



Full Length Article

Two-dimensional networks of brominated Y-shaped molecules on Au(111)

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ABSTRACT

In the design of supramolecular structures, Y-shaped molecules are useful to expand the structures in three different directions. The supramolecular structures of Y-shaped molecules with three halogen-ligands on surfaces have been extensively studied, but much less are done for those with six halogen-ligands. Here, we report on the intermolecular interactions of a Y-shaped molecule, 1,3,5-Tris(3,5-dibromophenyl)benzene, with six Br-ligands studied using scanning tunneling microscopy (STM). Honeycomb-like structures were observed on Au(111), and could be explained with chiral triple-nodes made of three Br...Br halogen bonds. Molecular models were proposed based on STM images and reproduced with density-functional theory calculations. Although the molecule has six Br-ligands, only three of them form Br...Br halogen bonds because of geometrical restrictions. Our study shows that halogenated Y-shaped molecules will be useful components for building supramolecular structures.

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1. Introduction

Supramolecular structures have been widely studied, because of their possible applications in material technology such as catalysis, data storage and computation [1–3]. The structures are formed via self-assembly processes that are driven by a multitude of intermolecular interactions such as hydrogen bonds, dipole interactions, van der Waals forces, π -interactions, metal-coordination bonds, and halogen bonds. Among them, halogen bonds drew relatively less attention for the last several decades, but they were recently reconsidered because of their complementary role to hydrogen bonds and their relevance in biochemical systems [4–17]. Specifically, halogen ligands have been exploited in various drug candidates to enhance membrane penetration, and they showed comparable bond strengths but different directionality to hydrogen bonds [15–17]. Halogen bonds are the interactions between donor halogen ligands (Br and I) and acceptor ligands (O, N, Br, and I). Such interactions are caused by peculiar charge distributions at covalently-bonded halogen ligands (X) that possess both positive and negative potential regions [4–8]. The negative regions allow the role of an electron donor to form X...O hydrogen bonds,

whereas the positive regions, termed a σ -holes, do the role of an electron acceptor to form X...O or X...N halogen bonds. It is also possible to have X...X halogen bonds between two halogen ligands. For the last several years, two-dimensional (2D) supramolecular structures formed with halogen bonds have been studied on crystal surfaces [18–32]. They have been found to form square, rectangular, hexagonal, chevron, or parallel-array structures, as revealed by scanning tunneling microscopy (STM). It has been suggested that Y-shaped molecules are useful in the design of supramolecular structures, because they can connect molecules in three different directions. Y-shaped molecules with three halogen-ligands including 1,3,5-tris(4-bromophenyl)benzene (TBB) and 1,3,5-tris(4-iodophenyl)benzene (TIB), have been actively studied on different substrates such as Au(111), Ag(111), Ag(110), Cu(111), graphite, boron nitride/Ni(111), and graphene/Ni(111) using STM [24–28]. In contrast, there are few reports on Y-shaped molecules with six Br-ligands on surfaces [29]. It was expected that six Br-ligands in a molecule might allow more halogen bonds per molecule than three Br-ligands.

In this paper, we present an STM study of the supramolecular structures of 1,3,5-Tris(3,5-dibromophenyl)benzene (TDBPB), a Y-shaped molecule containing six Br-ligands. We observed honeycomb-like structures on Au(111), and explained them with three Br...Br halogen bonds per molecule with the help of density-functional theory (DFT) calculations. Our study shows that the triple

