

double-stranded DNA through the central channel of its hexameric ring<sup>8</sup>.

Another addition to this protein superfamily came as a greater surprise. The core of RecA and many helicases is also seen in the  $F_1$ -ATPase<sup>9</sup>. This protein, found only in higher organisms, is part of the  $F_1F_0$ -ATP synthase, which makes ATP — the main source of energy for most cellular processes. So it seems that although the functions (and sequences) of proteins such as helicases and the  $F_1$ -ATPase have diverged greatly, aspects of their organization into hexameric rings have been preserved.

Gomis-Rüth *et al.*<sup>1</sup> now add the *E. coli* protein TrwB to the family. They have determined the structure of TrwB, and find that it exists as a hexameric ring that is remarkably similar to those formed by the  $F_1$ -ATPase, RecA and certain helicases (Fig. 1). The structure and topology of the core regions are also very similar.

The TrwB protein is embedded within the bacterium's outer membrane and is encoded in a small, circular DNA molecule that is not part of the main chromosome. TrwB is needed for conjugation — the transfer of singlestranded DNA between bacterial cells. This process is crucial for the spread of antibiotic resistance within a population of bacteria. Gomis-Rüth et al.'s crystal structure1 did not contain DNA, but a mechanism can still be put forward for how the TrwB ring transfers it between bacteria. TrwB requires energy from ATP hydrolysis to allow conjugation to proceed, so it seemed reasonable that TrwB might be acting as some form of energy-driven motor to move DNA between cells. It now seems likely that the protein not only forms the transmembrane pore that is needed for such transfer, but also acts as the ATP-driven pump that transfers the DNA, working in a similar way to RuvB, mentioned above8.

Gomis-Rüth *et al.*'s results<sup>1</sup> also have more general implications. Many proteins have been predicted to be helicases because they contain sequence motifs that are now understood to be part of the conserved core. But neither TrwB nor RuvB works by separating strands of DNA, so these predictions may be incorrect. The putative helicases might be DNA motors involved in pumping or moving along DNA.

Another implication is that proteins that are not classified as helicases, such as the protein SpoIIIE from the bacterium *Bacillus subtilis*, may also be part of this structurally similar superfamily. SpoIIE is involved in transferring DNA between a *B. subtilis* mother cell and a prespore. This protein actually has a similar amino-acid sequence to that of TrwB, and is capable *in vitro* of moving along DNA in an ATP-dependent manner<sup>10</sup>. Perhaps SpoIIIE also forms a hexameric ring around DNA, functioning *in vivo* as yet another DNA pump.

Further structural studies of such pro-NATURE | VOL 409 | 1 FEBRUARY 2001 | www.nature.com teins will be essential in working out how cells move DNA around. They may also tell us about the evolutionary history of some of the basic machinery for transforming energy and manipulating DNA.

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# Materials science Ultrafast colour displays

### Michael Grätzel

Materials that change their colour as a result of a simple electric potential could be key to a new generation of flat-screen displays. But the speed at which they undergo this change of hue has held them back, until now.

lectrochromic devices are transparent materials that become coloured when an electric potential difference is applied to them. This useful property has already been exploited commercially - for example, in car rear-view mirrors that can be darkened to stop lights from other vehicles from blinding the driver. But the full potential of electrochromic devices has yet to be realized. They could appear as electrochromic windows panes of glass that can be darkened at the flick of a switch to provide privacy. Alternatively, they could be used in high-contrast dynamic displays such as flat-panel television and computer screens. The main reason these applications remain on the drawing board is the long time it takes present electrochromic devices to switch between transparent and coloured states.

Writing in the *Journal of Physical Chemistry B*, Cummins *et al.*<sup>1</sup> report a new type of electrochromic system that promises to overcome this problem. Their device yields highcontrast images that can be rapidly created and erased. In addition, the optical appearance of the images does not depend on the angle from which they are viewed, an important attribute for use in display screens.

There are two basic types of electrochromic device in use at the moment. One uses a thin, transparent metal-oxide film, such as tungsten trioxide (WO<sub>3</sub>), which is deposited onto a conducting glass substrate. When a negative potential is applied to the glass, there is an influx of conducting electrons into the metal-oxide film, which turns the WO<sub>3</sub> blue. Because the system wants to be electrically neutral, this causes positive ions, usually lithium (Li<sup>+</sup>), to move into the film from the surrounding electrolyte. Without this charge compensation, the electrons could not be injected into the film. But the

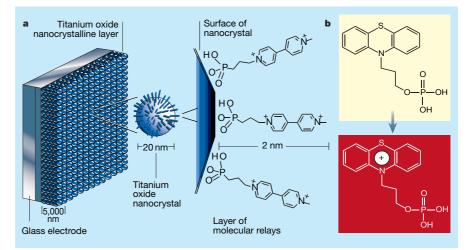


Figure 1 Ingredients for making a dynamic colour display. Cummins *et al.*<sup>1</sup> have built an electrochromic cell from two porous metal-oxide films, sandwiched between glass electrodes. a, The negative electrode is coated with a layer of TiO<sub>2</sub> nanocrystals, with viologen molecules anchored to the surface of the nanocrystals. Viologen molecules turn blue when injected with charge. b, The positive electrode consists of a nanocrystalline SnO<sub>2</sub>:Sb film, which is linked to phenothiazine molecules, which turn red when oxidized. When the electrochromic cell is filled with an electrolyte and a voltage is applied, the colour can be switched on and off in under 250 milliseconds.

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diffusion of the positive ions into the oxide layer is slow, taking minutes to complete.

