Maximizing the Third-Order Optical Nonlinearity in Organic Molecules for Photonic Applications

Joshua C. May, Prof. Ivan Biaggio
Department of Physics and Center for Optical Technologies, Lehigh University

Dr. Filip Bures, Prof. François Diederich
Laboratorium für Organische Chemie, ETH Zürich, Hönggerberg

We have made great strides in understanding the molecular origin of higher third-order nonlinear optical effects in smaller molecules. We are now able to target the two properties important to photonic device integration: 1) maximizing the molecular optical nonlinearity and 2) maximizing the density of nonlinear molecules in the solid state. We will also discuss how we plan to improve on our best molecules, whose third-order nonlinearities have recently broken the world-record for proximity to the quantum limit.

The third-order nonlinear optical response from a material ($\chi^{(3)}$) can lead to a large number of effects such as third-harmonic generation, the intensity-dependent refractive index and two-photon absorption. Applications that utilize these effects are well known, but are limited by strength of the nonlinearity in current materials and the speed at which the effects are realized (nanoseconds, 10^{-9} s). There is a drive to develop materials that have both high nonlinearity and have ultra-fast response times (femtoseconds, 10^{-15} s), which would be invaluable for all-optical applications. Organic molecules have two properties that make them attractive candidates for this field of research: (1) they can form loosely bound electron systems (molecular wires) that have a strong optical response and (2) their physical characteristics can be easily tuned to fit a particular need. Previous work has shown that very large nonlinearities can come from large molecules, but when considering that the *density* of molecules in the solid state needs to be high for a high nonlinearity in the bulk material, the large molecules are not well-suited for application. Our research focuses on maximizing the third-order optical nonlinearity in organic molecules, while keeping their size small so they may be densely packed into a solid state material[1].

The molecules we are investigating are donor-substituted cyanoethynyl-ethenes. An example of one of our best molecules, TDMEE (1,1,2-tricyano-2-[(4-dimethylamino-phenyl)ethynyl]ethane) is shown in Fig. 1. The molecule consists of a N, N-dimethylanilino donor (i) and three cyano acceptors (ii). The ground state of the molecule is set by the donor and is shown in the orbital plot (**A**). The first excited state is set by the acceptors and is shown in orbital plot (**B**). The optical response in these types of molecules is dominated by the charge transfer from donor to accepter (**A** to **B**). This is also outlined in the figure, which shows the three possible transfer paths: (a) *trans* (b) *cis* and (c) *cross.*

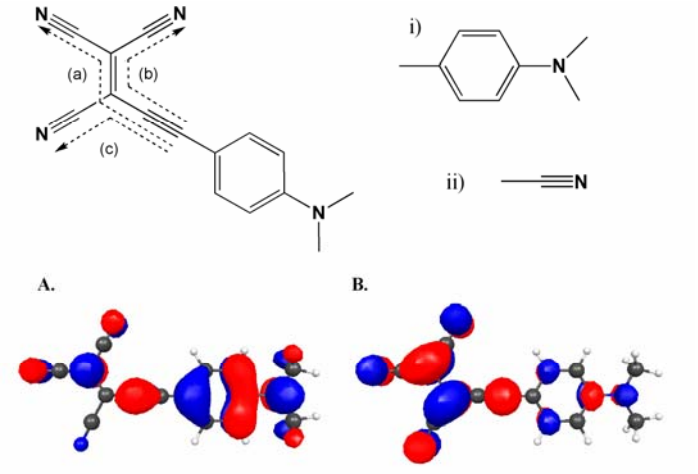

Fig. 1. The highly efficient third-order optical nonlinearity molecule, TDMEE. The figure is described in the text.

