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Design and synthesis of bichromophores for nonlinear optical applications in polymer films

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ABSTRACT

Three bichromophores were designed and synthesized by linking a vinylthiophene-conjugated chromophore with different tether groups via esterification. Second harmonic generation measurements of nonlinear polymer films revealed that the second harmonic generation coefficients of the films containing the bichromophore and using 3-phenoxypropane-1,2-diyl succinic diester as the tether group were improved in comparison with the mono-chromophore-doped polymer films. However, the second harmonic generation coefficients of the polymer films containing bichromophores using isophthalic ester as the tether group were decreased. Overall, the results indicate that the 3-phenoxypropane-1,2-diyl succinic diester tether group has potential applications in the design and synthesis of multi-chromophoric dendrimers with large macroscopic optical nonlinearity.

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1. Introduction

Organic nonlinear optical (NLO) materials have drawn considerable attention over the past two decades due to their potential applications in photonic devices [1–6]. Poled polymers that incorporate chromophores with high hyperpolarizabilities β into their polymeric host matrices and are poled by an electrical field to obtain a noncentrosymmetric arrangement are the most widely studied organic NLO materials [7–11]. Unfortunately, the strong dipole–dipole interactions between chromophores have led to unfavorable, antiparallel packing of the chromophores to large macroscopic optical nonlinearities a continual challenge [12–15].

In recent years, multi-chromophores synthesized by linking mono-chromophores via tether groups have become widely studied [16–18]. It has been reported that multi-chromophores exhibit a much higher figure of merit than their corresponding monochromophores [19–22]. Generally, multi-chromophores are synthesized by linking NLO chromophores with different tether groups, and the tether groups, in turn, greatly affect the electrooptic properties of the multi-chromophores [23]. In other words, the tether groups have been found to play an important role in the formation of multi-chromophores but require further study to determine which tether groups can improve the macroscopic optical nonlinearities [24].

In this study, we designed and synthesized three bichromophores by choosing tether groups with different electronic enrichments, lengths and flexibilities. Additionally, we systemically studied their optical nonlinearities in a polymer matrix. In this approach, a common thiophene containing FTC-type chromophore [25,26], was chosen as the mono-chromophore unit for construction of all of the bichromophores; it has a large β value and is a robust compound. In addition, esterification was used in the design and synthesis of the multi-chromophores and the NLO polymer materials because of its synthetic convenience and high yield [27,28]. The bichromophores studied were synthesized via esterification between the linking groups and the FTC chromophore. Furthermore, the macroscopic optical nonlinearities of the bichromophores and FTC chromophoredoped poly(4-vinylphenol)(PVPh) thin films were studied to evaluate the differences in the bichromophores with different tether groups. Our goal in this study was to search for tether groups that could enhance the macroscopic optical nonlinearity.

2. Experimental

2.1. Materials and measurements

All chemicals were purchased from Alfa Aesar and Aldrich and used as received. Dichloromethane and *N*,*N*-dimethylformamide (DMF) were distilled over drying agents before use. Isophthalic acid was commercially available and used without further purification. Chromophore **FTC1** and 5-(trimethylsilyloxy)isophthalic acid (compound **2**) were prepared according to procedures found in the literature [26,29].





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¹H and ¹³C NMR spectra were collected on a Bruker Avance DMX500 spectrometer. Mass spectrometry was performed on a Bruker Daltonics Esquire3000^{plus} mass spectrometer. UV-visible absorption spectra were obtained using a Perkin-Elmer Lambda 20 spectrophotometer. Elemental analyses were obtained from a ThermoFinnigan Instruments Flash EA1112 microelemental analyzer. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 at a heating rate of 10 °C min⁻¹ and under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed in a nitrogen atmosphere using a Netzsch Instruments 200 F3 with a heating rate of 10 °C min⁻¹; the DSC thermograms of the bichromophores were obtained from the second scan. Film thicknesses were measured using a Tencor Alfa-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 ($d_{11} = 0.5$ $pm V^{-1}$) as the Refs. [30,31].

