A NIRT on Organic Opto-Electronic Materials

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Design, synthesis and processing of new nanoscopic organic supermolecular architectures with greatly enhanced electronic and photonic properties has been accomplished. Two preparations of dipolar (noncentrosymmetric or ferroelectric) bulk material lattices are illustrated below.

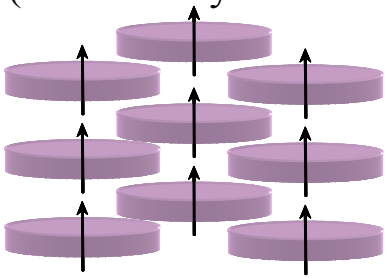

Fig. 1. New statistical mechanical methods explicitly considering the interplay of electronic and nuclear repulsive intermolecular electrostatic interactions are employed to predict the assembly of dipolar molecules of various nanoscopic shapes under the influences of electric poling fields and/or deposition surfaces. Discotic shapes such as shown to the right lead to dipolar material lattices exhibiting record hyperpolarizability and charge mobility..

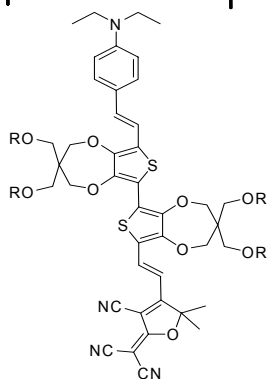

Fig. 2. One example of experimental implementation of theoretically-suggested structures is shown to the right. Systematic variation of the R groups by dendritic synthesis permits the molecular shape to be varied from prolate to oblate ellipsoidal leading to factors of 3 improvement in macroscopic (bulk material) electro-optic activity. Note that pi electrons dominate electronic interactions while all atoms including the ether substituents influence nuclear repulsive interactions. Molecular assembly is defined by controlling the interplay of these two anisotropic intermolecular interactions. This research accounts quantitatively for the formation of "H" and "J" molecular aggregates.

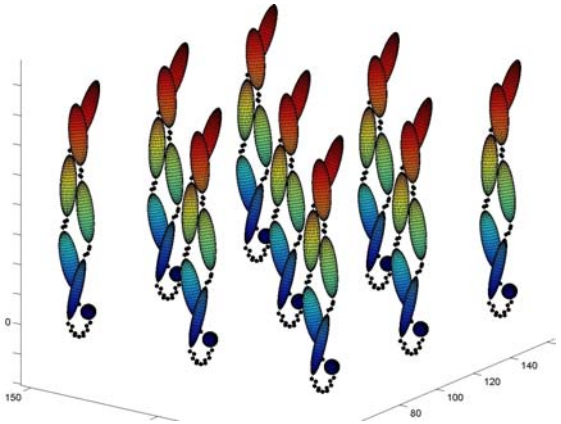

Fig. 3. Potential functions associated with covalent bonds and ionic charges also influence the nanoscopic assembly of molecules. Pseudo-atomistic calculations (where stiff molecules are treated in the united atom approximation and flexible segments are treated atomistically) permit prediction of final macroscopic structures as a function of variation of components. In the figure at the right, the assembly of prolate ellipsoidal nonlinear optical chromophores into a dipolar lattices is predicted theoretically. Again, dendritic synthesis schemes have been utilized to achieve experimental implementation of theoretically predicted structures with improved electronic and photonic properties.

Nanostructural engineering at the molecular and supermolecular level together with new nanofabrication techniques have permitted realization of the record performance for electro-optic, photovoltaic, and organic electronic (organic field effect transistor, OFET) devices.

Supermolecular Nanoscopic Engineering: This work has permitted, for the first time, the theoretically-inspired and systematic engineering of noncentrosymmetric material lattices with revolutionary properties; this has been achieved by nanoscopic control of intermolecular electrostatic interactions that drive molecular assembly (crystalization). Nanoscopic control has required the development of new synthetic chemistries and processing methodologies. The important consequence has been order of magnitude improvements in electro-optic activity (relevant to the control of electrical and optical signals central to information processing, display, and sensing) and charge mobility (central to the performance of photovoltaic and electronic devices).

