The Rational Design and Production of Organic Electro-Optic Materials and Devices

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Abstract
Recently, new theoretical design paradigms have facilitated the production of organic electro-optic materials that have been used to fabricate simple electro-optic devices characterized by halfwave voltages of less than 1 volt and demonstrated frequency response to above 100 GHz. Electro-optic circuitry has been vertically integrated with VLSI electronics and 3-D circuitry has been demonstrated. Several schemes have been introduced for overcoming the problem of mode mismatch leading to high insertion loss demonstrating that per facet losses of less than 1 dB can be achieved. New material design strategies have also resulted in dramatic improvement of auxiliary material properties: Optical loss has been reduced to values as low as 0.2 dB/cm, thermal stability of electro-optic activity has been extended to 250 C, and significant improvements in photostability have been achieved. These properties have not been achieved in the same material and the tradeoffs required are now becoming better defined. In this communication, we review the state-of-the-art of organic electro-optic materials and devices and the design paradigms that have defined that state-of-the-art. We present preliminary data suggesting that a design paradigm shift may lead to even more impressive improvements in the properties of organic electro-optic materials and devices fabricated from those materials.

Introduction and Chromophore Synthesis
The following steps are required to produce an electro-optic (EO) device based on organic materials: (1) Synthesis of chromophores characterized by large (> 10^{-44} esu) molecular first hyperpolarizability (β) dipole moment (μ) products, high thermal (> 300°C) and chemical stability, and good processability (e.g., solubility in spin casting solvents, etc.); (2) processing of these chromophores into acentric (electro-optic active) lattices by introduction of an appropriate host (dilutent) material and by application of an ordering force such as an electric poling field; (3) stabilization of acentric order by lattice hardening chemistry to facilitate subsequent EO circuit and device fabrication; (4) fabrication of buried channel electro-optic waveguides by reactive ion etching (RIE) or photolithographic techniques, deposition of cladding layers and metal drive electrodes; and (5) execution of all remaining steps necessary to achieve integration with optical transmission lines and VLSI drive electronics [1-3]. Organic EO chromophores are dipolar (charge-transfer) molecules consisting of an electron donor, an electron acceptor, and a pi-electron bridge providing communication between the donor and acceptor moieties. Control of single/double bond length alternation is critical to maintain pi electron communication between the donor and acceptor and thus to optimization of molecular hyperpolarizability. Bridges containing aromatic and heteroaromatic groups yield excellent thermal and chemical stability; however, the larger bond length alternation of these species frequently results in poor molecular hyperpolarizability. The largest hyperpolarizabilities have, to date, been obtained with protected polyene and multiple (including fused) thiophene ring containing bridges. A typical chromophore meeting the criteria of high hyperpolarizability and thermal stability is shown in Figure 1, which also shows the synthetic scheme used to produce the chromophore. In Figure 2, we show electro-optic data recorded for thin films of this chromophore dissolved in amorphous polycarbonate (APC) [4] to form a composite material. Electrically poled APC composite films typically exhibit waveguide loss of 1-1.5 dB/cm at the telecommunication wavelengths (1.3 and 1.55 μm). Such loss values are typically a combination of absorption (from C-H, N-H, or O-H vibrational overtones) and scattering (processing—spin casting, poling, and waveguide fabrication) losses. Reduction of loss to values less than 1 dB/cm requires reduction of proton density in both chromophore and host materials (e.g., by replacement of H with F) and attention to the details of processing to minimize scattering losses [1-3]. The thermal stability (the temperature at which > 95% EO activity is observed after 1000 hours) of poling-induced electro-optic activity of chromophore-APC composite materials typically lies in the range 60-80°C. Temperature stability can be increased by 20-50°C, or even higher, by lattice hardening chemistry that introduces covalent bonds tethering the chromophore at both ends to a 3-D crosslinked lattice. Stability is also enhanced by increasing the segmental rigidity of the host lattice (an EO chromophore is already a moderately stiff object due to the conjugated pi electron structure). Temperature stability can even be increased to above 200°C; however, more typical values lie in the range 100-125°C. Unfortunately, some attenuation of electro-optic activity is associated with the lattice hardening process, as both poling and lattice hardening are temperature-dependent processes.
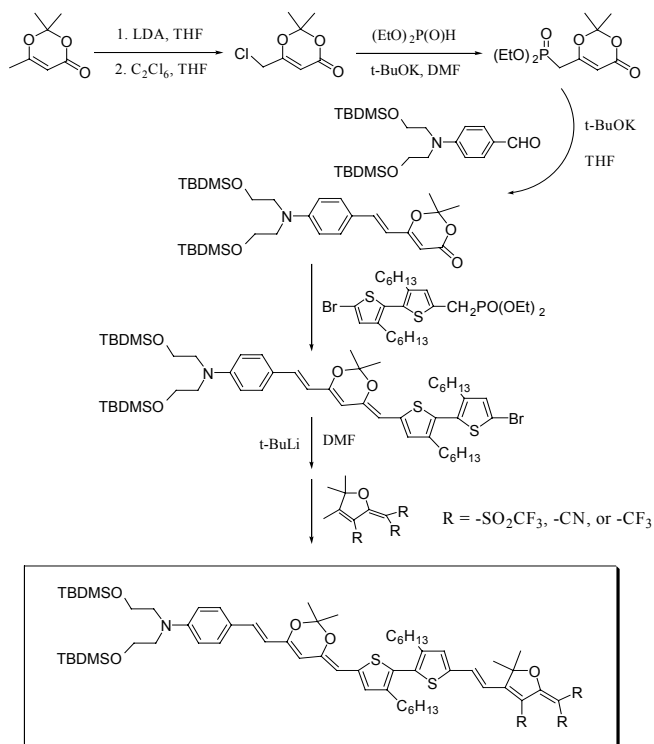
Figure 1: Synthesis of the CWC chromophore (R = CN) is shown. Removal of the dithiophene bridge gives the commonly used CLD chromophore.
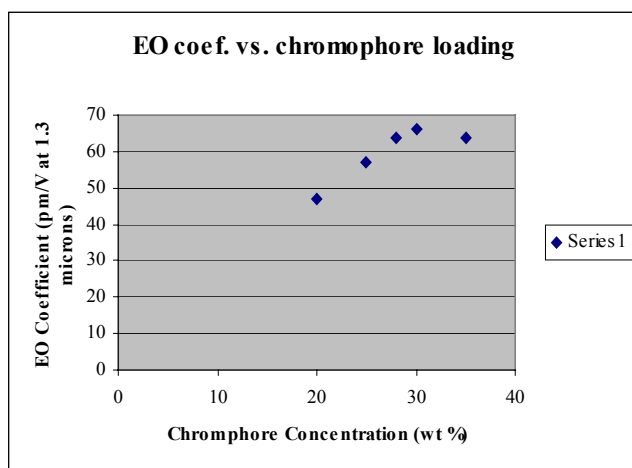

