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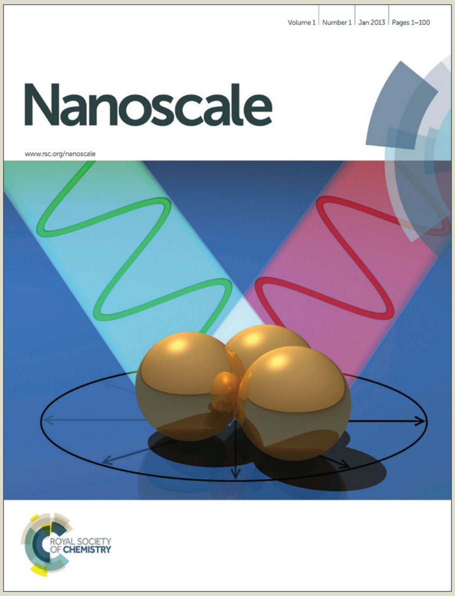

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Triangular-Shaped Molecular Random Tiling and Molecular Rotation in a Two-Dimensional Glassy Networks

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Macrocycle-1 molecules can self-assemble into glassy state networks via van der Waals force and form many triangular nanopores in networks. The nanopores can be expressed to triangular tilings, which lead to a particularly rich range of arrangements. Moreover an interesting molecular rotation phenomenon was observed in the glassy networks.

Glass and amorphous solids are materials whose atomic or molecular constituents lack long-range order in their structures,[1-3] which poses a tremendous challenge to the microscopic description of their structures. The structure of glassy solids has traditionally been studied by diffraction techniques, which provide a very detailed description of such materials at the macroscopic scale. [4-8] However, much less is known about the local structure of disordered solids at the molecular scale. Using the scanning tunneling microscopy (STM) some groups have identified the medium-range ordering of a 2D organic glass in real space, thus providing a general methodology to study the glassy systems at the submolecular scale.[9-16] This new insight may lead to new high-tech applications.

In previous, Blunt and Otero et al.[9,16] have studied some random molecular networks as glassy systems in a creative way, which have used some molecular tilings as model systems for the study of glassy. Until now, most of successful 2D glassy networks have been fabricated via hydrogen bonding or coordination interaction. These molecules with hydrogen bonding or coordination interaction, which may be distributed in a highly anisotropic way, have the potential to organize in random arrangements when deposited on an atomically flat solid surface. The structure and dynamics of such systems have been addressed by STM at the molecular level. However, the 2D glassy network fabricated via van der Waals force has barely been reported.

Larger macrocycles (**Macrocycle-1**) with long side groups have been synthetized.[19] The molecular structure is shown in Chart 1. Herein, we report a new kind of 2D glassy networks, which is fabricated by **Macrocycle-1** via van der Waals force. **Macrocycle-1** can form 2D glassy networks, in which translational symmetry is absent. Three **Macrocycle-1** molecules can form a triangular nanopore, which can be expressed to a triangular tiling. The triangular tilings lead to a particularly rich range of arrangements, which may be periodic, but random nonperiodic tilings are also permitted and have attracted great interest.

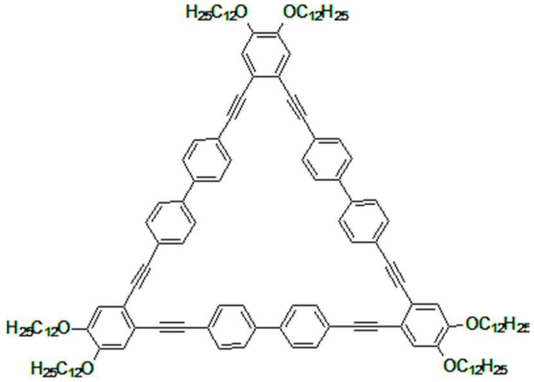


Chart 1 Chemical structure of **Macrocycle-1**.

Macrocyclic molecules are a kind of promising building blocks in fabricating 2D networks. [20-30] They can form adlayers when adsorbed onto the surface due to their side groups. In a general way, the macrocycles usually formed 2D crystal networks other than glassy ones. The length of side groups, solvents, concentration and their molecular symmetry define the shape of 2D crystal nanopattern, ranging from diamond to honeycomb, Kagomé and others 2D crystal nanopattern.[20,26,30] In this paper, we will report a kind of macrocyclic molecule (**Macrocycle-1**) with long side groups that can form 2D glassy networks on the surface. Besides the random tilling and 2D glassy networks, the molecular rotation is observed in the glassy networks.

