Unique intermolecular reaction of simple porphyrins at a metal surface gives covalent nanostructures†

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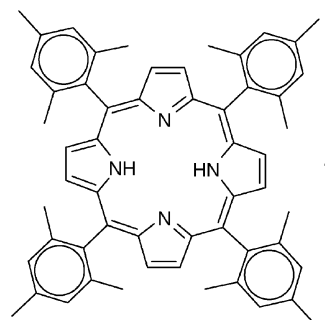**Deposition of a porphyrin onto metallic copper followed by heating leads to an unprecedented type of linking of the molecules giving a mixture of covalent multiporphyrin nanostructures at the surface.**

A prime challenge on the road to the bottom–up assembly of functional molecular nanosystems at surfaces is the formation of structures of large size using covalent or non-covalent bonds.[1] While the use of non-covalent bonds is elegant, spontaneous and widespread,[2] the structures that are created are somewhat fragile. In contrast, the creation of surface nanostructures through covalent bonds is almost non-existent despite the advantages of generating robust systems which can be manipulated.[3] Here, we will show the unexpected formation of covalent structures from very simple tetra(aryl)porphyrins at a copper surface, in a reaction which bears all the hallmarks of a condensation polymerisation. This result evokes the idea of combinatorial preparation of covalent nanostructures at surfaces, which would be amenable to direct addressing and screening with scanning probe techniques.[4]

The reaction which leads to the formation of the covalent porphyrin scaffolds involves a thermally-induced activation and reaction of tetra(mesityl)porphyrin **1** on metallic copper under ultrahigh vacuum conditions. Very recently, and in parallel to our own work, Grill *et al.* showed the formation of covalently-linked porphyrin arrays on a gold surface upon loss of bromine atoms from bromophenyl porphyrins.[5] Our results show that different chemistry on a different surface leads to related covalent structures, and that, therefore, the approach may indeed be general, as foreseen by Champness.[6] The unique contribution from our work is the demonstration that the molecules can be functionalised differently with simple organic groups and a new, potentially cleaner, chemistry has been uncovered. We also prove the robust nature of the covalent link by STM-monitoring of concerted movement of a covalent trimer on the surface. We were attracted to **1** because the eight methyl groups at the *ortho* positions to the porphyrin substituent on the phenyl rings ensure that the π systems are perpendicular and rigidly held with respect to the pyrrole ring.

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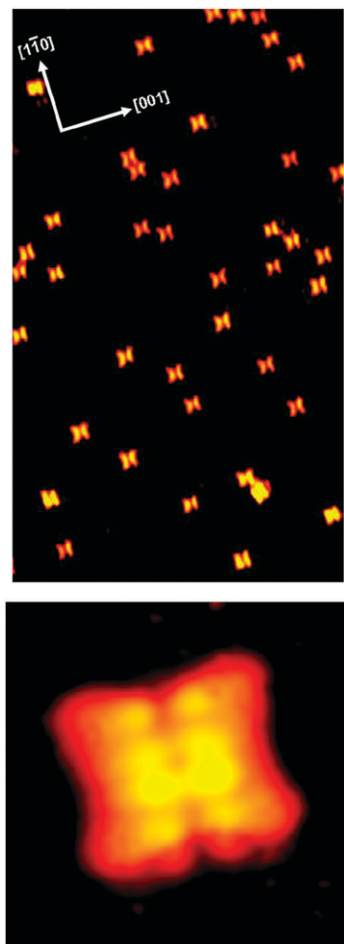† Electronic supplementary information (ESI) available: Supporting STM images. See DOI: 10.1039/b718865j

The molecule was purchased from Frontier Scientific.

Deposition of **1** was achieved by sublimation from a glass Knudsen cell heated to 150 °C with direct exposure onto a Cu(110) surface held at room temperature in an ultra-high vacuum chamber. After deposition, the adsorbed layer was characterised by reflection absorption infrared spectroscopy (RAIRS) which indicated the presence of intact molecules at the surface (see ESI†). The adsorbed molecules were imaged using a scanning tunnelling microscope (STM) in the ultra-high vacuum chamber at room temperature. The images in Fig. 1 show that the molecules (which appear as bright square protrusions when viewed at a relatively large scale) are located on individual sites on the metal surface, and rarely come into a position where contact would be possible. A close up STM image on an individual molecule shows submolecular resolution, in which a butterfly-like pattern appears, with an area of lower tunnelling current at the centre and eight bright lobes around it. The distance between diagonally opposite extremes of the STM image is ∼18 Å, corresponding to the calculated distance between diametrically opposite methyl groups. This data and the dimensions of the bright points in the images indicate that the porphyrins lie pseudo-planar to the surface, with no significant intermolecular interaction between them. Even at high coverage (see ESI†) no preferred order or associations emerge and the porphyrins do not have significant side-on contact.

