PYREX®
USA
26060

Any Color You Like

by Douglas L. Smith

On the fiber-optic lanes of the information superhighway, nonlinear-optic materials may one day provide the off ramps and cloverleaf interchanges.

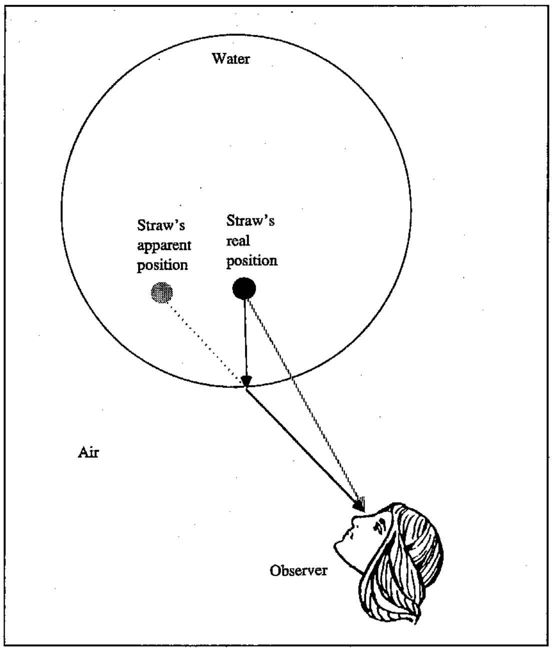
In Marder's lab, nonlinear-optical compounds are purified by running them through silica-gel-filled columns like this one.

If you shine a red light through a pane of glass, it comes out red. But shine that same light through a nonlinear-optic material, and it might come out blue. Or it might come out red, but at a funny angle. A nonlinear-optic material modifies light passing through it in a way that depends on the light itself, among other things. On the fiber-optic lanes of the information superhighway, nonlinear-optic materials may one day provide the off ramps and cloverleaf interchanges, routing data-laden pulses of light to their proper destinations. Seth Marder, a member of the technical staff at Caltech's Jet Propulsion Laboratory and a member of the Beckman Institute on campus, and Joseph Perry (PhD '84), leader of the optoelectronic materials group at JPL and a visiting associate at the BI, lead a group that has created a whole new class of substances with the highest nonlinear-optic properties yet found.

Light is an electromagnetic wave, so it's no surprise that it interacts with electrically charged things, including the electrons in a molecule. As light passes through a molecule, the molecule's electrons ride the waves like boats at anchor. As the electrons surge against their moorings, the molecule becomes polarized—it acquires a slight negative charge in the direction the electrons are moving, and a slight positive charge in the region they've vacated. In materials such as glass, the electrons move back and forth with equal facility, and the distance an electron moves in either direction is proportional to the wave's amplitude, at least to a first approximation. Thus a plot of polarization versus the applied field is a straight line—a linear, symmetric response.

But if the molecule is already polarized, applying an electric field in the direction of polarization can shove the electrons a considerable distance. Applying the same field in the opposite direction pushes the electrons against the tide, and they won't move nearly as far. Now the plot of net polarization versus the applied field is steep in one direction and flat in the other—a nonlinear, asymmetric response. This effect, called "hyperpolarization," is relatively weak, becoming noticeable only in the presence of strong fields. There, however, the effect becomes quite powerful, since it varies with the square of the field's strength. Only molecules lacking a center of symmetry are hyperpolarizable in this manner—a symmetrical molecule would have an equal desire to polarize in either direction. (This kind of hyperpolarization is what's called a second-order effect—there are other, higher-order hyperpolarizations beyond our scope here.)

The interplay of polarization and hyperpolarization has several useful consequences. You can bend light by manipulating the material's refractive index. When a beam of light hits a molecule at the edge of a chunk of matter and sets its electrons bobbing, the oscillating electrons themselves generate an electromagnetic field at the same frequency as the original wave. The new field travels to the next molecule, and the light propagates through the material. Each molecule imposes a tiny time lag as its electrons respond—in essence, the light slows down. This time lag, relative to that for light through air, is the material's refractive index. (This is why a straw sticking out of a glass of water appears bent: light



An overhead view of a glass of water. Light travels by the quickest path (solid arrows), and since light travels more slowly in water than in air, the quickest path is not the shortest path (shaded arrow). But we *know* that light travels in straight lines, so we see the straw in a different location from where it actually is.

travels one-third slower in water than in air. Light reaches your eye by the fastest possible route rather than the shortest possible route, and as a consequence takes the path that minimizes the time spent traveling through the slower medium.) Applying a second, nonoscillating field slows the wave further—the electrons have to fight harder to get back to their initial position to begin the next oscillation. As the second field intensifies, the refractive index gets higher, until eventually the light beam emerges from the material in a radically different direction. Thus, laser signals could be shunted from one fiber-optic line to another by applying a switching field to a nonlinear-optic material at the lines' junction. The switching field could be an applied voltage, or it could be another laser beam.