2.2. Synthesis

2.2.1. Synthesis of compound 3

To a solution of 3-phenoxypropane-1,2-diol (1.68 g, 10 mmol) and succinic anhydride (2.2 g, 22 mmol) in anhydrous dichloromethane (50 mL), DMAP (0.90 g) and pyridine (1.5 mL) were added. The reaction mixture was stirred at room temperature overnight, and the following day, the mixture was washed with brine and DI water for three times. The organic phase was dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was purified by silica column chromatography using 50% ethyl acetate in CH_2Cl_2 as the eluent to give the final product. Yield: 65%. ¹H NMR (500 MHz, CDCl₃, δ ppm): 2.65 (*m*, 8H, COCH₂), 4.11 (q, J = 6.2 Hz, 2H, CCH₂O), 4.35 (d, J = 8.8 Hz, 1H, higher field branch of AB quartet, ArOCH₂), 4.48 (d, J = 6 Hz, 1H, lower field branch of AB quartet, ArOCH₂), 5.41 (m, 1H, CHCH₂), 6.88 (*d*, *J* = 8 Hz, 2H, Ar**H**), 6.96 (*t*, 1H, Ar**H**), 7.27 (*d*, *J* = 8 Hz, 2H, Ar**H**), 9.82 (s, 2H, COOH). Elemental analysis calcd (%) for $C_{17}H_{20}O_9$: C, 55.43; H, 5.47. Found: C, 55.69; H, 5.63. MS (ESI): exact mass calcd for C₁₇H₂₀O₉ [M–H]⁻, 367.1. Found: 367.0.

2.2.2. Synthesis of bichromophore B1

A solution of chromophore FTC1 (1.03 g, 2.2 mmol) and isophthalic acid (0.17 g, 1 mmol) in anhydrous dichloromethane (60 mL) and DMF (0.5 mL) was stirred for 10 min at room temperature. Next, the mixture was cooled to 0 °C in an ice bath, and DMAP (0.54 g, 4.4 mmol) and EDC.HCl (1.26 g, 6.6 mmol) were added to the mixture. Once the additions were complete, the ice bath was removed, and the reaction mixture was stirred at room temperature for 24 h. After that time, the mixture was diluted with CH₂Cl₂ (120 mL) and washed with brine and DI water. The organic phase was dried over MgSO₄, and the solvent was evaporated under reduced pressure. The product was obtained by silica column chromatography using 10% ethyl acetate in CH₂Cl₂ as the eluent. Yield: 61%. ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 1.83 (s, 12H, C(CH₃)₂), 3.05 (s, 6H, NCH₃), 3.85 (t, 4H, NCH₂), 4.52 (t, 4H, OCH₂), 6.67 (*d*, *J* = 16 Hz, 2H, CH = CH), 6.83 (*d*, 4H, ArH), 7.17-7.29 (*m*, 6H, Ar**H**, C**H** = CH), 7.48 (*d*, J = 8.9 Hz, 4H, Ar**H**), 7.66 (t, 1H, ArH), 7.77 (d, J = 8.8 Hz, 2H, ArH), 8.12-8.15 (m, 4H, ArH)CH = CH), 8.38 (s, 1H, ArH). ¹³C NMR (125 MHz, DMSO-d6, δ ppm): 177.222, 174.870, 165.357, 153.679, 150.136, 140.862, 139.291, 138.153, 134.487, 134.136, 130.474, 130.103, 129.814, 129.220, 128.137, 124.187, 116.736, 113.455, 112.702, 112.549, 112.334, 111.639, 98.986, 96.894, 63.039, 53.290, 50.426, 38.654, 26.026. Elemental analysis calcd (%) for C₆₂H₅₀N₈O₆S₂: C, 69.77; H, 4.72; N, 10.50. Found: C, 69.88; H, 4.93; N, 10.29. MS (ESI): exact mass calcd for C₆₂H₅₀N₈O₆S₂ [M], 1066.3. Found: 1066.9.

