

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. □

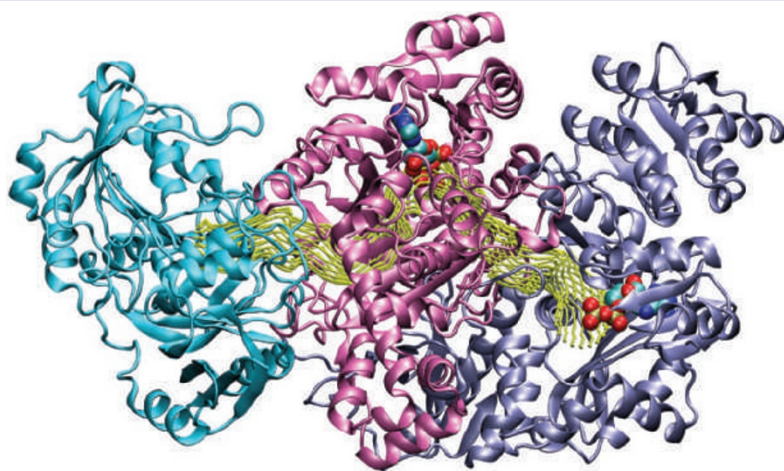
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References

1. Malliaras, G. & Friend, R. *Phys. Today* **58**, 53–58 (May 2005).
2. Braun, S., Salaneck, W. R. & Fahlman, M. *Adv. Mater.* **21**, 1450–1472 (2009).
3. Lindstrom, C. D. & Zhu, X. Y. *Chem. Rev.* **106**, 4281–4300 (2006).
4. Tseng, T.-C. *et al. Nature Chem.* **2**, 374–379 (2010).
5. Gimzewski, J. K., Modesti, S. & Shlittler, R. R. *Phys. Rev. Lett.* **72**, 1036–1039 (1994).
6. Otero, R. *et al. Nano Lett.* **4**, 75–78 (2004).
7. Bedwani, S., Wegner, D. & Crommie, M. F. *Phys. Rev. Lett.* **101**, 216105 (2008).
8. Witte, G., Lukas, S., Bagus, P. S. & Woll, C. *Appl. Phys. Lett.* **87**, 263502 (2005).
9. Koch, N., Duhm, S., Rabe, J. P., Vollmer, A. & Johnson, R. L. *Phys. Rev. Lett.* **95**, 237601 (2005).
10. Wang, S. D., Minari, T., Miyadera, T., Tsukagoshi, K. & Aoyagi, Y. *Appl. Phys. Lett.* **91**, 203508 (2007).

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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The original version of this story first appeared on the Research Highlights section of the *Nature Chemistry* website.