

# Organic and polymer transistors for electronics

Some of the major application areas for organic and polymeric transistors are reviewed. Organic complementary devices are promising on account of their lower power dissipation and ease of circuit design. The first organic large-scale integrated circuits have been implemented with this circuit approach. Organic transistor backplanes are ideally suited for electronic paper applications and other display schemes. Low-cost and other processing advantages, as well as improving performance, have led to organic-based radio frequency identification tag development. The chemical interaction between various organic and polymer semiconductors can be exploited in chemical and biological sensors based upon organic transistors.

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Organic- and polymer-transistor-based circuits are being investigated for a number of low-cost, large-area applications, particularly those that are compatible with flexible plastic circuits<sup>1-12</sup>. The organic materials that have been used as active semiconductor materials include both sublimed and solution-processed semiconductors such as pentacene<sup>6,7,13-24</sup>, oligothiophenes<sup>21,22,25-32</sup>, hexadecafluorocopper phthalocyanine<sup>28-33</sup>, polythiophene<sup>8,32,34-39</sup>, etc. This choice of materials opens up several possibilities to develop integrated circuit technologies based on organic transistors for various large-area, low-cost applications. Organic field-effect transistors (OFETs) have been proposed for applications such as display switches<sup>38</sup>, display drivers<sup>39,40</sup>, radio-frequency identification

(RFID) tags<sup>1,9,10,22,41-43</sup>, and sensors<sup>44,45</sup>. Organic/polymer transistors have also been integrated with optical devices such as light-emitting diodes (LEDs), electrophoretic cells<sup>11,46,47</sup>, and liquid crystals<sup>6,12,24,48</sup>, to name but a few examples.

In recent years, the complexity of circuits made with organic transistors has increased, and the first large-scale (864 transistor) complementary circuits have been fabricated<sup>29</sup>. Researchers have reported active-matrix displays and electronic paper with hundreds or thousands of transistors<sup>46</sup>. The speed of ring oscillators is now in excess of 100 kHz and the clock speed of clocked sequential circuits such as registers is in the kilohertz range. There is a need to develop technologies for relatively fast circuits (~100 kHz clock rate) for use in RFID tags and display drivers. One way to accomplish this is with a

complementary technology combining pentacene  $p$ -channel transistors (mobility typically  $0.3\text{--}2\text{ cm}^2/\text{Vs}$ ) with an  $n$ -channel technology utilizing materials with an electron mobility in excess of  $0.1\text{ cm}^2/\text{Vs}$ . There have been a few such materials reported in recent years<sup>49–55</sup>, with many more currently being synthesized. Calculations indicate that with such materials, ring oscillators with frequencies greater than or equal to 1 MHz and sequential circuits with clock rates of 100 kHz are possible.

In this review, we highlight developments in organic complementary circuits, RFID tags, chemical and biological sensors, and electronic paper.

## Organic complementary circuits

There are several advantages in designing circuits with  $p$ -channel (hole conducting) and  $n$ -channel (electron conducting) transistors. In the case of Si, complementary metal-oxide-semiconductor (CMOS) circuits dissipate power mostly while the constituent transistors are switching from one state to the other. There is very little static power dissipation, which means that CMOS circuits consume much less power than either  $n$ -MOS or  $p$ -MOS circuits. In organic circuits the same holds true and measurements, as well as simulations, have shown that complementary circuits require much less power. However, in the case of organic CMOS, power dissipation is dominated by leakage currents. Other advantages of complementary circuits include the ease of circuit design, greater speed, much better immunity to noise effects, and greater tolerance of variability and shifts in transistor operating characteristics. The chief disadvantage for organic CMOS has been that the electron-transporting semiconductor materials, which are needed for  $n$ -channel transistors, have tended to be more environmentally sensitive than  $p$ -channel transistor materials. The past few years have seen substantial advances in improving both the charge carrier mobility (which influences the speed) and the stability of  $n$ -channel FET materials. Some of the successful  $n$ -channel materials include hexadecafluorocopper phthalocyanine ( $F_{16}\text{CuPc}$ )<sup>29</sup>, as well as materials from the oligothiophene, fullerene, and rylene imide families with top-contact mobilities consistently in excess of  $0.1\text{ cm}^2/\text{Vs}$ <sup>49–55</sup>. Very recently, bottom-contact short channel length transistors ( $L < 5\text{ }\mu\text{m}$ ) with mobilities in excess of  $0.1\text{ cm}^2/\text{Vs}$  have been reported<sup>56</sup>. The structure of an organic thin-film transistor (OTFT) is shown in Fig. 1.

