On-surface synthesis of fused anthracenyl porphyrin derivatives

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For the last fifteen years, on-surface synthesis became an extremely popular and powerful method to fabricate nanostructures which otherwise would not have been accessible by conventional wet organic syntheses. The syntheses, realized in the chamber of high vacuum scanning tunneling microscope (STM), permitted the fabrication and the characterization of atomically defined nanostructures such as polycyclic aromatic hydrocarbons (PAH), graphene nanoribbons or 2D covalent networks.[1] Among the organic molecules studied by STM, porphyrins are of particular importance because of their electronic and optical properties. Initial studies were mainly devoted to the supramolecular organization of porphyrins and porphyrin derivatives on surface and it is only in 2004 that noble metal surfaces were used as catalytic surface to perform reactions on the porphyrin cores.[2] Since then, examples of open-shell porphyrin derivatives [3] and conjugated oligomers [4] were reported.

While the synthesis of fused bis- and tetra-4,5-bis-(2,4,6-trimethylphenoxy)anthracen-9-yl porphyrins containing Ni(II) was reported by Anderson about 10 years ago,[5] the formation π-extended porphyrin bearing unsubstituted anthracenyl moieties were never achieved. The formation of such compounds became possible by on-surface synthesis. Herein, we report on the synthesis of fused bis- and tetra-anthracenylporphyrin derivatives via the cyclodehydrogenation the parent meso-substituted molecules on a catalytic Au(111) surface.[6] Depending on the annealing temperature, anthracenylporphyrins with the four anthracene fully linked to the porphyrin core or over-oxidized porphyrin in which the anthracene are connected two by two in 2-2’ position were observed by STM (Figure 1).

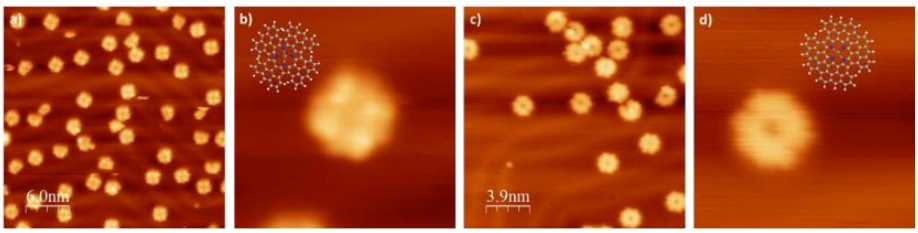

Figure 1. STM images of the fused tetra-anthracenylporphyrins and related porphyrin structures

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