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Manipulation and spectroscopy of individual phthalocyanine molecules on InAs(111)A with a low-temperature scanning tunneling microscope

Ch. Nacci^{1,*}, S. C. Erwin², K. Kanisawa³ and S. Fölsch¹

¹Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

²Center for Computational Materials Science, Naval Research Laboratory, Washington, D.C. 20375, United States

³NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi, Kanagawa, 243-0198, Japan

*Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Phthalocyanine is a promising class of organic molecules to explore new functionality concepts within a molecule-semiconductor hybrid scheme. We report on single free-base phthalocyanine (H₂Pc) molecules on the weakly binding III-V semiconductor surface InAs(111)A studied by low-temperature scanning tunneling microscopy (STM) at 5 K. InAs(111)A is an In-terminated surface characterized by completely saturated surface dangling bonds due to its intrinsic (2 × 2) In vacancy reconstruction [1]. H₂Pc adopts a planar adsorption geometry on InAs(111)A with the molecular center located at the In vacancy site. When probed by the STM tip, the discrete molecule performs in-plane rotational jumps between three equivalent in-plane orientations excited by inelastic electron tunneling (IET) [2]. STM-based molecule and atom manipulation techniques at low temperature [2,3] have been applied to quench the rotation and stabilize H₂Pc at the surface using native individual In adatoms (In_{ad}). This allows us to explore the intrinsic molecular switching behavior given by the tautomerization switching of the two inner hydrogen atoms. STM imaging of the In_{ad}-H₂Pc-In_{ad} complex reveals the presence of a left-handed and a right-handed conformer, suggesting that the adatom-induced single-molecule pinning leaves the tautomerization reaction unperturbed, and that it can be excited by IET. Density functional theory calculations reveal these experimental observations and show that the energetics of the switching process remains largely unaffected by both the surface and the stabilizing atoms [2].

The IET-induced in-plane rotation observed for discrete H₂Pc proves to be a generic property of phthalocyanines on InAs(111)A and was observed also for metal phthalocyanines (MPc, M: Cu, Sn) [4]. Finally, STM imaging of largely unperturbed frontier molecular orbitals of naphthalocyanine (NPc) molecules on InAs(111)A indicates that the molecule is in a physisorbed state. The molecular electronic structure of NPc is preserved to a large extent, indicating a weak electronic coupling to the semiconductor template [5].

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References:

- [1] A. Taguchi, K. Kanisawa, Appl. Surf. Sci. 252, 526 (2006)
- [2] Ch. Nacci, S. C. Erwin, K. Kanisawa, S. Fölsch, ACS Nano 6, 4190 (2012)
- [3] S. Fölsch, J. Yang, Ch. Nacci, K. Kanisawa, Phys. Rev. Lett. 103, 096104 (2009)PRL 103,
- [4] C. Nacci, K. Kanisawa, S. Fölsch, J. Phys.: Condens. Matter 24, 354008(2012)
- [5] G. Münnich, F. Albrecht, C. Nacci, D. Schuh, K. Kanisawa, S. Fölsch, J. Repp, J. Appl. Phys. 112, 034312 (2012)