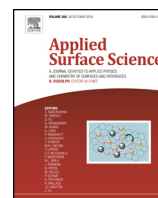




Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: [www.elsevier.com/locate/apsusc](http://www.elsevier.com/locate/apsusc)



Full length article

## Networks of non-planar molecules with halogen bonds studied using scanning tunneling microscopy on Au (111)

Min Hui Chang<sup>a</sup>, Won Jun Jang<sup>a</sup>, Min Wook Lee<sup>a</sup>, Un Seung Jeon<sup>a</sup>, Seungwu Han<sup>b</sup>,  
Se-Jong Kahng<sup>a,\*</sup>

<sup>a</sup> Department of Physics, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

<sup>b</sup> Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 10 October 2016

Received in revised form 24 January 2017

Accepted 25 January 2017

Available online xxx

#### Keywords:

Molecular nanostructures

Self-assembly

Scanning tunneling microscopy

Halogen bond

Non-planar molecule

### ABSTRACT

Molecular networks connected by halogen bonds have been actively studied due to their ubiquity in biological systems and complementary role to hydrogen bonds. Although networks of planar molecules with halogen ligands have been studied using scanning tunneling microscopy (STM), those of non-planar molecules have not. Here, we report on the network structures of non-planar molecules containing Br-ligands, tetrabromo-spirobifluorene on Au (111), studied using STM. One and two-dimensional networks were observed and their intermolecular interactions were investigated. In two-dimensional networks, a molecule forms 3.5 Br...Br halogen bonds and 2 Br...H hydrogen bonds, as supported by our density functional theory calculation results. Our study demonstrates that intermolecular structures of non-planar molecules with halogen bonds can be probed on surfaces using STM.

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### 1. Introduction

Increasing numbers of organic drug candidate molecules include halogen ligands to boost membrane permeability [1–3]. Halogen ligands have abnormal electrostatic potential distributions; a positive potential region called a  $\sigma$ -hole is surrounded by a negative potential region, showing cylindrical symmetry along the axis of the ligand bond [4–14]. The  $\sigma$ -hole of a halogen ligand attracts the negative potential regions of oxygen, nitrogen, and other halogen ligands, resulting in halogen bonds. Halogen bonds can be as strong as hydrogen bonds, but show different directionality. Thus they are considered as complimentary tools for forming supramolecular structures that can be applied to molecular recognition, storage, and catalysis [8–11]. The networks of supramolecular structures formed with halogen bonds have been actively studied for the last five years using scanning tunneling microscopy (STM) [15–26]. They have been found to form various two-dimensional networks such as square, rectangular, hexagonal, chevron, or parallel-array structures on crystal surfaces. These previous studies have been of planar molecules to guarantee the ease of the identification of single molecules and their interactions, but in nature there are more non-planar molecules than planar ones. As far as we are aware,

there has been no STM study of supramolecular structures formed from non-planar molecules through halogen bonding.

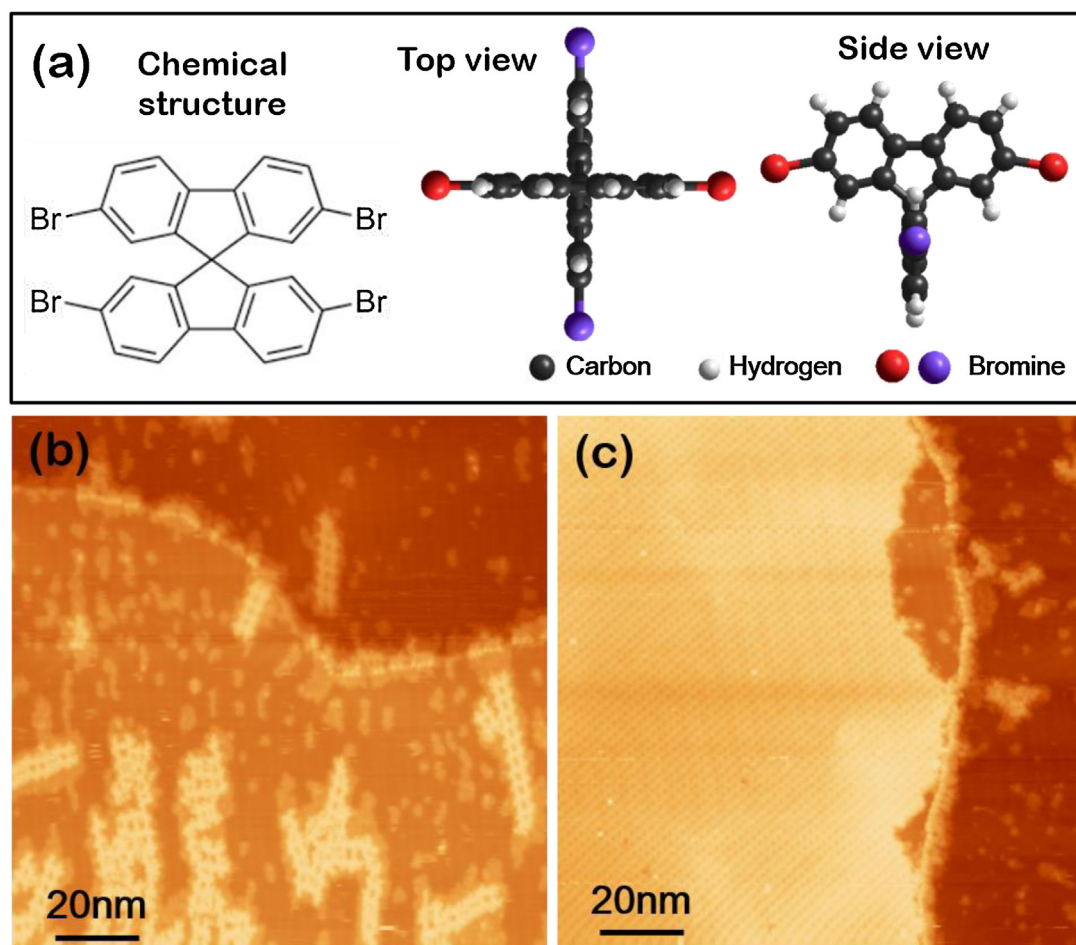
Here, we present an STM study of the network structures of tetrabromo-spirobifluorene (TBSBF), a non-planar molecule containing Br-ligands on Au (111). We observed one and two-dimensional networks and proposed their atomistic models. In the two-dimensional networks, a molecule forms 3.5 Br...Br halogen bonds and 2 Br...H hydrogen bonds, according to our density functional theory (DFT) calculations. Our study shows that the network structures and interactions of non-planar molecules with halogen ligands can be successfully revealed using STM on surfaces.

