# Bis-dioxaborine Polymethines with Large Third-Order Nonlinearities for All-Optical Signal Processing

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Synthetic Details for Compounds 1 and 2.
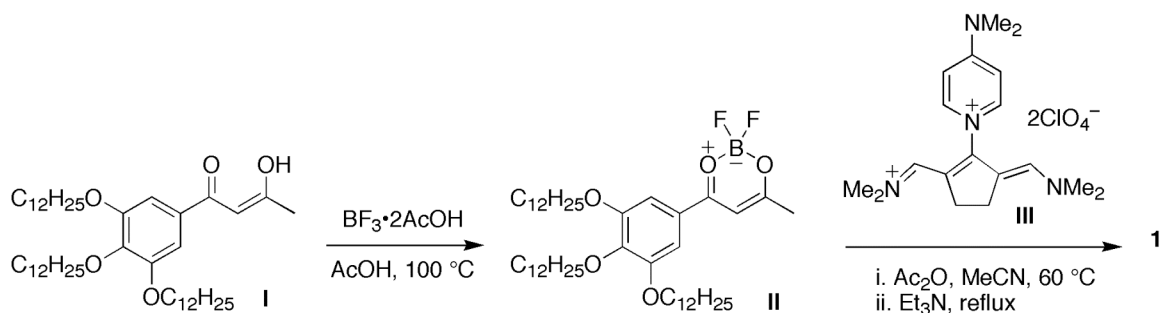

Scheme S1. Synthetic route to Compound **1**.

Intermediate II. $BF_3 \cdot 2AcOH$ (1.86 mL, 13.4 mmol) was added to a solution of $\mathbf{I}^1$ (7.1 g, 13.4 mmol) in acetic acid (100 mL) and the mixture was heated at 100 °C for 20 min. After filtration and washing with acetic acid, a yellow solid (6.56 g, 85%) was obtained. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.11 (d, J = 2.2 Hz, 2H), 6.71 (t, J = 2.2 Hz, 1H), 6.49 (s, 1H), 3.96 (t, J = 6.5 Hz, 4H), 2.38 (s, 3H), 1.77 (q, J = 6.5 Hz, 4H), 1.44 (m, 4H), 1.30

(bs, 32H), 0.86 (t, J = 7.0 Hz, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 192.22, 183.00, 160.64, 132.84, 108.60, 107.02, 97.67, 68.55, 31.91, 29.65, 29.62, 29.58, 29.56, 29.34, 29.11, 25.97, 24.72, 22.68, 14.11 (one alkyl CH not observed, presumably due to overlap). HRMS (EI) calcd for C$_{34}$H$_{57}$BF$_2$O$_4$: 578.4318; Found: 578.4334. Anal. Calcd for C$_{34}$H$_{57}$BF$_2$O$_4$: C, 70.58, H, 9.93. Found: C, 70.70; H, 10.03.

Intermediate III. The preparation of **III** has previously been mentioned to in reference 2, but without details. Specifically, [[2-chloro-3-[(dimethylamino)methylene]-1-cyclopenten-1-yl]methylene]dimethylammonium perchlorate[3] (10 g, 31 mmol), 4-(dimethylamino)pyridine (4.0 g, 32 mmol) and sodium perchlorate (4.5 g, 32 mmol) in acetonitrile (300 mL) were stirred for 12 h at room temperature. The mixture was then filtered and the filtrate was layered with ether to give a brown-red crystalline solid after one day (12 g, 77%).

Compound 1. A mixture of dioxaborane **II** (1.50 g, 2.6 mmol), cyanine **III** (0.647 g, 1.3 mmol), and acetic anhydride (0.65mL) in acetonitrile (16 mL) was heated at 60 °C for 20 min. To the mixture, triethylamine (0.53 g, 5.2 mmol) was added, upon which the mixture turned deep blue immediately. The resulting mixture was then heated to reflux for 30 min. After allowing to cool to room temperature, filtration, and washing with acetonitrile, a metallic golden brown solid was obtained and then purified by recrystallization from a dichloromethane / acetonitrile mixture to afford dark blue solid (1.40 g, 79%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.69 (d, J = 7.3 Hz, 2H), 7.07 (d, J = 13.2 Hz, 2H), 7.02 (d, J = 1.7 Hz, 4H), 6.89 (d, J = 7.4 Hz, 2H), 6.18 (s, 2H), 5.61 (d, J = 13.2

Hz, 2H), 3.94 (t, $J = 6.5$ Hz, 8H), 3.41 (s, 6H), 2.82 (s, 4H), 1.75 (q, $J = 6.4$ Hz, 8H), 1.41

(m, 8H), 1.24 (bs, 32H), 0.86 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 172.58,

170.26, 160.27, 156.79, 150.64, 141.86, 135.77, 132.62, 131.27, 111.38, 108.19, 105.51,

