

## Research Article

# Solvent-Dependent Self-Assembly of 4,7-Dibromo-5,6-bis(octyloxy)benzo[c][1,2,5] Thiadiazole on Graphite Surface by Scanning Tunneling Microscopy

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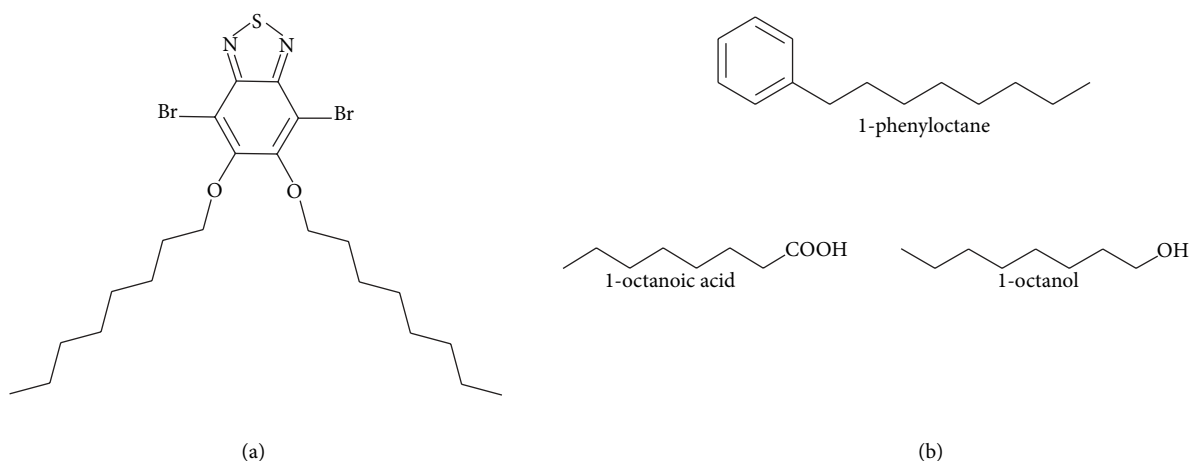
Solvent effect on self-assembly of 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5] thiadiazole (DBT) on a highly oriented graphite (HOPG) surface was investigated by scanning tunneling microscopy (STM) by using 1-phenyloctane, 1-octanoic acid, and 1-octanol as the solvents. Two different patterns were obtained in 1-phenyloctane and 1-octanoic acid, suggesting that the self-assembly of DBT was solvent dependent. At the 1-phenyloctane/HOPG interface, a linear structure was revealed due to the intermolecular halogen bonding. When 1-octanoic acid and 1-octanol are used as the solvents, the coadsorption of solvent molecules resulting from the hydrogen bonding between DBT and solvent made an important contribution to the formation of a lamellar structure. The results demonstrate that solvents could affect the molecular self-assembly according to the variational intermolecular interactions.