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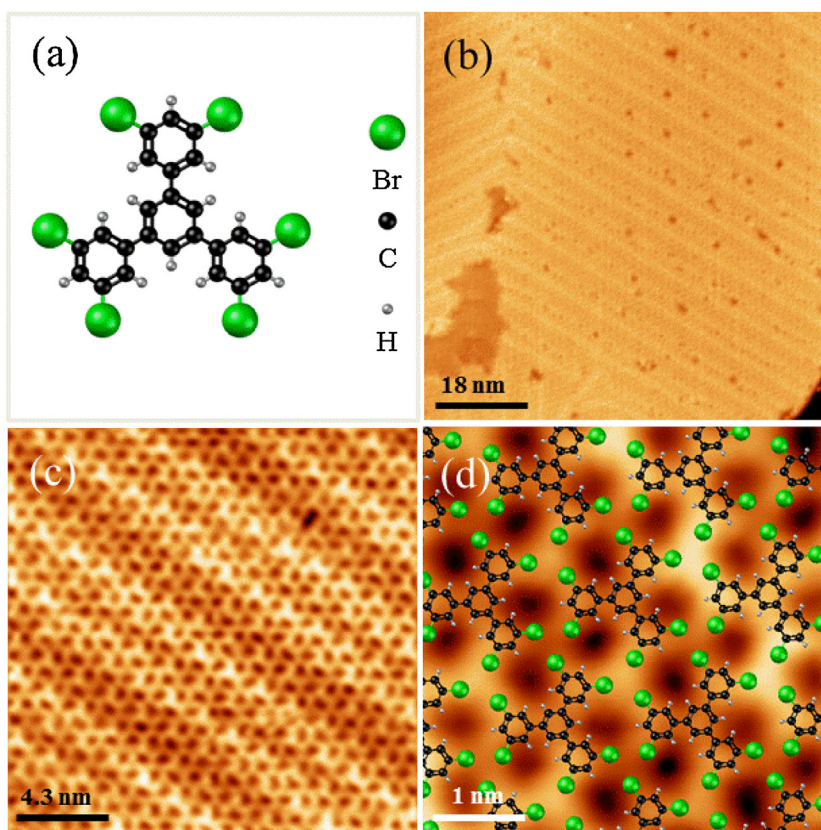


Fig. 1. (a) A ball and stick model of a TDBPB molecule. Grey, white and green balls in the molecular structure correspond to carbon, hydrogen and bromine atoms, respectively. (b)–(d) Typical STM images, measured at 80 K, of the two-dimensional supramolecular structures of TDBPB molecules as-deposited at 150 K. Honeycomb-like structures are visible in (c). In (d), a molecular model is superimposed over the STM image. The sizes of STM images: (b) $80 \times 80 \text{ nm}^2$, (c) $12 \times 12 \text{ nm}^2$, and (d) $4.5 \times 4.5 \text{ nm}^2$. For all images, tunneling current: $I_T = 0.1 \text{ nA}$ and sample voltage: $V_S = -1.8 \text{ V}$ (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

nodes made of Br...Br halogen bonds can play key roles in the formation of supramolecular structures.

1.1. Experimental methods

STM experiments have been performed using a home-built STM housed in an ultra-high vacuum chamber with a base pressure below 1×10^{-10} torr. The Au(111) was prepared from a 200 nm thick film of Au(111) on mica. It was exposed to several cycles of Ne-ion sputtering at 1 keV and annealing at 800 K over the course of 1 h. The surface cleanliness of Au(111) was checked by confirming the herringbone structures on the terraces in STM images. Commercially available TDBPB (Tokyo Chemical Industry) was outgassed in a vacuum for several hours and then deposited on Au(111) at sub-monolayer coverage by thermal evaporation using an alumina-coated evaporator. STM images were obtained at constant-current mode with a Pt/Rh tip while keeping the sample temperature at 80 K.

1.2. Theoretical calculations

Density-functional calculations (DFT) were performed using the Vienna *ab initio* simulation package (VASP) [33,34] and the projector-augmented wave (PAW) potential [35]. The exchange-correlation energies between electrons were described within the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [36]. The energy cutoff for the plane wave basis was set to 600 eV. To describe the non-bonding interactions between the molecules, particularly the van der Waals

type, the empirical correction scheme proposed by Grimme was adopted [37]. The energy and electrostatic potential for the isolated molecules were obtained using a $35 \times 35 \times 20 \text{ \AA}^3$ supercell. A simulation cell containing two TDBPB molecules was employed to describe the periodic structure. The height of the simulation box perpendicular to the molecule plane was fixed to 10 Å.

