

Organic Material Debuts as Both an Injection Laser and a Superconductor **FREE**

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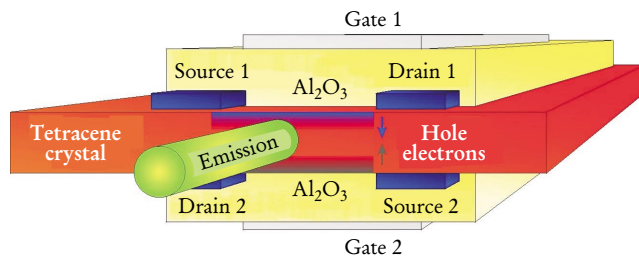
It's rare that a conference talk will sweep an audience off its feet, but those who heard Bertram Batlogg of Bell Labs address the International Conference on Synthetic Metals (ICSM) in Bad Gastein, Austria, this past July were reportedly blown away by what he had to say. Batlogg's group had achieved the long-sought goal of making an electrically pumped injection laser from an organic material, specifically tetracene.¹ Furthermore, the team had also shown that the same tetracene crystals could be made to superconduct, with a critical temperature of a few degrees kelvin.² But perhaps the most intriguing aspect of both demonstrations was the elegant and novel technique that the Bell Labs team had devised for adding charge: Rather than chemically doping their crystal, the experimenters injected charge through a field-effect-transistor arrangement, adding enough charge to convert the normally insulating tetracene crystal into a metal and even a superconductor. The control exerted by these experimenters over the current density allows them to study different regimes of behavior, as they did recently in exploring the fractional quantum Hall effect in tetracene and pentacene.³

Tetracene, which consists of a chain of four benzene rings, is one member of the acene family of compounds. Its cousins—pentacene (five rings) and anthracene (three rings)—have also been found to superconduct, and there appears to be no reason why these two couldn't be the basis for injection lasers as well. Because all three compounds are relatively simple in structure, Batlogg calls them "physicists' molecules." He expects to see lots of additional phenomena emerge in more complex molecules. "The richness and creativity of organic chemistry should lead to a much wider phase space to be investigated," he says.

Besides opening the door to a whole new range of behavior, the new results—the injection laser in particular—are of interest because of their potential optoelectronic applications. It's expected that manufacturers will

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be able to produce organic lasers far more cheaply than their semiconductor counterparts, and that the wavelength of organic lasers might be tuned from the infrared to the ultraviolet, thanks to the enormous variety of organic compounds. For several decades, researchers have studied a class of polymers known as pi-conjugated polymers and other lower-molecular-weight organic molecules in the hope of developing electronic devices. They have developed such optoelectronic components as light-emitting diodes and fast optical switches. Photo-excited lasers based on polymers doped with molecular dyes were made more than 30 years ago, and one based on pi-conjugated polymers in solution⁴ was reported in 1992. More recently, three reports of optically stimulated laser action in pi-conjugated polymers in solid films,⁵⁻⁷ presented at ICSM-1996, stimulated a lot of work on materials and resonators and brought the lasing



TETRACENE LASER features a tetracene crystal sandwiched between two gate electrodes and insulated from them by a layer of aluminum oxide, Al_2O_3 . A negative voltage on gate 1 induces a few monolayers of holes (blue region) near the top of the tetracene crystal, whereas a positive voltage on gate 2 produces a layer of electrons (grayish region) near the bottom. A potential applied across the crystal draws electrons and holes to the center, where they recombine to produce the laser emission. (Adapted from ref. 1.)

threshold for optically pumped organic devices down to values well below those available from inorganic semiconductors. But until the Bell Labs work, an electrically pumped organic laser had eluded researchers.

The electrically injected tetracene laser has now energized many in the organic electronics community. For one, Andrew Holmes of the University of Cambridge feels that the tetracene laser "means that there is real hope also for conjugated polymers, as recent experience is that polymers can be made to match what small molecules do." The challenge will be to impose on the spaghetti-like polymer strands a rigid order and high purity comparable to those achieved in the more ordered acene crystals grown at Bell Labs.