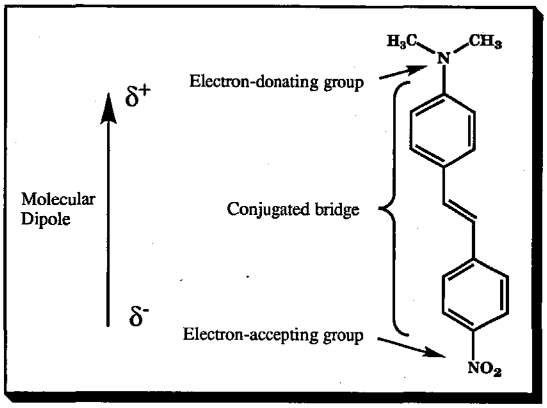
And you can change the light's color. The oscillating electrons not only rebroadcast the light at its original frequency, they also emit energy at twice that frequency. (These higher frequencies—harmonics—are analogous to the harmonics of sound waves. You can hear harmonic generation the next time you have a piano handy: Press down on the C above middle C slowly and gently, so that the note doesn't sound. While holding that key down, hit middle C hard. Let go of middle C, but continue to hold the other one. The ringing you hear is the second harmonic of middle C causing the string an octave above it to resonate.) Under the right circumstances, upward of 80 percent of the light can be rebroadcast as the second harmonic; 35 percent is routine for commercial devices. Additional frequencies can be generated by combining the fundamental frequency with other frequencies, an effect that comes in very handy when working with lasers. A laser emits light at one specific frequency that depends on what the laser is made of. But this frequency generally isn't the one that a researcher needs, so nonlinear-optic crystals are widely used to "tune" lasers to the right frequency—say, a particular spectroscopic resonance of some molecule. Outside the lab, surgeons need short-wavelength lasers to cut tissue, while longer wavelengths work better to cauterize the incision.

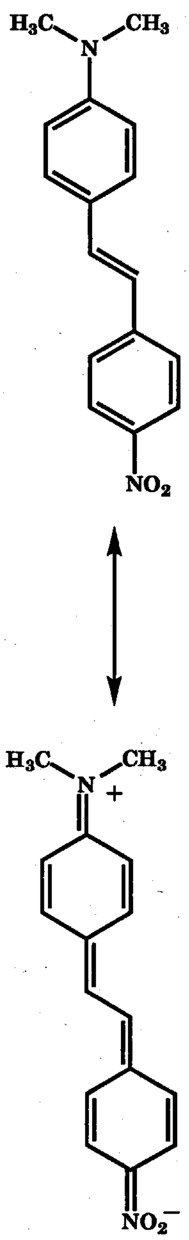
To date, all commercial nonlinear-optic materials have been inorganic compounds such as potassium dihydrogen phosphate and lithium niobate. But their nonlinear effects aren't that large, whereas some organic molecules are highly polarizable and thus should show strong effects. And while lithium niobate and its kin polarize in part by schlepping heavy ions back and forth, organic molecules polarize by whisking featherweight electrons around. Electrons are nimble enough to keep up with the highest frequencies—a very big advantage, says Marder, when you consider that the information superhighway's structural engineers want electro-optic switches capable of operating 10 billion times a second. "If you tried to do that with an inorganic," says Perry, "its efficiency drops way off. It becomes very power-hungry." Organics have other advantages—they can be formed into films and sheets, or molded into any shape you like; and best of all, the molecule's properties can be customized by altering its chemical composition. Lured by these promises, folks have been tinkering with organic molecules for the past two decades.

These molecules share a basic design: a cluster of atoms (the donor group) willing to give up an electron and acquire a positive charge; another cluster of atoms (the acceptor group) that attracts the electron and becomes equally negatively charged; and in between them a stiff bridge, several atoms long, that separates the charges to create a dipole. (The longer the bridge, the farther the charges are separated, and the greater the dipole—at least within limits. If the bridge gets too long—more than 13 atoms, say—the groups' influence fades.) In order to get the donated electron to the acceptor, the bridge contains what chemists call a conjugated π-bond system—a backbone of alternating single and double bonds along which a charge can flow.