## 1. Introduction

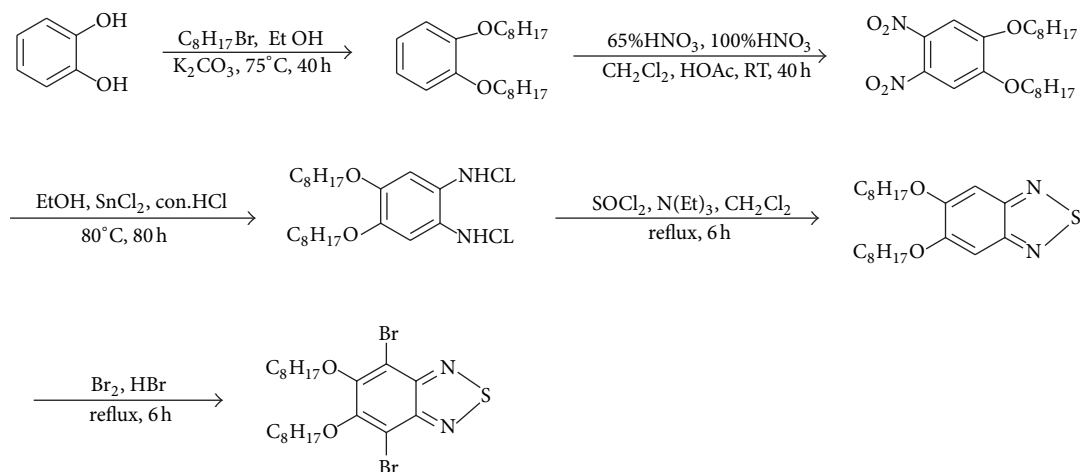
Self-assembly has been considered as an elegant “bottom-up” approach for fabricating nanostructured materials [1–4]. Due to the convenient and straightforward experimental methods, scanning tunneling microscopy (STM) is widely used to be an effective tool for studying assembly nanostructures in ambient conditions [5, 6]. Molecular self-assembly at the liquid/solid interface is that molecules arrange into well-defined nanopattern spontaneously, owing to the noncovalent bonds among the intermolecular, molecule-solvent and molecule-substrate interactions [7–10]. Weak intermolecular interactions such as hydrogen bonding, van der Waals interaction, dipole interaction, or metal coordination have been successfully displayed in supramolecular architectures [11–13]. Hydrogen bond is a prevalent type of interaction for formation of the molecular adlayers because of the advantages of selectivity and directionality. Recently, halogen bonding (X-bonding) has been less extensive in two-dimensional (2D) self-assembly [14–16], which is used as a binding motif in organic thin films and as a linker in the self-assembled nanoparticles.

For self-assembly from the solutions, solvents play an important part in the formation of the self-assembled monolayer. In some cases, if solvents contain alkyl chains, aromatic rings, or hydrogen bonding donor or acceptors, the solvent molecules can be coadsorbed on the surface by van der Waals interactions with the substrate, hydrogen bond or van der Waals interactions with the adsorbates, to form 2D nanostructure [9, 17, 18]. For example, the carboxyl groups of 5-(benzyloxy)-isophthalic acid derivative (BIC) were observed to form hydrogen bonds between neighboring molecules or between BIC molecules and 1-octanoic acids [19]. Mamdouh et al. reported that in aromatic alkylated solvents and *n*-alkanes, solvent molecules were coadsorbed and were part of a complex 2D molecular network of monodendron [20].

During the past few years, 4,7-dithienyl-2,1,3-benzothiadiazole (DBTD) unit was widely used as electron accepting moiety for the design and synthesis of low bandgap copolymers [21–24]. The photovoltaic property might have a relationship with the arrangement of DBTD unit, so it is a significant effort to interpret the essence from molecular scale. Herein, we studied the self-assembly of (DBT,  $C_{14}H_{34}O_2N_2Br_2S$ , Scheme 1) at the liquid/solid interface in



SCHEME 1: (a) Chemical structure of 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (DBT). (b) Different solvents and their chemical structures.



SCHEME 2: Synthetic route of 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (DBT).

different solvents by STM. As it is known, variation of the solvents was important to understand their roles in the assembly. In particular, the hydrogen bonding plays a very important role in the coadsorption of solvent molecules, including the formation of separated rows of strip structures. As detailed here in after, interfacial DBT monolayers show fully solvent-dependent phenomenon. The DBT molecules formed ordered nanostructure at the 1-phenyloctane/HOPG interface, while at the 1-octanoic acid or 1-octanol/HOPG interface, a linear lamellar pattern was observed. The study on solvent effect would shed on better control of the self-assembled nanostructures by changing the intermolecular interactions.

## 2. Experimental

**2.1. Synthesis of DBT.** The synthetic pathway to obtain the DBT molecule is depicted in Scheme 2. Organic starting materials were purchased from Sigma-Aldrich. Solvent was purified and dried by standard techniques. DBT has been synthesized according to a literature procedure [25].

**2.2. Scanning Tunneling Microscopy.** All experiments were performed at ambient conditions using a Nanoscope IIIa Multimode SPM (Digital Instruments, Santa Barbara, CA). Scanning tunneling microscopy (STM) was operated in constant-current mode. STM tips were prepared by mechanical cutting from Pt/Ir wire (80 : 20, diameter 0.2 mm). Prior to image, DBT molecule was dissolved (concentration =  $\sim 10^{-6}$  M) in 1-phenyloctane, 1-octanoic acid, and 1-octanol, respectively. A drop of this solution ( $1 \mu L$ ) was applied on a freshly cleaved surface of HOPG (quality ZYB, Digital Instruments, Santa Barbara, CA). Then STM experiment was carried out. All images were taken within 4 h of applying the solution on the HOPG surface. Different tips and samples were used to check the reproducibility and exclude image artifacts that were caused by the tips and samples. Tunneling parameters are given in the corresponding figure captions. The images were corrected for drift using the recorded HOPG images for calibration purposes.

