Chinese Chemical Letters xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chinese Chemical Letters

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

Original article

Pinning-down molecules in their self-assemblies with multiple weak hydrogen bonds of C—H···F and C—H···N

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ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form 27 October 2016
Accepted 28 October 2016
Available online xxx

Keywords:
Fluorinated pyridyl molecules
Grouped hydrogen bonds
Molecular self-assembly
Molecular design
Scanning tunneling microscopy

ABSTRACT

Two-dimensional self-assemblies of four partially fluorinated molecules, 1,4-bis(2,6-difluoropyridin-4-yl)benzene, 4,4'-bis(2,6-difluoropyridin-4-yl)-1,1'-biphenyl, 4,4'-bis(2,6-difluoropyridin-4-yl)-1,1':4',1''-terphenyl and 4,4'-bis(2,6-difluoropyridin-3-yl)-1,1'-biphenyl, involving weak intermolecular C—H···F and C—H···N hydrogen bonds were systematically investigated on Au(111) with low-temperature scanning tunneling microscopy. The inter-molecular connecting modes and binding sites were closely related to the backbones of the building blocks, i.e., the molecule length determines its binding sites with neighboring molecules in the assemblies while the attaching positions of the N and F atoms dictate its approaching and docking angles. The experimental results demonstrate that multiple weak hydrogen bonds such as C—H···F and C—H···N can be efficiently applied to tune the molecular orientations and the self-assembly structures accordingly.

1. Introduction

Self-assembled molecular architectures on metal surfaces have attracted great interest due to their structural ordering and abundance, and potential applications in the field of nanotechnology [1–3]. As one of the main driving forces among non-covalent bonding interactions, hydrogen bond (HB) has been extensively exploited to form various assembling patterns owing to its unique properties such as bonding strength, flexibility, directionality and selectivity [3–7]. Compared with their strong counterparts (7–8 kcal/mol) [8–10], weak HBs [11] are usually more flexible in bonding geometries which could be employed to control the orientations of the assembling molecules and hence ultimate assembling structures [12–14].

Weak HBs like C—H···O and C—H···N are frequently utilized to construct two-dimensional (2D) self-assemblies in the past [15–19]. Meanwhile, perfluoro-molecules such as copper hexadecafluorophthalocyanine (F_{16}CuPc), a potential molecular semiconductor serving as an electron acceptor in organic photovoltaic (OPV) devices [20–22] and as an n-type organic semiconducting material in light-emitting diode [23], have received substantial attention due to their extraordinary air-stability. Besides the layer thickness, the packing pattern of the F_{16}CuPc molecules governed by weak intermolecular interactions including C—H···F HBs may have great influence in the performance of the OPV devices. In terms of the F_{16}CuPc self-assembly on metallic substrates [20–22], previous research normally focuses on its co-assembly with other p-type organic molecules to form molecular p–n junctions or donor–acceptor pairs [23,24].

While perfluoro-molecules have been generally adopted to prepare organic semiconducting self-assembled membranes [29–32], nano-arrays [33] and networks [34,35] at surfaces, partially fluorinated molecules are less studied in the past. In our previous report [15], we have successfully assembled a whole series of 2D molecular porous networks whose pores possess all possible rotational symmetry, i.e., 2-, 3-, 4- and 6-fold rotations, by using the same building blocks, 4,4'-bis(pyridin-4-yl)-1,1'-biphenyl (BPBP) and trimesic acid (TMA). This is achieved by solely

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http://dx.doi.org/10.1016/j.cclet.2016.11.007

changing two physical parameters, substrate temperature and coverage ratio of TMA to BPBP. The driving force is the combined strong and weak HB networks formed between TMA and BPBP. Among all possible HBs, the weak ones such as C=O (TMA)···H—C (α- and β-H in the pyridyl group in BPBP) and N(pyridyl)···H—C (pyridyl) play an important role in tuning the final pore symmetry. Therefore, it would be very interesting to explore the assembling behavior of partially fluorinated BPBP derivatives upon substitutions of the α-H in pyridyl with F atoms. The replacing F atoms would accordingly change the acidity of their neighboring H atoms in the pyridyl groups. Such a motivation intrigues the present study of the self-assemblies of 1,4-bis(2,6-difluoropyridin-4-yl) benzene (BDFPB) and its derivatives which can form weak HBs like C—H···F and C—H···N.

