Modulated conjugation as a means for attaining a record high intrinsic hyperpolarizability

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We report on a series of chromophores that have been synthesized with a modulated conjugation path between donor and acceptor. Hyper-Rayleigh scattering measurements of the best molecule show an enhanced intrinsic hyperpolarizability that breaches the apparent limit of all previously-studied molecules.

Over the last 3 decades, many novel molecules have been designed and synthesized to improve the nonlinear response for a variety of applications. Quantum calculations using sum rules have been used to place an upper-bound on the molecular susceptibilities,[1, 2, 3, 4] but, the largest nonlinear susceptibilities of the best molecules fall short of the fundamental limit by a factor of $10^{3/2}$. A thorough analysis shows that there is no reason why the molecular hyperpolarizability can not exceed this apparent limit.[6] In this letter, we report on a novel set of molecules where the one with modulated conjugation[7] is found to have a hyperpolarizability that breaches the apparent limit of all previously-measured molecules.

Past work has shown that the polarizability is largest when the potential energy function oscillates in a way that localizes the eigenfunctions on different parts of the molecule.[7] This type of oscillation can be designed into a bridge that separates the donor and acceptor ends of a chromophore by varying the degree of conjugation. Our approach is based on the well-known difference in aromatic stabilization energy between benzene and heteroaromatics, such as thiophene rings.[8]

Figure 1 shows the series of molecules under study. The synthesis and the details of the linear and nonlinear optical characterization of this series of compounds will be published elsewhere.[9]

The hyperpolarizability, $\beta$, was determined at 800 nm using Hyper-Rayleigh scattering. The zero-frequency hyperpolarizability, $\beta_0$, was determined using the two-level model. Table I shows the measured molecular properties and Figure 2 shows a plot of $\beta_0$, normalized to the fundamental limit of the hyperpolarizability (this ratio is called the intrinsic hyperpolarizability, which is scale-invariant), where the fundamental limit, $\beta_{MAX}$, is given by

$$\beta_{MAX} = \sqrt{\frac{3e^3 \hbar}{m^2}} \frac{N^{3/2}}{E_{10}^{7/2}},$$

where $N$ is the number of electrons ($N$ is determined by counting methods described in the literature[10, 11]), $E_{10}$ the energy difference between state 1 and 0, $e$ is the electron charge, $\hbar$ Planck’s constant and $m$ the mass of the electron. The horizontal line in Figure 2 represents the apparent limit defined by the best past measurements, which is a factor of $10^{3/2}$ below the fundamental limit.

No single molecule has ever been reported to breach the apparent limit, though some have come close. For example, May and coworkers have shown that the second hyperpolarizability gets within a factor of 2 of the apparent limit.[12] However, a close analysis shows that their chromophores, being part of a cross-linked system, were strongly interacting – leading to an under-counting of the number of electrons. So, we believe our reported values to be the first example of single chromophores that breach the limit with record intrinsic hyperpolarizability.

Our molecular design focuses on modulating the amount of aromatic stabilization energy along the con-
jugated bridge between the donor and the acceptor. To induce the desired modulation, aromatic moieties with a different degree of aromaticity make up the asymmetrically substituted $\pi$-bridge. As an example, molecules 4 and 7 are both azo dyes, but while molecule 4 has 2 benzene moieties with identical (36 kcal/mol, or 1.57 eV) aromatic stabilization energy, molecule 7 has a benzene and a thiophene moiety. The latter is well known to have a reduced aromatic stabilization energy (29 kcal/mol, or 1.25 eV). This results in a significant variation of the degree of aromaticity for molecule 7, or in a modulation of the conjugation between the donor and acceptor. This degree of conjugation modulation yields an enhancement in the hyperpolarizability that breaches the apparent limit well outside the range of experimental uncertainty of 10%. Note that a demodulation technique is used to eliminate the background contribution from two-photon fluorescence,[14, 15, 16] insuring that the measured values are not overestimated due to this known source of systematic error.