Figure 2: Electro-optic activity at 1.3 microns as a function of concentration of CWC in APC.

The details of processing (e.g., stepped electric field/temperature poling protocols) necessary to minimize the tradeoff between optimized electro-optic activity and the thermal stability of that activity has been discussed elsewhere [1-3,5,6]. Unless care is exercised lattice hardening can lead to phase separation with resulting dramatic increase in optical loss. Indeed, lattice hardening, which is critical to both thermal and photochemical stability of organic EO devices, is the most demanding aspect of the fabrication of organic EO devices.

The photostability of organic EO devices is defined by reactions that chemically disrupt pi electron conjugation by substitution (oxidation) or by bond breaking. Photochemical decomposition is typically dominated by singlet oxygen pathways. As shown in Figure 3, partial exclusion of oxygen results in dramatic improvement in photostability.
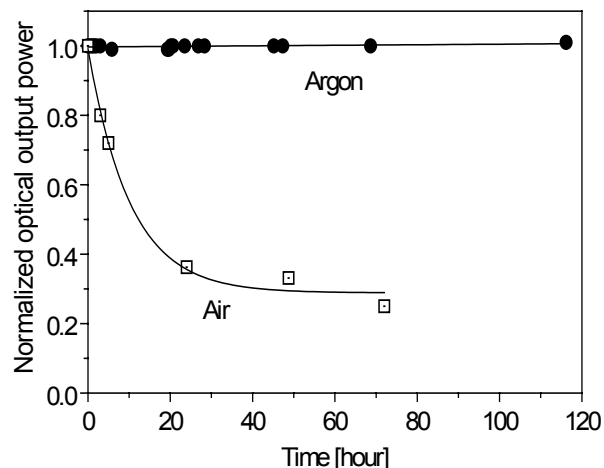

Figure 3: The photostability of an EO modulator fabricated from CLD/APC for a waveguide power of 20 mW (λ = 1.55 μm).