105.35, 98.07, 68.32, 40.72, 31.91, 29.66, 29.62, 29.60, 29.58, 29.40, 29.34, 29.25, 26.83,

26.00, 22.68, 14.11. HRMS (MALDI) calcd for C$_{82}$H$_{126}$B$_2$F$_4$N$_2$O$_8$: 1364.9636. Found:

1364.9658. Anal. calcd for C$_{82}$H$_{126}$B$_2$F$_4$N$_2$O$_8$: C, 72.13; H, 9.30; N, 2.05. Found: C,

71.78; H, 9.39; N, 2.15.
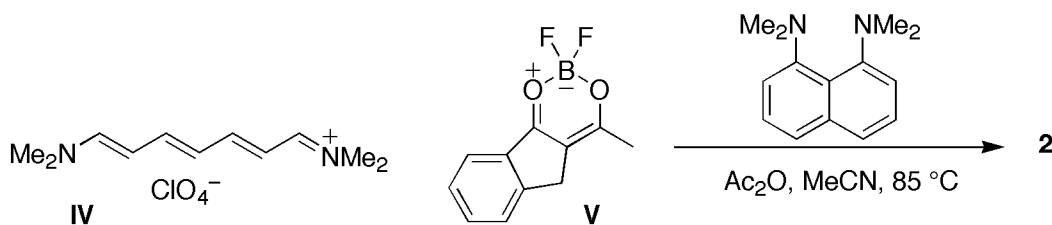
Scheme S2. Synthesis of Compound **2**.

Compound 2. A mixture of dioxaborine **IV**[4] (0.22 g, 1.0 mmol), cyanine **V**[5] (0.14 g, 0.5

mmol), proton sponge (0.33 g, 1.5 mmol) and acetic anhydride (0.25 mL) in acetonitrile

(4 mL) was heated at 85 °C for 20 min under nitrogen. The solution turned deep blue and

a golden brown precipitate forms. After allowing to cool to room temperature, filtration,

and washing with acetonitrile, a golden brown solid was obtained (0.20 g, 0.2 mmol,

40%). ^{1}H NMR (CD$_3$CN, 500 Hz) δ 8.03 (d, $J = 8.1$ Hz, 2H), 7.87 (d, $J = 7.5$ Hz, 2H),

7.69 (t, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 7.7$ Hz, 2H), 7.56 (t, $J = 13.1$ Hz, 2H), 7.53 (d, $J =$

7.7 Hz, 2H), 7.46 (dt, $J = 7.3, 1.2$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.06 (t, $J = 12.8$ Hz,

2H), 6.36 (t, $J = 12.8$ Hz, 2H), 6.33 (t, $J = 12.5$ Hz, 1H), 5.85 (d, $J = 13.1$ Hz, 2H), 3.57

(s, 4H), 3.09 (s, 12H). ^{13}C NMR (DMSO-d_6, 100 Hz) δ 170.38, 165.69, 149.86, 145.71,

145.08, 144.60, 136.90, 134.78, 130.34, 128.85 (t, J = 5.8 Hz), 127.23, 126.94 (t, J_{CF} = 4.0 Hz), 125.63, 125.17, 124.26, 121.78 (t, J_{CF} = 5.6 Hz), 120.60 (t, J_{CF} = 5.8 Hz), 118.97, 111.34, 107.96, 45.72, 30.74. HRMS (ESI) calcd for anion $C_{29}H_{21}B_2F_4O_4^-$: 531.1568. Found: 531.1597. UV-Vis-NIR (acetonitrile): λ_{max} = 926 nm (145000).

Materials Preparation and Linear Characterization Techniques. Absorption spectra were recorded on a dual-beam Cary-5E UV-Vis-NIR spectrophotometer. For all spectroscopic measurements on solutions, both linear and nonlinear, spectrophotometric grade solvents purchased from Sigma-Aldrich were used. Linear absorption measurements were performed in 1 cm pathlength quartz cuvettes. The DMSO solvent used for compound **2** was purged with nitrogen for approximately 20-30 minutes prior to making any solution. These solutions had concentrations that ranged between 1×10^{-6} and 1×10^{-5} M. The absorption spectra of the films were taken using microscope coverslides as references. A preliminary study involving absorption photolysis measurements showed that the dioxaborine-terminated polymethines studied in this paper showed better photo-chemical stability than benzthiazolium-terminated polymethines of comparable chain lengths similar to those found in Reference 9a. Further studies concerning the stability of these dioxaborine-terminated systems will be reported in a future paper.

The solutions used for the nonlinear characterization techniques were contained in 1 mm glass cuvettes with concentrations that ranged between 2×10^{-4} and 8×10^{-3} M. Nitrogen purging of DMSO solutions were carried out in a manner similar to the solutions used for linear spectroscopy. Linear absorption spectra taken of these highly concentrated

solutions in short pathlength quartz cuvettes (50 μm) revealed no evidence of aggregation at these concentrations.

