

SURFACE CHEMISTRY

Making the right connections

How do you create a molecular circuit board? Covalently coupling different molecules in a sequential manner in surface-based nanostructures opens up new possibilities and hopes for molecular electronics.

Neil R. Champness

The idea that electronic circuit boards can be made by connecting designed molecular components has fired the imagination of chemists for many years. Much research has focused on the construction of molecules that mimic the properties of wires, transistors and other devices that are typically associated with electronic circuitry. One of the questions that has always lurked in the shadows of such studies is how are these components, beautiful in their own right, going to be assembled into something that resembles a circuit board? And if a molecular circuit board could be built, then there would need to be a mechanism by which information, electronic or otherwise, could be introduced or read from the array.

These are difficult questions to answer but over the years steps have been made towards this challenging goal. Now, writing in *Nature Chemistry*, Leonhard Grill, Stefan Hecht and co-workers¹ have taken a significant step towards addressing some of the challenges in this field by demonstrating a method to rationally construct covalently bonded nanostructures from more than one component on a gold surface.

A common strategy that enables molecular arrays to be interrogated with an external probe is to deposit or grow the target system on a surface, facilitating direct molecular-resolution imaging and manipulation using a scanning tunnelling microscope. Back in 2007, Grill and

co-workers described a method for creating covalently linked arrays of porphyrin molecules on a gold surface². This relatively simple system exploited an aryl-aryl coupling reaction that linked bromo-aryl-functionalized porphyrins into two-dimensional arrays. The original strategy has been adapted to other molecules^{3,4} and other coupling processes⁵, but until now has been generally limited to the construction of arrays built from a single type of molecule.

Grill and co-workers have now developed their methodology to enable arrays to be assembled from two different molecular components by exploiting the different reactivities of bromo-aryl and iodo-aryl groups. Although examples of covalently

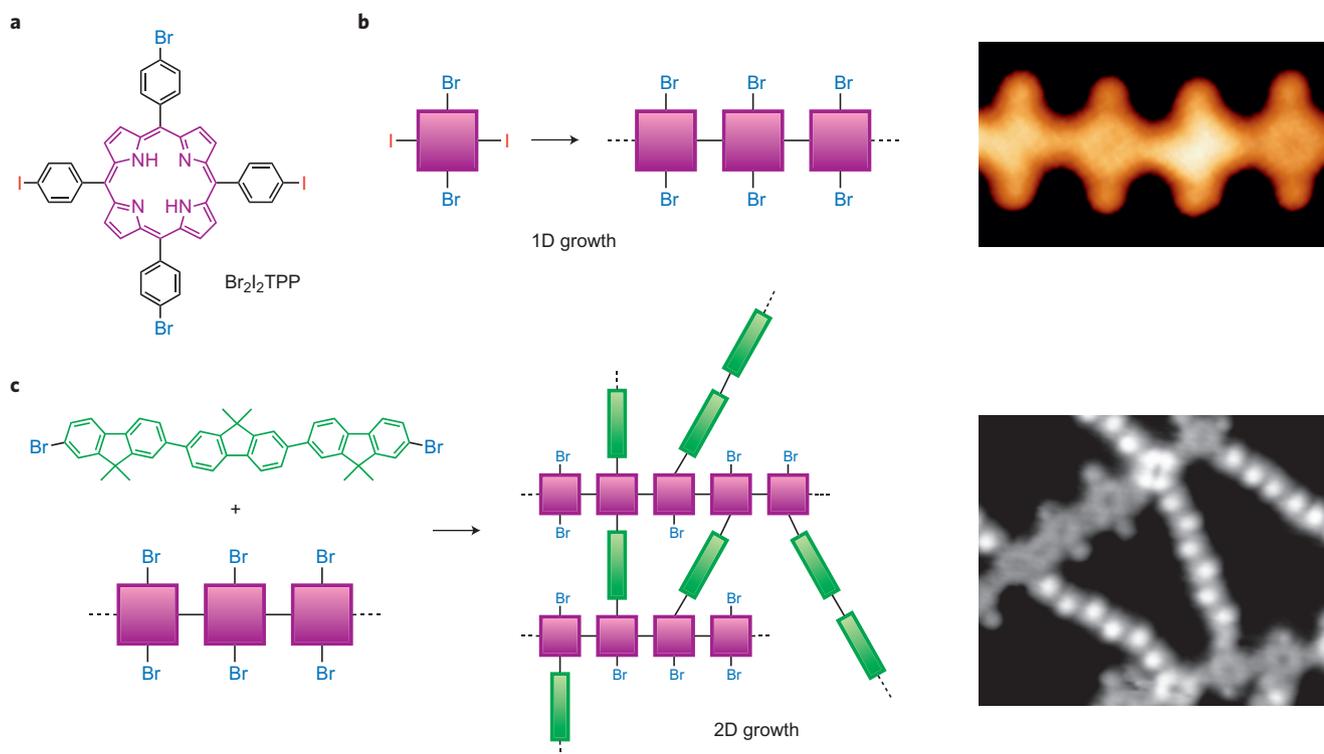


Figure 1 | Covalently coupled bimolecular arrays on surfaces. **a**, A porphyrin building block with two *trans* bromo-aryl substituents and two *trans* iodo-aryl substituents. **b**, Heating at 120 °C leads to aryl-aryl coupling between the iodo-aryl groups to form one-dimensional porphyrin chains. **c**, The bromo-aryl substituents along the porphyrin chain can be made to react by raising the temperature to at least 200 °C. In the presence of a different monomer with bromo-aryl groups — in this case dibromoterfluorene (green) — cross-coupling between the two different components leads to a complex two-dimensional covalent network in which porphyrin chains are linked through one or more terfluorene building blocks. (Right-hand images from ref. 1.)

bound bimolecular arrays exist⁶, this new approach could be readily adapted to allow the combination of a large range of component species. This relatively simple strategy leads to fascinating results and a potentially general method for developing increasingly complex molecular arrays on surfaces.