The largest complementary circuit that has been made to date is an 864 transistor 48-stage shift register circuit that operates at a clock rate of 1 kHz. This is illustrated in Figs. 2a and 2b. Other circuits that have been made include a decoder circuit and ring oscillators. With the use of improved materials, clock speeds of more than 10 kHz are anticipated, with 5 kHz recently achieved experimentally<sup>57</sup>.

Since CMOS circuits typically involve two types of semiconductors, the processing of such circuits is more complicated as both materials have to be deposited and patterned. There have been many attempts

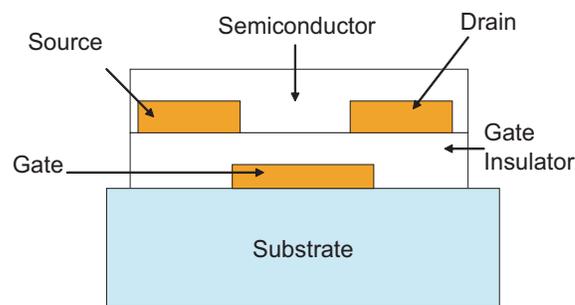


Fig. 1 Schematic showing the structure of a bottom-gate, bottom-contact, organic thin-film transistor showing the main layers and contacts.

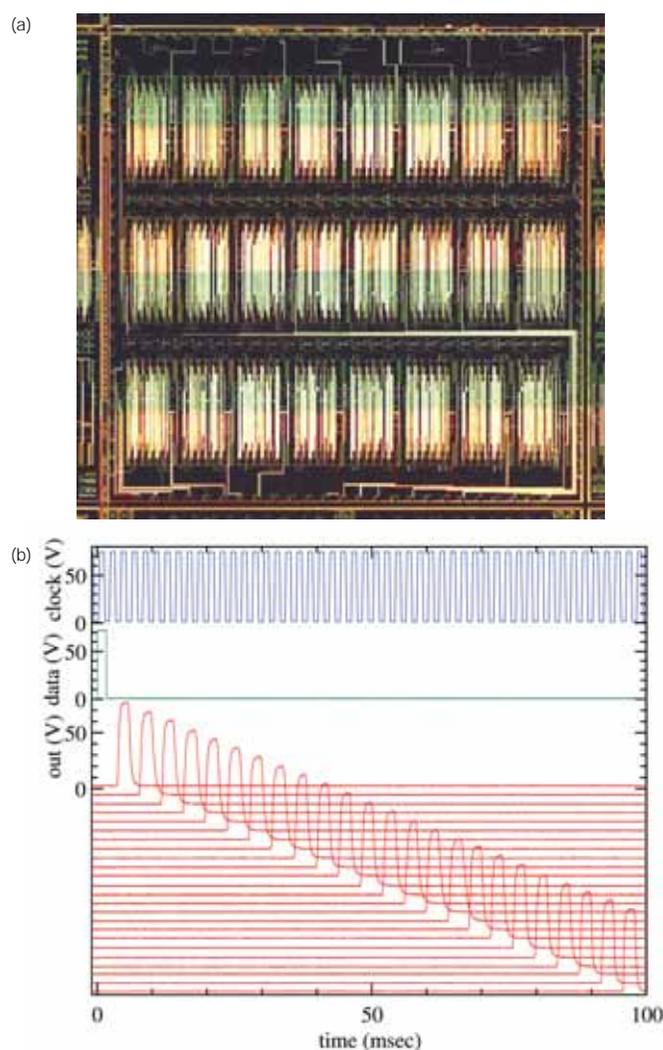


Fig. 2(a) Photograph of a 864-transistor organic complementary shift register with 48 stages. The bluish regions contain the  $n$ -channel  $F_{16}\text{CuPc}$  transistors and the yellow regions contain the  $p$ -channel oligothiophene transistors. (b) The electrical response of the 48-stage shift register. The data and clock pulses are shown. The output of alternate stages (24 in all) is shown vertically offset for clarity. The clock rate is 1 kHz. (Reproduced with permission from<sup>29</sup>. © 2000 Nature Publishing Group.)