2.2.3. Synthesis of B2

Compound 2 (0.15 g, 0.5 mmol) and FTC1 (0.47 g, 1.0 mmol) were dissolved in CH₂Cl₂ (60 mL), and the reaction mixture was cooled to 0 °C. Next, DCC (0.24 g, 1.2 mmol) and DMAP (0.14 g, 1.2 mmol) were added to the mixture, and the solvent was warmed to room temperature and stirred for 24 h. After that time, the solution was diluted with CH₂Cl₂ (100 mL) and washed with brine and DI 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: 68%. ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 0.18 (s, 6H, Si(CH₃)₂), 0.94 (t, 9H, C(CH₃)₃), 1.78 (s, 12H, C(CH₃)₂), 3.00 (s, 6H, NCH₃), 3.79 (s, 4H, NCH₂), 4.47 (t, 4H, OCH₂), 6.62 (*d*, *J* = 16 Hz, 2H, CH = CH), 6.77 (*d*, *J* = 9 Hz, 4H, ArH), 7.14–7.23 (m, 6H, ArH, CH = CH), 7.41 (d, I = 8.6 Hz, 4H, ArH), 7.48 (d, I)*I* = 8.8 Hz, 2H, ArH), 7.73 (*d*, *J* = 8.8 Hz, 2H, ArH), 7.96 (*s*, 1H, ArH), 8.11 (d, I = 16 Hz, 2H, CH = CH), 13C NMR (125 MHz, DMSO-d6, δ ppm): 177.213, 174.876, 165.069, 155.815, 153.685, 150.146, 140.871, 139.314, 138.165, 134.497, 131.983, 129.231, 128.127, 125.131, 124.145, 123.440, 116.700, 113.471, 112.718, 112.491, 112.340, 111.637, 98.987, 96.920, 63.236, 60.233, 53.323, 50.361, 38.548, 26.048, 25.906, 18.382, 14.562, -4.219. Elemental analysis calcd (%) for C₆₈H₆₄N₈O₇S₂Si: C, 68.20; H, 5.39; N, 9.36. Found: C, 68.27; H, 5.35; N, 9.44. MS (ESI): exact mass calcd for C₆₈H₆₄N₈O₇S₂Si [M–H]⁻, 1195.4. Found: 1195.7.

2.2.4. Synthesis of B3

Reaction of compound **3** with **FTC1** was performed as described for **B1**, except with subsequent purification by silica column chromatography using 8% ethyl acetate in CH₂Cl₂ as the eluent. Yield: 72%. ¹H NMR (500 MHz, DMSO-d₆, *δ* ppm): 1.79 (*s*, 12H, C(CH₃)₂), 2.63 (m, 8H, COCH₂), 3.31 (s, 6H, NCH₃), 3.61 (s, 4H, NCH₂), 4.11 (*d*, 2H, CCH₂O), 4.16 (*t*, 4H, OCH₂), 4.28(*d*, *J* = 4.6 Hz, 2H, ArOCH₂), 5.28(s, 1H, CHCH₂), 6.63 (d, J = 16 Hz, 2H, CH = CH), 6.73 (d, J = 8.8 Hz, 4H, Ar**H**), 6.93 (*m*, 4H, Ar**H**), 7.16 (*d*, J = 15.7 Hz, 2H, CH = CH), 7.23–7.28 (*m*, 6H, ArH), 7.46 (*d*, *J* = 8.8 Hz, 4H, ArH), 7.73 (*d*, *J* = 8.8 Hz, 2H, Ar**H**), 8.08 (*d*, *J* = 16 Hz, 2H, C**H** = CH). 13C NMR (125 MHz, DMSO-d6, δ ppm): 177.238, 174.889, 172.302, 172.219, 172.092, 171.884, 158.481, 153.728, 149.933, 140.866, 139.296, 138.166, 134.521, 130.006, 129.247, 128.153, 124.160, 121.568, 116.763, 115.074, 113.481, 112.723, 112.398, 112.342, 111.661, 98.998, 96.884, 70.167, 66.430, 62.642, 61.947, 53.310, 50.412, 38.807, 29.056, 28.904, 26.042. Elemental analysis calcd (%) for C₇₁H₆₄N₈O₁₁S₂: C, 67.18; H, 5.08; N, 8.83. Found: C, 66.70; H, 5.24; N, 8.48. MS (ESI): exact mass calcd for C₇₁H₆₄N₈O₁₁S₂ [M-H]⁻, 1267.4. Found: 1266.7.

