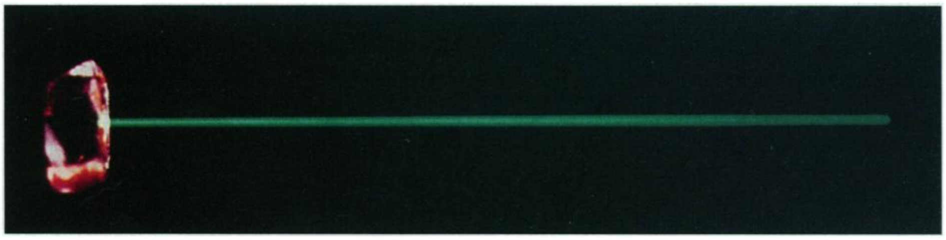
Plastics That Play on Light

By minutely tailoring molecules and their arrangement, researchers are turning out organic materials that could serve as switches and transformers in future optical circuits

When light passes through a sheet of glass or a pool of water, the process seems utterly stealthy. Yet, in fact, the light vibrates electrons in those materials—ringing them like the strings of a musical instrument. In most materials, the "strings" respond with the same note, only louder, when played harder, with brighter light. The frequency of the vibration remains the same. That's why light of any intensity passing through a window emerges basically unchanged, save for being weakened or bent by refraction.

But in certain optical materials, the instrument transforms the notes. Take a quartz crystal, for example. Shine a beam of light from a common infrared laser at it and you would expect infrared to emerge. But that's only part of what actually happens. Some infrared light does make it through—but if the beam is bright enough, some of the light will be transformed to green, because its frequency is doubled as it passes through the crystal.

Frequency doubling, commonly used to change the wavelength of laser light, is only one example of a nonlinear optical (NLO) effect: an effect that arises when light itself changes the optical properties of a material. Other NLO effects alter transparency or refractive index. Far from being curiosities, these effects enable materials to, say, become opaque to protect sensors or eyes the moment an intense flash of light strikes them, or to serve as optical switches—the optical analogue of a transistor—in which one beam of light can redirect a second beam. As technologies for communicating and computing with light take shape, the search for NLO materials that are good at manipulating light while still being practical as materials is heating up. And much of that heat is coming from the effort to develop nonlinear optical polymers.



The greening of a laser. An inorganic crystal doubles the frequency of infrared laser light, an effect that materials scientists are trying to reproduce in polymers.

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Traditional NLO materials are mostly inorganic crystals, such as quartz, lithium niobate, and potassium dihydrogenphosphate—all fragile, hard to grow as large crystals, and vulnerable to cracking under intense laser light. Organic molecules, incorporated into plastics, should fit the bill much better, says materials scientist David Bloor of Durham University in England: "Polymers are the ideal materials for mass applications." As chemist Harry Milburn of Napier University in Edinburgh explains, "[Organics] can be molded and crystallized and applied as coatings, and they are robust." What's more, because of organic chemistry's power to tailor materials at will, investigators see the potential for much larger nonlinear effects in organic molecules than in traditional materials.

So far, though, says materials scientist Simon Allen of ICI's Materials Research Center in Wilton, England, "device manufacturers do not see organics as being quite good enough." The NLO effects in many materials haven't been strong enough for application. Nor have they been persistent enough; in many of the polymers devised so far, subtle molecular rearrangements eventually wipe out the nonlinear behavior. But in the past few years, Bloor, Allen, and others have been tailoring the molecules and their arrangements to transcend those limitations. The result: relatively stable organic materials whose nonlinear behavior approaches that of lithium niobate, now a staple of nonlinear optics.

Molecular harmonies

Guiding this new molecular tailoring is an understanding of how the NLO effects arise. When the electric field of light vibrates the electrons in a material, it produces a secondary field at the same frequency as the light—the displacement of the electrons is linearly related to the strength of the light's field. But if the field is strong enough, the vibrating electrons themselves induce another, changing electric field, which in turn affects the electrons. The result is something like a violin note: a complex mixture of the fundamental frequency and harmonics, rather like the overtones of the violin, that have two, three, or four times the frequency of the fundamental. This response has a complex, "nonlinear" relation to the field strength.

