Cyanine Dyes with Exceptional Third-Order Nonlinear Optical Figures-of-Merit for All-Optical Switching

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Abstract: A molecular design strategy that involves favorable control of one- and two-photon absorption resonances to produce exceptional nonlinear optical figures-of-merit for all-optical switching has been realized in a series of cyanines dyes.
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OCIS codes: (190.0190) Nonlinear optics; (190.4710) Optical nonlinearities in organic materials; (190.7110) Ultrafast nonlinear optics; (070.6020) Signal processing

1. Introduction

The development of organic chromophores for nonlinear optical (NLO) applications has been a subject of research for the last thirty years. However, third-order NLO chromophores that possess the characteristics necessary to perform all-optical switching (AOS) in the telecommunications bands (1300 – 1550 nm) still remain elusive. With recent breakthroughs in the development of silicon-organic hybrid waveguide geometries [1], which provide a robust platform to make these applications feasible, identification of optimal third-order NLO materials has become even more critical. While molecules with moderately large third-order nonlinearities have been identified [2], perhaps an even greater obstacle to the development of such materials for AOS is that most molecular materials examined to date exhibit unacceptable optical losses, i.e. linear and/or nonlinear (in particular, two-photon) absorption. Consequently, a significant challenge is to identify materials that possess good two-photon figures-of-merit (FOM) [3], i.e. simultaneously possess very large nonlinear refractive indices and very small two-photon absorption (2PA) coefficients, which are related to the real and imaginary parts of the third-order susceptibility, respectively. At the molecular level, this implies $|\text{Re}(\gamma)/\text{Im}(\gamma)| > 10$, where γ is the third-order polarizability.

While minimizing 2PA can be accommodated by working at photon energies ($\hbar\omega$) less than half the energy of the lowest lying 2PA transition (see Fig. 1a), the magnitude of $\text{Re}(\gamma)$ at this wavelength cannot reach its full potential. This is a consequence of a large detuning energy, i.e. $\Delta = (E - \hbar\omega)$, which is detrimental as a reduction of this detuning energy can lead to pre-resonant enhancement of γ by well over an order-of-magnitude. An alternative approach depicted in Fig. 1b is possible. This involves operating at photon energies relatively close to the lowest-lying 1PA transition such that γ can be pre-resonantly enhanced while twice the photon energy falls *in between* potentially detrimental 2PA bands. This latter approach, while promising, clearly requires a more careful molecular design strategy to achieve favorably spaced states and sufficiently narrow absorption features to minimize losses. In this report, we describe a series of remarkably efficient NLO molecules that satisfy these conditions and consequently possess very large non-resonant values of $\text{Re}(\gamma)$ *and*, for one member of the series, a ratio of $|\text{Re}(\gamma)/\text{Im}(\gamma)|$ that exceeds 100 throughout the telecommunications spectral window from 1300 to 1550 nm.
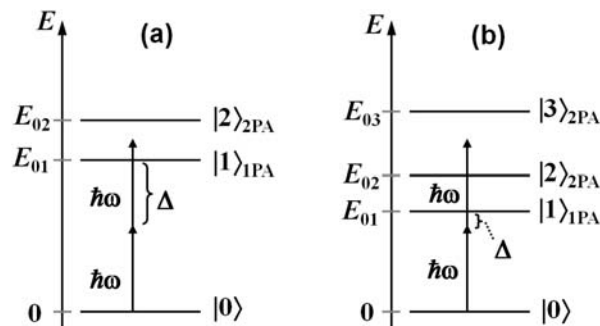

Fig. 1. State energy schematic depictions for avoiding 2PA in organic chromophores: (a) twice the excitation photon energy ($2\hbar\omega$) is less than the 2PA state energy (E_{02}), (b) $\hbar\omega$ lies below E_{01} and $2\hbar\omega$ lies in between two-photon state energies (E_{02} and E_{03}).

2. Bis(dioxaborine)- and chalcogen-based cyanines

Cyanine systems are of particular interest for use as NLO materials in AOS applications because they possess a

number of unique properties such as optimized vales of γ for discrete molecules, high order power law scaling of γ with increasing conjugation length, and sharp absorption band edges resulting in modest optical losses below E_{01}. Nonetheless, it is known that extended cyanines will undergo a symmetry-breaking process that places practical restrictions on the length of molecules in which one can achieve very large values of γ. Consequently, while we recently identified a bis(dioxaborine)-terminated nonamethine cyanine (**DOB-9C**) that resists symmetry breaking and exhibited promising NLO characteristics (i.e. Re(γ) $\approx$ -5×10^{-32} esu and |Re(γ)/Im(γ)| $\leq$ 10, in the telecommunications spectral region) [4], additional improvements along this route were limited by such restrictions.