As is well known, the structures of the molecular building blocks are of extreme importance in tailoring and engineering the molecular self-assemblies. To do this, several strategies including re-designing the molecular backbones [36–38], introducing additional functional groups [39–42] and changing the number and positions of the substituents [43–46] have been developed, aiming at precisely controlling the assembled architectures on the substrates.

To achieve tuning the 2D molecular self-assembly patterns in a controlled manner, the BPFBP molecule and its three derivatives such as 4,4'-bis(2,6-difluoropyridin-4-yl)-1,1'-biphenyl (BDFPBP), 4,4"-bis(2,6-difluoropyridin-4-yl)-1,1':4',1"-terphenyl (BDFPTP) and 4,4'-bis(2,6-difluoropyridin-3-yl)-1,1'-biphenyl (BDFP-3-BP) were deposited onto an atomically flat Au(111) substrate. Their corresponding self-assembly patterns were subsequently scrutinized in detail with scanning tunneling microscopy (STM), a powerful tool to unveiling surface molecular assembling structures at the sub-molecular level. A major experimental observation was that these molecules could be pinned down in their self-assemblies by synergic multiple weak HBs of C—H···F and C—H···N.

2. Results and discussion

In a previous study [5], a porous honeycomb network was prepared by grouped HBs, exhibiting a much stronger hetero- as opposed to homo-molecular hydrogen bonding between perylene tetra-carboxylic di-imide (PTCDI) and melamine (1,3,5-triazine-2,4,6-triamine) on a silver-terminated silicon surface. Such a honeycomb network contains vertices formed by melamine and straight edges formed by PTCDI. Here, we adopt grouped weak HBs formed by bent F—C—N=C—F and H—C=C—C=C—H in the F-containing molecules to govern the assembling structures.

At the coverage of one monolayer (ML), the BDFPB molecules assembled into a close-packed structure denoted Pattern X (Fig. 1b). In this pattern, one BDFPB molecule perpendicularly approaches to another at the X sites, as marked in the molecular model in Fig. 1a. Such a connection mode is termed as Mode X. Apparently, Pattern X is formed solely via the X mode. One unit cell of this close-packed structure is schematically modelled in Fig. 1d and defined by the cell parameters: $a = (1.2 \pm 0.1)$ nm, $b = (1.8 \pm 0.1)$ nm, and $\alpha = (86 \pm 2)°$. Further annealing at 400 K led to partial desorption of the BDFPB molecules (Fig. 1c). However, regardless of the surface coverage decrease or temperature elevation of the sample, Pattern X is the sole structure observed at surface.

Similar to the case of BDFPB, BDFPBP also assembled into a close-packed Pattern X (Fig. 2a) at 1 ML. Two interacting BDFPBP molecules in adjacent rows formed an angle of about $(84 \pm 2)°$. It should be pointed out that these two molecules are not strictly perpendicular to each other due to the repulsion interaction of the F atoms in them. Subsequent thermal treatment of the sample led to several new patterns correspondingly labelled as XYI, XYII and Y in Fig. 2b–d. The unit cell parameters for the four assembled patterns are given below: (1) Pattern X, $a = (1.1 \pm 0.1)$ nm, $b = (2.4 \pm 0.1)$ nm, and $\alpha = (89 \pm 2)°$; (2) Pattern XYI, $a = (2.1 \pm 0.1)$ nm, $b = (2.1 \pm 0.1)$ nm, and $\alpha = (75 \pm 2)°$; (3) Pattern XYII, $a = (1.7 \pm 0.1)$ nm, $b = (1.9 \pm 0.1)$ nm, and $\alpha = (96 \pm 2)°$; (4) Pattern Y, $a = (1.9 \pm 0.1)$ nm, $b = (1.9 \pm 0.1)$ nm, and $\alpha = (93 \pm 2)°$. All unit cells are highlighted in the STM images in Fig. 2, and the corresponding schematic models for the patterns are given in Fig. 2e–h.