2.3. Thin film fabrication

Each chromophore was mixed with solid PVPh, and the solid components were dissolved into cyclopentanone (8% of total solid weight), stirred in a vial for 1 h, filtered through 0.22- μ m Teflon membrane filters and spin-coated onto indium-tin oxide (ITO) glass substrates. Once the coatings were complete, the films were dried in a vacuum oven at 85 °C for 12 h to remove the residual solvent.

3. Results and discussion

3.1. Synthesis and characterization

Structures of the bichromophores are shown in Fig. 1, and all of the bichromophores were synthesized via esterification between the linking groups and FTC chromophore. The first linking group synthesized, compound **2**, was specifically designed to introduce



Fig. 1. Structures of FTC1 and the bichromophores.

an electron-rich group, *tert*-butyldimethylsilyloxy, to the 5-position of isophthalic acid and was produced by a protection and deprotection procedure with 5-hydroxyisophthalic acid, as shown in Scheme 1. Interestingly, isophthalic acid and its derivative, compound **2**, are widely used as linking groups in the synthesis of dendrimers [19,32]. Another linking group we synthesized was formed by reacting 3-phenoxypropane-1,2-diol with succinic anhydride to produce a carboxylic acid functionalized compound **3**. Applications of this long, flexible linking group in multi-chromophore and dendrimer syntheses have not been reported in the literature.

The overall synthetic route of the bichromophores is shown in Scheme 2. Here, bichromophore **B1** was based on the isophthalic acid linking group, where esterification between isophthalic acid and chromophore **FTC1** produced a relatively short, inflexible isophthalic ester tether group. The reaction between **2** and **FTC1** yielded **B2** with 5-(*tert*-butyldimethylsilyloxy)isophthalic ester as the tether group. In bichromophore **B3**, 3-phenoxypropane-1,2-diyl succinic diester was used as a long, flexible tether group.

The structures of the bichromophores were confirmed by elemental analysis, ¹H NMR, ¹³C NMR and mass spectrometry. The details of the syntheses and characterizations are provided in the Experimental Section.

Thermal properties of **FTC1**, **B1**, **B2** and **B3** were explored by DSC and TGA, as shown in Figs. 2 and 3. Compound **FTC1** displayed a melting point (T_m) of 250 °C, whereas all of the bichromophores showed a range of glass transition temperatures (T_g) instead of melting points. The T_g of compound **B1** was 135 °C, and for **B2**, the T_g was 130 °C, which was 5 °C lower than that of **B1**. The difference in the temperatures was attributed to the introduction of the flexible *tert*-butyldimethylsilyloxy group in compound **B2**. Compound **B3** showed the lowest T_g , which was 93 °C, resulting from the longer, more flexible 3-phenoxypropane-1,2-diyl succinic diester tether group. The decomposition temperature (T_d) of **FTC1** was found to be 258 °C; however, all of the bichromophores showed much higher T_d than **FTC1**. Compound **B2** gave the highest T_d , which was 32 °C higher than that of **FTC1**. The T_d of compound



Scheme 1. Syntheses of compounds 2 and 3.



Scheme 2. Synthesis of bichromophore B1.



Fig. 2. DSC thermograms of compound FTC1, B1, B2 and B3: (a) FTC1, (b) B3, (c) B2 and (d) B1.



Fig. 3. TGA curves of FTC1 and the bichromophores: (a) FTC1, (b) B1, (c) B2 and (d) B3.

B1 and **B3** showed less improvement, 27 °C and 21 °C, compared with that of **FTC1**, indicating that the molecular thermal stability could be efficiently improved in the bichromophores that were more suitable for photonic device fabrications.

