

Self-Assembly of Para-Hexaphenyl-Dicarbonitrile on Graphitic substrates: H-bonding and Metal-Organic Coordination

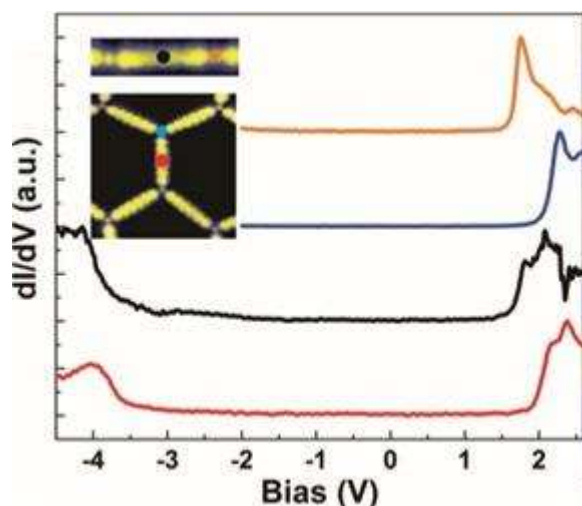
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Graphene is a material with outstanding properties in mechanical strength as well as in thermal and electric conductivity. Self-assembled networks of molecules on graphene are often studied as a method to steer especially the electronic properties. On the other hand, graphene can be also employed as a decoupling layer to preserve the intrinsic properties of adsorbed species. This allows for real space investigation of their electronic properties with scanning tunneling microscopy (STM). Herein we present an STM and scanning tunneling spectroscopy (STS) study of para-hexaphenyl-dicarbonitrile (P6) on graphitic substrates with respect to both molecule-graphene interactions and the effect of decoupling for the preservation of molecular properties. To study the influence of the substrate, onto which graphene is placed, we compared the adsorption behavior of P6 on three graphitic substrates [1]: highly oriented pyrolytic graphite (HOPG), graphene on Cu(111) (g/Cu) and graphene on Ir(111) (g/Ir). At submonolayer coverage, close packed networks formed on all three substrates with the molecules arranging in stripes. Within each stripe, the molecules arranged parallel to each other. On HOPG, for every fourth molecule a shift along the molecule axis of about one phenyl ring was observed while on g/Cu and g/Ir, two phases formed, with the shift occurring either every fourth or fifth molecule. The observed shift is suggested to alleviate the screening of the unequal charge distribution of the P6 molecules by graphene. When adding Cu atoms to P6 adsorbed on g/Ir, metal-organic coordination networks could be fabricated [2]. Depending on the ratio between molecules and atoms (P6:Cu) we observed different structures. For a ratio of 6:1, a basketweave-like pattern occurred, with some packets of parallel arranged molecules rotated by 60° with respect to the other molecules and some molecules positioned head-to-head were involved in metal-ligand interactions with Cu atoms. For a 3:2 ratio we observed a hexagonal porous arrangement, stabilized by threefold coordination between the P6 molecules and Cu atoms. At a ratio of 1:1, long 1D chains with twofold coordination dominated. We performed STS on the hexagonal network and the 1D chains and observed significant differences between the electronic properties of both structures, as shown in figure 1.



References

- [1] N. Schmidt et al., Chemistry: A European Journal, 19 (2019), 5065-5070
- [2] J. Li et al., Journal of Physical Chemistry C, 123 (2019), 12730-12735

Figure 1: Comparison of STS spectra taken at the Cu atoms (orange, blue) and molecules (black, red) on the chains and the porous network. The insets show the positions where the spectra were taken.