to make the processing of organic complementary circuits easy. The traditional complementary circuit design paradigm, which evolved from Si technology, involves different compositions for the  $n$ -channel and  $p$ -channel devices. However, in organics, it is possible to create a device that functions as a  $p$ -channel and an  $n$ -channel device, depending upon the electrical bias conditions. This is done by mixing up the active semiconductor to have two components: one electron transporting and the other hole transporting. Such mixing can be done at the molecular level by using donor-acceptor combinations akin to those employed in solar cells<sup>58</sup> or at a spatially coarser level. It is also possible to have two thin layers instead of a mixture<sup>59</sup>. More recent work has shown that some semiconductor materials act as ambipolar semiconductors and transport both electrons and holes. This is accomplished by suitable chemical treatments of the semiconductor/dielectric interface to reduce electron trapping<sup>60,61</sup>.

Despite the additional complexity involved, the practical motivations to switch to CMOS are many. For example, in RFID tag circuits the total power budget needs to be minimized. If complementary circuits, which dissipate less power, are used then the tag can be read from a greater distance. This will in turn enhance the acceptance of this technology in the marketplace. Another key advantage is speed. For the same mobility, complementary circuits are about ten times faster than  $p$ -channel FETs and require fewer transistors. This difference can be vital in some applications. It can mean that the clock rate of display drivers can be increased by a factor of ten in CMOS circuits, making them acceptable for a wider range of applications.

## Electronic paper

One of the earliest prototypes based on organic transistors that was realized was active-matrix electronic paper. In such systems, an organic or polymer transistor backplane drives display elements such as electrophoretic cells. The display elements have a memory effect and are often electric field driven. This means that the drive circuitry needs to be on only when the information is changed and frequent refreshes, which are characteristic of liquid crystal displays, are not required. The current drive requirements are typically much less than those required for an active-matrix organic light-emitting diode (OLED) display. This factor and the binary nature of the display element means that the requirements of the transistor in terms of current drive, as well as uniformity of electrical performance across the entire array, are much less stringent. Electronic paper is often required to be flexible and necessitates processing over relatively large areas. These factors also play to the strengths of organic transistor technology. In the first report on organic-transistor-based electronic paper, pentacene transistors were used along with soft lithographic methods to pattern the conductors<sup>46</sup>. The backplane sheet is shown in Fig. 3. More recently, many companies have attempted to commercialize electronic paper based on polymer electronics.

## RFID tags

Another major application area for organic and polymeric transistors is that of RFID tags. RFID tags are expected eventually to be deployed at the item level (meaning that such tags will be used in the identification of individual retail goods in much the same way as barcodes are presently employed). The main barrier to this happening is the high cost of Si-based tags, which, although steadily falling, is unlikely to be low enough to warrant large-scale deployment. This application space therefore represents an opportunity for organic- and polymer-transistor-based systems. In the following section, we describe the schematic block-diagram level structure of a typical RFID tag and discuss how some of the functionality can be implemented with organic transistors.

A typical RFID tag is shown in Fig. 4 and contains three major functional blocks and an antenna coil. The antenna coil is used to magnetically couple radio frequency (RF) energy from an RFID reader into the tag. An RF energy rectifier in the RF interface provides a dc power supply to the entire RFID tag and must operate at the frequency of the signal from the antenna coil. This frequency can be 125 kHz or 13.56 MHz, which are the presently allowed frequencies for this type of RF device. The RF interface also contains a capacitor that stores energy from the rectifier and powers the rest of the circuitry in the tag. 125 kHz tags have very long antennae and have other disadvantages that have led to the evolving emergence of 13.56 MHz as the preferred frequency for item-level tags.

In order for organic transistors to rectify at 13.56 MHz, they need to operate in the non-quasi static (NQS) regime<sup>62,63</sup>. In the NQS regime of operation, the transistor drain currents have not yet reached the equilibrium (quasi-static) value expected for a given set of bias voltages. During this time, channel formation is taking place and there is a build-up in drain current with time. Transport in this regime can be