3.2. Linear and nonlinear optical properties

The linear optical properties of the bichromophores were studied by UV-visible absorption spectroscopy. The UV-visible

absorption spectra of FTC1 and the bichromophores in CHCl₃ are shown in Fig. 4. Chromophore FTC1 showed a maximum absorption wavelength (λ_{max}) of 644 nm in CHCl₃. However, the maximum absorption wavelengths (λ_{max}) of bichromophore **B1**, **B2** and **B3** in CHCl₃ were 634 nm, 636 nm and 639 nm, respectively. Small blue shifts were observed for all of the bichromophores compared with mono-chromophore **FTC1**. Specifically, the λ_{max} of the isophthalic ester tether group attached to **B1** displayed the largest blue shift, approximately 10 nm. This shift was mainly attributed to the electron-withdrawing inductive effect of the ester group, which reduced the electron-donating ability of the amine donor site of the FTC1 mono-chromophore [23,32]. The detrimental reduction of electron density to the donor site decreased the intramolecular charge transfer band, which, in turn, led to the hypsochromic shift [33]. The blue shift of λ_{max} was also influenced by the inter-chromophore interaction between the sub-chromophores of the bichromophores, as reported in the literature [34,13]. The λ_{max} of **B2** showed a blue shift of 8 nm, which was smaller than that of **B1**. Compared with the isophthalic ester tether group in B1, the 5-(tert-butyldimethylsilyloxy)isophthalic ester tether group in **B2** contained an electron-rich *tert*-butyldimethylsilyloxy group. In other words, the electron-donating conjugation of the tert-butyldimethylsilyloxy group via the phenyl decreased the polarity of the ester group, which reduced the detrimental effect the ester group played on the amine donor and resulted in a smaller blue shift. The smallest blue shift (5 nm) was observed for the λ_{max} of **B3**, indicating that the 3-phenoxypropane-1,2-diyl succinic



Fig. 4. UV-visible absorption spectra of FTC1 and the bichromophores in CHCl₃.

diester tether group was able to minimize the detrimental influence of the ester on the electron-donating ability of the donor site.

NLO thin films containing FTC1 and the bichromophores were prepared by choosing PVPh as the polymer matrix [35]. Due to the poor solubility of **B1** in the organic solvents, only a doping level of 10 wt.% was achieved. The doping levels of the other three compounds were only able to reach 20 wt.% without phase separation. The bichromophore doped polymer films were fabricated and compared with the FTC1-doped polymer films with the same doping level because the active chromophore units were almost equal when using the same loading densities. Generally, the thickness of the films was in the range of 500-600 nm. The second-order NLO properties of the polymer films were characterized by their SHG measurements using the Maker fringe technique [36,37]. The second harmonic coefficient (d_{33}) of the film can be calculated by comparing the film's SHG with the SHG intensity of a standard Y-cut quartz crystal plate. In this case, the films were poled by applying a 6-kV dc voltage at 140 °C for 1 h; the d_{33} values of the films are shown in Fig. 5. When the chromophore doping level was 10 wt.%, the d_{33} value of the films containing **B1** (film-B1) was 12 pm V⁻¹; however, the d_{33} values of films containing **B2** (film-B2), B3 (film-B3) and FTC1 (film-FTC1) were 17 pm V⁻¹, 26 pm V^{-1} and 23 pm V^{-1} , respectively. Film-B1 and film-B2 showed reduced d_{33} values compared to that of **film-FTC1** with the same doping level; moreover, the d_{33} value of **film-B1** was the smallest, only half that of film-FTC1. The reason for the decrease in the d₃₃ values for **film-B1** and **film-B2** could be attributed to the inflexible and short isophthalic ester tether group that made the mono-chromophores difficult to rotate under the poling field. On the other hand, for **film-B3**, the largest d_{33} value was 42 pm V⁻¹ (20 wt.%), which was an improvement in comparison with film-**FTC1** (20 wt.%). The largest d_{33} value of **film-FTC1** that was achieved was 32 pm V⁻¹ (20 wt.%), and the largest d_{33} value of **film-B2** was 24 pm V^{-1} (20 wt.%).

