From porphyrins to nanoribbons: STM and synchrotron studies of molecules on surfaces.

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Porphyrins are a ubiquitous class of naturally occurring molecules involved in a wide variety of important biological processes ranging from oxygen transport to photosynthesis and from catalysis to pigmentation changes . The common feature of all these molecules is the basic structure of the macrocycle, which consists of four pyrrolic subunits bridged by four (meso) carbon atoms (Figure 1a). This macrocycle is an aromatic system, the size of which is perfect to bind most metal ions. Many of the transition metals (e.g., Fe, Zn, Cu, Ni, and Co) can be inserted in the centre of the macrocycle forming metallo-porphyrins (Figure 1b). Porphyrin-based biological molecules include hemes, chlorophylls and vitamin B-12. Given the capabilities of porphyrins to bind and release gases and to act as an active centre in catalytic reactions in biological systems, porphyrin-based films on surfaces are extremely appealing as chemical and gas sensors as well as nano-porous catalytic materials in novel synthetic bio-mimetic devices . Moreover, the role of porphyrins in photosynthetic mechanisms indicates a good ability of these molecules to mediate visible photon-electron energy transfer processes. For this reason metallo-porphyrins and porphyrin-substrate systems (in particular on Au, Ag, Cu) are of major interest for applications in opto-electronics, data storage, solar cells and gas sensors and an increasing number of porphyrin based assemblies have been studied for these purposes .

The first part of this presentation will give a general overview of the interesting properties of porphyrins and their many applications. In the second part I will present results from recent scanning tunnelling microscopy (STM) and synchrotron based studies of the self-assembly and temperature-assisted covalent bonding of porphyrin molecules on metal surfaces. I will discuss the formation of porphyrin based nano-networks and nano-lines formed via radical addition following thermal activation of functionalised porphyrin molecules. These nanostructures offer a powerful approach to the development of molecular devices possessing functions such as sensing, rectifying and switching. Such molecular assemblies can be probed with STM, to reveal the arrangement and conformation of molecules with sub-molecular resolution while their electronic and chemical bonding can be probed by synchrotron based x-ray photoemission and x-ray absorption techniques. Finally, I will briefly discuss a bottom-up approach for the formation of graphene nanoribbons and their functionalisation using porphyrin molecules.

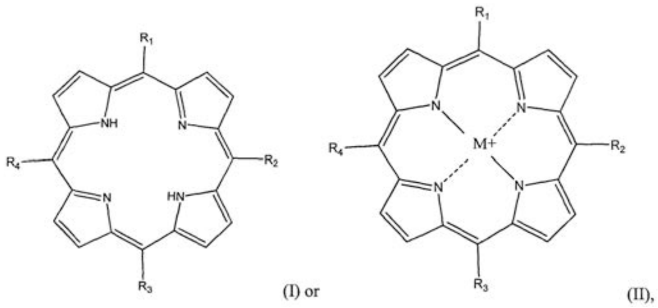

Figure 1: Structure of a ‘free-base’ porphyrin (a), and metallo-porphyrin molecule (b).

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