

ORGANIC/METAL INTERFACES

Seeing both sides

To improve organic electronic devices, the principles underlying organic-film/metal-electrode interfaces must be understood. A comprehensive study of the organic electron acceptor TCNQ on a copper surface reveals a structural rearrangement of both the organic molecule and the metal surface atoms after charge transfer across the interface.

Clara Santato and Federico Rosei

Organic electronics is a field of research of growing importance and impact¹. In an organic electronic device, a thin film of an organic semiconductor is used as active material for rectification and illumination (light-emitting diodes); current modulation (field-effect transistors (FET)); a typical layout of this type of device is shown in Fig. 1a); current modulation and light emission (light-emitting FET); or solar-energy conversion (photovoltaic cells). Some important advantages of organic semiconductors over their inorganic counterparts are their processability in solution and the opportunities they present for tailoring properties — such as the colour of the light they emit — through rational chemical synthesis.

Despite continuous progress in this field there are still, however, significant hurdles to be overcome at a fundamental level. The main challenges in organic electronics are: (1) identifying new ambipolar materials, able to transport both electrons and holes; (2) controlling the molecular arrangement in the film to increase charge carrier mobility; (3) designing and realizing molecular structures that are stable (for example, against air oxidation) for long-term operation; and (4) improving the properties of the organic-film/metal-electrode interface (inset in Fig. 1a)^{2,3}, where charge carrier injection (diodes and transistors) and charge carrier collection (photovoltaic devices) take place. Indeed, progress in organic electronics requires a detailed understanding of all the relevant chemical and physical processes that occur at organic-film/metal interfaces. For example, the efficiency of organic light-emitting devices depends critically on charge injection from the metal electrode into the organic film. Although significant progress has been made in materials design and synthesis, interface engineering still needs significant improvement².

Writing in *Nature Chemistry*, a collaboration led by Roberto Otero and Stephen Tait reports a model study of the interface between the strong electron acceptor tetracyano-*p*-quinodimethane

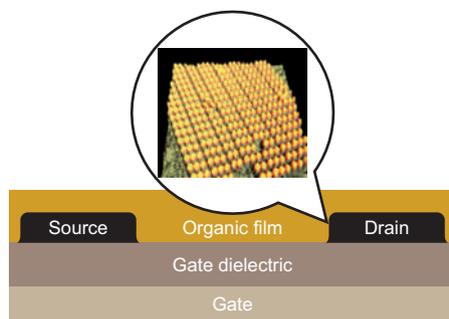


Figure 1 | Organic/metal interfaces. **a**, Scheme of an organic FET. The inset is a STM image of TCNQ on copper, representing the organic/metal electrode interface. **b**, Three-dimensional representation of a TCNQ molecule adsorbed on a metal surface. Images courtesy of R. Otero.

(TCNQ; Fig. 1b) and copper. This work provides new insight into the properties of organic-film/metal interfaces and their mutual interactions⁴. Otero, Tait and co-workers illustrate one of the most complete investigations so far on this type of interface, combining a multitude of techniques such as high-resolution scanning tunnelling microscopy (STM), low-energy electron diffraction, near-edge X-ray absorption fine structure, X-ray photoelectron spectroscopy and density functional theory (DFT) calculations. In particular, they describe a significant structural rearrangement at both sides of the TCNQ/copper interface induced by charge transfer.

Surface reconstruction induced by molecular overlayers has been observed since the early 1990s (ref. 5), and local reconstructions induced by individual molecules were observed during the past decade⁶. In a recent, elegant study, Bedwani *et al.* combined STM and DFT to investigate the adsorption of tetracyanoethylene on copper⁷, reporting that the adsorption is so strong that it induces a local reconstruction of the surface, in which the top-most copper atoms bound to tetracyanoethylene undergo significant buckling. Otero, Tait and co-workers have taken this concept an important step further. The power and depth of their research stems

from the combination of a complete suite of surface sensitive techniques that yield complementary information. Scanning probe microscopes are able to visualize organic molecules adsorbed at surfaces with unprecedented resolution, allowing the investigation of the conformation and adsorption properties of anything from a few molecules up to a saturated monolayer. Understanding the interaction between a molecular film that consists of several stacked layers and an underlying surface, however, requires more knowledge. This knowledge can only be accessed through probes that integrate over large areas and measure electronic and chemical properties at the interface, with adequate depth resolution. Most studies of similar systems have used X-ray and ultraviolet photoelectron spectroscopy as the main probes, sacrificing 'local' resolution to obtain information on extended properties^{8,9}. Conversely, combining STM and DFT, although elegant and powerful, focuses on a few molecules and very small areas because of resolution and computational constraints, and observations cannot necessarily be extrapolated over large areas.