Conjugated systems really contain *two* sets of electrons. One set actually holds the structure together, and lives in well-defined bonds between the atoms. The other set—the π electrons proper, and the second half of each double bond, as it

Right: DANS's anatomy. The line segments are carbon-carbon bonds; their intersections are the carbon atoms themselves. The δ+ indicates a partial positive charge, δ- a partial negative charge. Left: DANS can be thought of as existing in two forms: the electrically neutral form (top); and the charge-separated form (bottom), in which the nitrogen atom at the molecule's top end has given an electron to an oxygen atom at the molecule's bottom end. Note how all the double bonds have shifted as a result.





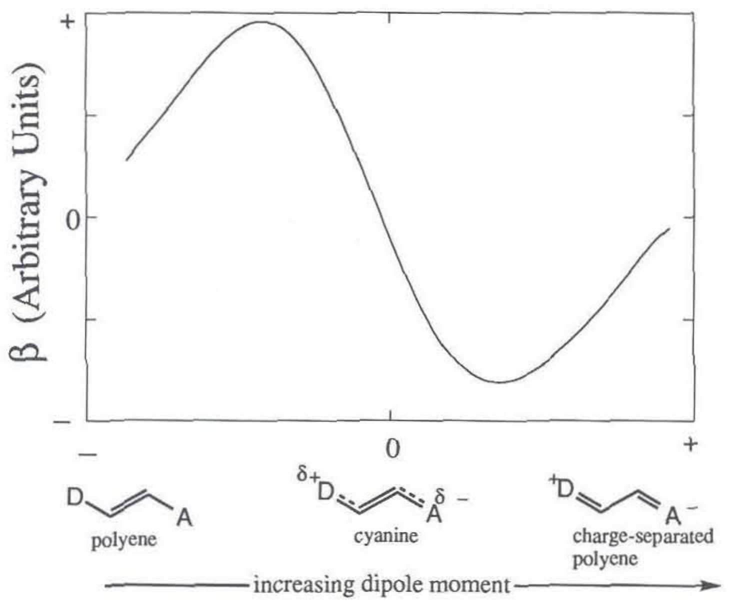
were—is more gregarious. If the opportunity permits, they spend as much time visiting neighboring atoms as they do at home. The π electrons will cruise up and down the system for as far as the alternating double and single bonds extend.

The archetypal nonlinear-optic organic molecule is called DANS (4-N,N'-dimethylamino, 4'-nitrostilbene to the chemically literate). DANS's structure is shown above. DANS has an electron-greedy nitro group—NO_2—and an electron-generous amine—$(CH_3)_2N$—and a bridge of 10 conjugated carbon atoms to carry the charge. Researchers had worked their way up to DANS by attaching progressively stronger donors and acceptors to the bridge. "These are among the strongest donors and acceptors known—at least, as far as things that don't combust spontaneously in air are concerned," says Perry. And, in fact, the nonlinear response was getting stronger, but nobody knew how high it could go. "They hadn't gotten to the end of the rainbow yet."

Marder and David Beratan (PhD '86, now at the University of Pittsburgh), decided to start afresh, working from chemical first principles. "All of the equations for nonlinear optics were derived by physicists," Marder explains. "They played around with things like DANS because they could buy it. You can buy a dye called Disperse Red in kilo quantities, and it's essentially the same stuff. The chemists learned from the physicists what molecules to make—were told the rules—and to a great extent didn't try to derive the rules for themselves. What we did was make the connection between the physics and the chemistry."

The chemistry told Marder and Beratan something very important. Conceptually, a molecule containing an electron donor and an acceptor exists in two forms (shown at left). In one—the electrically neutral form—the donor keeps its spare electron in its trouser pocket. In the other—the charge-separated form—the donor surrenders its electron completely, acquiring a charge of +1, and the acceptor acquires a charge of −1. But as long as the π electrons are loose, the molecule actually exists in a state somewhere between these extremes—a combination of the two forms that resembles the charge-separated one more closely as the donor and acceptor get stronger. If both forms contribute equally to the molecule's character, the donor and acceptor act as if they have charges of plus and minus one-half, respectively. At this balance point, a light wave's oscillating field finds it just as easy to push electrons in one direction as the other. In other words, the molecule no longer responds asymmetrically to the field (i.e., does not hyperpolarize), even though the molecule itself is polarized.