**2.3. Computer Simulation.** Molecular models of the observed assembled structures were built by Materials Studio 4.4.

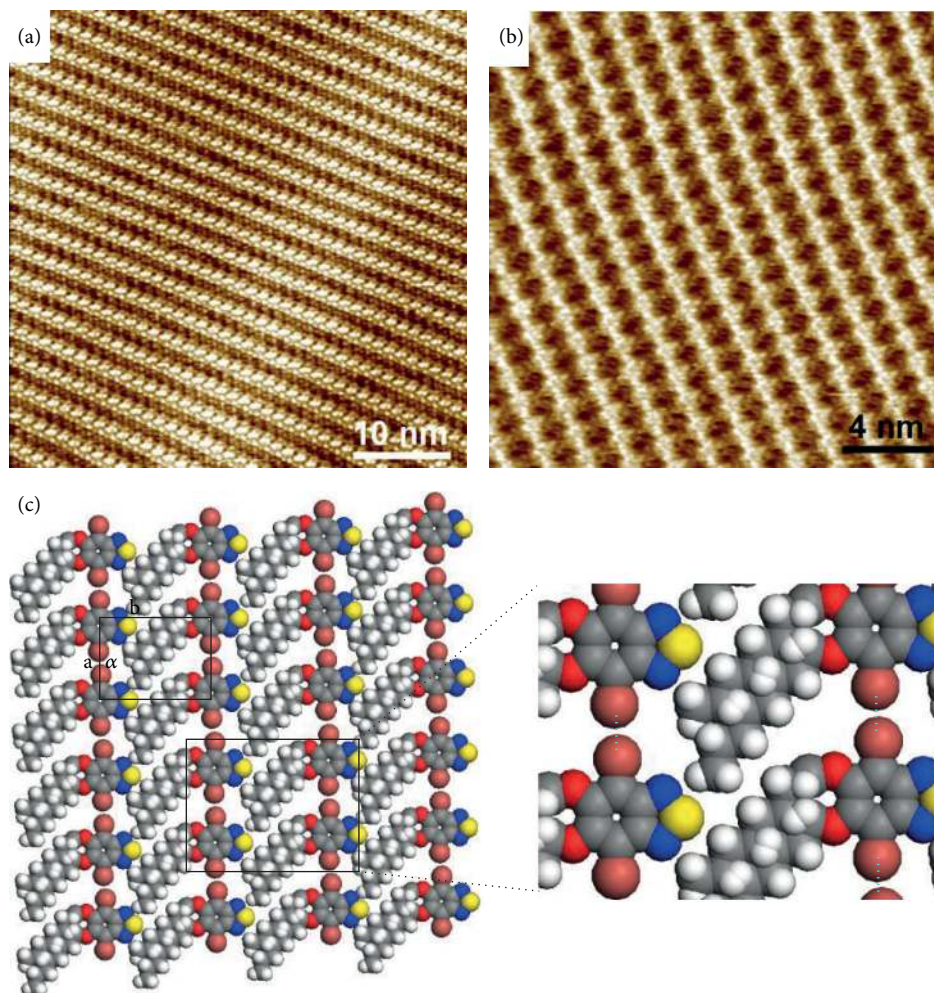


FIGURE 1: (a) Large-scale STM image of DBT adlayer in 1-phenyloctane. Tunneling parameters:  $I_t = 520$  pA and  $V_b = 730$  mV. (b) High-resolution STM image of DBT adlayer. Tunneling parameters:  $I_t = 520$  pA and  $V_b = 730$  mV. (c) Structure model for the DBT adlayer. Possible halogen bonds are shown in the enlarged inset by black dashed lines.

The model of monolayer was constructed by placing the molecules according to the intermolecular distances and angles obtained from analysis of STM images.

