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Revisiting organic optical nonlinearity leads to a new class of materials

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Theory-guided definition of key structure and function relationships has dramatically improved the performance of organic nonlinear optical materials.

In the late 1980s and 1990s, researchers in industry and academia became captivated by so-called organic nonlinear optical (ONLO) materials, as is evident from SPIE Proceedings of that period. The ultrafast response of the π-electrons of ONLO materials to time-dependent electric fields—which translates into active control of light—clearly afforded a unique opportunity vis-à-vis ultrahigh (terahertz) bandwidth devices for information processing, computing, and sensing. The second- and third-order nonlinearities of ONLO materials also promised radically enhanced performance.

But the quantum and statistical mechanical theoretical methods needed to realize these advantages still had to be worked out.[1,2] Also, auxiliary material issues, including optical loss, thermal stability, and photostability, were neglected. Moreover, the processing advantages of ONLO materials, e.g., amenability to low-temperature techniques such as nanoimprint lithography[3] and compatibility with a wide range of disparate other materials and device architectures,[4–6] have only just begun to be explored and demonstrated. As a result, application of ONLO materials never moved past the prototype stage, and most companies abandoned their research and development efforts in the area. Lockheed Martin appears to be the noticeable exception: since 2000 the company's researchers have made substantial progress in understanding optical loss.[7,8]

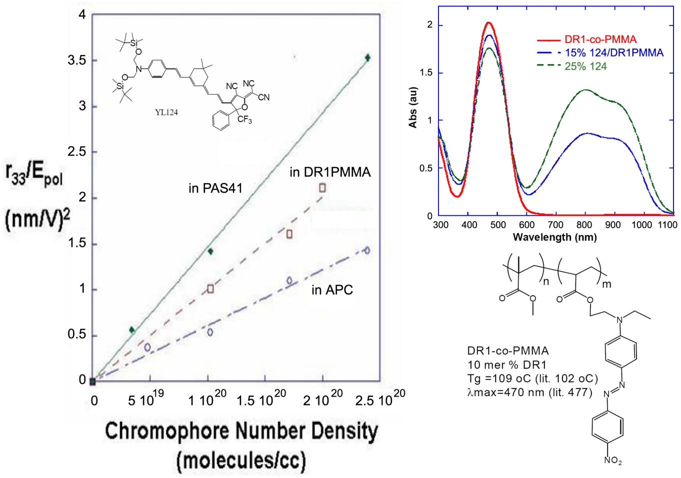

Figure 1. *The exceptional linear and nonlinear optical properties of BCOGs. (Left) The variation of normalized electro-optic activity (r33/E_{pol}, where r33 is the principal element of the electro-optic tensor and E_{pol} is the applied electrical poling field) with number density is shown for doping of the YL124 chromophore into different host materials. These are, respectively, a DR1-co-PMMA polymer (structure shown at the bottom right) and a multi-chromophore-containing dendrimer denoted as PAS41.[1,2] The doping leads to dramatic enhancement of electro-optic activity. (Right) BCOGs are also characterized by the absence of spectral line broadening and solvatochromic shifts, as shown in the graph. Abs: Absorption.*

Now, greater understanding of electro-optic activity and auxiliary issues, together with improved performance, has led to renewed attention to ONLO materials. This interest is heightened by their amplified response in devices with nanoscopic dimensions (e.g., slotted silicon photonic devices such as ring microresonators[4]). Electro-optic coefficients in the range of 200–450pm/V (at telecommunication wavelengths) have been observed in materials with optical loss on the order of 2dB/cm and material glass transition temperatures of 200°C. Superior organic electro-optic materials have resulted in drive (V_π) voltages in Mach–Zehnder interferometers as low as 0.3V.[9] These voltages suggest the intriguing possibility not only of achieving gain in radio frequency (RF) photonics (electrical-to-optical-to-

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electrical signal transduction) but also of realizing the potential of ONLO materials for commercial applications.