Photostability can also be improved dramatically by lattice hardening and by the incorporation of scavengers. Lattice hardening acts to both decrease oxygen diffusion rates and to promote the recombination of radicals formed by bond breaking. Photochemical stability can also be improved by eliminating points of chemical reactivity in the pi electron structure or by modification of chromophores to sterically protect those sites.

Theory and Acentric Order
A major problem in the development of organic electro-optic materials is the aggregation (centrosymmetric lattice crystallization) of chromophores at high concentrations. This chromophore intermolecular association both attenuates the maximum achievable electro-optic activity (see Figure 2) and at the highest concentrations leads to optical loss due to light scattering from aggregates. It is driven by chromophore intermolecular electrostatic (dipole-dipole) interactions, which compete with dipole-electric poling field driven acentric ordering. Not only do intermolecular dipole-dipole interactions lead to a maximum in graphs of electro-optic activity versus chromophore loading but the detailed shape of the curves and the position of the maximum

depends upon molecular dipole moment and chromophore shape. Several years ago we realized that to optimize electro-optic activity we needed to have a theory that was capable of quantitatively predicting the maximum electro-optic activity that could be achieved for a given pi electron backbone structure and how that activity depends upon the details of chromophore structure and processing conditions. For chromophores dissolved in polymers such as APC, the problem can be treated using statistical mechanical methods providing that a realistic potential function describing long-range interaction among many chromophores could be defined. We have shown that such a potential function can be defined either analytically or by Monte Carlo calculations [7]. As shown in Figure 4,
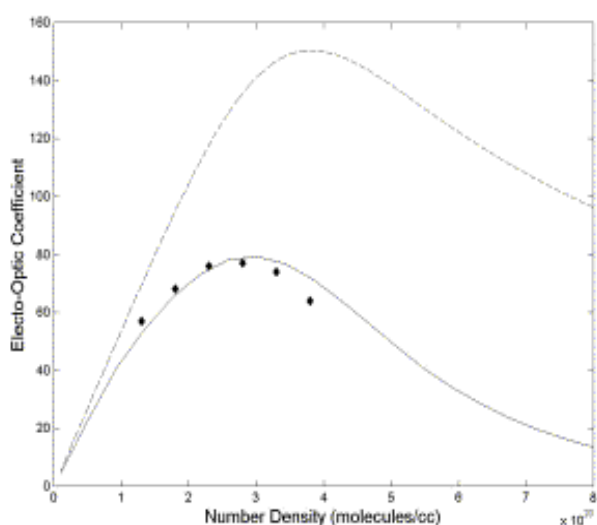

Figure 4: Comparison of experimental (symbols) and theoretical (lines) EO activity (at 1.06 μm) is shown for a CLD chromophore/polymer composite. The lower curve is for a prolate ellipsoid structure with dimensions matching the chormophore. The upper curve would be obtained if the chromophore were of spherical rather than ellipsoidal shape.

theory provides a simple prescription for improving electro-optic activity; namely, modification of chromophores to make them more spherical in shape. Simple derivatization of the bridge region of chromophores resulted in factor of two improvement of EO activity for the same pi electron backbone [8,9]. Theory also permits ready definition of the chromophore/host material composition that leads to optimum electro-optic activity and explains why maximum obtainable electro-optic activity is only weakly dependent on electric poling field strength for high dipole moment chromophores.

Recently, we have observed that use of dendritic synthetic schemes provide a systematic method of altering chromophore structures to make them more spherical [1,3,10]. A new fabrication

paradigm has been suggested by the synthesis of multi-chromophore-containing dendrimers [3,10]. Not only is electro-optic activity of chromophores improved in dendrimer structures compared to the same chromophores in conventional polymer hosts but also thermal stability and optical loss is improved. The improvement in electro-optic activity is easily understood in a qualitative sense when it is realized that the covalent bonds of dendrimer structures act to sterically inhibit centrosymmetric aggregation (crystallization). The branched nature of dendrimers naturally leads to reduced proton density in materials and the homogeneous size distribution of dendrimers leads to very uniform crosslinked 3-D material lattices. Polymers, by the very nature of variable chain lengths and packing, are naturally more heterogenous with chromophores existing in regions characterized by different free volumes. The nature of dendrimers, however, leads to a theoretical complication. Chromophores can no longer be adequately approximated as rigid objects moving in a medium of uniform viscosity and dielectric constant. The segmental flexibility of dendrons and the folding/packing of dendrimers under electric field poling must be understood to predict electro-optic activity. Atomistic kinetic Monte Carlo calculations are required to predict results and more sophisticated simulations codes must be developed before theory can usefully guide the development of new materials.