### 3. Results and Discussion

**3.1. Self-Assembly of DBT in 1-Phenyloctane.** After deposition of a solution containing DBT molecule on the HOPG surface, a ribbon featured-pattern was observed after several minutes. Figure 1(a) displays a large-scale STM image of the adsorbed monolayer. A highly ordered adlayer with only one single-crystalline domain size more than 200 nm could be clearly resolved, which is rarely observed in the self-assembled monolayer at the liquid/solid interface. In our numerous experiments, no domain separation was observed within the same terrace of HOPG surface. Detailed molecular packing pattern of DBT assembly can be seen from the high-resolution STM image (Figure 1(b)), which is composed of dark troughs and bright stripes. Owing to the high electron density of state, the bright stripes are attributed to the DBT aromatic cores, whereas the dark troughs are occupied by

the side chains. The length of side chain is measured to be  $1.0 \pm 0.1$  nm. The van der Waals interactions between the short side chains and HOPG surface are weak so that the side chains could not be resolved more clearly. Thus, the higher-resolution STM image could not be obtained.

On the basis of the STM image, a structural model is proposed in Figure 1(c). A unit cell with the parameters of  $a = 1.2 \pm 0.2$  nm,  $b = 1.7 \pm 0.1$  nm, and  $\alpha = 88 \pm 1^\circ$  is outlined in the model. In view of the total system energy, densely packed assembly is most frequently favored. The adsorbate-substrate and adsorbate-adsorbate interactions could be maximized in the densely arrangement, especially when the intermolecular interaction lacks directionality [4]. Therefore, two side chains of the DBT molecule locate at the same side of the conjugated cores and arrange in parallel. Halogen bonds occur due to polarisation of the halogen atom in a C–X bond, the resulting nonspherical charge distribution, and electrostatic potential. These influence factors are strong enough to stabilize supramolecular monolayers under the equilibrium conditions of liquid/solid interfaces [26]. Because of the nonspherical charge distribution of bromine atom and the parallel