In most optical materials, these effects are slight, and the fundamental is the main note sounded. But in NLO materials, the electrons are exceptionally easy to polarize, or displace along the molecule, yielding a strong response at one or more of these harmonics. The harmonic at twice the original frequency, for instance, generates light at twice the frequency of the incoming beam. Materials that generate a strong second harmonic signal can serve as frequency doublers for lasers, yielding shorter-wavelength beams that can be focused more precisely. Because these "second order" materials also change their refractive index in response to an ordinary electric field, they have also found their way into electro-optic switches for communications, in which an applied voltage causes the material to switch a light beam from one path to another or turn it on or off.

To allow the electrons to oscillate freely, NLO polymers generally have double or triple bonds alternating with single bonds between the carbon atoms along each long polymer or molecule. Electrons in these "conjugated" bonds aren't pinned down, as in most compounds, but are free to skip up and down the molecule in step with the oscillating electric field of light. For strong second-order effects, however, there's another requirement: The material must also have an electronic asymmetry, so that the electrons, like springs, are "stiffer" in one direction than the other. Otherwise the oscillation of the electrons in one direction cancels the oscillation in the other and no second harmonic is generated.

One way to create that kind of asymmetry in a molecule or polymer is to create a "donor-acceptor" or "push-pull" compound. An electron-attracting chemical group—a nitro, for example, consisting of a nitrogen atom attached to two oxygens—gives a pull at one end, and an electron-repelling group such as a methoxy, consisting of an oxygen attached to a methyl group, gives a push at the other. Many researchers have fashioned such lopsided molecules. But preventing adjacent molecules from canceling out each other's effects by aligning head to tail, or push to pull, has proved difficult.

Milburn and his team are trying to do so by building short push-pull molecules, then locking them together in the right orientation in a polymer. They start with diacetylene molecules—short, four-carbon units with alternating triple and single bonds—then add push and pull groups to these monomers. They orient the monomers with a weak electric field, then apply heat, light, or gamma rays to link the monomers into a chain, forming a polymer. Because the pushes and pulls all maintain the same orientation, the polymers preserve the asymmetry needed for strong second order effects. In fact, the strategy paid off in polydiacetylene polymers more effective at frequency doubling than lithium niobate.

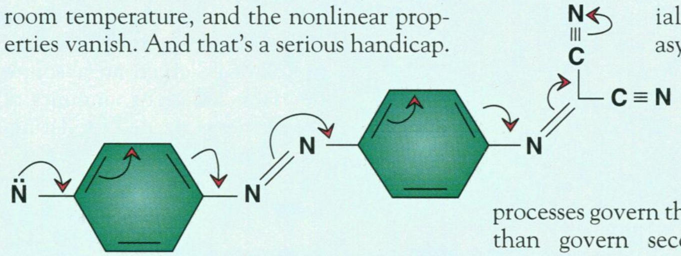
Seth Marder and his colleagues at the California Institute of Technology and DuPont, meanwhile, are looking for ways to produce stronger second-order effects by easing the passage of electrons across the links between push-pull groups. Standard nonlinear molecules often contain carbon rings, like benzene, in place of some of the straight links. But the rings, Marder and his group found, often interfere with the asymmetric oscillations needed for strong second order effects, because the stable arrangement of electrons around the ring—their "aromaticity"—is reduced when light sets the electrons oscillating. The loss of aromatic stability sets up a roadblock to free motion of electrons along the molecule.

By clever molecular design, Marder and company have turned this effect around and used it to their benefit in making nonlinear materials. The links in their molecules are actually joined pairs of rings—one that loses aromatic stabilization when the electrons vibrate and the other that gains it. Together, these countervailing effects can actually increase the extent and asymmetry of the oscillations, boosting the second-order nonlinearity. Marder's group recently applied this strategy to make molecules 20 to 30 times more effective at frequency doubling than the standard push-pull molecule dimethylaminonitrostilbene.