### 2. Experimental methods

The experiments were performed using a home-built STM housed in an ultrahigh vacuum (UHV) chamber with a base pressure below  $1 \times 10^{-10}$  torr. The Au (111) surface was prepared from a 200 nm thick film of Au on mica that had been exposed to several cycles of Ne-ion sputtering and annealing at 800 K over the course of 1 h. The surface cleanliness of the Au (111) was checked by confirming the typical herringbone structures on the terraces in STM images. Commercially available TBSBF molecules (Tokyo Chemical Industry, Japan) were thermally evaporated onto the surface to form a sub-monolayer coverage from an alumina-coated crucible, maintaining the substrate temperature at 150 K. The molecular sources were outgassed for several hours prior to deposition. Once

\* Corresponding author

E-mail address: [sjkahng@korea.ac.kr](mailto:sjkahng@korea.ac.kr) (S.-J. Kahng).



**Fig. 1.** (a) The chemical structure and the ball and stick 3D model of a TBSBF molecule. (b), (c) Typical STM images of TBSBF molecules on Au (111) surface after heating at (b) 200 K and (c) 300 K. The size of STM images:  $128 \times 128 \text{ nm}^2$ . Tunneling current:  $I_T = 0.03 \text{ nA}$ . Sample voltage: (b)  $V_S = 0.8 \text{ V}$  and (c)  $V_S = 0.7 \text{ V}$ .

prepared, the sample was transferred to the STM, and measured at 80 K using a Pt-Rh alloy tip.

### 3. Theoretical calculations

DFT calculations were performed using the VASP code [27,28]. Interactions between ions and electrons were approximated by the projector-augmented wave (PAW) potential [29]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange-correlation energies between electrons [30]. The energy cutoff for the plane wave basis was set to 500 eV. To include the non-bonding interactions between the molecules, especially those of the van der Waals type, the empirical scheme proposed by Grimme was adopted [31]. Parallelepiped simulation cells containing two TBSBF molecules were adopted to form the periodic structure. The side lengths  $a$  and  $b$  of the parallelogram parallel to the molecular plane were varied to find the most stable structure. The height of the simulation cell perpendicular to the molecular plane was fixed at 50 Å, while the lateral cell parameters  $a$  and  $b$  were optimized such that the residual stress was reduced to under 1 kbar.

### 4. Results and discussion

Fig. 1(a) shows the chemical structure and three-dimensional (3D) ball and stick model of a TBSBF molecule made up of two bibromo-fluorene (BBF) molecules. Two planar BBF molecules share a carbon atom to form a “+”-like non-planar TBSBF structure.

When the molecules were deposited at 150 K, rather than forming ordered structures, they formed cluster structures randomly distributed on the terraces. Fig. 1(b), (c) show the STM images obtained at 80 K after depositing the TBSBF molecules on Au (111) at a sub-monolayer coverage and annealing at 200 and 300 K, respectively. After annealing at 200 K, the cluster structures are still visible, and one-dimensional (1D) structures are observed on top of mono-layer islands. However, when the sample was annealed at 300 K, the molecules formed two-dimensional (2D) structures. The 2D structures also formed on top of the mono-layer islands whose structures are not clear from our experiments. It is expected that interaction between the molecules and substrate is marginal. Still, the 2D networks reflect the herringbone structures of Au (111) as shown in Fig. S1(a). The angle between the  $[1\bar{2}1]$  direction of Au (111) and the direction of a molecular row is estimated to be  $30^\circ$ .

Fig. 2(a)–(d) show higher resolution STM images of the 1D and 2D structures. We considered molecular models in which both BBF planes of the single TBSBF molecules were in  $90^\circ$  configurations with respect to a surface plane. One BBF is close to the surface (the lower BBF), while the other is far from the surface (the upper BBF). A bar-like structure that represents one side of the upper BBF of the TBSBF molecule was regarded as a single molecule. Molecular models are superimposed over the STM images of the 1D structures in Fig. 2(b) and the 2D structures in Fig. 2(d).

To explain the molecular models deduced from our experiments, we calculated the intramolecular electrostatic potential distributions of isolated molecules using DFT calculations. Fig. 3(a)

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