Real-time, time-dependent density functional theory[10] has led to better simulation of both linear and nonlinear optical properties (including dispersion and dielectric dependence) of molecules. Moreover, theory has guided the design of molecules with improved hyperpolarizabilities. But the major breakthrough in macroscopic optical nonlinearities has been new understanding of intermolecular electrostatic interactions derived from Monte Carlo/molecular dynamics statistical mechanical simulation algorithms.[2] These calculations have demonstrated the importance of chromophore (π-electron molecules with special optical properties) shape and of the covalent bond potentials that connect chromophores to supermolecular architectures such as dendrimers and polymers.

Theory has also inspired the development and use of a new class of ONLO materials, namely, binary chromophore organic glasses (BCOGs).[1,11] Intermolecular electrostatic interactions in BCOGs actually promote the high acentric order necessary for second-order optical nonlinearity, whereas in conventional chromophore/polymer composites they strongly favor centric order and highly attenuated electro-optic activity. The unique behavior of BCOGs is illustrated in Figure 1, which shows doping of the YL124 chromophore (see inset) into a conventional polymer (amorphous polycarbonate, APC) and two BCOG materials: a polymethylmethacrylate (DR1PMMA) and a 4000Da multi-chromophore-containing dendrimer (PAS41). The interaction between guest and host chromophores in BCOGs permits high loading without phase separation and leads to enhanced acentric order of the molecules.[1,2]

The DR1PMMA material permits further test of theory. Optical poling can be used to drive the DR1 chromophore (through photo-induced trans-cis-trans isomerization-induced molecular reorientation) toward either a Bessel or 2D lattice using linearly polarized light, or an Ising or 1D lattice using circularly polarized light. The consequence is a further increase in electro-optic activity as predicted by theory[1] with coefficients on the order of 400pm/V at 100V/μm electric poling fields (see Figure 1).

The variation of normalized electro-optic activity (r_{33}/E_{pol}, where E_{pol} is the electric poling field strength) with chromophore number density is shown for YL124 doping into APC (from Aldrich Chemical, first used by Lockheed Martin[7,8]), DR1PMMA (also from Aldrich Chemical, see lower right of figure), and PAS41.[2] At low number density, doping into a conventional polymer yields a linear dependence characteristic of noninteracting versions of the chromophores. At higher concentrations, the chromophores in conventional composite materials strongly interact. In addition, electro-optic activity decreases with increasing concentration: with densities of 4×10^{20} molecules/cm^3, activity is highly attenuated. In contrast, the BCOGs activity continues to increase in a linear manner to the highest densities ($>7\times10^{20}$ molecules/cm^3). The slope is greater than that of the 'noninteracting chromophore limit,' which suggests that electrostatic interactions between guest and host molecules favor acentric order. The behavior of linear optical properties is quite different as well. Doping chromophores into conventional polymers such as APC leads to spectral line broadening and solvatochromic (i.e., solvent-induced color change) 'red' shifts of the linear absorption spectra.[7,8] For BCOG materials, such effects are absent (see Figure 1, upper right).[1,2]

Thermal stability is defined by material glass transition temperature, and so-called Diels–Alder/retro-Diels-Alder crosslinking enables convenient production of materials with glass transition temperatures in the range 200–300°C.[1,12] Photostability is determined by singlet oxygen chemistry, and stability for given chromophores is increased by as much as five orders of magnitude by actions that inhibit singlet oxygen–related photodegradation.[13,14] It is also becoming more widely recognized that ONLO materials afford many processing advantages, including conformal and flexible devices by lift-off techniques,[15] as well as highly integrated (including 3D photonic circuitry) applications.[16] Novel structures, too, including ring microresonators,[4,17] have recently been demonstrated. Finally, ONLO materials appear to have potential advantages for space applications related both to weight and resistance to high-energy radiation.[18]

Over the past seven years, better knowledge of critical structure and function relationships has led to marked improvement in the performance of ONLO materials, in some cases exceeding a rate consistent with Moore's Law. These same relationships suggest even greater advances in the future. While ONLO materials are not likely to displace inorganic electro-optic and electro-absorptive materials, their unique properties of ultrafast response to electric fields, large optical nonlinearities, and their numerous processing and device fabrication options should promote new applications that are not possible with inorganic materials. Manufacturing cost (largely packaging) reduction and in-field reliability testing represent the most probable final hurdles that ONLO materials must pass before they can gain wide acceptance.

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