

## SURFACE CHEMISTRY

## Building with molecules

Linking individual molecular building blocks with covalent bonds leads to new surface-based nanostructures, which could open up new possibilities for molecular electronics.

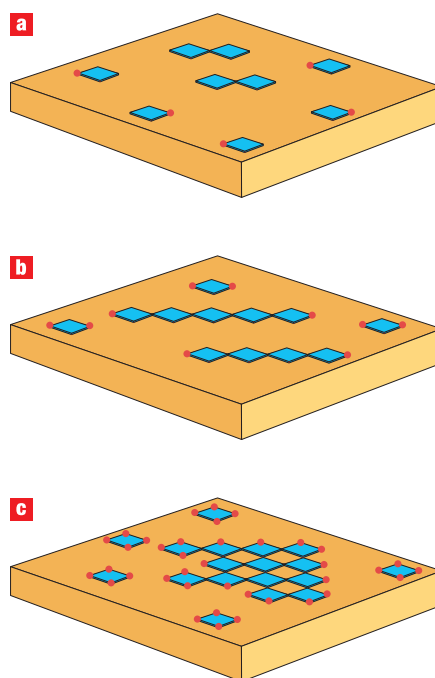
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One of the great hopes of nanotechnology is that molecules can be connected together to make pre-designed structures with useful functions. By combining carefully chosen molecules it should, in principle, be possible to build nanoscale electronic devices such as wires, or more complex examples such as transistors, capacitors and memories. The integration of these components into a so-called 'molecular computer' is one of the ultimate goals of such endeavours, but there are enormous scientific challenges that must first be overcome. On the *Nature Nanotechnology* website today, Leonhard Grill and co-workers<sup>1</sup> from the Freie Universität Berlin and the University of Liverpool begin to address some of these obstacles by showing how molecular building blocks can be rationally combined to form covalently bonded nanostructures — with predefined geometries — on a gold surface.

The building blocks used by Grill and colleagues are flat square-shaped molecules known as porphyrins that have four equally spaced 'arms' — one protruding from each edge. These molecules can be synthesized so that some or all of the arms have a bromine atom at their end. The bromine atoms can be removed by heating up the molecules, most probably leaving behind highly reactive carbon radicals that combine through covalent carbon-carbon bonds to link the porphyrin molecules together. The number and arrangement of the bromine atoms determines the type of nanostructures that are ultimately assembled (Fig. 1). Whereas porphyrins with just a single brominated arm form discrete dimers, those with two bromine-modified arms — disposed 180° apart — string themselves into one-dimensional chains,



**Figure 1** The formation of covalently bonded nanostructures on a gold surface from porphyrin molecules. When the porphyrins (blue) are heated either on the gold surface or in the evaporator prior to deposition, bromine atoms can be removed to generate reactive carbon radicals (red). The porphyrins are linked together when the radicals combine to form covalent carbon-carbon bonds. The shape of the resulting nanostructures is determined by the number and arrangement of bromine atoms originally present in the porphyrins: dimers (a) are the only product when one bromine atom is present, whereas linear chains (b) and grids (c) are made from porphyrins with two and four bromines, respectively.

and porphyrins with a full complement of four brominated arms link together into two-dimensional sheets.

The synthesis works in one of two ways: the bromine atoms can either be removed before the molecules are put on the surface — by raising the temperature at which they are evaporated — or after they have been deposited by simply

heating up the gold substrate. Moreover, because the nanostructures are formed on a surface, they can be characterized by scanning tunnelling microscopy, enabling precise identification of the molecular arrangement within the different architectures.

So what is so special about this particular study? The answer lies in the type of bonding and the environment in which the process takes place. The ability to self-assemble molecules into intricate and complex arrays has been the speciality of the chemist — and particularly the supramolecular chemist — over recent years<sup>2</sup>. The vast majority of studies have been solution-based, however, and only recently have surface-based processes been investigated in detail<sup>3-5</sup>. Working on a surface significantly enhances the possibility of creating devices from molecules, but raises problems in terms of how the molecules are deposited, particularly for large molecular arrays. Thus the possibility of working with small molecular building blocks that will spontaneously assemble themselves on a surface is particularly attractive because it simplifies the overall synthetic procedure.

Typically, non-covalent bonds, such as hydrogen bonds and van der Waals interactions, have been used to self-assemble increasingly complex nanostructured arrays on surfaces. Hydrogen bonds are particularly useful because they can be highly directional — resulting in geometric control — and multiple hydrogen bonding links between adjacent building blocks can give structures additional strength. So, if hydrogen bonds are so versatile and successful, why is it necessary to develop methods that rely on covalent bonds?

The answer lies in one of the fundamental differences between non-covalent and covalent bonding interactions: whereas non-covalent bonds are formed reversibly, most covalent bonds — although not all<sup>6</sup> — are formed irreversibly and, as such, are

generally much more robust than their non-covalent counterparts. Therefore, although non-covalent self-assembly enables the formation of highly optimized structures through a self-correcting process of bonds forming, breaking and reforming, the final products can be relatively fragile. To make more stable assemblies, therefore, the only realistic approach is to use covalent bonds. Moreover, covalent bonds offer another very significant benefit over non-covalent interactions — the possibility of efficient electron transport through the bond. If rationally constructed molecular electronic components are to be made in this fashion, then covalent bonds offer the greatest chance of success.

So what is the next step forward for this area? Clearly this demonstration is limited to a single type of molecule and a single reaction pathway. However, there is no obvious reason why the approach described would be specific to this particular system, and thus this study opens up the possibility of a generic application for the synthesis of nanostructures from diverse molecular building blocks. The next step should be to build covalently bonded arrays in a surface environment from molecules encoded with a specific function, and, importantly, to demonstrate useful properties. It is clear that the strategy described by Grill and co-workers for producing nanostructured arrays at

the molecular level has many possible applications, not only in electronics, but also in magnetism, catalysis and even for the recognition and activation of biomolecules.

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### References

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