When the Cu(110) sample with a low coverage of **1** was annealed at between 150 and 200 °C and then imaged by STM at room temperature, a completely different picture arises (Fig. 2). While individual porphyrins are observed, the majority are linked up together in lines, angular structures, and grids, with a specific, almost colinear attachment or linkage.

The linear, angular and grid-like structures have all the characteristics of covalent structures. The porphyrins are connected *via* specific parts at the corners of the four-point

Fig. 1 Top, 27 nm × 47 nm STM image of **1** on Cu(110) ($I = 0.2$ nA $V = 363$ mV); bottom, a close up of an individual molecule (image size 2.8 nm × 2.8 nm; $I = -0.26$ nA $V = -284$ mV).

Fig. 2 Room-temperature STM image of annealed **1** on Cu(110). Image size 38 nm × 71 nm ($I = -0.5$ nA $V = -267$ mV).

be expected to produce higher valencies and highly non-linear structures, which are not observed. The average core-to-core distance between linked porphyrins is approximately 18.5 Å, a value very close to that corresponding to the calculated value for formation of an ethylene linkage (19 Å).[10] Furthermore,

Fig. 3 A close-up STM image of annealed **1** showing lines and a grid. Image size 12.6 nm × 20.6 nm ($I = -0.26$ nA $V = -243$ mV). A graphic of a trimer is also shown (not scaled to the STM image).

features of the porphyrins, and not at the interstices. Our experiments show that the covalent nanostructures arise from heating the Cu surface. We note here that the creation of phenyl radicals on the Cu(110) surface upon annealing has been reported recently.[7] Thermal desorption data obtained from our system shows evolution of hydrogen (amu = 2) over the temperature range in which coupling occurs. Furthermore, the sub-molecular details of STM images recorded of individual porphyrins after thermal annealing are markedly different to the non-annealed sample, suggesting that the chemical nature of **1** is altered. It is, therefore, reasonable to propose that reaction with the copper reduces a methyl group on the mesityl functionality[8] generating a $CH_2^{\bullet}$ radical[9] group which could then homocouple in a similar way to the debrominated porphyrin reported recently.[4]

An analysis of the STM distances measured between the cores of the porphyrin units supports the idea of a covalent link between the methyl substituents at the *para* position of the benzene rings relative to the porphyrin ring. Each unit, therefore, has a maximum valency of four, with two and three connections being the most common. Any substitution pattern other than that proposed (*e.g.* at the *meta*-positions which are the interstices between the methyl groups, for example) would
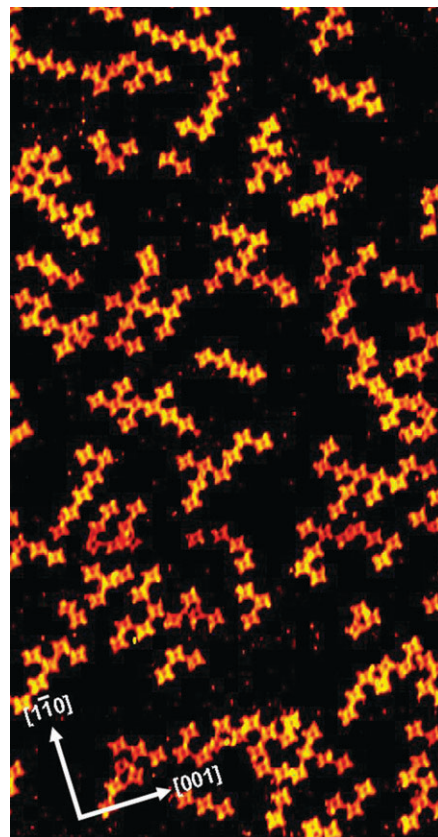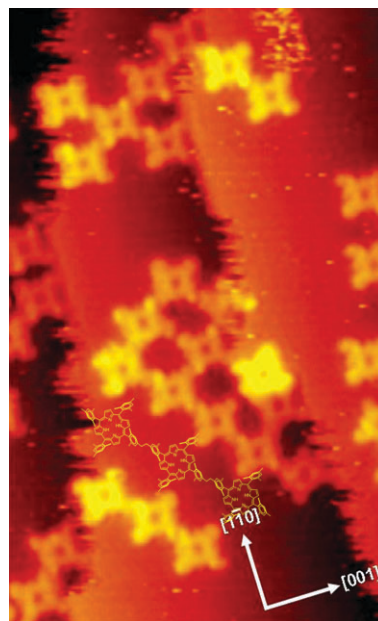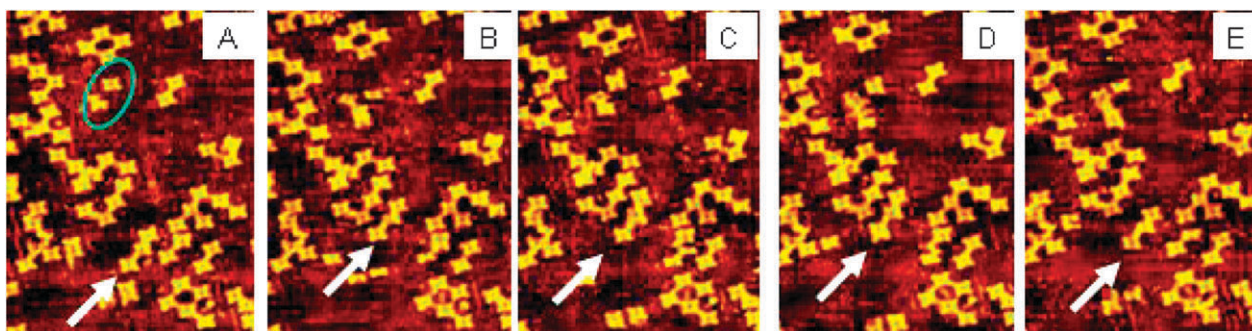
Fig. 4 A series of STM images of annealed **1** on Cu(110) at 120 °C taken over a 200 s time-span, with the mobile trimers (indicated by white arrow) and monomers (blue circle in A).