Devices: Active Wavelength Selective Filters
The fabrication of 3-D EO circuitry and low insertion loss device structures has been described elsewhere [11] as has the vertical integration of organic EO circuitry with semiconductor VLSI circuitry [2,3]. A variety of prototype devices have been demonstrated including photonic radiofrequency phase shifters for phased array radar applications [12], time stretching devices for ultrafast A/D conversion [13], ultrahigh bandwidth oscillators [14], acoustic spectrum analyzers [15], a variety of optical switches and intensity modulators [3,16], laser beam steering devices [17], and optical gyroscopes. Halfwave voltages as low as 0.7 volts and bandwidths as high as 113 GHz have been reported for simple device structures.

Military and civilian telecommunication data handling applications are logical candidates for high bandwidth, low drive voltage organic materials. While organic EO devices have bandwidths that may permit massive data handling requirements to be met simply exploiting time division multiplexing, it is interesting to explore organic EO materials and devices for wavelength division multiplexing (WDM) applications and particularly for chip scale WDM. The critical element is a wavelength selective filter shown in Figure 5. In preliminary studies, we have investigated the performance of simple ring
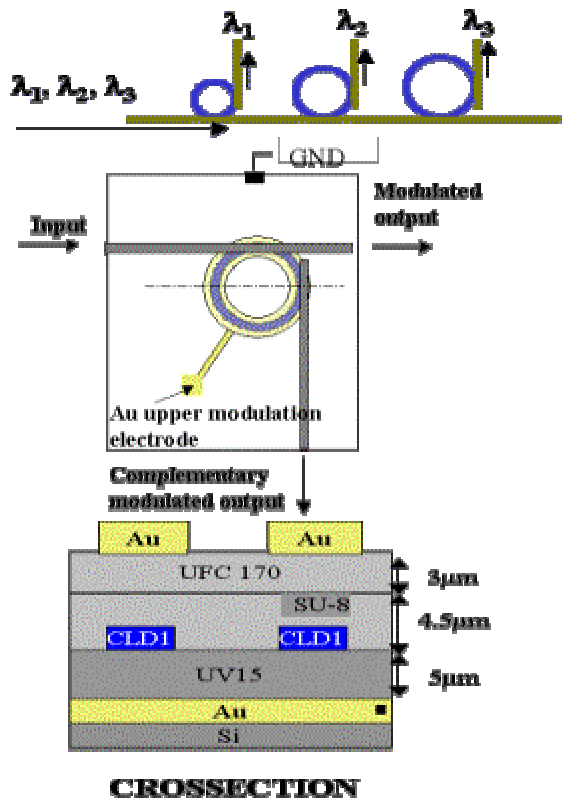
Figure 5: The dimensions of the ring microresonator determines the wavelength selected. Various views of the microresonator are shown.

microresonator structures for both analog and digital data handling and for operation at both 1.3 (see Figure 6) and 1.55 telecommunication bands.
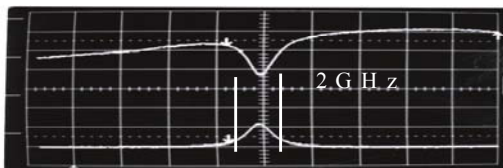

Figure 6: The response of a 200 μm radius ring resonator at 1.310 microns wavelength is shown. Q = 1.3 x 10^5, $\Delta\lambda$ = 0.01 nm, FSR = 0.8 nm.

At 1550 nm, we observed for a 20 mm radius ring a Q of 10,000 and a free spectral range (FSR) of 10 nm. A Teflon cladding was used to increase the index contrast. In Figure 7, we show the digital response.

Figure 7: Eye diagram, 1 Gb/s, V$_{peak}$ = 1 V.

The performance of these prototype structures, including photostability, is surprisingly good.

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