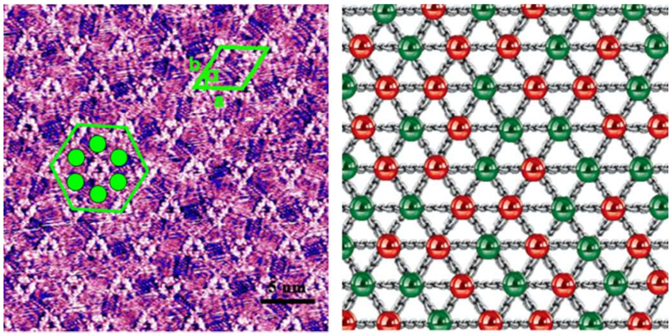


Figure 1. (a) An STM image (32 nm × 32 nm) of a typical area of **Macrocycle-1** network at the TCB/HOPG interface. The group of biphenyl rings constituting the backbone of the **Macrocycle-1** molecules appear as bright triangle-shaped features in the image. The hexagonal orientational order of the structure is highlighted by the group of green dots in the left section of the image. A unit cell is indicated in green for the structure. Tunneling conditions: Iset = 284 pA, Vbias = 1000 mV. (b). The coloration of (a) represents the two directional orientations of **Macrocycle-1**. The **Macrocycle-1** molecules directing upwards are denoted to the red balls. The **Macrocycle-1** molecules directing downwards are denoted to the green balls.

The detailed experimental process is shown in the supporting information. Typically, a droplet of the **Macrocycle-1** and 1,2,4-trichlorobenzene (TCB) mixed solution was deposited on a freshly cleaved HOPG (Highly Oriented Pyrolytic Graphite) surface. An area of the **Macrocycle-1** networks adsorbed on the surface is shown in Figure 1a. The biphenyl backbones of the molecules appear as bright triangle-shaped features, and the molecular arrangement is unusual because it exhibits hexagonal orientational order without translational symmetry, which is rarely observed in macrocyclic 2D nanopatterns. The lengths of the side groups and biphenyl edges are calculated to be 2.0 and 2.3 nm, which is in good agreement with the STM images results. We can also observe that two kinds of molecular direction of triangle exist in the network. One kind of triangle is directing upwards, which is denoted to the red balls in Figure 1b. The other kind of triangles are directing downwards, which are denoted to the green balls in Figure 1b. The hexagonal order can be discerned from the array of green and red balls in Figure 1b, and these two kinds of triangle distributed disorderly in networks. We found that six nanopores (denoted green dots in Figure 1a) existed in a hexagonal array. Although the pores are regularly arranged, the triangular molecular network enclosing them is not translationally ordered as shown in Figure 1a. According to the hexagonal orientational order of the structure, a unit cell (a = b = 4.2 ± 0.1 nm, α = 60 ± 2°) is superimposed in Figure 1a.

The topology model is important to analyse the glassy networks.[9-10] The direction of triangle-shaped molecules could only illustrate the 1D glass lines. So we choose three adjacent molecules that can form a triangle-shape nanopore as shown in Figure 2 to characterize the systems. In other words, a nanopore is embraced by three **Macrocycle-1** molecules. These nanopores can be abstracted into unites to tile the 2D networks.

According to the formula of permutation and combination (formu1a 1), we can know that four kinds of nanopores should exist in networks, which is in good agreement with the STM images results.

$$\frac{n!\times n!\times n!}{2}=\frac{2\times 2\times 2}{2}=4 \qquad (1)$$

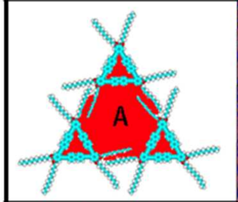
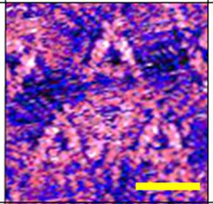
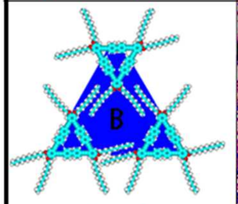
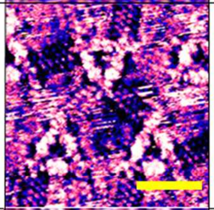
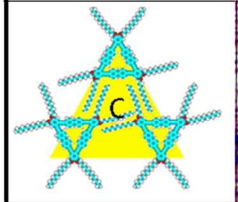
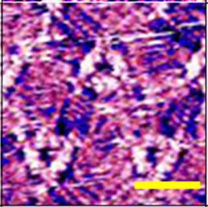
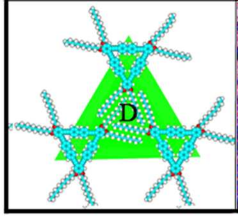
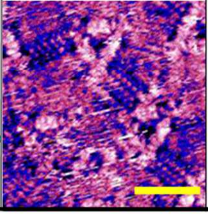
Model	STM image	Energy (kcal/mol)
		-10.28
		-32.73
		-34.71
		-10.52

Figure 2. Overview of the four well-ordered nanopores formed by **Macrocycle-1** at the 2D glassy networks. A type nanopores (Iset = 299 pA, Vbias = 989 mV); B type nanopores (Iset = 272 pA, Vbias = 998 mV); C type nanopores (Iset = 285 pA, Vbias = 899 mV); D type nanopores (Iset = 266 pA, Vbias = 899 mV); The corresponding tentative models are shown in the left column. The scale bars correspond to 2.5 nm. The corresponding interaction energy of nanopores are shown in the right column.