2. Results and discussion

An atomic model of TDBPB molecule is shown in Fig. 1(a). Because the molecule is terminated with 6 Br-ligands and 12 H-ligands, they are expected to form Br...Br halogen bonds or Br...H hydrogen bonds. When the TDBPB molecules are deposited on Au(111), they formed self-assembled molecular islands. We deposited 0.8 monolayer TDBPB to Au(111) at 150 K, cooled down the sample to 80 K, and afterward obtained STM images. Fig. 1(b)–(d) show typical STM images at different length scales. We observed a monolayer-high molecular-layer that still reflected the herringbone corrugations of Au(111). The formation of self-assembled layer at low-temperature and the preserved herringbone corrugations implies that the interaction between the molecules and surface is reasonably modest. The molecular layer showed honeycomb-like network structures, as shown in Fig. 1(c) and (d). In the small scale images of Fig. 1(d), an individual molecule was identified as a Y shape, and molecular models were superimposed to the STM image.

To identify intermolecular interactions in the observed structures, we calculated the electrostatic potential distribution of a single TDBPB molecule using DFT methods based on the GGA.

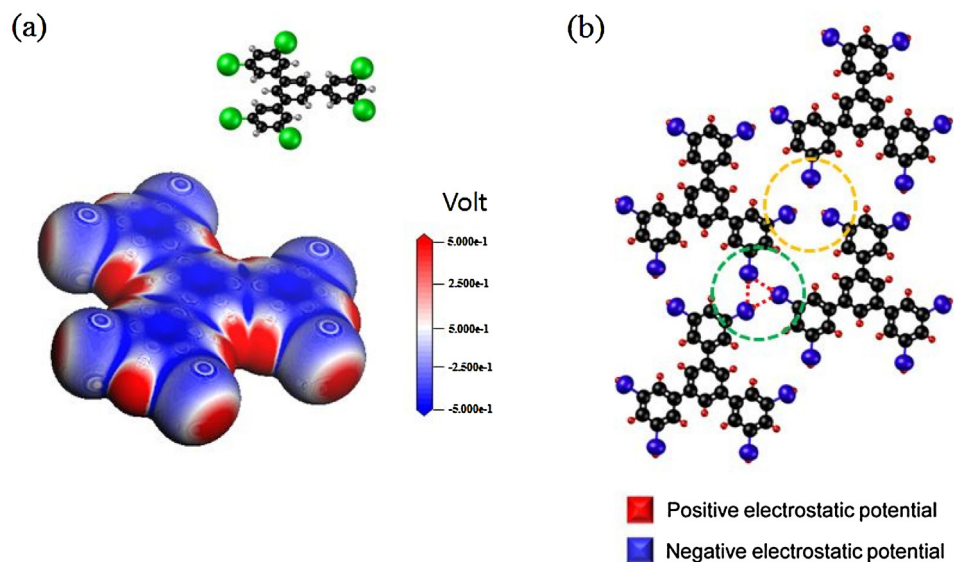


Fig. 2. (a) An isodensity-surface plot of computed molecular electrostatic potential for a TDBPB molecule, shown in red (positive) and blue (negative), along with a molecular model. (b) A schematic illustration of four nearest neighbor TDBPB molecules with simplified electrostatic potential distributions around the H and Br atoms. Green and yellow-dotted-circle indicate triple nodes with three Br-ligands. Red-dotted-lines inside the green-dotted-circle denote possible Br...Br halogen bonds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