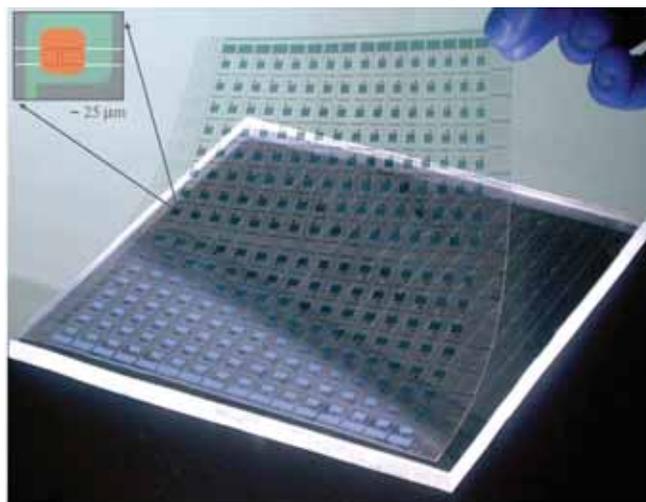


Fig. 3 The backplane for a 256-element electronic paper system described in detail elsewhere<sup>46</sup>. Each pixel consists of an organic transistor with channel length  $<20 \mu\text{m}$ .

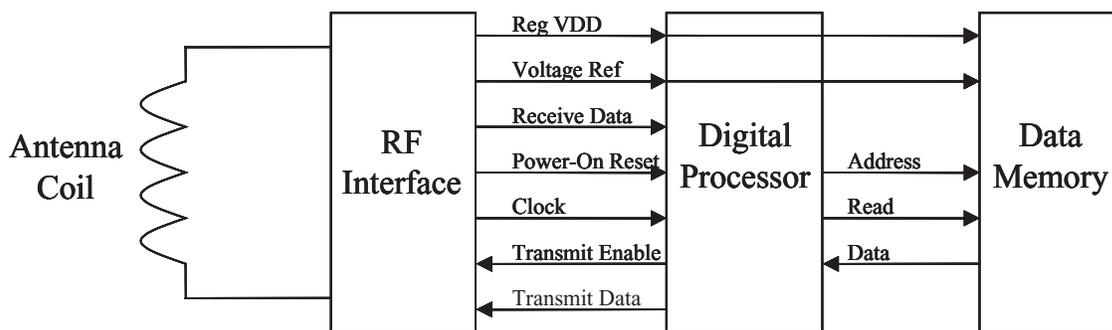


Fig. 4 Block diagram of an RFID tag showing the important components. (Reproduced with permission from<sup>62</sup>. © 2005 Materials Research Society.)

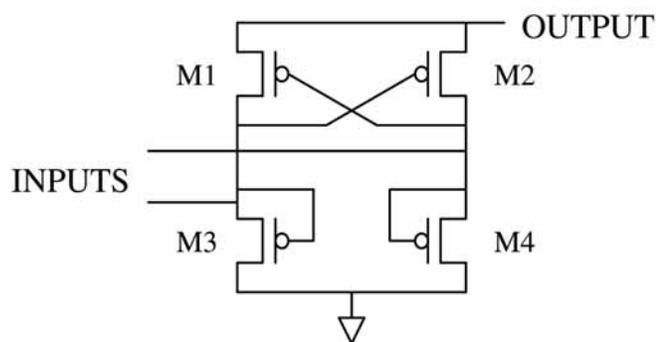


Fig. 5 Circuit diagram of a full-wave rectifier circuit based on *p*-channel organic transistors. (Reproduced with permission from<sup>62</sup>. © 2005 Materials Research Society.)



Fig. 6 Photo of an RFID tag component circuit. (Courtesy of OrganicID Corporation.)

understood by examining the transient response of an organic transistor to a voltage step input applied to the gate and drain simultaneously<sup>64</sup>. Charges are injected from the source electrode and drift toward the drain under the influence of the source-drain field. For an initial period there is no external drain current measured as the carriers are transiting between the source and drain electrodes. The fastest carriers arrive at the drain and at this point an external drain current is measured. There is then a gradual buildup in drain current as the channel carrier density approaches its equilibrium value, at which point the drain current stabilizes. With pentacene transistors, 13.56 MHz rectifiers with useful

efficiency have been fabricated by the OrganicID Corporation<sup>62,63</sup>. The circuit diagram of such a rectifier is shown in Fig. 5 and a photo of the flexible circuit in Fig. 6.

The digital processor contains several thousand transistors and can be either *p*-MOS or CMOS. The advantages of CMOS for this application have been described previously. The clock rates needed in the processor are significantly less than the carrier frequency. It is expected that organic and polymer transistor circuits will be fast enough to accomplish the required functionality.