Molecule 6 is isoelectronic to molecule 7, but due to the additional Cl atom in molecule 6, steric hindrance induces a twist in the conjugation path, resulting in a decreased hyperpolarizability. Molecules 2 and 5 are homologues of 4 and 7; and show a similar enhancement. However, the larger and more geometrically linear molecules show a more dramatic effect, which is predicted by the theory (steric hindrance caused by the chlorine atom suppresses the enhancement of molecule 5.).[7] In particular, the best molecules are ones that are long with many undulations in the potential energy function, which allows for the electron densities of the eigenstates to be well separated. So, future design strategies should focus on longer molecules with stronger modulation of conjugation.

In addition to increased length, future efforts must also focus on keeping the chain linear. Special attention should be devoted to mimic the optimal undulation[7] by making use of not only benzene and thiophene, but also of other aromatic moieties that exhibit an even wider range of stabilization energies (like pyrrole and furan with aromatic stabilization energy values of 22 and 16 kcal/mol, or 0.98 and 0.69 eV, respectively).

While our best measured values of the hyperpolarizability are still more than an order of magnitude from the fundamental limit, our design strategy appears to be
a promising new paradigm for making better molecules.

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[1] M. G. Kuzyk, “Fundamental limits on third-order molecular susceptibilities,” Opt. Lett. 25, 1183-1185 (2000).
[2] M. G. Kuzyk, “Physical Limits on Electronic Nonlinear Molecular Susceptibilities,” Phys. Rev. Lett. 85, 1218-1221 (2000).
[3] M. G. Kuzyk, Opt. Lett. 28, 135 (2003).
[4] M. G. Kuzyk, “Erratum: Physical Limits on Electronic Nonlinear Molecular Susceptibilities,” Phys. Rev. Lett. 90 039902 (2003).
[5] M. G. Kuzyk, “Fundamental Limits of Nonlinear Susceptibilities,” Optics & Photonics News 14, 26 (2003).
[6] K. Tripathi, J. Pérez-Moreno, M. G. Kuzyk, B. J. Coe, K. Clays, and A. M. Kelley, “Why Hyperpolarizabilities Fall Short of the Fundamental Quantum Limits,” J. Chem. Phys. 121 7932-7945 (2004).
[7] J. Zhou, M. G. Kuzyk, and D. S. Watkins, “Pushing the hyperpolarizability to the limit,” Opt. Lett. 31 2891-2893 (2006).
[8] L. T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken, and C. W. Spangler, “Experimental Investigations of Organic Molecular Nonlinear Optical Polarizabilities. 2. A Study of Conjugation Dependences,” J. Phys. Chem. 95 10643-10652 (1991).
[9] Y. Shen, L. Qiu, J. Hao, Y. Zhao, J. Pérez-Moreno, M. G. Kuzyk and K. Clays, manuscript in preparation.
[10] M. G. Kuzyk, “Fundamental limits on two-photon absorption cross sections” J. Chem. Phys. 119, 8327-8334 (2003).
[11] J. Pérez-Moreno and M. G. Kuzyk, “Fundamental limits of the dispersion of the two-photon absorption cross section,” J. Chem. Phys. 121, 194101-194114 (2003).
[12] J. C. May, J. H. Lim, I. Biaggio, N. N. P. Moonen, T. Michinobu, and F. Diederich, “Highly efficient third-order optical nonlinearities in donor-substituted cyanoethynylethene molecules,” Opt. Lett. 30, 3057-3059 (2005).
[13] Q. Y. Chen, L. Kuang, Z. Y. Wang, and E. H. Sargent, “Crosslinked C60 polymer breaches the quantum gap, Nano Letters,” Nano. Lett. 4, 1673-1675 (2004).
[14] K. Clays and A. Persoons, “Hyper-Rayleigh scattering in solution,” Phys. Rev. Lett. 66, 2980-2983 (1991).
[15] K. Clays and A. Persoons, “Hyper-Rayleigh scattering in solution,” Rev. Sci. Instrum. 63, 3285-3289 (1992).
[16] G. Olbrechts, R. Strobbe, K. Clays, and A. Persoons, “High-frequency demodulation of multi-photon fluorescence in hyper-Rayleigh scattering,” Rev. Sci. Instrum. 69, 2233-2241 (1998).