From insulator to superconductor

Many organics become semiconductors only when they are doped with an electron or hole donor. To add charge carriers to crystals of the acene family, Batlogg and coworkers used the geometry of a field-effect transistor (FET). The figure on this page essentially shows two such devices put together to form a laser. The simplest FET consists of a single crystal of, say, tetracene, on which is deposited just

one pair of source and drain electrodes (such as source 1 and drain 1). An insulating layer of aluminum oxide is laid down next, followed by deposition of a gate electrode (gate 1) on top. A negative voltage applied to gate 1 induces positive charges (holes) to amass in a few monolayers just below the crystal's top surface (as shown). Conversely, a positive voltage on gate 1 gives rise to a sea of electrons. Increasing the gate voltage raises the charge carrier density.

With a single-FET geometry, Batlogg and colleagues Christian Kloc and Jan Hendrik Schön found they could inject as many electrons as one per molecule, assuming that only the topmost molecular layer takes part in conduction. The three measured the resistance of crystals of the acene family as a function of temperature.

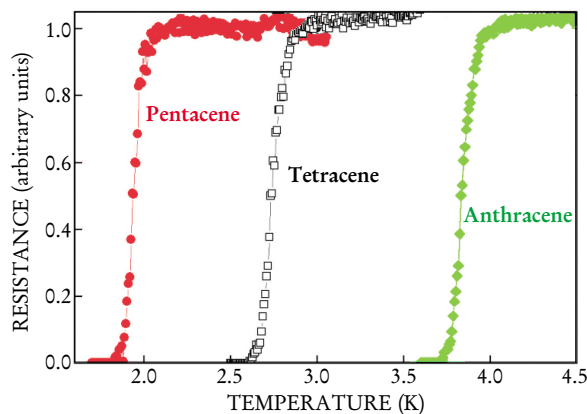
As seen in the adjacent figure, the resistance plummets sharply to zero at temperatures of roughly 2.0 K, 2.7 K, and 4.0 K for pentacene, tetracene, and anthracene, respectively. No one knows the mechanism for this observed superconductivity, although electron–phonon coupling is a strong candidate. The mechanism is something for theorists to chew on. Any models will have to explain why the critical temperature T_c rises as the size of the molecule decreases. (Such a size dependence has already been predicted in one theoretical paper.⁸) Schön, Kloc, and Batlogg also measured the upper critical field for this superconductor, extrapolating to a value of 4.1 T at 0 K. The upper critical field gives a measure of the coherence length, which in this case corresponds to about 80–90 Å.

The Bell Labs researchers can generate a kind of phase diagram, plotting resistance as a function of the temperature and carrier concentration. The resistance is a measure of the phase of the material—metallic or superconducting, for example—so that the plot is much like the phase-space diagram of high-temperature oxide superconductors that is often the subject of debate among theorists these days. For the acenes, T_c does not seem to vary with carrier concentration, as it does for the oxide materials, but Batlogg and company want to see if that remains true even at higher concentrations.

Fred Wudl of UCLA, who says he has “spent more years studying organic superconductors than I care to count,” thinks the new class of superconductors “is a terrific piece of work; it’s going to engender a great deal of physics.”

Mobility is the key

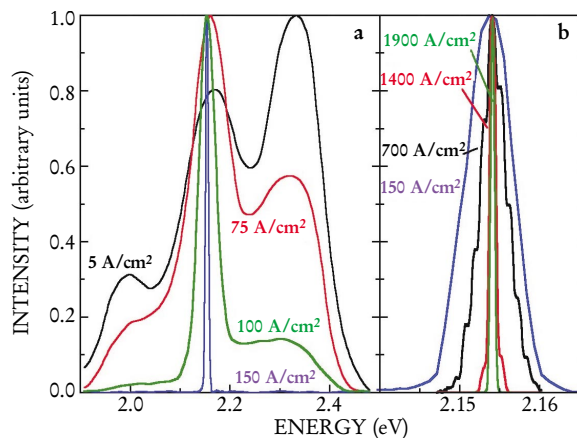
The Bell Labs researchers first took interest in members of the acene family when they realized that, at room temperature, the mobility of holes—that is, the ease with which they can move through the crystal—was about the same as that of other semiconducting organic crystals they had been studying, around $2 \text{ cm}^2/(\text{V s})$, and several orders of magnitude higher than those of conjugated polymers. Kloc, the chemist of the group, grew very pure crystals of pentacene for his colleagues to characterize. They were surprised to find that, for these crystals, the mobility greatly increased at