Although the observed mutual 'restructuring' is a mechanical effect, from an electronic point of view the metal surface actually acts as the 'soft' and the

molecular overlayer as the 'hard' partner. The adsorption of organic molecules, attracted to the surface by van der Waals forces, causes a lateral displacement of electronic charge, and effectively 'pushes' back the electron density of the underlying metal substrate that previously extended into vacuum (known as the 'cushion' or 'push-back' effect).

The metal-surface reconstruction caused by molecular adsorption can influence the nucleation and growth of the organic film, affecting both charge carrier injection and transport. For example, structural defects in the organic film at the organic/metal interface may lead to a high density of trapped charge carriers in proximity to the electrode, ultimately contributing to a high contact resistance in FET devices¹⁰. It is now well recognized that the figures of merit of charge transport in the FET configuration are not merely materials properties — only dependent on the organic semiconductor used — but actual device properties — that is, dependent on the choice of device structure, including electrode work function and the quality of the organic/metal and organic/substrate surface interfaces.

The chosen TCNQ/copper surface interface is a highly idealized version of

interfaces found in actual devices. For example, electrodes are generally not highly oriented, smooth single crystals, but rather have a high degree of roughness and disorder, which in itself can heavily affect the morphology of the organic film. Smoother surfaces promote the nucleation of larger islands where the number of grain boundaries is lower, leading to improved transport.

Future studies should extend these concepts well into the third dimension, bridging the gap between the early stages of growth and more realistic systems made of thicker organic films. It will also be necessary to evaluate the role played by complex electronic effects such as band bending. Another important aspect is to carefully examine the effect of the most common contaminants such as oxygen and hydrocarbons, which affect both the morphology and the electronic properties of the interface. This can be achieved for example by introducing selected gases into the ultrahigh-vacuum chamber, mimicking more realistic device-fabrication conditions in a controlled way. Although much is still to be investigated, the research of Otero, Tait and colleagues shows that the dramatic consequences of mutual restructuring

induced by charge transfer should be taken into account and used to help guide the choice of organic–metal pairs when designing devices. □

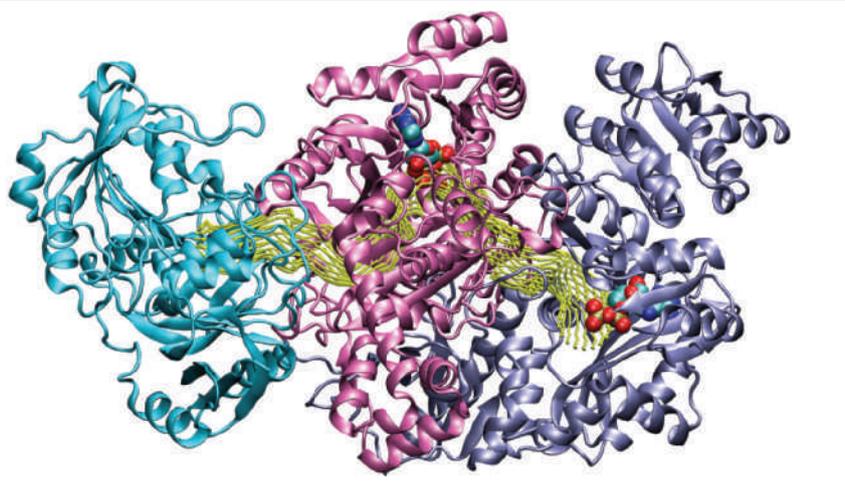
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THEORETICAL ENZYMOLOGY

Carbamate tunnel syndrome



Some enzymes that carry out multiple reaction steps are known to contain tunnels that are used to direct the transport of reactive intermediates. One such enzyme is carbamoyl phosphate synthetase from *Escherichia coli*, which catalyses the production of carbamoyl phosphate — an intermediate in nucleotide

and arginine synthesis. An important step in this synthesis is the transport of carbamate, after its formation, through a ~40-Å-long tunnel within the enzyme to another active site where it is phosphorylated to give the final product.

Now Frank Raushel, Yi Qin Gao and colleagues from Texas A&M University have

used molecular dynamics simulations to reveal that the tunnel is composed of three pockets filled with water connected by two narrow passages (pictured; *J. Am. Chem. Soc.* **132**, 3870–3878; 2010). To understand the factors that influence carbamate transport, they also calculated the potential energy of the system under different substrate–product binding conditions with carbamate at different positions along the tunnel.

The researchers found that phosphate, a by-product from the carbamate-forming reaction step, must be released from that active site before the carbamate can enter the tunnel. This release causes the rotation of an arginine residue within the enzyme that unblocks the tunnel entrance, and also shields the carbamate from undesirable electrostatic interactions with three glutamate residues within the tunnel.

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