

CARBON ELECTRONICS

DAVID FILMORE



Organic transistors are on their way to forging a low-cost, lightweight, and bendable electronic future.

The changes promised are impressive—plastic “smart” cards that could keep track of things like an individual’s prescription drug and insurance information, radio wave-interrogated identification tags for applications like tracking luggage, and large-area electronic displays that can be rolled up like paper. The goal for these products is to be inexpensive, easy to use, and flexible. It’s a new model for electronics that is attracting significant industrial interest. In terms of data requirements, these applications are by no means groundbreaking. Today’s digital circuitry, made of silicon-based field-effect transistors (FETs), provides ample processing speed and memory.

On the other hand, “inexpensive”, “easy”, and “flexible” are product descriptors not currently highlighted in modern microchip catalogs. The high-vacuum photolithographic-based procedure for fabricating the densely packed silicon microchips is technologically challenging, costly, and heat-intensive, requiring very robust and heavy substrates. This is fine for high-performance computing, but for wallet-ready cards or “electronic paper”, a more economical and versatile means of production is desirable.

Enter the organic chemist. Organic synthesis has produced a wide range of highly conjugated compounds—both polymers and small molecules—with semiconducting properties. Some of these compounds, which emit light, have already entered the market as organic light-emitting diode displays (see “Thinner, Lighter, Better, Brighter”, *Today’s Chemist at Work*, Nov 2001, p 30). In

the wake of this success, there is tremendous interest in developing organic semiconductors into actual electronic circuitry, specifically by constructing working organic thin-film transistors (OTFTs). OTFTs can’t begin to compete with the high speed of finely etched silicon chips, but their performance is rising to levels that are expected to meet the needs of lower-resolution applications. Most promising for commercial interests is the potential they offer for low-cost, solution-based processing methods that present the opportunity for printing press-like (reel-to-reel) circuit manufacturing on plastic substrates.

Carbon Current

FETs consist of two electrodes—a source and a drain—connected by a semiconductor and a third electrode, called the gate, which is separated from the semiconductor with an insulator. Basically, the gate turns the semiconductor on and off, thus controlling the source-drain current flow. For instance, with a p-type semiconductor (which transfers positively charged “holes”), the gate can supply a small negative voltage (relative to the source voltage) and holes will swarm to the semiconductor-insulator border, creating a channel for positive current flow (see Figure 1). A positive voltage, on the other hand, will repel the holes and effectively “pinch off” the current channel and turn off the transistor (the inverse occurs with electron-transferring n-type semiconductors). Large transistor setups work together to perform logic functions (intricate combinations of grounded and ungrounded current translating into 0’s and 1’s) and also provide the back-plane circuitry that drives the pixels to change colors in flat panel display applications.

Highly conjugated organic materials have the potential to work as semiconductors in this arrangement because of their

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strong π -orbital overlap. When an electron is added or a hole is injected (formal physics-speak for removing an electron), the resultant charge becomes delocalized across the conjugated system. This injected charge is able to act as a carrier for current through the molecule. The potential for implementing these types of compounds into actual FETs depends on both the electronic properties of individual semiconductor molecules and the structural ordering of the molecules in the solid film that will act as a macroscopic source-drain connection.

An effective organic semiconductor must have a redox potential that is open to charge injection by a small applied voltage. In other words, the molecular orbitals (MOs)—that is, the highest occupied MO for hole injection or the lowest unoccupied molecular orbital for electron injection—must be energetically accessible. On the other hand, the orbitals shouldn't be so easily accessible that the semiconductor can't be effectively turned off (i.e., have a high $I^{\text{on}}/I^{\text{off}}$ ratio), which is vital to accurate logic functions and to display resolutions. This also means that a good semiconductor should not be reactive to potential contaminants like oxygen, which could change its conductivity. Sophisticated synthetic work has produced a wide range of compounds with electronic properties that could fulfill these demands. However, the parameter that is more likely to become the deciding factor for FET application is an organic chemical's capacity to form a continuous thin film that, when turned on, allows charge to move through at a quick enough pace for use in actual electronic applications.

Molecular Masonry

Unlike silicon-based semiconductors, which consist of atoms connected by strong covalent bonds, organic thin films are crystalline or amorphous collections of molecules interacting through weak van der Waals forces. Corresponding orbitals in the inorganic system mesh into continuous bands, allowing unfettered movement of charge, but in the organic case, charge carriers must move via a much slower process of hopping between localized molecular π -orbitals, upon which vibrational transitions tend to inefficiently scatter the charges.

