

STRUCTURAL AND ELECTRONIC PROPERTIES OF SUPRAMOLECULAR ASSEMBLY DRIVEN BY HALOGEN BONDING ON GRAPHENE: A COMBINED STM/STS AND DFT STUDY

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The bottom-up construction of molecular nanomaterials on surfaces is an active research area due to fundamental interests in self-assembly processes as well as potential applications in nanotechnology and molecular electronics. Epitaxial graphene on metal (Gr/M) has emerged as an appealing substrate as it offers a versatile testing ground for investigating the formation of 2D molecular networks [1]. Based on the fact that self-assembly at surfaces is governed by a subtle balance between intermolecular and molecule-substrate interactions, we exploit the idea to tailor molecular arrangements by varying the graphene-metal interaction. This can be realized by the intercalation of foreign atoms (X) leading to Gr/X/M interfaces. Moreover, intercalation offers the possibility to create nanostructured graphene [2] and therefore to investigate the influence of spatial constraints on self-assembly. In this framework, we have investigated the growth of 1,3,5-tri(4'-bromophenyl)benzene (TBB) on Gr/Ir(111) and Gr/Cu/Ir(111) by means of scanning tunneling microscopy and spectroscopy (STM/STS) at 77 K. A Density-Functional-Theory (DFT) study of TBB adsorbed on graphene has been carried out using a fully atomistic description of the molecules in interaction with the Gr/Ir(111) substrate. Structural and electronic properties of the TBB self-assembly on Gr/Ir are determined. The impact of the underlying metallic layer upon the self-assembly behavior of the molecules and their properties is discussed. When adsorbed on Gr/Cu/Ir interfaces, TBB also forms 2D supramolecular networks that can be confined at the surface of Cu intercalated nanoislands. This work opens new routes towards the realization of original molecular architectures with novel properties.

References

- [1] J. M. MacLeod and F. Rosei, *Small* 10, 2014, pp. 1038.
[2] M. Sicot et al., *Appl. Phys. Lett.* 105 2014 pp. 191603.

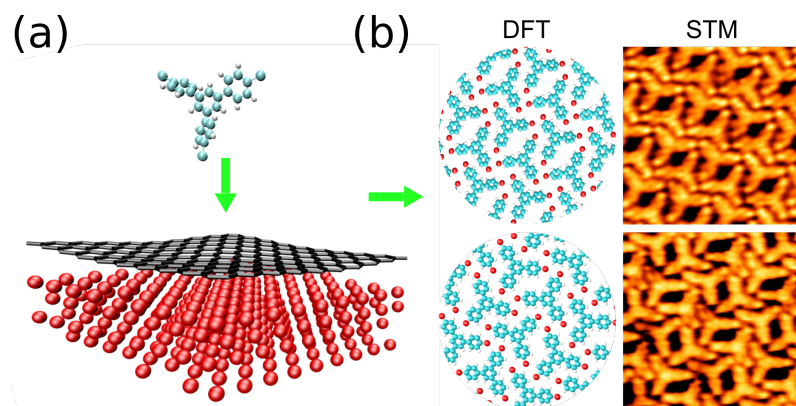


Figure : (a) 3D schematic drawing of TBB adsorption on epitaxial graphene on Ir(111), (b) Left panel: models of molecular phases of TBB obtained using DFT. Right panel: corresponding STM images.