To correct for the absorptions that could lead to resonance enhancement of the SHG, the nonresonant $d_{33}(0)$ values of the NLO thin films were obtained by using the approximate two-level model and are summarized in Table 1 [38,39]. The maximum $d_{33}(0)$ values of **film-FTC1** and **film-B2** were determined to be 10 pm V⁻¹ and 7 pm V⁻¹, respectively. However, **film-B3** displayed a $d_{33}(0)$ value of 13 pm V⁻¹, which was higher than the maximum $d_{33}(0)$ values of **film-FTC1** and **film-B2**. To characterize the poling efficiency of the polymer films, the order parameter φ ($\varphi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the film before and after poling) was also calculated and tabulated in Table 1. The φ values of **film-FTC1**, **film-B2** and **film-B3** at 20 wt.% were 0.11, 0.10 and 0.18, respectively. Once again, the bichromophore **B3** doped polymer films showed a much higher value than the other films. In



Fig. 5. *d*₃₃ values of the polymer films as a function of chromophore loading densities: (a) **film-B3**, (b) **film-FTC1**, (c) **film-B2** and (d) **film-B1**.

Table 1

Wavelength of maximum absorption (λ_{max}) and maximum second harmonic coefficients of the NLO thin films.

Films	λ_{\max} (nm)	φ	$d_{33} ({\rm pm}{\rm V}^{-1})$	$d_{33}(0) (\mathrm{pm}\mathrm{V}^{-1})$
Film-FTC1	656	0.11	32	10
Film-B2	654	0.10	24	7
Film-B3	651	0.18	42	13

comparison with the isophthalic ester tether group, 3-phenoxypropane-1,2-diyl succinic diester created a long and flexible structure that allowed the mono-chromophores to rotate freely in the presence of the poling field, thus increasing the poling order and the d_{33} values [23]. Overall, the results indicated that the inflexible isophthalic ester tether group decreased the macroscopic optical nonlinearities, and the longer and flexible 3-phenoxypropane-1,2-diyl succinic diester tether group improved the optical nonlinearities. Additionally, with proper modification, the 3-phenoxypropane-1,2-diyl succinic diester could be used in the syntheses of multi-chromophore dendrimers for enhanced optical nonlinearities; this work is now in progress.

The thermal dynamic stabilities of the poled films were also investigated through a depoling experiment in which the temperature was ramped at a rate of 10 °C min⁻¹, as shown in Fig. 6. The half-decay temperatures determined for the d_{33} values of **film-FTC1** and **film-B2** (20 wt.%) were about 125 °C and 116 °C, respectively, whereas the d_{33} signal of **film-B3** (20 wt.%) was stable at 80 °C. In contrast, the signal of **film-B3** then decayed rapidly with the further increase of temperature and almost disappeared when heating to 100 °C. This result could be attributed to the low T_g of bichromophore **B3**, which was about 93 °C. In addition, due to the much higher T_g of bichromophore **B2**, the half-decay temperature of the d_{33} values for **film-B2** was 28 °C higher than that for **film-B3** (88 °C). Therefore, the results indicate that improvement of the T_g for the multi-chromophores could enhance the thermal stability of the poled films.

4. Conclusions

A series of bichromophores were synthesized by attaching different tether groups with a vinylthiophene-conjugated FTC-type chromophore, and their NLO activities in a polymeric matrix were studied and compared. The results indicated that the inflexible isophthalic ester tether group in **B1** and **B2** reduced the d_{33} value of the NLO polymer films. However, the polymer films containing bichromophore **B3**, with its longer, flexible 3-phenoxypropane-1, 2-diyl succinic diester tether group, displayed a d_{33} value of



Fig. 6. Decay of the normalized *d*₃₃ values as a function of temperature for **film-B2**, **film-B3** and **film-FTC1** at 20 wt.% and poled at 140 °C for 30 min.

42 pm V⁻¹, which was larger than that of the films containing **FTC1**. Based on the improvement in optical nonlinearity made with the 3-phenoxypropane-1,2-diyl succinic diester, potential applications in the design and synthesis of multi-chromophoric dendrimers with quite large macroscopic optical nonlinearity are possible.

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