Another route for achieving large nonlinearities while avoiding symmetry breaking in cyanines is to optimize Re(γ) for a fixed conjugation length. In this manner, the terminal group (1) participates efficiently in extending the overall conjugation length and (2) increases the transition densities towards the periphery which gives contributions to the transition dipole, all while maintaining a bridge of modest length that could help prevent the onset of symmetry breaking. We chose a chalcogen-containing terminal group with the expectation that the lower electronegativity of these highly polarizable atoms could effect these properties. In particular, we synthesized chalcogen-based cyanines with varying polymethine bridge lengths (**Cy-3C**, **Cy-5C** and **Cy-7C**).

3. Results and discussion

To determine the extent to which this choice of terminal group could help generate large values of Re(γ) at modest chain lengths, the third-order NLO properties of these dyes were investigated in solution using the femtosecond-pulsed Z-scan technique and degenerate four-wave mixing. For these chalcogen-based cyanines, it was found that the magnitude of Re(γ) increased by an order of magnitude with the addition of each double bond in the conjugated bridge, leading to an exceptionally large value of -2.2×10^{-31} esu at 1300 nm for **Cy-7C**, the system with seven carbons in the bridge. This value of Re(γ) compares very favorably to reported values for other organic systems in this spectral region [2], including the **DOB-9C** cyanine discussed above.

Furthermore, **Cy-5C** and **Cy-7C** exhibit exceptional values of |Re(γ)/Im(γ)| >> 10 at 1300 nm, i.e. much larger molecular two-photon FOMs for AOS than other chromophores previously reported. Fig. 2a illustrates the dispersion of |Re(γ)/Im(γ)| from 1300 – 1550 nm for all the chalcogen-based compounds. While **Cy-5C** exhibits a ratio at 1300 nm of nearly 100, **Cy-7C** possesses similarly large values but maintains this over the entire spectral region of interest. It is also interesting to note that these ratios dwarf those of **DOB-9C** (see Fig. 2a). In order to determine the positions of the 2PA resonances in these systems, non-degenerate 2PA spectra were measured for all the dyes in solution; the spectrum for **Cy-7C** is shown in Fig. 2b. Typical of all the cyanines studied, the spectrum exhibits a favorable region over which 2PA is relatively weak; furthermore, this low-loss window appears to be tunable simply by modifying the position of E_{01} (or equivalently molecular length). It therefore becomes apparent that the unprecedented two-photon FOMs indicate that detrimental 2PA can be avoided by the approach outlined in Fig. 1b above. Thus, the observations here have important implications for the design of a new generation of materials that could enable low power and high contrast AOS.
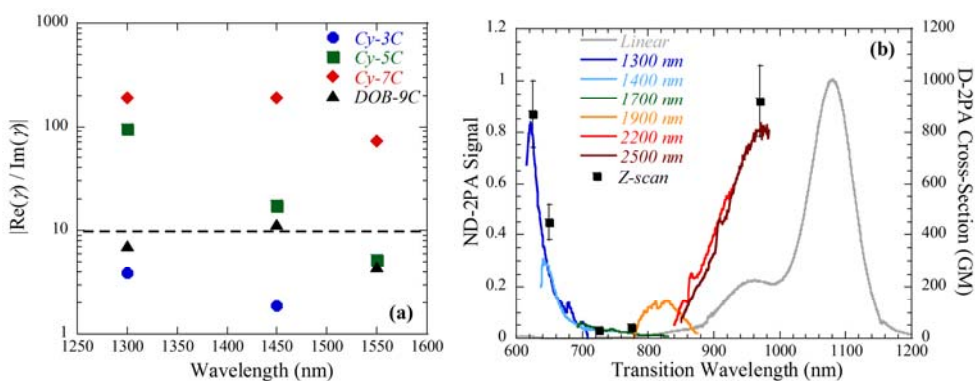

Fig. 2. Plots of (a) the dispersion of |Re(γ)/Im(γ)| for all the cyanine compounds discussed here and (b) the non-degenerate 2PA spectrum for **Cy-7C**. Different pump wavelengths (shown in legend) were employed to observe the full ND-2PA spectrum. Filled squares are 2PA cross-sections derived from femtosecond-pulsed Z-scan measurements. 1 GM is defined as 1×10^{-50} cm^4 s photon^{-1}. Experimental uncertainties in the values were estimated to be ±15%. The linear absorption spectrum is shown as a reference.

[1] M. Hochberg *et al.*, *Nat. Mater.* **5**, 703-709 (2006).
[2] J. M. Hales, J. W. Perry, *Introduction to Organic Electronic and Optoelectronic Materials and Devices,* (CRC Press, 2008), Chap. 17.
[3] V. Mizrahi, K. W. Delong, G. I. Stegeman, M. A. Saifi, M. J. Andrejco, *Opt. Lett.* **14**, 1140-1142 (1989).
[4] J. M. Hales, S. Zheng, S. Barlow, S. R. Marder, J. W. Perry, *J. Am. Chem. Soc.* **128**, 11362-11363 (2006).