



Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb



Concentration-dependent supramolecular patterns of C₃ and C₂ symmetric molecules at the solid/liquid interface

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ARTICLE INFO

Article history:

Received 9 October 2017

Received in revised form

27 November 2017

Accepted 28 November 2017

Available online xxx

Keywords:

STM

Concentration dependent

Solid/liquid

HOPG

Symmetry

ABSTRACT

Here we report on a scanning tunnelling microscopy (STM) investigation on the self-assembly of C₃- and C₂-symmetric molecules at the solution/graphite interface. 1,3,5-tris((E)-2-(pyridin-4-yl)vinyl)benzene and 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethane are used as model systems. These molecules displayed a concentration dependent self-assembly behaviour on graphite, resulting in highly ordered supramolecular structures, which are stabilized jointly by van der Waals substrate-adsorbate interactions and in-plane intermolecular H-bonding. Denser packing is obtained when applying a relatively high concentration solution to the basal plane of the surface whereas a less dense porous network is observed upon lowering the concentration. We show that the molecular conformation does not influence the stability of the self-assembly and a twisted molecule can pack into dense and porous architectures under the concentration effect.

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1. Introduction

Molecular self-assembly at surfaces and interfaces has been widely exploited during the last three decades to nanopattern surfaces with an atomic precision, becoming a reliable route to generate functional nanostructures [1,2]. The virtually unlimited degrees of freedom offered by organic chemistry grant access to molecules possessing different sizes and characterized by multiple and regiospecific substitutions with functional groups at the core, in the scaffold and/or in the periphery [3,4]. In this framework, π -conjugated molecules exhibit unique opto-electronic properties, which render them interesting building blocks for application in opto-electronics [5,6].

In general, the self-assembly of molecules at surfaces and interfaces is ruled by the interplay of intramolecular, intermolecular and interfacial forces. The use of a rigid π -conjugated scaffold limits, to a certain extent, the conformational degrees of freedom of the molecules [7]. On the other hand, the functionalization of the molecular peripheries with specific moieties enables the use of dipolar interactions to stabilize in-plane adjacent molecules, resulting in controlled two-dimensional (2D) crystallization and

ultimately the formation of robust self-assembled networks [8–10]. Among non-covalent interactions, hydrogen bonding combines specificity, cooperativity, reversibility and directionality, the latter offering high control over the geometry of the assemblies [11–15]. H-bonding occurs between polar molecules where a hydrogen (H) atom can interact with more electronegative atoms such as oxygen (O) or nitrogen (N). It has been exploited to design and to build various molecular nano-architectures, in particular on solid surfaces resulting in linear and cyclic motifs [16–21].

Both the structure of chemisorbed and physisorbed molecular self-assembled monolayers, as well as their nanoscale electronic density states on electrically conductive solid surfaces, can be explored by means of scanning probe techniques, and in particular by scanning tunnelling microscopy (STM), which has proven to be the most convenient tool to probe the physisorbed molecules with sub-molecular resolution in real space. It is an excellent tool to unravel structure and dynamics of molecules at surfaces under different environmental conditions including ultra-high vacuum (UHV), solid/air or solid/liquid interface. The latter environment offers many advantages when performing molecular self-assembly studies: (i) the experiments do not require a complicated or expensive set-up, (ii) it facilitates choice of the solvent in view of the selected solute and substrate, (iii) it allows the investigation of large molecules that can be difficult to sublime under vacuum, (iv) the reversible nature of self-assembly enables defect reparation via self-healing by taking advantage of the dynamic exchange between

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<https://doi.org/10.1016/j.colsurf.2017.11.065>

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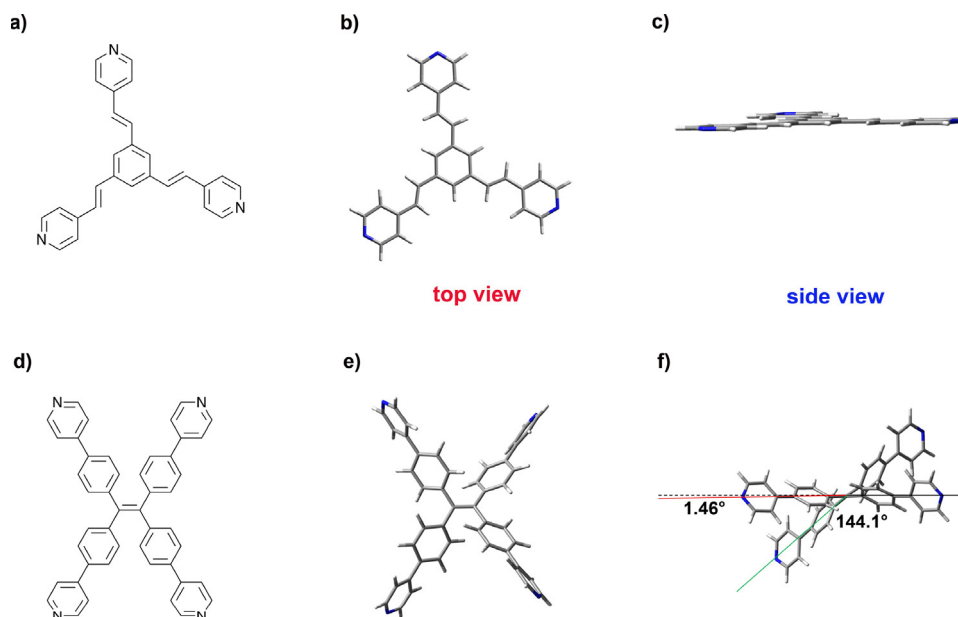