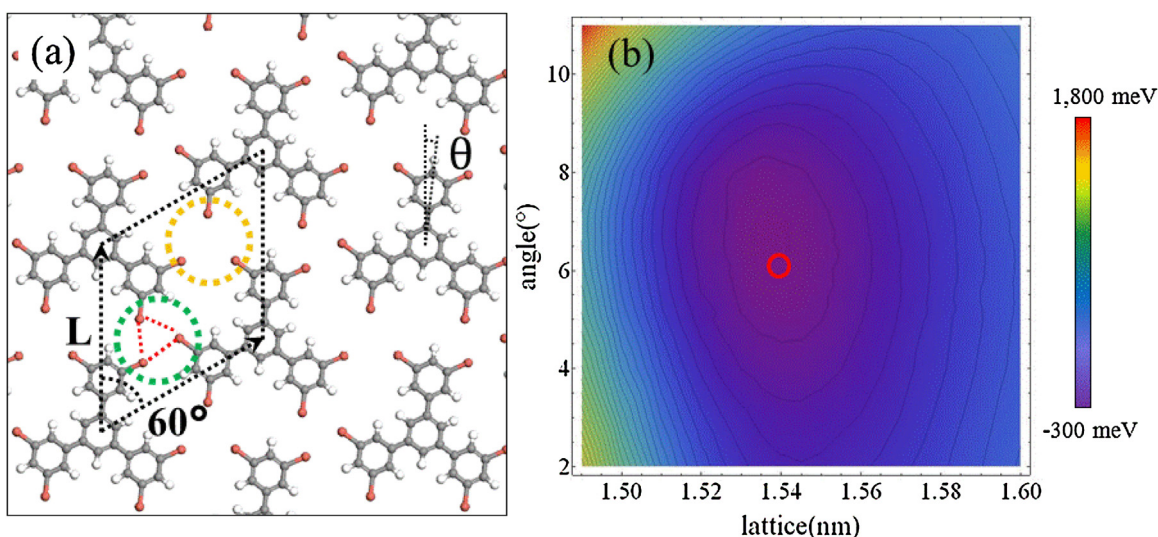


Fig. 3. (a) The relaxed structures of TDBPB obtained by DFT calculations. A black-dotted rhombus shows a unit cell with the side length of L and angle of 60° . θ is the molecular rotation angle. Green- and yellow-dotted circles indicate triple nodes with three Br-ligands. Red-dotted lines denote Br...Br halogen bonds. (b) The computed formation energy per molecule plotted as a function of the side length L and molecular rotation angle θ . The minimum-energy configuration is found at $L = 1.54$ nm and $\theta = 6.2^\circ$ with the formation energy 300 meV/molecule.

The result is mapped on isosurfaces of $0.003 e/\text{Bohr}^3$, as shown in Fig. 2(a). As expected, H atoms showed a positive electrostatic potential, whereas Br atoms showed both positive and negative potential regions. They have a positive region (σ -hole) embedded in a negative region, still showing cylindrical symmetry about the axis of covalent bond. As shown in Fig. 2(b), the structure of four neighboring molecules are drawn based on the single molecule potential distributions around the Br and H-ligands. Using that, we speculate that the network has two different triple nodes made of Br-ligands, which are denoted in Fig. 2(b) as green and yellow-dotted-circles. In the green-dotted-circle, the positive region of a Br-ligand in a molecule points toward the negative region of a Br-ligand associated to a neighboring molecule. So the three Br-ligands take a cyclic structure that is known to be a typical behavior of Br...Br halogen

bonds. In contrast, the triple node in a yellow-dotted-circle does not show such cyclic structure. Rather, all the positive regions of three Br-ligands point toward the center of an equilateral triangle which has Br atoms at each corner. Therefore, we expected that only the triple node in the green-dotted-circle might form Br...Br halogen bonds, whereas the other one in the yellow-dotted-circle did not form halogen bonds.

