% of total solid weight). The solutions were stirred in a vial for 1 h and then filtered through a 0.22 μm Teflon membrane filter and spin-coated on the indium-tin oxide (ITO) glass substrates. The films were then dried in a vacuum oven at 85 °C for 10 h to remove the residual solvent.



Scheme 1. Synthesis of bichromophore **B1**.

3. Results and discussion

3.1. Synthesis and characterization

The detailed synthetic procedure of bichromophore **B1** was presented in Scheme 1. Chromophore **1** was synthesized via Knoevenagel reaction of 4-((2-hydroxyethyl)(methyl)amino) benzaldehyde with TCF acceptor 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene) malononitrile. The reaction between succinic anhydride and chromophore **1** produced the carboxylic acid functionalized chromophore **2** to create an attachment point. Compound **2** was then attached to 3-phenoxypropane-1,2-diol via esterification under DCC coupling conditions to create bichromophore **B1**. The reaction was performed in anhydrous CH_2Cl_2 with 4-(dimethylamino)-pyridine (DMAP) as a catalyst and the mixtures were stirred overnight with the satisfied yield (71%). The structure of **B1** was confirmed by elemental analysis, ^1H NMR and mass spectrometry. The details of the synthesis and characterizations are provided in the Experimental Section.

Thermal properties of compound **1** and **B1** were explored by thermalgravimetric analysis (TGA) and differential scanning calorimetry (DSC). The decomposition temperature (T_d) of compound **1** and **B1** were 283 °C and 300 °C respectively. Bichromophore **B1** showed much higher thermal stability than chromophore **1**. Compound **1** displayed a melting point (T_m) of 281 °C. Bichromophore **B1** showed a range of glass transition temperature (T_g) instead of melting point which was about 78 °C. It was attributed to the long and flexible tether group that connected the monochromophore **1** together.

3.2. Linear and nonlinear optical properties

The linear optical properties of bichromophore **B1** were studied by UV–visible absorption spectra. Fig. 2 shows the UV–vis spectra of chromophore **1** and bichromophore **B1** in tetrahydrofuran (THF) and DMF. The maximum absorption wavelengths (λ_{max}) of **B1** are 546 nm in THF and 573 nm in DMF and show a red shift of 27 nm with the increase of solvent polarity. This behavior is quite similar with that of monochromophore **1**, while the λ_{max} of **1** shows a red shift of 24 nm from THF (563 nm) to DMF (587 nm). The red shift was attributed to the functional monochromophore in **B1** since chromophore **1** shows red shift behaviors with the increase of solvent polarity. In THF, the λ_{max} of **B1** displayed a blue shift of 17 nm compared with that of compound **1**. This blue shift may be attributed to the spatial interactions between the two

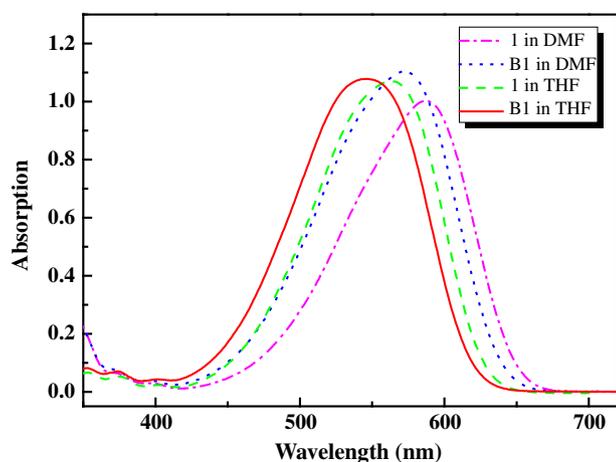


Fig. 2. UV–visible absorption spectra of compound **1** and **B1** in THF and DMF.

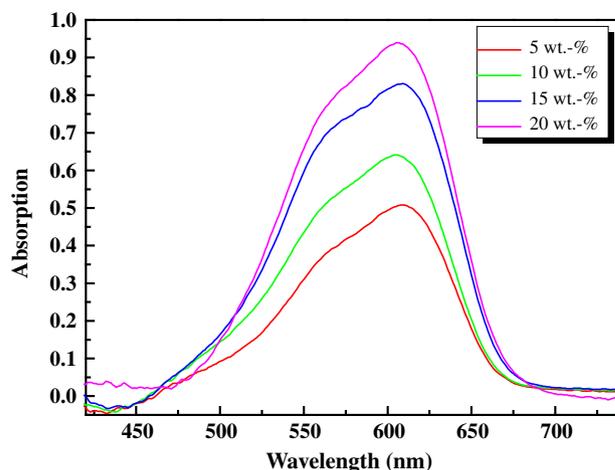


Fig. 3. UV–Visible absorption spectra of thin films of chromophore **1** in PVPh with different loading densities.

sub-chromophores in **B1** [21,31,32]. Also, the absorption spectra was slightly broadened from monomer to bichromophore, which is could be resulted from the larger conformational disorder in the bichromophore [32,33]. The same trend was also observed in DMF.

