

Covalent self-assembly to steer highly directional nanostructures on a substrate

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The control of covalent molecular self-assembly is very important as it enables to produce robust nanostructures, as opposite to "fragile" assemblies mediated by weaker interactions. This allows the realization of stable structures that could be exploited in molecular devices operating in extreme conditions, even much above room temperature. Structures with distinctively directional properties were obtained by heating a system of tri-methyl-tetra-phenyl-porphyrin (TMTTP) molecules on Cu(110)[1]. Here, using techniques based on DFT, we give a complete characterization of the self-assembly via an analysis of the structures on the substrate and the phenomena bringing to the bonding. We find that the assembly result from de-hydrogenation processes catalyzed by the substrate happening at high temperature ($T > 500\text{K}$) and involving only specific, peripheral chemical groups. Upon de-hydrogenation, the molecules are driven to connect by diffusing mainly along the Cu(110) rows. The unique features realized here and other distinct patterns achieved with different substituents [2], suggest that the use of this class of porphyrins is very promising to realize and control vertical, horizontal or diagonal networks of molecules with coverage-dependent dimensionality.

[1] In't Veld M., Iavicoli P., Haq S., Amabilino D. B. and Raval R., *Chem. Commun* 1536 (2008).

[2] Sam Haq, Felix Hanke, Matthew S. Dyer, Mats Persson, Patrizia Iavicoli, David B. Amabilino and Rasmita Raval, *JACS* 133, 12031 (2011).