## Chemical and biological sensors

There are numerous chemical sensor technologies that have been explored and a few of these have been successfully commercialized<sup>65</sup>. The utility of organic and polymeric transistors for sensor applications arises from the fact that these materials are first and foremost organic chemicals and can form weak chemical interactions with a variety of vapor analytes. The semiconducting behavior of the organic materials permits the transduction of chemical information to electronic information in the solid state. The availability of a large number of semiconductors will permit analyte identification through 'fingerprinting', in which a particular analyte produces a unique pattern of responses with different semiconductors. These basic requirements for the creation of a viable sensor technology have already been demonstrated and are reviewed below.

The drain current of an organic transistor with the active semiconductor dihexyl  $\alpha$ -sexithiophene is shown (in red) in Fig. 7 as a function of time with the device in a normal air ambient<sup>66</sup>. There is a slight decrease in current with time, which is very common in organic transistors and is referred to as the bias stress effect. The current in the same device is also shown (in green) when a stream of hexanol-containing vapor is delivered for 5 s. There is a marked change in current that reflects the effect of the chemical interaction between the alcohol and the semiconductor on the semiconducting properties. Such changes in current are reversible and the original current can be restored by reverse biasing the transistor. The change in current for more than 60 successive exposures of the device to alcohol is shown in Fig. 8. In each case there is an electrical refresh that takes

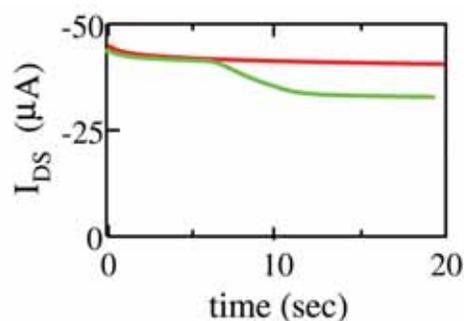


Fig. 7 Drain current of an organic transistor chemical sensor under normal ambient air (red) and under a stream of alcohol vapor (green). The alcohol is delivered for a 5 s period between 5 s and 10 s. The reduction in current is the result of charge trapping caused by the alcohol. (Reproduced with permission from<sup>44</sup>. © 2001 American Institute of Physics.)

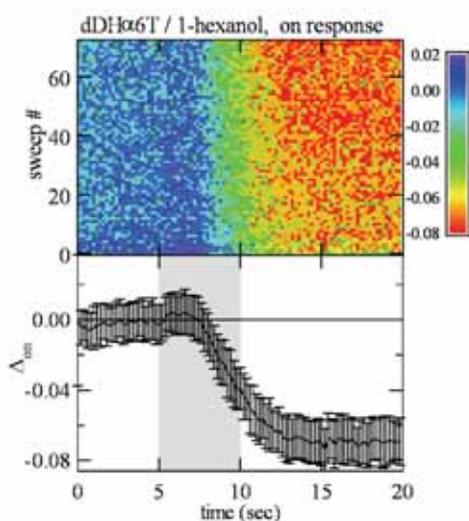


Fig. 8 Response of an oligothiophene transistor sensor after repeated exposure to hexanol, which is delivered for 5 s between 5 s and 10 s. In the top figure, the fractional change (decrease) in drain current is color coded. After each exposure, the sensor is electrically refreshed to bring the drain current back to within 2% of the original current. In the bottom figure, the change in current is shown for over > 60 runs. (Reproduced with permission from<sup>44</sup>. © 2001 American Institute of Physics.)

approximately 1 min and consists of a reverse bias step to release trapped charge and restore the device to close to its original state. This repeatability is an important requirement for sensor technology. The next requirement is that the responses of different semiconductors to a particular analyte are also different. This will facilitate the construction of an electronic-nose-type sensor<sup>66</sup>, as illustrated in Fig. 9.