The flat porphyrin molecules used by Grill and colleagues are synthesized such that one functionalized 'arm' protrudes from each of the four sides of the square-shaped building blocks. Unlike related molecules that have been studied previously in this context, the four arms of the porphyrins are not identical. The arms on opposite sides of the porphyrin are the same, but are different from those located on adjacent sides. As shown in Fig. 1a, the 'north' and 'south' appendages are bromo-aryl substituents, whereas those found to the 'east' and 'west' comprise iodo-aryl groups. This subtle distinction in the type of halogen functionalization leads to different reactivity between arms on different sides of the porphyrin molecules.

Following deposition of the dibromo-diiodo-porphyrin ($\text{Br}_2\text{I}_2\text{TPP}$) molecules onto a gold surface, heating the sample leads to the covalent coupling between adjacent porphyrin species. The degree of intermolecular coupling and precise identification of the molecular arrangement can be readily determined using scanning tunnelling microscopy. Owing to the lower bond-dissociation energy of the C–I bonds, in comparison with C–Br bonds, the

iodo-functionalized arms couple at a lower temperature than the bromo-functionalized arms, leading to the formation of one-dimensional chains of coupled porphyrin building-blocks at 120 °C (Fig. 1b). As long as the temperature is kept below 200 °C only the iodo-functionalized arms react, leaving the bromo substituents intact and opening up the possibility of further reaction. It is possible to react the bromo-functionalized arms of the one-dimensional chains at higher temperatures, resulting in the formation of a two-dimensional porphyrin island, mirroring the previously reported observations².

The novelty of this particular study, however, is that the stepwise reaction of the $\text{Br}_2\text{I}_2\text{TPP}$ building-blocks enables the one-dimensional porphyrin chains to react with a secondary species, in this case dibromoterfluorene. When dibromoterfluorene is co-deposited with the porphyrin building blocks, once the iodo-aryl groups have coupled at low temperature to give porphyrin chains, the remaining bromo-aryl substituents along the chain can subsequently be induced to react by raising the temperature. These bromo-aryl groups can couple with others that are either located in different porphyrin chains or those at the ends of the dibromoterfluorene monomers.

Thus, coupling of the bromo-aryl groups on the porphyrin chain and the terfluorene molecules leads to decoration of the porphyrin chains with terfluorene groups (Fig. 1c). Indeed, crosslinking of adjacent porphyrin chains is observed resulting in

the formation of a complex two-dimensional array of coupled porphyrin chains and terfluorene moieties. The simple strategy of exploiting dissimilar chemical reactivity and thermal activation barriers for building-block appendages leads to the formation of a bimolecular array, a significant step-forward in the creation of more complex covalently coupled molecular arrays on surfaces.

Another notable advance of this study is that the method is potentially adaptable to a large variety of components — all you need are appropriate building blocks that are carefully functionalized with either bromo-aryl or iodo-aryl groups. The next step will be to develop functional arrays demonstrating real properties⁷, such as electronic conductivity, and to reveal the nature of the interplay between different components of the coupled arrays. If such properties can be established, a number of avenues of research in sensing, display devices, and even complex molecular circuit boards, will become realistic targets. □

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CHIRALITY

Spin and gravity give a helping hand

The handedness of supramolecular helices formed from achiral monomers has been controlled by applying rotational and gravitational forces, but at the start of the assembly process only. This demonstrates that a falsely chiral influence is able to induce absolute enantioselection.

Laurence D. Barron

A controversy going back over 30 years has finally been resolved. Writing in *Nature Chemistry*, Monsù Scolaro and co-workers now provide compelling evidence that a combination of rotational and gravitational forces can bias a chemical process in favour of either the left- or the right-handed form of a chiral assembly¹.

Understanding how chirality arises has important implications for, among other things, the search for the source of homochirality in life's chemistry — based

almost exclusively on L-amino acids and D-sugars — and perhaps even for life's origins. In 1980, an experiment² similar to that of Monsù Scolaro and colleagues had reported the induction of chirality — albeit only a slight enantiomeric excess — through rotational and gravitational forces. At the time, however, this conclusion had attracted strong criticism, based on fundamental symmetry arguments that seemed to show it to be a physical impossibility³. So, what exactly is going on?

Scientists have been fascinated by handedness in the structure of matter ever since the concept arose in the early years of the nineteenth century, as a result of the discovery of natural optical activity. Having found in 1848 that individual molecules could exhibit chirality, Louis Pasteur then attempted to extend this concept to other aspects of the physical world in his search for forces that might be connected with handedness in the molecules of life⁴. For example, he was correct in suggesting that