SIGNALS OF SUPERCONDUCTIVITY in three crystals of the acene family are the precipitous drops in resistance with temperature. Note that pentacene (a chain of five benzene rings) has a lower critical temperature than anthracene (three rings). (Adapted from ref. 2.)

lower temperatures, rising to values on the order of $10^5 \text{ cm}^2/(\text{V s})$ below about 2 K. Furthermore, the mobility of electrons, typically very low because electrons are readily trapped, was nearly as high at room temperature as that for holes, and rose to about $10^4 \text{ cm}^2/(\text{V s})$ below 2 K, indicating a very low density of impurities that can trap charges.

At low temperatures, the pentacene and tetracene crystals have mobilities comparable to the two-dimensional gases created in a metal-oxide-semiconductor FET, and can be used in a comparable way to study fundamental charge interactions.



EMISSION SPECTRA of a tetracene laser at 5 K narrow as the current density increases. (a) Spectrum of the central peak changes to a sharp spike as the current density rises to 150 A/cm^2 . (b) Shown on a magnified energy scale, the spectrum continues to narrow as current density rises to 1800 A/cm^2 . (Adapted from ref. 1.)

Thus, Schön, Kloc, and Batlogg have been able to explore such phenomena as the fractional quantum Hall effect³ (see PHYSICS TODAY, May 2000, page 23). The control over the charge density gives the team another experimental knob to turn.

High mobility for both electrons and holes is an essential ingredient for an electrically injected laser. If the mobility is too low, the threshold current will be too high, resulting in undesirable heat losses. A second prerequisite for an electrically pumped laser is a quantum efficiency for photon emission that is higher than roughly 5%. That efficiency has not yet been measured, but the Bell Labs researchers, collaborating with Vally Vardeny and his coworkers at the University of Utah, measured the quantum efficiency for photoluminescence and found it to be 10–20% at room temperature.

Injection laser

To build a solid-state injection laser, Schön, Kloc, and Batlogg enlisted the aid of their Bell Labs colleague, Ananth Dodabalapur. The design is shown schematically in the figure on page 17. To operate the laser, the experimenters apply a negative voltage (around -50 V) to gate 1 and a positive voltage (about 50 V) to gate 2, inducing thin regions of holes and electrons on opposite edges of the crystal. Then, the experimenters maintain a fixed potential difference

of 5 V across the crystal—from one pair of drain and source electrodes to the other. The potential across the crystal draws holes and electrons into the center, where they radiatively recombine. Schön and coworkers cleaved the front and back surfaces of the crystal, so that the cleaved edges act as mirrors, but with reflectivities of only about 8%.

This method of charge injection circumvents perhaps the biggest problem plaguing the effort to build an injection laser from conjugated polymers or

other organic materials: the losses introduced by the electrodes themselves. As Alan Heeger of the University of California, Santa Barbara, explains, electrodes for carrier injection are typically lossy; even the best metals have reflectivities for visible light of 96–98%. The resulting losses overwhelm the gain for organic thin films. Heeger said the Bell Labs’s

method of using two FETs to inject the current “is a beautiful idea, and it works!” There are also losses associated with carrier-induced absorption, but the problem can be avoided with proper choice of material to get the material to absorb at a different wavelength than that at which it emits. It remains to be seen whether the Bell Labs approach can be successfully generalized to other materials.