DFT calculations were performed to understand the precise arrangement of TDBPB molecules in honeycomb-like structures. A rhombus unit cell with side length L , 60° angles, and molecular rotation angle θ was used to construct denoted with black dotted lines in Fig. 3(a). In Fig. 3(b) for various sets of L and θ , binding energies were calculated, and the results are plotted by color. The most stable structure yielded by calculations appeared at $L = 1.54$ nm and $\theta = 6.2^\circ$, and this finding was in good agreement with the experi-

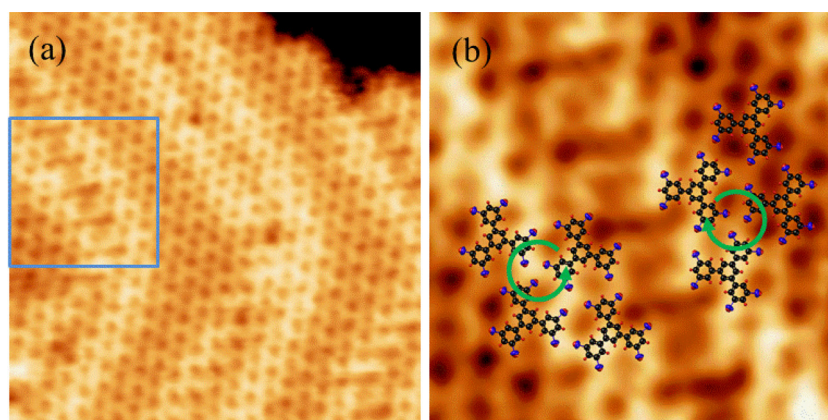


Fig. 4. (a) An STM image (1 V, 0.1 nA, $19 \times 19 \text{ nm}^2$) with domain boundaries. (b) The high resolution STM image (1 V, 0.1 nA, $6.5 \times 6.5 \text{ nm}^2$) from the squared area of (a) Circular green arrows indicate different chirality of triple nodes in the two domains. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mentally observed value of 1.6 nm and 6° . Since the DFT results well reproduce the model in Fig. 1(d), the likely lengths of the possible intermolecular bonds in Fig. 2(b) are determined from the computational results. The DFT calculations also reveal two different triple nodes denoted by green- and yellow-dotted circles. Br...Br distances in these circles were 0.37 and 0.45 nm, respectively. Because the sum of the van der Waals radii is 0.39 nm, only the former can be considered as halogen bonds, in line with the speculation mentioned in the previous paragraph. Thus a single TDBPB molecule forms three Br...Br halogen bonds in the honeycomb-like structures. The formation energy at the equilibrium structure was 300 meV per molecule in Fig. 3(b). Thus each Br...Br halogen bond carries 100 meV. It can be a question why a single TDBPB molecule forms only three halogen bonds, not six. We tried to construct a molecular model by tuning L and θ such that a single TDBPB molecule forms six halogen bonds, but in vain. To form six Br...Br halogen bonds, three Br-ligands in each triple node should make a cyclic configuration with a short enough distance. We found that whenever one set of three Br-ligands satisfies this condition, the other does not. For example, a simple case of $\theta = 0^\circ$ was considered but turned out to be less stable than the above one in our calculations. That is basically due to the geometrical configurations of Br-ligands in TDBPB molecules. Because the molecules make use of only three Br-ligands out of six, the honeycomb-like structures possess surface chirality. It has been known that non-chiral molecules can have surface chirality because of the cyclic nature of binding nodes. As shown in Fig. 4(a) and (b), two opposite chirality domains separated by boundaries were observed in our STM images.

3. Conclusions

In conclusion, intermolecular interactions were studied in the 2D self-assembled layers of TDBPB on Au(111) using STM. Honeycomb-like molecular structures were observed, and their molecular models were explained on the basis of DFT calculations. The molecular structures were stabilized by Br...Br halogen bonds without any hydrogen bond. Although the molecule has six Br-ligands, only three of them form Br...Br halogen bonds because of geometrical restrictions. Our study shows that brominated Y-shaped molecules are useful to grow halogen-bond-based supramolecular structures.

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