A common measure used to judge the processing speed of FETs is field effect mobility, which is the average charge carrier drift velocity per unit electric field. High-performance silicon transistors have values well over $100 \text{ cm}^2/\text{Vs}$, while the best-performing organic semiconductors over the past five years or so have generally ranged between 0.1 and $1 \text{ cm}^2/\text{Vs}$. Thankfully, OTFTs are not expected to replace silicon in high-end products like computer processors, but are likely to be used in applications in which the $0.1\text{--}1 \text{ cm}^2/\text{Vs}$ range should suffice ($0.1 \text{ cm}^2/\text{Vs}$ is the minimum value needed to realistically drive liquid crystal display pixels; closer to $1 \text{ cm}^2/\text{Vs}$ could be necessary for smart cards). What this points out, however, is the vital importance of the solid-state alignments of the semiconducting molecules for making effective OTFTs, specifically, the importance of having significant π -orbital overlap. (This would not be an issue, of course, for semiconductor channels consisting of only one molecule, which could theoretically provide the means to attain silicon-level speeds with organic semiconductors. This is the burgeoning endeavor of

molecular, or nano-, electronics. For more information, see *Chem. Eng. News* **2002**, *80*, 38–43.)

The most successful and widely tested semiconductors for OTFT films—molecules like pentacene, α -sexithiophene, and regioregular polythiophenes (all p-type semiconductors; see Figure 2)—are indicative of the importance of molecular alignment. Over the

past five years, mobilities at or above $0.1 \text{ cm}^2/\text{Vs}$ and $I^{\text{on}}/I^{\text{off}}$ ratios of more than 10^6 (the minimum resolution value needed for the circuit drivers in liquid crystal displays) have been observed repeatedly. Pentacene has even shown values approaching $2 \text{ cm}^2/\text{Vs}$ in at least one published report (1). Their effectiveness comes from their "herringbone" geometry, or edge-to-face interaction, in the solid state, which maximizes π -orbital overlap. Small changes in their chemical

structures can make all the difference. For instance, a polythiophene with a defined pattern of side chain attachments (i.e., head-to-head or head-to-tail) likely has similar electronic properties in solution compared with a regiorandom version with the same side chains, but charge mobilities have been shown to be markedly higher in the "regular" versions, due to greater structural ordering.

If parameters for real applications have been met, why are OTFTs still only in the research stage? One big reason is that most of the high charge mobility has come from organic semiconductors that were vacuum-deposited on glass or metallic substrates. This approach has been of great use for studying the aggregate electronic properties of the molecules, but commercially, the interest in OTFTs rests with the production and cost advantages that solution-based processes can provide. Methods such as spin-coating or solution-casting a semiconductor from a solvent like toluene or chloroform require much lower temperatures and cheaper materials. In addition, they are more amenable to high-volume manufacturing. But since these strategies do not provide as much control over solid-state morphology, they have led to cuts in mobility performance.

For instance, oligothiophenes, which have attained greater than $0.1 \text{ cm}^2/\text{Vs}$ in numerous vacuum-deposited FETs, have commonly ranged between 10^{-3} and $10^{-2} \text{ cm}^2/\text{Vs}$ when solution-cast. Refining the conditions by adjusting solvents or temperature used for the deposition can be an effective strategy for improving results and has led to a few reports of $0.1 \text{ cm}^2/\text{Vs}$ mobility levels for solution-processed oligothiophenes. In addition, synthetic efforts aimed at engineering organic semiconductor crystal structures through slight adjustments in chemical substituents have become an important aspect of OTFT design.

Another challenge to moving to solution processing is a dependence on the solubility of the semiconductor molecule. Case in point: Pentacene, generally the best-performing thin film, is virtually insoluble. Synthetic endeavors have attempted to combine the molecular shape of pentacene with thiophene end groups that provide points of attachment for solubilizing substituents. An example, dihexylanthradithiophene (Figure 2), is solution processable, but has shown mobility values between 0.01 and $0.02 \text{ cm}^2/\text{Vs}$, compared with 0.15 for the vacuum-deposited film (2). Another strategy to get around the pentacene solubility problem is the precursor method. A recent study from scientists at the IBM Research

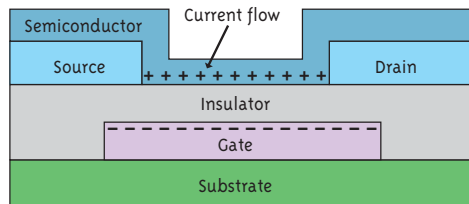


FIGURE 1: A negative gate voltage applied to a p-channel field-effect transistor forms a channel of positive current (holes) flow. Various arrangements of the different layers are possible.

Division (Yorktown Heights, NY) reported a maximum mobility of $0.89 \text{ cm}^2/\text{Vs}$ (among the highest mobilities reported for OTFTs fabricated by solution processing) from a FET that had been generated from spin-coating a soluble pentacene derivative to a substrate and briefly heating at $200 \text{ }^\circ\text{C}$ to form the active semiconductor. Longer heating at $130 \text{ }^\circ\text{C}$, which is more compatible with plastic substrates, attained the still high value of $0.13 \text{ cm}^2/\text{Vs}$ (3).

Flexible Electronics

Promising results for individual transistors are one thing, but implementing OTFTs into feasible electronic components will be necessary for them to reach any sort of commercial potential. Demonstrations have popped up over the past few years that have pushed such potential closer to reality.