Fundamental challenges include understanding, for the first time in a quantitative manner, the role that strong intermolecular interactions among high dipole moment molecules has upon molecular order, e.g., the formation of ferroelectric or anti-ferroelectric material lattices. Other fundamental challenges include developing new synthetic and processing protocols for the realization of theoretically-inspired nanoscopic supra- and super-molecular structures leading to improved material performance.

Achievements include the development of new theoretical methods for condensed matter physics and the synthesis and characterization of new and radically different nanoscopically ordered objects. These new materials were fed into a program developing new fabrication methodologies for the realization nano- and microscopic device structures.

Nano- and Microscopic Fabrication: Techniques such as soft lithography (popularized by Professor George Whitesides at Harvard and basically involving the development of device structures by "printing", "molding", or "stamping") have been used to fabricate a variety of "stripline" and "ring microresonator" electro-optical and all-optical device structures. Soft lithography has the potential for dramatically reducing manufacturing costs. To realize the importance of this consider the following: Lithium niobate modulators typically cost $5,000 to $50,000 for a single modulator. Lithium niobate modulators are inflexible and cannot be directly integrated with semiconductor electronics or silica fiber optics. In contrast, a hundred or more organic electro-optic devices can be fabricated directly on top of a semiconductor electronic wafer. Flexible and conformal devices are readily fabricated. Organic electro-optic devices are very light and do not damage with exposure to space-based radiation (e.g., gamma rays). These latter characteristics make organic electro-optic materials ideal for satellite (space) based applications such as phased array radar antennae. Processing methodologies, such as soft

lithography, could reduce manufacturing cost to a few dollars per modulator. Soft lithography fabrication is illustrated in Fig. 4.

Fundamental challenges include developing electro-optic materials appropriate for nanofabrication methodologies. For example, the development of "hardened" materials using "Retro-Diels-Alder" chemistry represented a new and extremely important advance in soft lithography processing. Retro-Diels-Alder materials are "hard (crosslinked)" at low (device operating) temperatures but "soft" (uncrosslinked) at high (device stamping or soft lithography processing) temperatures.

Achievements include fabrication of both stripline (e.g., Mach Zehnder interferometer or electrical-to-optical signal transducers) and ring microresontor (for active wavelength division multiplexing or color coding of telecommunication information; optical switching or optical network reconfiguration; laser wavelength tuning; etc.).

Why is realization of order of magnitude improvement in electro-optic (Pockels coefficient) activity and charge (electron and hole) mobility important? With the electro-optic coefficients that we have realized, device drive voltages on the order of 0.2 V can be achieved. This permits integration of photonic (e.g., silica fiber transmission circuitry) directly with the fast families of electronic devices enabling data handling at terabit/sec rates. Costly and bandwidth limiting amplifiers can be avoided. The bandwidths of several of the devices that we fabricate are in the ten terabit/sec range and device 3 dB bandwidths of 200 GHz are quite common. Devices based on organic electro-optic materials afford order of magnitude advantages over devices based on current inorganic materials in terms of drive voltage requirements, power consumption, bandwidth, weight, and cost. From another perspective, large electro-optic coefficients permit, for the first time, gain to be realized in the electrical-to-optical-to-electrical signal transduction process. Such signal transduction is central for example to downloading computer files to the internet. However, the impact is actually much larger as a great many new devices relevant to defense, telecommunications, computing, transportation, and entertainment depend of the material properties that we are advancing. For example, optical gyroscopes, ultrafast analog-to-digital converters, spatial light modulators, optical switches, etc. are being developed from our materials.

Tangible impact: One publicly traded (Nasdaq) company (Lumera Corporation of Bothell, WA) has been developed from the IP associated with our SIRG and NIRT grants. The research noted here has strongly influenced companies such as Boeing, Intel, Lockheed Martin, Corning, and Lucent to pursue research in the area of organic electro-optic devices. A variety of small businesses (such as Microcoatings Technologies) are also pursuing research based on our materials. Federal programs in several defense agencies have been launched.

Why is the realization of charge (electron and hole) mobilities greater than 1 cm2/Vs important? Stated simply this is necessary to achieve acceptable light conversion efficiencies (on the order of 10% or greater) for organic photovoltaics and acceptable performance of organic electronic devices. We believe we currently define the state-of-the-art of organic electronics and have achieved a significant breakthrough.