The fall in drain current with time is the result of charge trapping at the grain boundaries and interfaces. Careful studies of the extent of current decrease with channel length indicate that the longer the channel length the greater the extent of the trapping, which results in a threshold voltage shift and/or change in mobility<sup>67-69</sup>. When the channel length is reduced, the sensor functions in the contact injection limited regime and the current increases, sometimes very sharply, with analyte delivery. This opens up a new type of sensor action in which

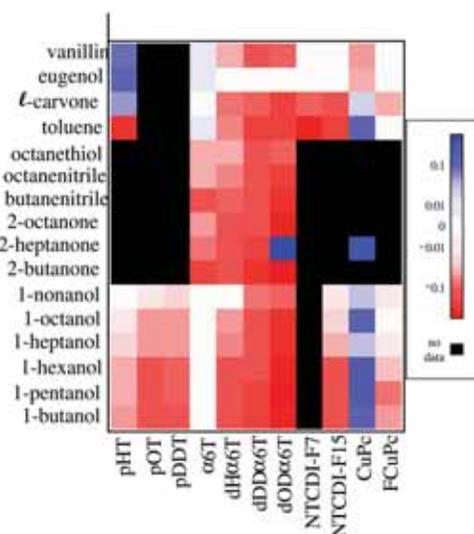


Fig. 9 The response of several organic/polymeric semiconductors to various analytes. The change in drain current is color coded with blue representing a current increase and red a current decrease. The different response of the various semiconductors to an analyte will permit the construction of an electronic nose in which a characteristic 'fingerprint' of responses is used to identify the analyte. With the use of more semiconductors and receptors, the fingerprint becomes more unique. (Reproduced with permission from<sup>44</sup>. © 2001 American Institute of Physics.)

the analyte molecules influence the charge injection properties of the contact<sup>70,71</sup>. A scanning electron micrograph of a nanoscale polymer transistor is shown in Fig. 10 along with the response to analyte delivery (Fig. 11).

The extension of sensing to water-based analytes has also been achieved and opens up a new area of opportunity for polymer and organic transistor sensors in sensing various biochemicals and biological materials. In the initial report, a carefully prepared organic transistor was used to sense analytes such as lactic acid and glucose<sup>72</sup>. The

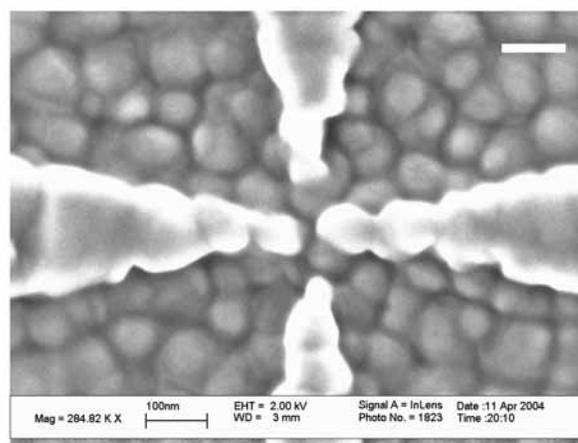


Fig. 10 Scanning electron micrograph of a nanoscale organic transistor sensor. Two of the electrodes are source and drain, while the other two are guard electrodes to collect spreading currents. The operation of such sensors is described in detail elsewhere<sup>69</sup>.

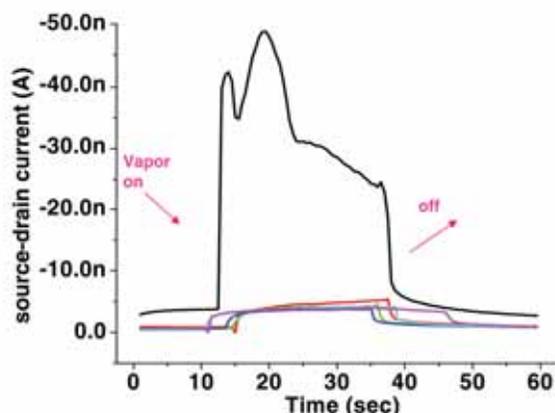


Fig. 11 Electrical response of a nanoscale polymer FET sensor upon exposure to an alcohol. The substantial rise in current makes such sensors very sensitive. (Reproduced with permission from<sup>71</sup>. © 2006 Elsevier Ltd.)

transistor was operated under water with the channel in contact with the analyte, which was dissolved in the water. In order for the device to function without electrical shorts, the source and drain contacts had to be covered with a hydrophobic insulator. This protects the high electric field regions from contact with the water. The structure of the sensor transistor is shown schematically in Fig. 12a. For practical utility, such sensors must be integrated with microfluidics to facilitate analyte delivery. This has also been demonstrated, with a microfluidic channel running along the transistor electrical channel. Two inlets were provided to the fluidic system: one being the analyte (which was lactic acid solution) and the other water. The transistor current clearly and repeatedly was able to sense the analyte delivery, during which time the source-drain current fell. Flushing the microfluidic channel with water restored the source-drain current to close to the original value, as show in Fig. 13. Recent work is building on this early development and holds great promise in a number of sensing applications<sup>73</sup>.