Fleeting effects

The dramatic nonlinearities seen in laboratory materials haven't been enough to convince many conservative manufacturers. There are a few exceptions. For example, Akzo Electronic Products of Redwood City, California, soon hopes to market optical switches based on a second-order organic material. But for the rest of the commercial competitors, a stumbling block has been the short life of nonlinear properties. Strong as the effects may be in a freshly synthesized material, they often fade, sometimes within hours.

The problem is creeping disorder. Strong second-order effects depend on molecular order, which materials scientists often create by a "poled polymer" approach. The trick is to dissolve NLO molecules in a polymer, heat the polymer until the chains begin to move, then apply an electric field that lines up the NLO molecules like iron filings near a magnet. Cooling the material freezes the polymer chains, locking the NLO molecules in place. However, random thermal motions can overcome the molecular order, even at room temperature, and the nonlinear properties vanish. And that's a serious handicap.



Push and pull. In an organic molecule with alternating single and double bonds, light sets electrons oscillating between electron-attracting *(right)* and electron repelling *(left)* groups, giving rise to nonlinear optical effects.

As Allen says, "Telecommunications companies are naturally reluctant to dig up their equipment every 3 years to replace devices!"

One solution is to attach many short NLO molecules to the polymer backbone, all in the correct orientation—the so-called side-chain approach. That provides a measure of order, but a polymer chains themselves can reorient over time. To overcome that tendency, some researchers, including Rick Lytel and Jeong Wu, who were then at Lockheed, have been locking NLO molecules into polymers that remain rigid at very high temperatures. That approach recently yielded a material with nonlinear properties that remained stable at 300 degrees C.

Instead of trying to lock the NLO molecules in place, Milburn and his colleagues are trying another approach with their diacetylene polymers, detailed in a forthcoming paper in the journal *Molecular Crystals, Liquid Crystals*: periodically restoring order. Because some of these materials are liquid crystals, the polymers can temporarily align, like logs on a lake, at room temperature. They drift out of alignment fairly quickly, but by "tickling" the molecules with a low-voltage electric field, the researchers can switch the NLO effect on or off or fine tune it.

At the frontier of research on nonlinear optical materials lie polymers with third-order effects. These effects, generated by a harmonic with three times the frequency of the light's electric field, are as tempting as second-order effects. They include light-induced changes in a material's refractive index and its ability to absorb light, and a tripling—rather than a doubling—of a laser beam's frequency as it passes through the material. But so far, the best third-order effects in polymers, seen in such materials as polydiacetylenes and polyphenylacetylenes, are less than half as strong as needed for such applications as optical switches, frequency tripling for lasers, or instant-response light shields. Says Marder, "Some dramatic advances are needed."

Dramatic advances in these properties, however, have been slow in coming. That's somewhat surprising, because third-order effects can arise in materials lacking any electronic asymmetry. But researchers attempting to improve third-order effects run into a stumbling block because far more molecular processes govern the strength of these effects than govern second-order effects. That makes it more difficult for theorists to guide experimenters—and for experimenters to interpret their results.

The net result of these obstacles is that until recently, organic chemists had learned very little about the bases of third-order nonlinear optical effects. About the only solid fact they had was that molecules with longer conjugated regions exhibit stronger third-order effects. But Marder's team has now turned up a second clue to tailoring molecules for strong third-order effects. They have found that the average difference in length between the single and double bonds that alternate along a conjugated chain affects the third-order effects. Since nearby chemical groups affect the lengths of these bonds, Marder thinks the finding may guide investigators in designing polymer chains with stronger third-order effects.

All of which convinces Marder and his colleagues that in future light-based information technologies, polymers—now relegated to serving as insulation and support—will play a much more active role in carrying and controlling the signals. Once industry also begins to see the light, plastics may be controlling light in everything from supercomputers to CD players.

–David Bradley

David Bradley is a science writer based in Cambridge, England.

Additional Reading

R.A. Hahn and D. Bloor, editors. *Organic Materials for Non-Linear Optics II,* Royal Society of Chemistry, Cambridge (1991).

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S.R. Marder *et al.*, "Relation Between Bond-Length Alternation and Second Electronic Hyperpolarizability of Conjugated Organic Molecules," *Science* **261**, 186 (1993).