Engineering organic materials for hybrid electro-optics

Larry Dalton

A new molecular template permits nano-engineering of soft matter materials to optimize optical and optoelectronic properties.

Organic materials offer exceptional electro-optic activity, bandwidth, and processability. They are also low-cost, flexible, and compatible with diverse materials. Hybrid devices (that combine organic materials with silicon technologies) offer chip-scale integration of electronics and photonics, which could support applications in telecommunications, high-performance computing, radio-frequency (RF) photonics, and sensing technologies. Such integration requires organic materials that are adaptable to a range of processing options and conditions. They also need to have optimal optical and optoelectronic properties, which depend on order and lattice dimensionality. It has proven very difficult to prepare organic (soft matter) materials with the high molecular order and reduced (2D or 1D) lattice dimensionality needed to optimize technologically relevant physical properties such as electro-optic activity. Organic materials are typically randomly organized 3D structures dominated by van der Waals interactions that do not impart any spatial preference.

Previously, the dominant technique for controlling order in organic electro-optic materials used shape-engineering of fundamental electroactive molecular units called chromophores to control their packing.1 We recently introduced a new paradigm for systematic and theory-guided preparation of soft matter materials with the desired molecular order and dynamic properties (viscoelasticity) necessary for materials processing and device fabrication.2,3 We created a molecular template using a chromophore (an active \(\pi\)-electron moiety) that is modified to allow dipolar or quadrupolar chemical groups to be attached at critical points (see Figure 1).

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Figure 1. Molecular units or chromophores of FTC (thiovinylene or heteroaromatic bridge)-type or CLD (isophorone-protected polyene bridge)-type are modified to permit attachment of dipolar or quadrupolar moieties at points A, B, C, and D. Chromophore cores can be modified to control close chromophore approach while the dipolar and quadrupolar moieties are used to control long-range chromophore cooperativity and organization.
The desired electroactivity arises from the conjugated π-electrons of the fundamental chromophore (molecule) in the template while the systematically incorporated intermolecular soft interactions control chromophore organization (order and lattice dimensionality) and length scale of chromophore molecular cooperativity (dynamics).

These soft interactions control the phase transitions of materials, such as the temperature of glass transition as well as that of transitions to lattices of reduced dimensionality. They also offer control over viscoelasticity, which is necessary for materials processing, for example in melt processing, molding, nanoimprint lithography, and electric field poling. By selecting the spatially anisotropic dipolar or quadrupolar interactions used, molecular cooperativity can be tuned from a few nanometers to nearly a micron and lattice dimensionality can be tuned from 3D to nearly 1D with corresponding tuning of phase transition temperatures. If melt processability is desired, however, care must be taken to avoid strong intermolecular interactions that elevate material glass transition temperatures above material decomposition temperatures.

For a material to have electro-optic activity it needs to be different on either side of a plane drawn through its center (acentric order). Lattice symmetry can have a dramatic effect on the efficiency of electric field poling, for example, by introducing acentric order in a dipolar chromophore system near its glass transition temperature (see Figure 2).²³ Electro-optic activity can be measured to characterize acentric order.²–⁴ Cenetric order, where the material is the same on both sides of a central plane, can be defined using variable angle spectroscopic ellipsometry and/or variable angle polarization referenced absorption spectroscopy.⁴⁻⁵ The ratio of these order parameters can be used to define lattice dimensionality, including fractional dimensionality.²⁻⁴ Fractional lattice dimensionality can provide a continuous measure of the effect of intermolecular electrostatic interactions of various strengths in defining molecular order. Dynamic techniques, such as shear modulation force microscopy (see Figure 3), intrinsic friction analysis, and dielectric relaxation spectroscopy, can be used to define phase transitions associated with changes in lattice order and symmetries, the length scale of molecular cooperativity, and thermodynamic properties defined by the various interactions.³⁶

Combining data from order parameter measurements and measurements of dynamics provides a very complete picture of the effect of selectively incorporated dipolar and quadrupolar interactions. This understanding can also be further enhanced by nuclear magnetic resonance, x-ray, and neutron scattering techniques.

Our template for exploiting spatially anisotropic intermolecular interactions for engineering materials with desired order and

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**Figure 2.** The variation of acentric order (<cos^3θ>) versus normalized electric poling field energy f is shown as a function of lattice dimensionality.³ The shaded area is the region relevant to practical poling experiments. (Reprinted from reference 3 with permission of the American Chemical Society.)

**Figure 3.** The shear modulation force microscopy of a typical template material (coumarin molecules attached to the A and D positions of a FTC-type chromophore) is shown. The region between T_1 and T_g corresponds to a region of approximately 2-D order.³ a.u.: Arbitrary units.
dynamics can be considered to be analogous to the engineering of organic molecules starting with the atomic template of hybridized carbon. By realizing covalent bond symmetries defined by hybridization of carbon and nitrogen atomic orbitals, Linus Pauling was able to anticipate the helical structures of proteins and DNA. In a similar manner, we have produced ordered helical structures exploiting soft (non-covalent-bonding) intermolecular interactions and the template. In designing our template, we were motivated by the need to modify chromophores for a broad range of hybrid material device applications.\(^7\)\(^\text{-}^{10}\) The template can be generalized to different core and pendant structures. Further control can be achieved by systematic variation of the shape of the core and the total molecular weight of the macromolecular unit.

In conclusion, we developed a template for introducing soft interactions at specific points on a core molecule. The result is an organic material that naturally organizes into a lattice of molecules of defined symmetry. This gives control over order, which defines photonic and electronic properties, as well as viscoelasticity, which gives processability. We are currently exploring stronger soft spatially anisotropic interactions that push closer to the 1D lattice dimensionality limit. We are also exploring the integration of organic electro-optic materials into a variety of silicon, silicon nitride, plasmonic, and metamaterial device architectures, including novel metamaterial phased-array radar receivers and transmitters.

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**Author Information**

Larry Dalton  
University of Washington  
Seattle, WA

Larry Dalton is the Seymour Rabinovitch Chair Professor of Chemistry and Electrical Engineering at the University of Washington. He is the founding director of the National Science Foundation Science and Technology Center on Materials and Devices for Information Technology Research.

**References**