NLO polymer films containing bichromophore **B1** (Film-**B1**) were fabricated by choosing poly(4-vinylphenol) (PVPh) as polymer matrix. The molecule loading densities were up to 20 wt% without phase separation. Chromophore **1** doped polymer films (Film-**1**) were also prepared and compared with **B1** doped films in the same doping level, since the active chromophore units were almost the same in the same molecule loading densities. The thickness of the films was in the range of 500–600 nm. The UV–visible absorption spectra of Film-**1** and Film-**B1** in different doping levels are shown in Figs. 3 and 4. The λ_{max} of Film-**1** was about 607 nm, and a red shift was occurred compared with that of chromophore **1** in solvents. A slight shoulder (571 nm) was observed with the increasing of molecule density. It was attributed to the H-type aggregation of the molecules which lead to the blue shift of the linear absorption maximum [25,34,35]. The λ_{max} of Film-**B1** was about 594 nm, and a shoulder also appeared around 560 nm with the increase of doping level which was resulted from H-type aggregation of the bichromophores. When the molecular loading density was 20 wt%, the λ_{max} of **B1** in PVPh shifted to 560 nm.

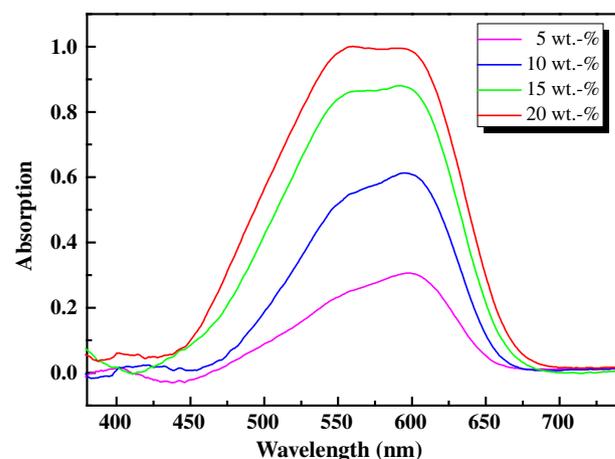


Fig. 4. UV–Visible absorption spectra of thin films of bichromophore **B1** in PVPh with different loading densities.

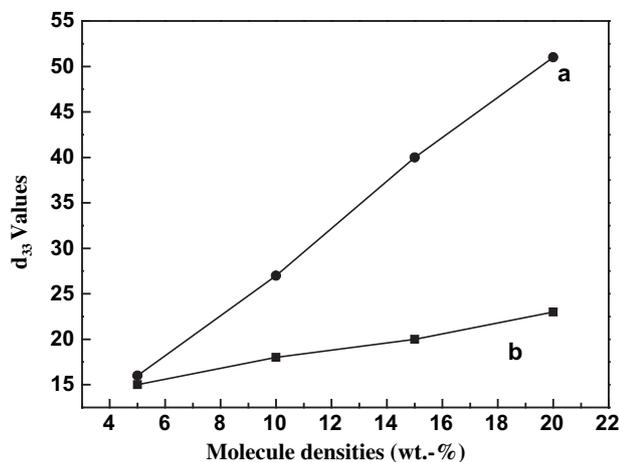


Fig. 5. d_{33} values of polymer films as a function of molecule loading densities of compound **1** and **B1**: a, Film-B1; b, Film-1.

The second-order NLO properties of the polymer films were characterized by SHG measurement using the Maker fringe technique [36,37]. The second harmonic coefficient (d_{33}) of the film can be calculated by comparison with the SHG intensity of a standard Y-cut quartz crystal plate. The films were poled by applying a 6 kV dc voltage. The d_{33} values of the films were shown in Fig. 5. With the increase of molecule loading densities, the d_{33} values of **Film-B1** showed almost linear improvement. The highest d_{33} values was 51 pm V^{-1} when the loading density was 20%. The d_{33} values of **Film-1** was up to 23 pm V^{-1} when the molecule loading density was 20%. A 2.2-fold enhancement in the second harmonic coefficient was achieved in bichromophore **B1** doped polymer films compared with monochromophore **1** doped films. The results indicated that 3-phenoxypropane-1, 2-diol linked bichromophore could efficiently improve the bulk optical nonlinearities of organic materials due to its supramolecular morphology. 3-phenoxypropane-1, 2-diol derivatives can be easily synthesized by the reaction between 3-chloropropane-1, 2-diol and phenols compounds under basic conditions [38]. It provides an efficient approach to design and synthesize tether cores for the use of multichromophore dendrimers.

4. Conclusions

A new type of bichromophore was synthesized by using 3-phenoxypropane-1,2-diol as the linking group. The esterification between carboxylic acid functionalized TFC-type chromophore and 3-phenoxypropane-1, 2-diol under DCC coupling conditions produced bichromophore **B1**. The d_{33} value of films containing **B1** increased almost linearly with the increase of chromophore doping levels. The highest d_{33} value was 51 pm V^{-1} (20 wt%), which was about 2.2 times the value of the films containing chromophore **1**. The easy approach to synthesis and effective improvement in macroscopic optical nonlinearity made 3-phenoxypropane-1, 2-diol derivatives have potential applications in the design and synthesis of multichromophore dendrimers with quite large EO coefficients.

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