So Marder and Beratan, in collaboration with Lap-Tak Cheng from DuPont, embarked on a series of calculations to see just what combination of donor and acceptor would maximize the asymmetric response. The calculations spanned a continuum having very strong donors and acceptors on one end and very weak donors and acceptors on the other end, and tested the π electrons' ease of motion along the bridge in both directions. "No one had done this kind of detailed analysis before," says Marder. "What we found is that you don't want the *strongest* donors and



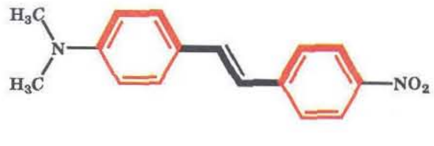


Figure of Merit = 470 x 10^{-48} esu

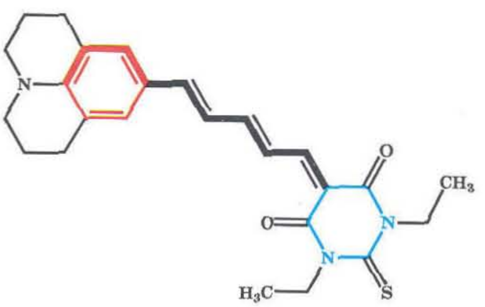


Figure of Merit = 7150 x 10^{-48} esu

Above: A plot of hyperpolarizability (β) versus dipole moment. In the generic molecules across the bottom, D stands for donor and A for acceptor. The "polyene" structure (left) is the neutral form. The "cyanine" structure (center) is the balance point. Here electron mobility is equal in either direction, as shown by the dashed lines, and the molecule's two ends have half a charge each. In the neutral form and the fully charge-separated form (right) the π electrons are pinned to the locations shown by the double bonds.

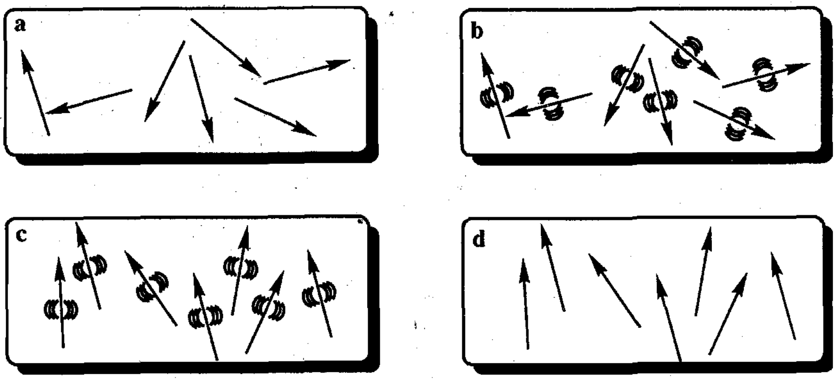
Right: The larger the figure of merit in esu, or electrostatic units, the more nonlinear the compound. Both compounds have 10-carbon bridges (bold lines), so the choice of donor and acceptor make all the difference. Top: DANS; bottom: a thiobarbituric acid derivative made in Marder's lab. Red rings lose aromaticity upon polarization. Blue rings gain aromaticity upon polarization.

acceptors you can possibly find; you want the *optimal* donor and acceptor."

The analysis showed that there's a balance between the electrons' lopsided reaction to the wave's alternating tugs and pushes that makes the molecule want to hyperpolarize, and the electron mobility that allows the hyperpolarization to occur. Plotting hyperpolarizability against the degree of charge separation, called the dipole moment, gives a double-humped curve. At the curve's very ends are molecules with very highly asymmetric responses, but whose π electrons are tied down. Molecules that are 100 percent in the neutral state lie at the curve's far left, and molecules that are fully charge-separated lie at the extreme right. In each case, there's only one direction the electron can be pushed—as skewed a response as you can get—but the π electrons are frozen in place because the opposite state does not contribute to the molecule. In the exact center lie molecules whose π electrons are free as the wind, but whose response is perfectly symmetric—the balance point. The molecule's hyperpolarizability is zero in all three instances. The curve's maximum occurs to the left of center. Here the response is asymmetric—you haven't yet gotten to the balance point, but you're far enough from the neutral state that the π electrons can move. On the curve's right-hand hump, which is actually a valley, the charge-separated form dominates. There's a similar hyperpolarizability, but with the opposite sign.