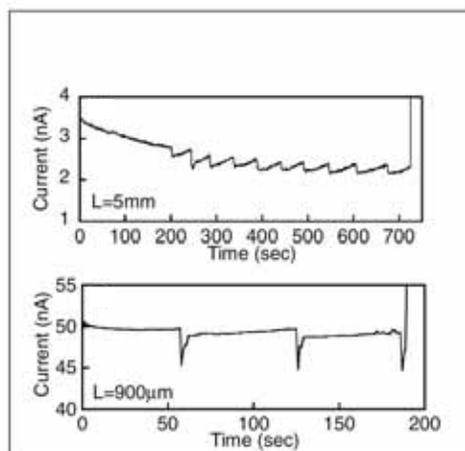


Fig. 13 Photo (right) of an organic transistor biochemical sensor in which a microfluidic channel is integrated with the device and is located in the middle of the transistor channel. Analyte (lactic acid) and water are delivered to the system. When lactic acid is delivered, the current falls; the current is restored when the channel is flushed with water. This is illustrated in the figure on the left. (Reproduced with permission from<sup>72</sup>. © 2002 American Chemical Society.)

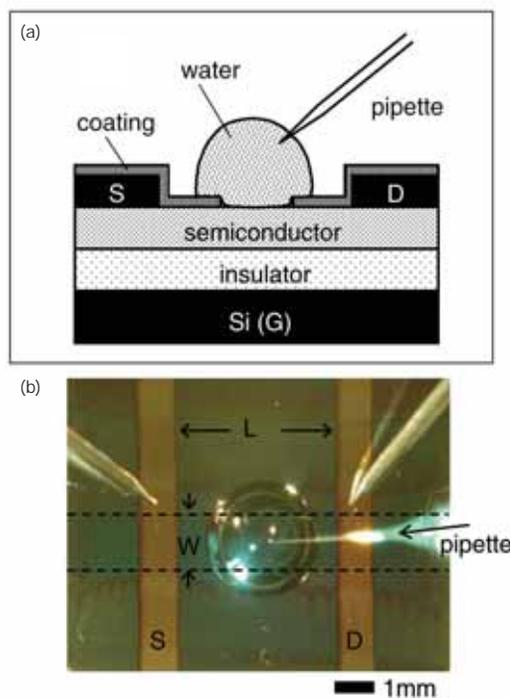
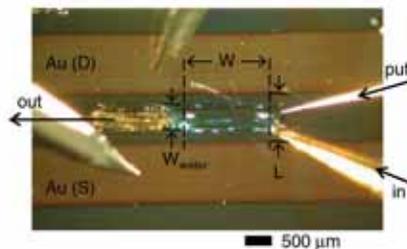


Fig. 12 Schematic (a) and photo (b) of an organic transistor biosensor designed to operate under water. The source and drain electrodes are protected by a hydrophobic insulator. The analyte can interact with the channel of the transistor that is exposed. (Reproduced with permission from<sup>72</sup>. © 2002 American Chemical Society.)

## Other applications and future outlook

In addition to the applications reviewed above, organic transistors have been proposed for other applications. Since the first reports of integrated OLEDs and transistors<sup>74</sup>, there have been advances in the performance of both organic/polymer LEDs and transistors. This has led to increased research activity in designing organic FET-based pixel



electronics for active-matrix OLED displays<sup>75</sup>. Light emission from an organic transistor has been proposed<sup>76</sup> and subsequently observed by several groups<sup>77-79</sup>. This promises to be an interesting area of device research in terms of both the materials that need to be developed for efficient light emission and transport, and the device design challenges and opportunities that exist. Another applications area that appears promising is the use of OFETs in large-area sensor and detector circuits<sup>80,81</sup>. Along these lines, it is anticipated that new and innovative applications that take advantage of the unique properties of organic

and polymer transistors will continue to appear, providing added impetus for advances in both materials and processing development. 

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