the slight kink in between the porphyrins (as seen clearly in the trimer and grid in Fig. 3) supports the presence of an ethylene bridge formed in this way. This link slightly offsets the diagonal axes of joined molecules, but is also flexible, as witnessed by slight distortions in some places in the images.

We note that the distribution of sizes and shapes of oligomeric molecules indicates a condensation-type (or stepwise) polymerisation, with very few monomeric porphyrins being observed in comparison with the oligomers, which contain mainly difunctional units, often three-connected units, and very rarely four-connected ones. Furthermore, the alignment of the central pyrrole ring along the high-symmetry axes of the Cu(110) surface means the connections mediated *via* the *para* methyl groups occur along non-symmetry directions. This combination of mechanistic and structural detail leads to most of the covalent nanostructures created being chiral.

Finally, the presence of a robust covalent link holding the nanostructures together was also indicated by time-resolved STM experiments, monitoring motion of the structures in a series of images at 120 °C (Fig. 4). It can be seen that the linear trimer in these images clearly changes position, relative to the "F" shaped molecule just to its right. We find that monomeric species present in this area are much more mobile, while the trimer is slow to move, presumably because of its molecular weight which results in slower diffusion. The linear and cyclic tetramers and other higher structures present in the images do not move at all on the timescale of the experiment.

The additional possibility of Cu incorporation into the tetrapyrrolic core also needs to be considered. In fact, this is a rather ready occurrence as confirmed by heating a sample of the porphyrin deposited from chloroform onto a large excess of copper filings in vacuum to 180 °C. The laser desorption–ionisation time-of flight (LDI-TOF) mass spectrum shows the presence of free base and copper porphyrins (see ESI). The proportion of the copper porphyrin is increased when copper filings are stirred in DMF at 100 °C with the porphyrin under an inert atmosphere.

In a separate set of experiments, the roles of metal ion and the mesityl functionality were evaluated by studying Co-tetraphenylporphyrin and Co-tetra(mesityl)porphyrin on Cu(110) in UHV. Whereas, the former showed no evidence of covalent coupling upon thermal annealing, the latter yielded very similar structures to those shown in Fig. 2, suggesting that the methyl groups are key to this reaction.

To conclude, the surface-confined reaction of tetra(mesityl)-porphyrin molecules leads to a combinatorial mixture of covalent nanostructures, which have been observed using STM, and the generality of the surface-assisted bond-forming approach seems certain. Our work also shows how metal surface-induced chemistry of highly functional organic molecules is a highly promising method for creating covalently linked superstructures at a surface from simple building blocks. Specifically, suitable linking of functional units such as porphyrins yields robust structures with potential electronic, optical, catalytic and magnetic properties. We are presently exploring this playground.

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