DANS, it turned out, was a bad choice in any case. Donor and acceptor groups aside, DANS suffered from having a bridge that actually impeded charge transfer. The bridge contains two benzene rings—carbon-atom hexagons containing six π electrons each. By a quirk of molecular orbital theory, rings containing six π electrons are especially stable, a beatified state known to chemists as "aromaticity." But in order for the charge separation to occur, each benzene ring would have to surrender some of its π electrons. The rings' reluctance to do so, and lose their aromaticity in the process, put the molecule on the very left-hand end of the curve, where the response was small.

Armed with this knowledge, Marder began synthesizing new molecules whose donors and acceptors had the right strength to put the molecule near the curve's peak. The bridges contained no aromatic rings, just chains of carbon atoms with alternating single and double bonds, and thus venturesome π electrons. In fact, the researchers were able to use aromaticity to their advantage. By choosing an acceptor group that contains a ring that becomes aromatic upon



How poling works. (a.) The molecules and the polymer are dissolved in a solvent, which is then evaporated off. This leaves the molecules trapped in the polymer and oriented at random, as shown by the arrows representing their dipoles. (b.) The polymer is heated above its glass transition temperature, allowing the molecules to jiggle about. (c.) A strong electric field orients all the molecules in roughly the same direction. (d.) The field is turned off after the polymer cools, freezing the molecules in their new orientation.

receipt of an electron, they were able to move the molecule farther to the right, toward the peak. "After we published that study, people jumped to the conclusion that aromaticity was bad," says Marder. "What we're really saying is that aromaticity is neither intrinsically bad nor good—it's just another way to position a molecule on the curve."

But getting the molecule right is only half the job. If the molecules assemble themselves into a crystal containing a center of symmetry, as Marder says some 75 percent of asymmetrical molecules are wont to do, then you're no better off than you were with a symmetrical molecule. It's the same old bugaboo—the asymmetric polarization response vanishes, and the bulk material will be inactive. But there are ways around this. One is a method called poling (which Marder and company did not invent). This method imprisons the active molecule in a polymer matrix. Then you heat the polymer until it goes rubbery, and apply a strong electric field. The active molecules' dipoles will line up more or less with the field. If you let the material cool back down while maintaining the field, the molecules will remain trapped in that alignment. The alignment isn't perfect, like a crystal's could be, and the molecules will slowly come unstuck again with time, but the technique is good enough for many applications.

Marder and Perry have made polymers using some of their molecules, and are measuring the polymers' "figure of merit"—a package of properties including the dielectric constant (which measures an individual molecule's polarizability), bulk susceptibility, thermal and chemical stability, and so forth, all of which have to be optimized in order to make real-world devices. The molecules they have made to date are far from optimal, but they still expect to beat lithium niobate's figure of merit for an electro-optic switch by a factor of four. This means that the polymer requires one-quarter as much power to operate and generates one fourth the waste heat to be dissipated, both important practical considerations. "They won't give you many watts on a spacecraft," says Perry. "Everything has to be lightweight and low-power. If a switch takes a watt to drive, you can't use it. But if it only takes 100 milliwatts, you might be able to. Technology like this lets us think about putting fiber-optic LANs [a type of communications network] on a spacecraft—you could run the whole switching network on one or two watts."

One of the first applications of these materials will probably be in sensors that react to changes in the voltage applied to them. "We could use these sensors to monitor, and perhaps eventually manage the national power grid," says Perry. "In areas of high demand, you want to equalize the load—the way the current is sucked through the lines. By evening out how the current is split, you minimize the power loss. Fully automating the distribution system might increase its efficiency by perhaps 0.1 percent, but that still translates into billions of dollars saved." The polymeric sensor would be applied to the lines at points near transformers and switching stations. "Like all technologies, we're chasing a moving target," says Marder. "Inorganic materials are constantly getting better, too. The goal is not to displace inorganics, but to complement them."

Perry agrees. "I think that we won't make a big dent in frequency conversion, but waveguides and polymer voltage sensors are where the cost benefits should allow these materials to find a real commercial life. Like plastics, they're really easy to process. You can mold them, you can spin them onto silicon wafers, and then you just mask, etch, and metallize them like any other circuit component." Waveguides are to light what wires and switches are to electricity, and could replace much of the soldered metal that shuttles information between the chip's microcircuits. The chip's logic elements would still be electronic, but they would communicate via tiny diode lasers and photodiodes. Data would travel faster and generate less heat. "This is the limiting step in chip design now—getting the waste heat off the chip. The more stuff you put on a chip and the faster it goes, the more heat you make." And with that, we're back to the information superhighway. ☐