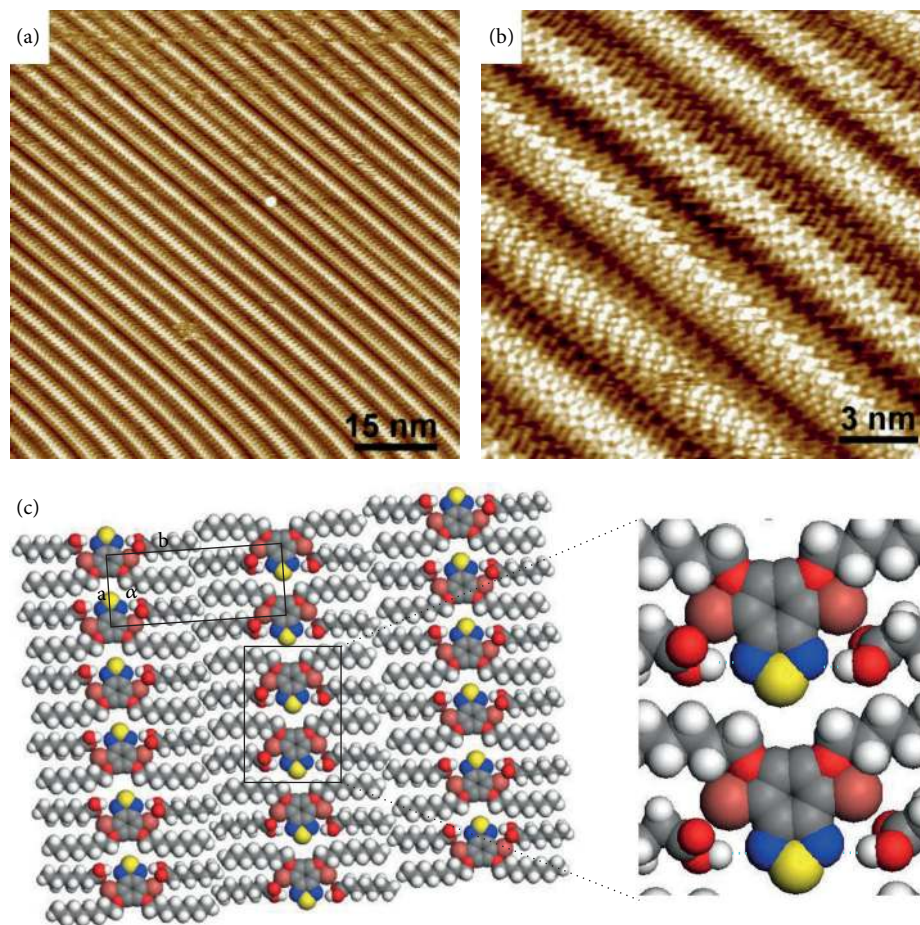


FIGURE 2: (a) Large-scale STM image of the DBT adlayer in 1-octanoic acid. Tunneling parameters:  $I_t = 570$  pA and  $V_b = 820$  mV. (b) High-resolution STM image of the DBT adlayer. Tunneling parameters:  $I_t = 570$  pA and  $V_b = 820$  mV. (c) Structure model for the DBT adlayer. Possible hydrogen bonds are shown in the enlarged inset by black dashed lines.



FIGURE 3: The optimized conformation of DBT calculated by Gaussian W03.

orientation, a halogen-halogen interaction is formed between the bromine atoms of the neighboring DBT molecules in each lamella. So, we propose that the Br–Br halogen bonds indicated by green lines in the enlarged inset of Figure 1(c) are the most dominant interactions stabilizing the 2D self-assembled structure.

**3.2. Self-Assembly of DBT in 1-Octanoic Acid.** In some cases, solvent molecules could control the self-assembled structure

of adsorbates significantly according to the solvent-adsorbate interactions [27, 28]. The nitrogen in the conjugated moiety of DBT has the isolated electron pair, which could act as hydrogen-bond acceptors to form hydrogen bonds with other donor functional groups or molecules. So, we choose 1-octanoic acid as the solvent in order to change the self-assembly of DBT by the hydrogen bonding between the DBT molecules and the 1-octanoic acids.

A distinctly dissimilar self-assembled pattern could be observed after adding a drop of DBT solution on the HOPG surface by using 1-octanoic acid as the solvent. Figure 2(a) is a large-scale STM image of a highly ordered DBT linear structure. Bright stripes and dark troughs can be distinguished easily from the STM image. Similarly, the scanning surface, more than 200 nm, was covered by one domain.

In the high-resolution STM image (Figure 2(b)), it is found that the bright stripes consisting of dot aggregations, arranged in a linear fashion. The dark area between bright molecular rows is attributed to the alkyl chains. Two kinds of alkyl chains are observed, which are the octoxy chains of DBT and the coadsorbed heptane chains of 1-octanoic acid. In the packing pattern, the side chains of DBT molecules arrange on either side of the conjugated groups, which approximate

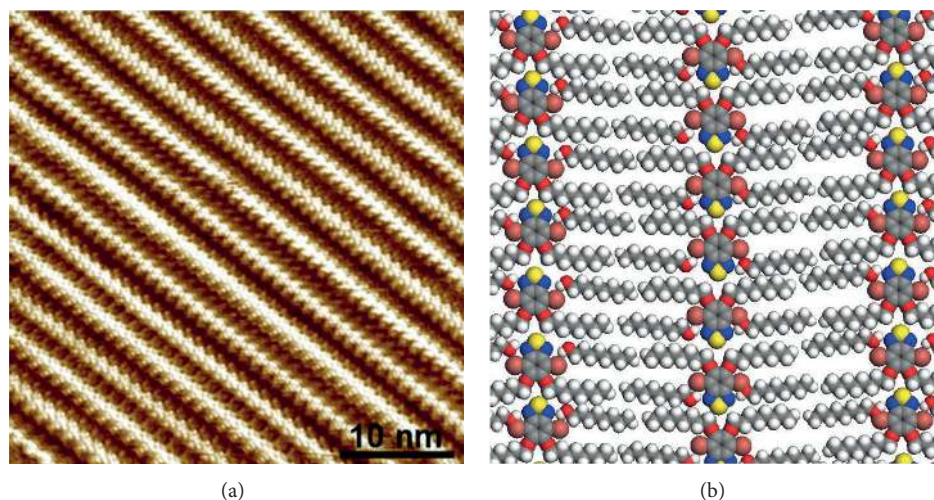


FIGURE 4: (a) Large-scale STM image of the DBT adlayer in 1-octanol. Tunneling parameters:  $I_t = 550$  pA and  $V_b = 710$  mV. (b) Structure model for the DBT adlayer.

