Bisdioxaborine Polymethines with Large Third-Order Nonlinearities for All-Optical Signal Processing

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Organic materials with large third-order optical nonlinearities in the near-infrared spectral regime are of interest for nonlinear all-optical signal processing (AOSP). While there has been much research aimed at increasing the magnitude of $\chi^{(3)}$, a key problem is that many materials are limited by large nonlinear absorption values ($Im\chi^{(3)}$), large linear absorption loss, and lack of processability into optical quality films. Strategies that have been pursued to increase nonlinearity include extending conjugation length in polymers such as polyacetylene and polydiacetylenes[1,2] and optimizing the bond length (or bond order) alternation in donor–acceptor conjugated molecules or polymethines.[3–5] In the latter approach, it has been shown that cyanine-like molecules with vanishing bond length alternation show optimized negative third-order polarizability for discrete molecules of relatively short chain lengths. In this Communication, we report on "cyanine-like" bisdioxaborine polymethines that show very large negative $Re\chi^{(3)}$ and small $Im\chi^{(3)}$ values in the near-infrared spectral region.

Previously, it has been shown both theoretically[4] and experimentally[3] that the third-order polarizability, γ, can be optimized through the correct combination of donor and acceptor substitution of a polyene molecule. In particular, γ is predicted to show a maximum negative peak at the so-called "cyanine limit" where the C–C bonds along the polyene backbone exhibit essentially equivalent lengths. At this particular ground-state geometry the π-electrons along the conjugated backbone are strongly delocalized resulting in the large and negative value for γ. These studies have shown that true cyanine-like molecules, such as symmetrically substituted polymethine cations or anions, should possess the largest magnitude of γ for a discrete polyene molecule of a given chain length. Furthermore, it has been reported that γ for cyanines rapidly increases with the length of the conjugated chain.[6,7] These features, coupled with the fact that cyanines possess sharp electronic absorption edges that should serve to reduce optical loss in the near-infrared, make these materials attractive for use in AOSP.

Here we report the synthesis and nonlinear optical properties of two bisdioxaborine-terminated polymethines (Chart 1; see Supporting Information (SI) for synthetic details). Compound **1** is a zwitterionic compound, in which the central carbon of the polymethine backbone is covalently linked to a pyridinium cation, that exhibits moderate solubility in a variety of common organic solvents and was synthesized in analogy to previously reported systems differing only in the substituents on the terminal aryl rings.[8] We also synthesized a more extended dioxaborine-terminated polymethine in the form of a salt of an anion, **2**, through the proton-sponge-induced condensation of the appropriate 4-methyl-dioxaborine with $[Me_2N(CH)_7NMe_2]^+[ClO_4]^-$. Solution spectra of **1** and **2** are shown in Figure 1 and exhibit typical cyanine-like spectra with characteristically sharp electronic absorption bands and edges. The spectrum of **2** is particularly interesting in that it shows no sign of the extensive broadening observed in other polymethines of similar

Chart 1
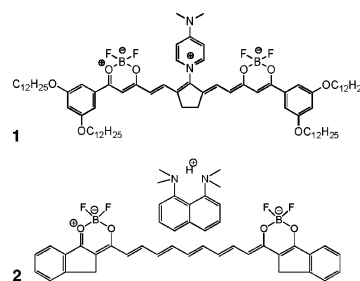
conjugation lengths, PD 1659 and DPy9 in ref 9, parts a and b, respectively;[10] in the former example this broadening was attributed to symmetry breaking resulting in reduced delocalization.[9a]

The third-order polarizabilities (γ) were measured using femtosecond pulse degenerate four-wave mixing and Z-scan methods (see SI for details) at a wavelength of 1.3 μm for **1** and **2** in solution. Both **1** and **2** exhibited sizable nonlinearities (see Table 1), with compound **2** possessing a larger value of γ in accordance with the aforementioned length scaling. Compound **2** also possessed a 3-fold larger nonlinearity than a direct analogue of PD 1659[9a] (with only the counterion ClO_4^- differing) despite possessing a similar effective conjugation length; this is likely the result of symmetry breaking leading to nonzero bond length alternation in the latter compound. The real part of γ for **2** was found to be quite large, -5.7×10^{-32} esu. Whereas the real part of γ can be exploited in AOSP applications, the imaginary part is associated with two-photon absorption, which can reduce transparency and device performance.[11] Consequently, the imaginary part of γ for this molecule was also determined and was found to have a modest value of 7.9 $\times 10^{-33}$ esu. Furthermore, the measurement of γ for compound **2** at two other wavelengths in the near-infrared spectral regime (see Table 1) indicated that **2** exhibits similarly attractive characteristics (i.e., large $Re(\gamma)$, small $Im(\gamma)$) over the entire telecommunications band.[12]
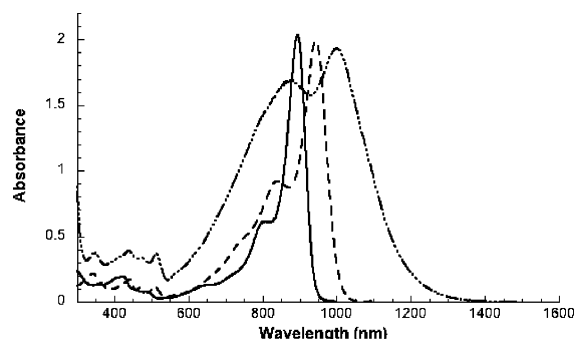

Figure 1. Linear absorption spectra of **1** in toluene (solid line), **2** in dimethyl sulfoxide, DMSO, (dashed line), and **2** as a 230 nm spin-coated film (dashed–dotted line).