According to the models given in Fig. 2e–h, two distinct connection modes, namely, X and Y, can be immediately identified. Obviously, each BDFPB molecule possesses four identical X sites. In the Y mode, one BDFPBP molecule perpendicularly approaches another one via the Y sites that bisect the molecule. The distance between the approaching sites for the Y mode and either end of the molecule is about 0.71 nm. Again the repulsion interaction of the F atoms in two connecting BDFPB molecules leads to their docking angle and distance deviations. The proposed molecular models suggest that both C—H···F and C—H···N weak HBs are involved in either X or Y modes.

The close-packed Pattern X is built solely via the X mode (Fig. 2a), and Pattern Y, solely via the Y mode (Fig. 2d). Pattern XY is made possible via a mixture of the X and Y modes. In our experiments, only two large-area ordered XY patterns were observed, namely Pattern XYI (Fig. 2b) and Pattern XYII (Fig. 2c). Both possess different X mode/Y mode ratios. For Pattern XYI, there are six intermolecular binding sites in a unit cell, four of which adopt the X mode to interact with the nearest molecule, while the other two adopt the Y mode (Fig. 2b and f). For Pattern XYII, one unit cell contains four binding sites, two X modes and two Y modes (Fig. 2c). Accordingly, the ratio of X mode to Y mode is 2:1 for Pattern XYI and 1:1 for Pattern XYII, respectively.

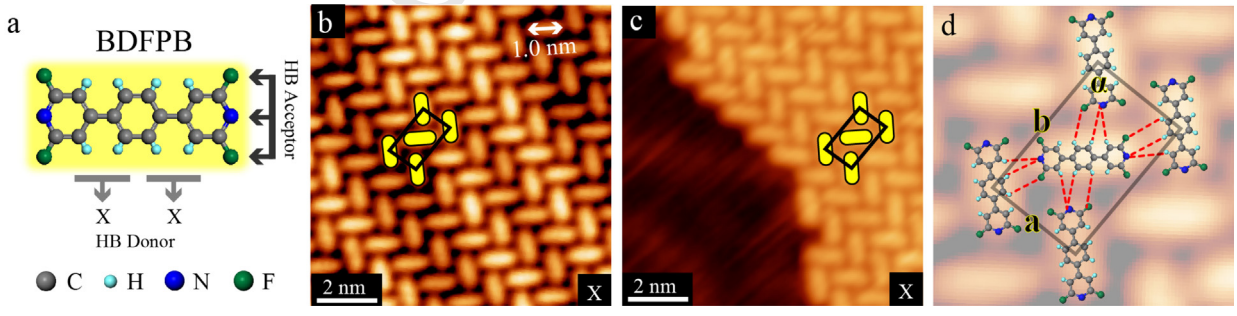

Fig. 1. (a) Schematic model of BDFPB, in which the HB acceptor groups and HB donor groups are marked by short lines and arrows. (b–c) STM images of the self-assembled Pattern X at full coverage (b) and after partial desorption (c). The yellow rods highlight the arrangements of BDFPB in within a unit cell, as marked by the black rectangle for eye guidance. (d) Schematic model for Pattern X superimposed onto an enlarged STM image. Imaging conditions: (b–c) bias voltage (V) = 1.5 V, feedback current (I) = 50 pA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Please cite this article in press as: X. Jin , et al., Pinning-down molecules in their self-assemblies with multiple weak hydrogen bonds of C—H···F and C—H···N, Chin. Chem. Lett. (2016), http://dx.doi.org/10.1016/j.cclet.2016.11.007