As mentioned above, a major future application of OTFTs is as circuitry for flat-panel displays that could be folded or rolled up. Last year, researchers from Lucent Technologies' Bell Laboratories (Murray Hill, NJ) and E Ink Corp. (Cambridge, MA) demonstrated such a "paperlike" electronic display using 256 p-type OTFTs (with several different p-channel semiconductors, including regioregular poly(3-hexylthiophene) and α -sexithiophene) patterned on a flexible plastic sheet (Mylar), which acts as the back plane for 256 pixels containing charged pigment compounds (4). An "on" voltage to a transistor generates an electric field to a corresponding pixel electrode and the field causes movement of the pigment, which changes the pigment color, compared to an "off" voltage. Although the prototypes do not have the number of pixels needed for most consumer applications, the researchers feel that "many of the processing approaches can be extended to systems with more pixels and/or higher resolution."

Another significant aspect of the Bell Labs research is the manner in which they deposited the transistor electrodes. Generally, metallic electrodes such as gold have been used for the source, drain, and gate of OTFTs and are usually deposited with the very photolithographic processes that the organic semiconductors are there to avoid. In this work, a technique much more attuned to integration into reel-to-reel processing called microcontact printing was used, in which a finely patterned stamp applies "ink" (hexadecanethiol) to a thin film of gold. The ink molecules form a self-assembled monolayer covering the desired spots for the source and the drain, and the rest of the gold is etched away.

Work done by researchers at the University of Cambridge (U.K.) and Dow Chemical Co. (Midland, MI) in constructing an all-polymer transistor has also moved OTFTs closer to a manufacturing reality. They used a piezoelectric ink-jet printer to deposit a

conductive polymer as the electrodes and spin-coated continuous films of a polymer insulator and the active p-type semiconductor polymer, which showed a field-effect mobility of 0.02 and an $I^{\text{on}}/I^{\text{off}}$ value of 10^5 . Even "via-hole" interconnects, which are needed in integrated circuits to provide electrode connections between transistors, were fashioned by ink-jet methods.

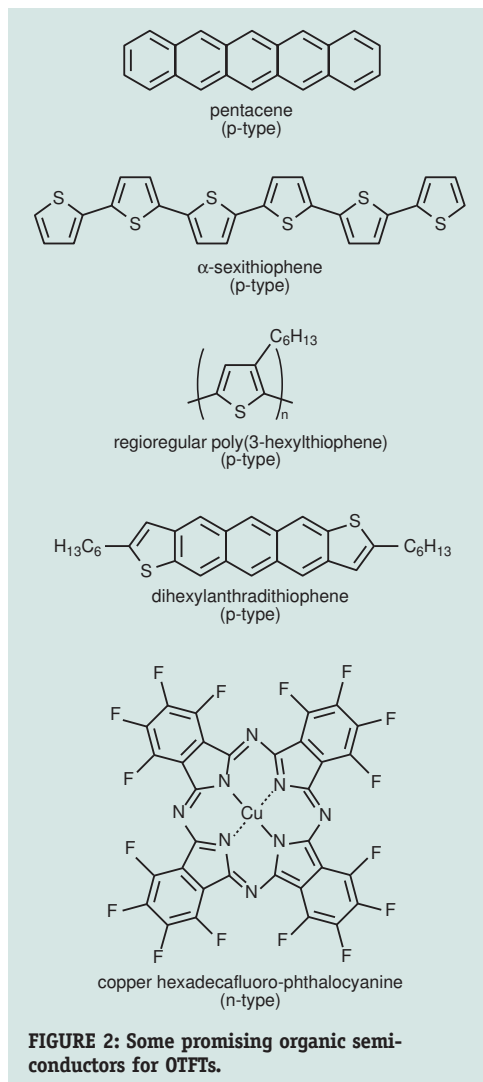


FIGURE 2: Some promising organic semiconductors for OTFTs.

Smart Cards and IDs

For applications like smart cards and remotely activated identification tags, integrated circuits that perform logic functions are necessary. Most digital circuitry uses complementary logic, in which p- and n-type transistors are incorporated into a circuit that contains both hole and electron charge carriers. This setup is ideal for performance stability and minimal power dissipation (an important factor, for example, for the ID tags powered by an ambient field). The Bell Labs group constructed complementary circuits made from 864 OTFTs per circuit, interconnecting α -sexithiophene (Figure 2) as the p-type and hexadecafluoro-copper phthalocyanine (Figure 2), one of the few air-stable n-type organic semiconductors that have been reported (6). This circuit showed operational speeds of about 1 kHz and is one of the largest-scale OTFT integrated circuits to date.

None of these examples represents a consumer-ready application, but they illustrate the capability of OTFTs to be incorporated into the types of environments—displays, integrated logic circuits—that will be necessary for this next step. They also make evident the low cost and portability aspects of the products—factors that could fundamentally change how people interact with electronic systems. As the performance parameters of solution-processed transistors continue to improve and electronic giants like IBM and Lucent continue to lead the way in research, it

seems that this new level of interaction is just a matter of time.

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David Filmore is an associate editor of *Today's Chemist at Work*. Send your comments or questions regarding this article to tcaw@acs.org or to the Editorial Office address on page 6. ♦