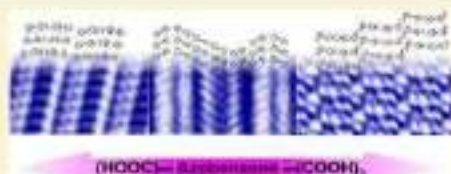


Controlling Self-Assembly of Switchable Azobenzene Derivatives on Highly Oriented Pyrolytic Graphite at Ambient Conditions

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Supporting Information

ABSTRACT: Ultrathin films prepared at the solid/air interface of azobenzene (AB), 4-(phenylazo) benzoic acid (PABA), 3,4'-azodibenzonic acid (meta-ADB), and 4,4'-azodibenzonic acid (para-ADB) have been studied on highly oriented pyrolytic graphite using scanning tunneling microscopy (STM) and atomic force microscopy (AFM). While AB molecules form compact hexagonal pattern stabilized via van der Waals interaction, AB derivatives with carboxyl groups show patterns formed through strong dimeric hydrogen bonds. Depending on the number and the position of carboxyl group(s), we show that the assembly can be controlled at a global level. Due to the right balance of weak and strong intermolecular interactions, PABA molecules show a unique growth at global level; meta/para-ADB molecules form chains stabilized through carboxyl groups; however, possible adsorption-induced defects influence the growth behavior and restrict it to limited site on the surface.



INTRODUCTION

Molecules with possible electrical functions like switching, rectification, conductivity, etc. may be useful in making single-molecule-based devices, which can add new perspectives to future molecular electronics. Azobenzene (AB) and its derivatives form a unique class of photoactive molecules that are appealing candidates for future molecular electronic applications. These derivatives undergo reversible *cis-trans* isomerization upon illumination of light^{1–5} and hence have the ability to convert light into molecular mechanical motion.⁶ Several derivatives of AB have revealed molecular level switching on surfaces not only by illumination with UV–visible light^{7–13} but also by electric fields¹⁴ and tunneling current.^{15–19} On surfaces, the switching function of these molecules depends on the molecular pattern,^{20–26} and therefore the control of their self-assembly plays a key role in their application on surfaces. Hydrogen bonding and weak van der Waals interactions are typically used in controlling assemblies of molecules on surfaces.^{27–33} Hydrogen bonding, in particular due to the directional nature and strength of the interaction, is useful in controlling the assembly. Using STM, self-assembly of AB and its derivatives has been studied at solid/liquid interfaces^{34–37} and in ultrahigh vacuum (UHV).^{38–44} However, the studies of such derivatives are scarce at the solid/air interface.⁴⁵

Carboxyl functional groups are particularly suitable for controlling the directionality of intermolecular interactions in molecular assemblies due to the cyclic nature of hydrogen

bonds.^{46–48,49} However, this group is susceptible to temperature and hence limited for deposition in UHV. The strength and the specificity of the intermolecular interactions offered by carboxylic groups have not been explored yet for controlling the patterns of AB at the solid/air interfaces. Here, we explore ultrathin films of azobenzene (AB), 4-(phenylazo) benzoic acid (PABA), 3,4'-azodibenzonic acid (meta-ADB), and 4,4'-azodibenzonic acid (para-ADB) as depicted in Figure 1 on highly oriented pyrolytic graphite (HOPG)/air interfaces prepared by the drop-casting method. Both STM and AFM at ambient conditions are applied for the understanding of growth and the assembly at the molecular level. The experiments are controlled at submonolayer coverage to understand the initial growth behavior. We show that attaching one or two carboxyl group(s) to AB assists in the interaction through dimeric hydrogen bonds. Addition of one carboxyl group to AB (PABA) leads to the formation of a dimer row pattern. This unique assembly pattern of PABA grows over several μm without defects. Attaching two carboxyl groups to different positions on AB (meta/para-ADB) facilitates dimer chain formation. The growth of these molecules is limited to a few hundreds of nanometers and shows polymorphism in the growth. We infer that different types of isomers of monomers and oligomers (a few units of molecules) induced due to adsorption of meta/para-ADB are at the origin of this limited

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