The neat films were fabricated by first filtering a ~50 mM solution of molecule **2** in DMSO through a 0.2 μm PTFE filter to remove dust particulates. The films were subsequently spin-coated on microscope coverslides and left overnight to dry. The thicknesses of the films were determined using a Dektak 3ST profilometer. The refractive indices of the films at 1.3 μm were determined to be 1.7 from interference fringes in their linear absorption spectra.[6] Anecdotal evidence of the stability of these films was obtained by linear and nonlinear spectroscopic investigations that were carried out on a single film over a six month period with negligible degradation observed.

Nonlinear Characterization Techniques. The light source used was a Spectra-Physics regeneratively amplified Ti:Sapphire system (Spitfire) that produces ~100 fs pulses at 800 nm with a repetition rate of 1 kHz which in turn pumps a Spectra-Physics optical parametric amplifier (OPA-800CF) that provides output pulses of <100 fs in the appropriate spectral band.

The Z-scan technique permits the determination of the real and imaginary components of a sample's nonlinearity and the optical layout is a standard one.[7] In order to determine the third-order polarizabilities of the molecules in solution it was necessary to perform a Z-scan measurement on both the solution as well as the neat solvent. This permitted subtraction of the signal due to the neat solvent from the solution to determine the contribution of the solute alone. It should be noted that for the 1 kHz amplified system used for the measurements, thermal nonlinearities were found to slightly obscure the

closed aperture results.[8] In order to eliminate these effects the repetition rate of the system was reduced to 10 Hz. This was found to reduce the thermal contributions to the resulting closed aperture signals to a negligible level. Z-scan measurements performed at 1 kHz on the spin-coated films exhibited no substantive thermal contributions to the closed aperture signals.

The degenerate four-wave mixing (DFWM) technique allows for determination of the magnitude of a sample's nonlinearity using a referential method[9] (a 540 μm slab of fused silica was used as the reference material) as well as its temporal response through the use of a computer-controlled delay line in one of the three pump beams. The optical layout consists of a forward scattering geometry with angular beam separation of ~1.5°. In order to extract both the real and imaginary parts of γ for the molecules in solution from DFWM measurements, the bulk values of $|\chi^{(3)}|$ for solutions of varying concentrations had to be carried out. These concentration dependent measurements can then be fit to extract out both the magnitude and phase of the γ.[10] Only the magnitude of $\chi^{(3)}$ could be determined for the solid films. Thermal nonlinearities were not found to obscure the DFWM signals for either solution or film measurements even at the 1 kHz repetition rate. The two nonlinear characterization techniques, DFWM and Z-scan, gave results that showed good agreement with one another. Averages of the results from the two techniques are the values reported in the paper.

Conversion for Nonlinear Optical Parameters. The proper conversions to n_2 and β from the real and imaginary parts of $\chi^{(3)}$ are as follows:

$$n_2 = \frac{3\mathrm{Re}\,\chi^{(3)}}{4\varepsilon_o c n_o^2}$$

and

$$\beta = \frac{3\pi \operatorname{Im}\chi^{(3)}}{\varepsilon_o c n_o^2 \lambda}$$. These conversions require $\chi^{(3)}$ to be converted from cgs to SI units according to Reference 8. The definitions for γ and $\chi^{(3)}$ and any conversions used here are the same as those used in Reference 11.

The high-number density extrapolation of γ to $\chi^{(3)}$ can be made using the following equation:

$$\chi^{(3)}(-\omega;\omega,\omega,\omega) = N \cdot L(\omega)^4 \cdot \langle \gamma(-\omega;\omega,\omega,\omega) \rangle \qquad (1)$$

where N is the number density of chromophores present and $\langle\gamma\rangle$ is the orientational averaged third-order polarizability as reported in Table 1 in the paper. $L(\omega)$ is the Lorenz local field factor that is defined as

$$L(\omega) = \frac{n(\omega)^2 + 2}{3} \qquad (2)$$

where $n(\omega)$ is the refractive index of the medium at frequency ω. Assuming a film density of 1 g/cm^3 and using the molecular weight of compound 2 (746.3 g/mole), the number density of the film was calculated to be 8.07×10^{20} molecules/cm^3. Using the refractive index of the film quoted above and Equation (2), the field factor is found to be 1.63. Inserting these two values along with the value for γ at 1.3 μm from Table 1 (-5.7×10^{-32} esu) into Equation (1) gives a value for $\chi^{(3)}$ of -3.2×10^{-10} esu. This value is in good agreement with the value of -3.6×10^{-10} esu found for the actual film.

Full references from paper:

Ref. 15:

Simonsen, K. B.; Geisler, T.; Petersen, J. C.; Arentoft, J.; Sommer-Larsen, P.; Greve, D. R.; Jakobsen, C.; Becher, J.; Malagoli, M.; Brédas, J. L.; Bjornholm, T. *Eur. J. Org. Chem.* **1998**, *12*, 2747-2757.

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