Fig. 1. Chemical structure (a), top (b) and side view (c) of optimized geometry of 1,3,5-tris((*E*)-2-(pyridin-4-yl)vinyl)benzene (**3Py**). Chemical structure (d), top (e) and side view (f) of optimized geometry of 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethane (**4Py**).

the liquid phase and the adsorbed molecules [8,22]. Working at the solid/liquid interface environment, the nanostructures can be influenced by a number of experimental conditions such as the chosen solvents, [23–26] the temperature, [27–29] and the concentration [30–33]. The formation of concentration-dependent nanostructures at surfaces and interfaces is a 2D crystallization phenomenon. It has been shown that densely packed molecular assemblies are produced when operating at a relatively high concentration and the porous networks are obtained at low concentration [34–36]. It is however important to note that the range of concentrations in which one phase is favoured over the other cannot be generalized. The strength of both inter and intramolecular forces varies from one molecule to the others and it is moderated also by the chosen solvent. Controlling the formation of the concentration-dependent 2D molecular networks can therefore be considered as a key factor to tune the self-assembly on surfaces [37,38].

The concentration-dependent self-assembly of C_3 -symmetric molecules has been reported in the literature but to the best of our knowledge C_2 -symmetric molecules are not yet investigated for concentration effects. The molecular symmetry C_3 refers to obtaining the equivalent configurations by a rotation of the molecule around an axis with 120° while the symmetry C_2 takes the molecule to the same structure by a rotation of 180° .

In this work, we report on the STM investigation of a concentration dependent formation of 2D molecular self-assembly at the solid/liquid interface. We focus our attention on two molecular building blocks with C_3 and C_2 -symmetry. 1,3,5-tris((*E*)-2-(pyridin-4-yl)vinyl)benzene (**3Py**) and 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethane (**4Py**) are physisorbed on highly oriented pyrolytic graphite (HOPG) surface. In both molecules the pyridyl N atom in the *para* position promotes the formation of directional H-bonds [34,35]. The choice of pyridine based chemistry enables the formation of weak hydrogen bonding, resulting in the generation of directional H-bonds that operate under full thermodynamic control [34–36,39,40].

2. Results and discussion

Fig. 1 displays the chemical structure and the optimized geometries of the C_3 -symmetric **3Py** and the C_2 -symmetric **4Py**. The

geometry optimization was done in the gas phase using density functional theory (DFT) calculations with three-parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP) and 6–31G basis set within Gaussian 09 [41]. **3Py** exhibits a flat stilbene core with a *trans* configuration, whereas **4Py** exhibits a twisted configuration due the steric hindrance brought into play by the interaction among the protons decorating the closest phenyl rings.

As previously reported, [34,35,39] triangular molecules can assemble on solid surfaces in parallel (P) or anti-parallel (A) fashion. Two different self-assembly motifs formed through (pyridyl)N...H–C(pyridyl) H-bonds can be proposed for **3Py**, and are characterized by the formation of P1 and P2 pairing (see Fig. 2a). Such pairing allows the generation of three distinct self-assembly motifs, i.e. [**3Py**]_nP1, [**3Py**]_nA1 and [**3Py**]_nP2 (Fig. 2a). [**3Py**]_nP1 and [**3Py**]_nA1 display dense parallel and anti-parallel molecular packing respectively while [**3Py**]_nP2 features a parallel porous network. On the other hand, since **4Py** has a C_2 symmetry, it can be self-assembled only in the parallel configurations P1 and P2 via H-bonds (Fig. 2b). Such interactions can promote the molecular packing of **4Py** into two supramolecular architectures, i.e. the dense [**4Py**]_nP1 and the porous [**4Py**]_nP2 motif (Fig. 2b).

The molecular self-assembly at the solid/liquid interface on HOPG was explored *in-situ* by STM. A 4 μ L droplet of a 250 μ M solution of **3Py** in 1-phenyloctane was drop cast on a freshly cleaved surface. Fig. 3a displays a STM height image of the physisorbed monolayer. It shows a 2D densely packed network of molecules lying flat on the basal plane of the surface. Due to their extended π -conjugated system, the individual molecules in the self-assembled pattern appear bright and exhibit a C_3 -symmetric contrast. All the molecules are oriented along the same direction with a parallel configuration. **3Py** is adsorbed in parallel fashion leading then to dense molecular architectures that are stable for 3–4 h. The 2D self-assembly can be described by the formation of six (pyridyl)N...H–C(pyridyl) H-bonds per molecule. A representative molecular model is presented in Fig. 3b.

We then extended our investigation to the formation of **3Py** films by lowering the concentration of the solution applied to the surface. STM height image in Fig. 3b displays the physisorbed monolayer of **3Py** at the solid/liquid interface obtained with a con-

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