We use degenerate four-wave mixing (DFWM) to determine the nonlinearity of our molecules dissolved in solution. The DFWM technique measures the ability of a material to convert three

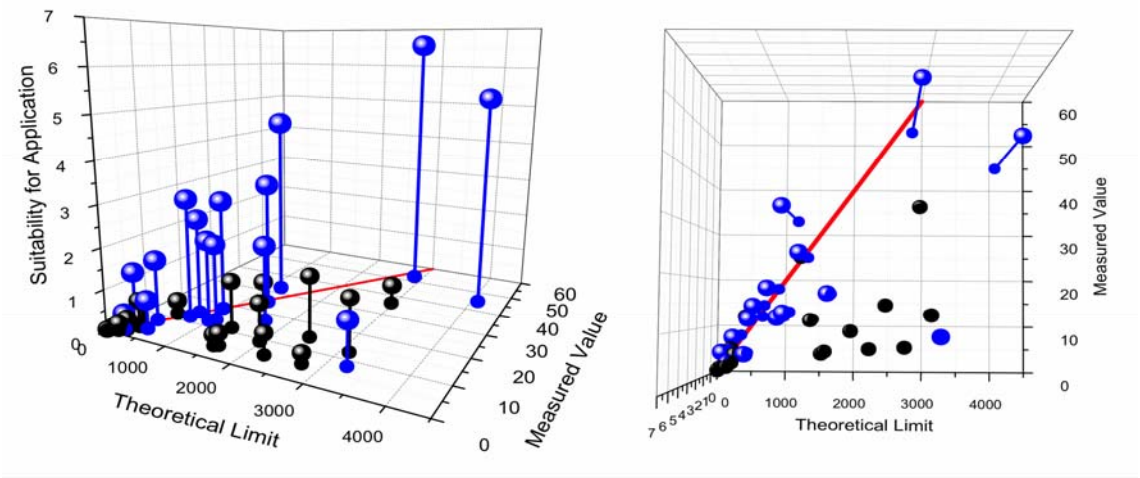

Fig. 2. The third-order optical nonlinearities (measured value) and the suitability for application for each molecule measured in this work (blue) are compared to those published in the literature (black) and plotted against the absolute maximum value allowed by quantum mechanics (theoretical limit). Left: Perspective that gives emphasis to the order of magnitude improvement that our molecules have in terms of their suitability for application. Right: Perspective that shows that our best molecules consistently fall within a factor of 50 (shown as red line) of the theoretical limit, which puts them among the best molecules measured to date.

incoming light beams into a fourth beam. This ability is directly related to the nonlinearity of the material and using simple considerations such as the concentration of molecules, we can determine the optical nonlinearity of each individual molecule.

The results for our molecules are presented in Fig. 2 and are shown in blue, the results from other publications are shown in black. The figure shows two perspectives of the same three-dimensional graph, where on the left, it is readily apparent that our molecules show an order of magnitude improvement in terms of suitability for application. On the right, the majority of our molecules fall within a factor of 50 of the theoretical limit (plotted as a red line), which is the current record for all molecules.

Through measurements and computer simulations we have been able to understand how the donors and acceptors lead to large nonlinearities in these small molecules. Our poster will discuss this in detail and we will also discuss our ideas for new molecules that we believe will lead to even more efficient third-order nonlinearities.

Joshua C. May is a fifth year PhD candidate in the Department of Physics working under Professor Ivan Biaggio and is also part of Lehigh's Class of 2000, where he graduated with an Engineering Physics degree. He is investigating the third-order nonlinear optical response in novel organic materials and is also using nonlinear optical methods to determine solid-state material properties. After completing his degree, he plans to seek a research position in industry or academia.

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[1] "*Highly Efficient Third-Order Optical Nonlinearities in Donor-Substituted CEE Molecules*." J. C. May, J. H. Lim, I. Biaggio, N. N. P. Moonen, T. Michinobu, F. Diederich, Opt. Lett. 30, 3057 (2005)
"*Property Tuning in Charge-Transfer Chromophores by Systematic Modulation of the Spacer Between Donor and Acceptor*." F. Bures, W. B. Schweizer, J. C. May, C. Boudon, J. Gisselbrecht, M. Gross, I. Biaggio, F. Diederich, Chem. Eur. J. (accepted for publication) (2007)
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