Part of the proof that the Bell Labs group had indeed formed a laser was the observed narrowing of the emission line as the current density increased—that is, as the laser was pumped harder and harder. As shown in the bottom figure on page 18 for two scales of energy, at low density the emission spectrum has several peaks. But as the gate voltages are raised to give higher current densities, the line continues to narrow. The first sign of optical gain sets in at current densities of about 30 A/cm², but the transition to lasing doesn’t occur until about 500 A/cm². Above that threshold, the emission line is centered at about 580 nm. The laser operates in a continuous-wave mode up to 200 K and in a pulsed mode up to room temperature.

Vardeny noted two particularly nice features of the Bell Labs laser. One is the balance that is maintained between the current of electrons and holes. In present-generation light-emitting diodes, he points out, the holes outnumber the electrons and the holes that are left behind can serve as nonradiative combination centers, reducing luminescence. The balance in the tetracene laser is of course made possible only because the high-purity crystals have few traps for either electrons or holes. In most organic conductors, there are many more traps for electrons than holes, so that holes become the dominant carriers. Another special feature, Vardeny says, is the separation of controls: In the FET design, one can increase the current (through the gate electrode) without having to increase the voltage across the device.

Batlogg admits that the new laser is only a demonstration and is far from being optimized. “Most of the work is ahead of us,” he claims. He and his colleagues believe they can reduce the threshold current by two orders of magnitude, for example. Among the obvious steps to further

improve the laser are to get a proper feedback mechanism rather than the simple cleaved mirrors they now use and to introduce a low-loss waveguide surrounding the active region. Doda-balapur says they are working on resonator designs, including one based on photonic crystals. Such photonic crystals, particularly two-dimensional ones, will enable the laser light to be coupled out in technologically useful directions.

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Solid-State NMR Reveals Key Structural Features of Membrane Transport Proteins

Only small neutral molecules can pass unaided through cell membranes. Other kinds of particles—ions that mediate neural signaling, sugars that provide energy, amino acids that form proteins, and so on—enter and leave cells through specialized molecular portals known collectively as membrane transport proteins. To do their vital jobs, these proteins must recognize and grant passage, when required, to only one kind of molecule. And if getting that molecule into or out of a cell involves pushing against an electrical or concentration gradient, the transport protein has to marshal the necessary energy.

Membrane transport proteins can pull off these feats of molecular processing thanks to their intricate structures. And only by knowing these structures can biophysicists begin to discover how membrane transport proteins work.

Most proteins are found in the aqueous interiors of cells and cellular compartments, but membrane transport proteins inhabit a quite different environment: the flexible double layer of lipid molecules that constitutes the cell membrane. For a membrane

▶ With carefully chosen pulse sequences, practitioners of solid-state NMR are closing in on a much-sought prize in structural biology: the ability to unravel the molecular structure of membrane transport proteins.

transport protein to remain attached to the membrane, the protein’s outer surface must match the electrical nonpolarity of the membrane’s interior. This property renders the protein insoluble in water, hard to purify, and very difficult to crystallize.

That last disadvantage is unfortunate. Without crystalline samples, x-ray diffraction—the structural biologists’ workhorse—can’t be used to solve a protein’s molecular structure. Of the 20 000 or so solved structures in the Protein Data Bank—a repository for the processing and distribution of three-dimensional macromolecular structure data—only a few handfuls correspond to membrane proteins.

Structure-solving techniques based on nuclear magnetic resonance (NMR) don’t require crystalline samples, but they have proved just as challenging

as x-ray crystallography to apply to membrane proteins. Recently, however, a significant milestone has been reached in NMR-based structure determination. Two groups—Francesca Marassi and Stan Opella at the University of Pennsylvania¹ and Tim Cross and his collaborators at Florida State University²—have independently demonstrated a method that can straightforwardly measure the position and orientation with respect to the membrane of a protein’s alpha helices, key elements of the protein’s structure.

Although this advance falls short of the ultimate goal of solving the complete structure of an arbitrary membrane protein, “determining the alpha helices’ disposition of is,” says the University of Cambridge’s Richard Henderson, “a magnificent achievement.”

Chemical shifts

Unlike crystallography, NMR doesn’t provide a picture in reciprocal space of a complete molecule. Rather, NMR data consist of a set of resonance peaks whose properties are shaped by the chemical environment of each