to the optimized structure of DBT as shown in Figure 3. The conjugated moieties arrange with an opposite direction in the adjacent lamellae. The side chains could be resolved clearly indicating that the van der Waals interactions of alkyl-alkyl and alkyl-substrate are enhanced significantly. On the aforementioned analysis, a proposed model is shown in Figure 2(c). A unit cell is outlined with the lattice constants of  $a = 0.69 \pm 0.05$  nm,  $b = 2.5 \pm 0.1$  nm, and  $\alpha = 89 \pm 1^\circ$ .

**3.3. Self-Assembly of DBT in 1-Octanol.** In a parallel experiment, the 2D self-assembled adlayer of DBT has been also investigated by using the solvent of 1-octanol containing DBT molecules. The self-assembled adlayer was fabricated after the solution was dropped on the HOPG surface, as shown in Figure 4(a). A well-ordered linear lamellar structure can be seen in the image, similar to the DBT assembly in 1-octanoic acid. No other structures could be obtained by STM. On the basis of the STM image, a structural model can be proposed for the coadsorption, as shown in Figure 4(b). The hydrogen bonds are formed between the DBT molecules and 1-octanoic acids. The solvent molecules play an important counterpart role in the assembly, leading to a stable and hydrogen-bonded coadsorbed pattern.

The question arises as to why in 1-phenyloctane no solvent molecules are coadsorbed, while in 1-octanoic acid and 1-octanol solvent coadsorbed patterns are observed. Clearly, the nature of the functional group must play an important role. The interaction of phenyl-substituted alkyl chain with the substrate is unlikely compared to  $-\text{COOH}$  functionalized alkyl chain. At relative low temperature ( $<15^\circ\text{C}$ ), the monolayer of 1-octanoic acid or 1-octanol in pure solvent conditions might be observed. This is never observed for 1-phenyloctane under comparable experimental conditions. In the self-assembly of DBT molecule, the  $-\text{COOH}$  or  $-\text{OH}$  groups of coadsorbed hydrophilic solvent molecules could interact by the hydrogen bonding with DBT molecules in the solution, hence, stabilizing their coadsorption. In other words, the

self-assembled structure formation involves the hydrogen bonding between the nitrogen atoms of DBT molecule and the carboxyl acid or hydroxyl of solvent molecules. The results also demonstrate that the hydrogen bonds are stronger than the Br-Br halogen bonds.

#### 4. Conclusions

Self-assembly of DBT molecule on HOPG surface in different solvents is investigated by STM. Dramatic differences in the 2D ordering are observed depending on the nature of solvents. When using 1-phenyloctane as the solvent, a linear structure is fabricated. Br-Br halogen bonds are found and were responsible for the formation of the packing pattern. However, a lamellar structure is formed by using 1-octanoic acid or 1-octanol as the solvent, in which the solvent molecules act as a coadsorbed component due to the hydrogen bonding between DBT molecules and solvent molecules rather than a dispersant. The distinct solvent effect reflected in the self-assembled structures could be ascribed to the polarity of the solvent and related solvent-solute interactions. The results are of significance to understand the solvent effect on the molecular self-assembly and to control nanostructures on solid surfaces.

#### Conflict of Interests

The authors declare that they have no direct financial relation with the commercial identities mentioned in this paper that might lead to a conflict of interests for any of the authors.

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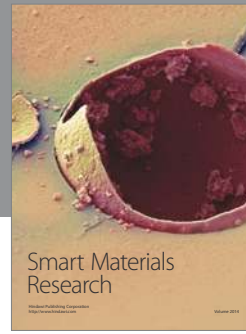
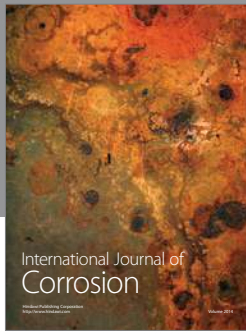
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