Other outcomes: The materials developed in this program have also led to record performance for organic light emitting devices (OLEDs) and various types of sensors including sensor paints used in wind tunnel testing of aircraft and land vehicle designs. This has led to important patents, licensing, and start-up activity.

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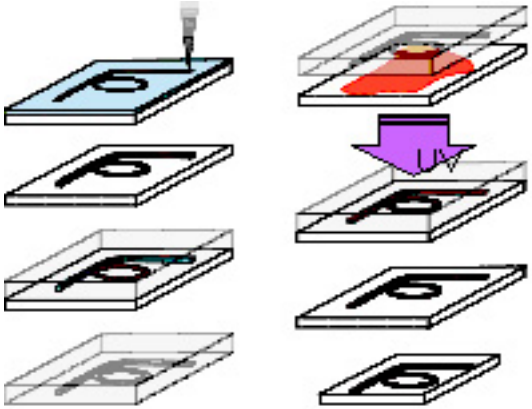

Fig. 4. The fabrication of an electro-optic ring microresonator by inexpensive soft lithography (i.e., stamping, molding, or printing) is schematically illustrated. On the left side, the preparation by e-beam etching of a master device (optical filter) is shown in blue. The master is then used to prepare a stamp. The stamp is then pressed into an electro-optic material (shown in red) and a replicate device structure is produced. The stamp can be used many times resulting in low-cost, mass production of the device structure. Typically, ring microresonator device structures range in size from several hundred nanometers to two hundred microns (smaller than a human hair in diameter).

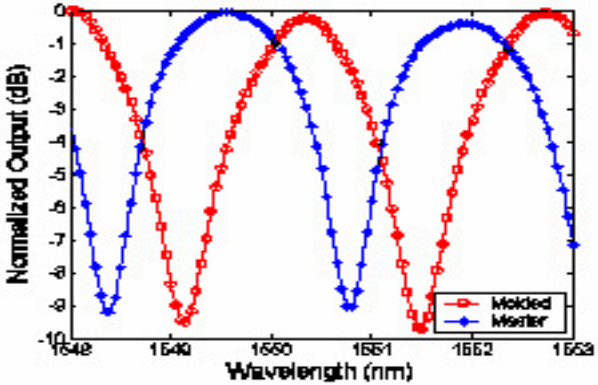

Fig. 5. The performance of master (blue) and replicate (red) ring microresonator optical filters is compared to the right. No degradation in performance is observed in the stamping process. Note that for an electro-optic filter the positioning of the pass band (the offset between the red and blue curves) is tuned by the application of a voltage. Both all organic and hybrid (silicon photonic/organic electro-optic) active optical filters have been fabricated. With all organic structures, both conformal and flexible device structures have been produced. Stripline structures have also been fabricated.

Education and Knowledge Transfer:

Chapters in *Encyclopedia of Modern Optics* and *Kirk-Othmer Encyclopedia of Chemical Technology*. Edited special issue of the *Journal of Physical Chemistry*. Eastman Lecture at the University of Akron. Special symposia at GE Global Research and Intel. Organized AAAS Symposium on 21st Century Photonics. Delivered ACS, IEEE and SPIE tutorials. Frontiers in Nanotechnology course developed and taught.

Soft lithography (low cost stamping or printing) techniques have been developed and used to fabricate stripline, cascaded prism, and ring microresonator photonic device exhibiting record performance. Highly flexible and conformal device structures have been demonstrated.

Soft lithography (stamping or printing), as illustrated in this slide, affords the potential for low cost manufacture. Moreover, conformal and flexible device structures have been fabricated. This research has proven to be immediately relevant to industry and intellectual property (joint with Boeing Corporation as well as independent of commercial companies but licensed to various corporations) has been developed. A variety of novel device structures have been fabricated including coupled ring microresonator systems appropriate for active wavelength division multiplexing (WDM), optical routing (reconfigurable optical interconnection), laser wavelength tuning, etc.

This research has served as the basis of new course material used in several courses including the flagship course of the UW Nanotechnology Ph.D. program (Frontiers in Nanotechnology). Invited lectures have been presented at symposia around the world.

Critical chapters in technology reference sources have been invited and prepared.