Slow charge diffusion also limits the switching speed of the second type of electrochromic device. Here the colour change arises from the oxidation (removal of electrons) or reduction (addition of electrons) of molecules known as 'molecular relays'. A typical example is methyl viologen, which is not coloured in its normal oxidation state, but turns deep blue when reduced. Such relays have so far been used either in solution or incorporated into a polymeric film.

Attempts have been made to overcome the charge diffusion problem by attaching the relays to the rough surface of a porous oxide film<sup>2-4</sup>. Typically, the film consists of a network of interconnected semiconducting or conducting metal-oxide nanocrystals, deposited onto a conducting glass electrode. The particles are fused together by heating to form a network that allows electric charges to move through it easily. Because the oxide crystals are so small, the film has an extraordinarily large internal surface area. The ratio between the internal surface area and the electrode's geometrical area (its 'roughness factor') approaches 1,000 for a film that is only a few micrometres thick. This means that a high number of molecular relays can be contained in a relatively small area.

Cummins et al.1 have developed this concept and assembled an electrochromic cell that uses two metal-oxide films - one at the negative electrode and, unusually, one at the positive electrode. The negative glass electrode is coated with a porous titanium dioxide  $(TiO_2)$  film, which is itself coated with a single layer of viologen molecules. These molecular relays are anchored firmly to the surface of the TiO<sub>2</sub> nanocrystals by phosphonate groups (Fig. 1a). The positive glass electrode features another nanocrystalline film, this time made up of antimony-doped tin dioxide (SnO<sub>2</sub>:Sb). This film has a layer of phosphonated phenothiazine molecules attached to it. In their normal state, these molecules have a weak yellow colour, but when they are oxidized, they turn red (Fig. 1b). The electrochromic cell is filled with an electrolyte and sealed.

The device can be switched from an uncoloured to a deeply coloured state by applying a potential difference of 1.2 volts to the system. This reduces the viologen, turning it blue, and oxidizes the phenothiazine. The overall result is a blue–red colour (Fig. 2). Similarly, reversing the potential removes the colour from the system. The cycle can be repeated many thousands of times without significant degradation of performance. Moreover, the colour persists for more than 600 seconds after the voltage is switched off.

Several remarkable features make this system very attractive for use in dynamic displays. The huge internal surface area of the two nanocrystalline films makes the electrochromic process very efficient, even though



Figure 2 Prototype of a fast switching, high-contrast electrochromic device viewed at a low angle.

the electron relay forms just a single molecular layer across the surface of the film's porous interior. On a flat surface the optical absorbance (colour change) caused by reduction or oxidation of the relay would be hardly visible. But when deposited on a nanocrystalline film, the coloration of the molecular relays is amplified by more than 1,000 times because of the high number of relay molecules present. The coloration efficiency, expressed as the change in the film's optical absorbance per unit of injected charge, is higher for these systems than for conventional electrochromic layers. This is because an electric charge injected into an organic molecule, such as viologen, which produces intensely coloured radical ions, causes a larger change in optical absorbance than when it is transferred to an oxide such as WO<sub>2</sub>.

But the most striking aspect of this work is the fast rate at which the device can be switched. Its speed can be attributed to a combination of rapid charge-motion within the metal oxide, ultrafast electron-transfer from the nanocrystalline metal-oxide to the relay molecule, and efficient movement of the charge-balancing ions in the electrolyte within the pores<sup>3,4</sup>. The switching times achieved by Cummins *et al.* are in the range of milliseconds, which is about a thousand times shorter than is possible with conventional electrochromic systems. Further acceleration of the switching cycle into the microsecond range appears possible by judicious choice of the nanocrystalline materials and by reducing the electrical resistance within the electrochromic device.

High-contrast images created in electrochromic devices retain their quality even when viewed at a low angle - in contrast with conventional liquid crystal displays. And with molecular relays there is a wide choice of molecules that can generate a specific colour, unlike devices that use WO<sub>3</sub>, which are limited to the colour blue. The colour change depends in an exponential way on the applied potential, allowing the device to be fashioned into a passive matrix display where the surface is divided into pixels. Each pixel can be addressed individually by applying a voltage difference locally at the edge of the panel. The combination of a molecular charge-relay with a porous support opens up exciting new opportunities for low-cost, thin-film molecular electronics. Michael Grätzel is in the Laboratory for Photonics and Interfaces at the Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland. e-mail: michael.graetzel@epfl.ch

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#### Oceanography

# The Rossby rototiller

David A. Siegel

Planetary waves, also known as Rossby waves, propagate throughout the world's oceans on very large scales. They influence the ocean–climate system and also, it seems, the delivery of nutrients to the ocean surface.

Data from Earth-viewing satellite systems have advanced to the point that marine scientists can carry out global analyses that were inconceivable just a few years ago. An excellent example can be found in the papers by Uz *et al.* on page 597 of this issue<sup>1</sup> and by Cipollini *et al.*<sup>2</sup> in the 15 January issue of *Geophysical Research Letters*. Both groups find a significant covariation of global chlorophyll concentrations with satellite determinations of sea level. The upshot of their investigations is the recognition that so-called planetary or Rossby waves provide a physical mechanism for bringing nutrients

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to the surface layers of the open ocean and feeding phytoplankton productivity.

Like all plants, phytoplankton require both light and nutrients to grow. But only in the upper 50 to 150 m of the water column of the open sea is there enough light for phytoplankton photosynthesis to occur. In this thin, well-lit euphotic zone, available nutrients are rapidly assimilated. Typically, then, it is the supply of new nutrients from deeper water that limits productivity in the open ocean.

In most coastal and high-latitude regions of the sea, vertical mixing and upwelling provide sufficient vertical fluxes of nutrients to