Table 1. Experimentally Determined Third-Order Nonlinearities[a] at Different Wavelengths for Compounds **1** and **2** in Solution and for **2** in a 230 nm Solid Film

	λ	1.30 μm	1.45 μm	1.55 μm
1 (soln)	$\mathrm{Re}(\gamma)$	-5.5×10^{-33}		
	$\mathrm{Im}(\gamma)$	1.9×10^{-33}		
2 (soln)	$\mathrm{Re}(\gamma)$	-5.7×10^{-32}	-5.3×10^{-32}	-5.3×10^{-32}
	$\mathrm{Im}(\gamma)$	7.9×10^{-33}	4.6×10^{-33}	1.2×10^{-32}
2 (film)	$\mathrm{Re}\chi^{(3)}$	-3.6×10^{-10}	-2.8×10^{-10}	-2.1×10^{-10}
	$\mathrm{Im}\chi^{(3)}$	3.8×10^{-11}	2.4×10^{-11}	3.3×10^{-11}

[a] All values are given in units of esu and their associated errors were determined to be $\pm 10\%$.

Table 2. T Figures of Merit[a] for Neat Film of **2** and Benchmark AOSP Materials at $\lambda = 1.3$ μm

material	n_2 (m^2 W^{-1})	β (mW^{-1})	T
GaAs[17]	4.1×10^{-18}	1.9×10^{-10}	60
silicon[16]	-6.6×10^{-17}	3.2×10^{-10}	6.3
PTS[b,2]	7.5×10^{-17}	6.0×10^{-11}	1.0
2 (film)	-4.9×10^{-16}	5.0×10^{-10}	1.3

[a] $T = \beta\lambda/n_2$, where β is the two-photon absorption coefficient and n_2 is the nonlinear refractive index. [b] Poly[2,4-hexadiyne-1,4-diyl bis(para-toluenesulfonate)].

Compound **2** exhibited good solubility in DMSO, permitting solution processing and fabrication of neat solid films, which is crucial to obtain the high bulk nonlinearities required for AOSP applications. The absorption spectrum of a neat film of **2** (shown in Figure 1) exhibits a broadening and splitting of the band compared to the solution spectrum, most likely due to excitonic effects upon aggregate formation;[13] yet the film still maintains relatively low linear absorption for wavelengths greater than 1.35 μm. With the use of degenerate four-wave mixing and Z-scan methods, the third-order macroscopic nonlinearity, $\chi^{(3)}$, was determined for the film. Table 1 shows that $\mathrm{Re}\chi^{(3)}$ at 1.3 μm is -3.6×10^{-10} esu, with the imaginary part nearly an order of magnitude lower. Interestingly, good agreement was found between a high-number density extrapolation of the value of γ and the value of $\chi^{(3)}$ (see SI for comparison), suggesting that the system retains its cyanine character upon processing into a neat film.[14] Although the third-order polarizabilities of certain extended cyanines have been examined in the past,[6,7,15] successful transition of cyanine-like molecules with large γ values to solid films with large values of $\chi^{(3)}$ has not previously been reported. Furthermore, time-resolved measurements on the film of **2** indicated a strong ultrafast component to the nonlinearity (response time < 100 fs) with a weaker decay component that relaxed to <1% of the peak signal in less than 8 ps.

Certain figures of merit (FOMs) for AOSP have been developed[11,16] that are based on the optical properties of the material. The two-photon FOM, or T, relates to the material's ability to perform despite potential losses because of two-photon absorption. For a material to be useful the criterion for this FOM is $T < 1$ (for definition see Table 2). The T FOMs for a few benchmark materials are given in Table 2 along with the values for the film of **2**. Because of the order of magnitude difference between the real and imaginary parts of $\chi^{(3)}$, the solid film performs quite well in terms of T. Furthermore, the measured dispersion of $\chi^{(3)}$ (Table 1) indicates that the film possesses good FOMs throughout the telecommunica-

tions band. An additional FOM, W, rates the material's ability to perform certain AOSP tasks and is dictated by the strength of the nonlinearity and its transparency. While films of **2** are semicrystalline and exhibit some scattering loss, chemical modifications that lead to the formation of an amorphous phase should yield low optical loss, which, coupled with the large nonlinearity of the film, would result in high W FOMs.

We have designed and synthesized a polymethine material that exhibits an extremely large microscopic nonlinearity in the near-infrared for a discrete (i.e., nonpolymeric) molecule. Upon solution processing into high-number density films, this material shows a large real part of $\chi^{(3)}$ with ultrafast temporal response as well as a relatively small $\mathrm{Im}\chi^{(3)}$. With these critical features for AOSP, extended highly delocalized cyanine-like systems in high optical quality films should result in photonic devices that utilize modest drive powers while performing at ultrahigh bit rates (>100 GHz).

Supporting Information Available: Complete synthetic procedures for molecules **1** and **2**; details of linear and nonlinear characterization techniques; appropriate conversions for nonlinear optical parameters; complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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