In STM results, Figure 2 shows the four kinds of nanopores (A B C and D), matched to the formula 1, constructed by three triangular **Macrocycle-1** molecules. For example, three edges (the biphenyl backbones) of respective three **Macrocycle-1** molecules are embracing a nanopore. This kind of pores is denoted to A type. The pore, which is denoted to B type nanopore, is embraced by two edges and one vertex of macrocycles. Similarly, the C type nanopore is formed by two vertexes and one edge of macrocycles. And the D type nanopore is fabricated by three vertexes of macrocycles. The 2D glassy molecular networks, such as Figure 1a, can be tiled by combining these four structural units in an arrangement that exhibits orientational symmetry but no translational order.

To illustrate the tiling, we have converted each of the triangular nanopores units discussed above into four kinds of triangles (Figure 2). We differentiate the different nanopores by different colors. These colourful triangles show that, at a molecular level, the mapping is possible because the molecules on vertex of nanopores are located at the vertex of the triangle. Each nanopore in the glassy networks points along one of three high-symmetry directions. For example, the molecular glassy networks displayed in Figure 3a can be mapped into different color triangles, and the resultant tiling is shown in Figure 3b. The mapping directly accounts for the presence of orientational symmetry combined with an absence of translational order because the color triangle vertexes (**Macrocycle-1** molecules in the STM images) fall on a hexagonal lattice, even though the arrangement of color triangle is not ordered. Thus, we demonstrate that the molecular array is equivalent to a triangle tiling.

We can use these four kinds of nanopores to tile networks as shown in Figures 3a and b, and found that the distribution of B and C type nanopores is almost equal. But the A and D type nanopores is very less in glassy networks. We observed there is average 0.2-0.3 A or D type nanopores in one hundred of nanopores.

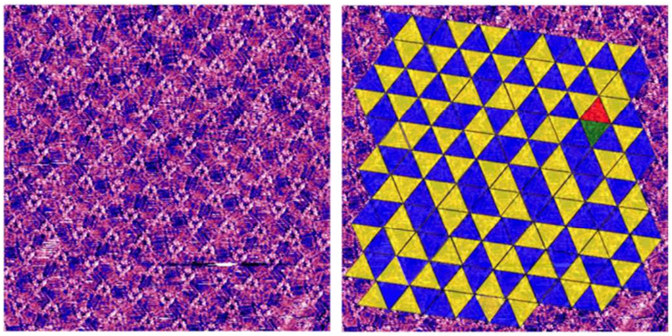


Figure 3. (a) STM image of (42nm × 42 nm, Iset = 272 pA, Vbias = 998 mV) a typical area of Macrocycle-1 network. (b) Corresponding tiling representation of (a). The coloration of (a) represents the four possible orientations of triangles within the tiling (red, green, yellow and blue). Idealized representations of the molecular positions are shown faintly in the tiling.

Besides the 2D glassy networks, we also observed molecular rotations in the form of special shaped molecules as shown in Figure 4. As everyone knows, the glassy and amorphous solids are materials whose atomic or molecular constituents lack long-range order in their structures. Some defects is in the glassy structures. Thus some physical properties, such as the thermal conductivity, of glassy is different from that of crystal. Herein the molecular rotations can be regard as a kind of defect that has been considered theoretically but has not previously been observed.[29-31] Moreover, in previous 2D crystal networks, the molecular rotation phenomena were observed in guest molecules rather than the host networks.[34-35] In our study, some molecular rotation phenomena were observed in glassy networks. These molecular rotations with a certain molecular shape are rarely observed. As shown in Figure 4a, two kinds of special shape molecules exist in the centre of six **Macrocycle-1** molecules. They are diamond-shaped (◊) molecules and Ж-shaped molecules which are marked by green and red rings respectively in Figure 4a. The reason of special molecular configurations is the rotation of **Macrocycle-1**, as shown in right section of Figure 4. The phenomenon of molecular rotation is attributed to the lack of structural symmetry in glassy networks, which results in the molecules not being tightly packed in glassy networks.

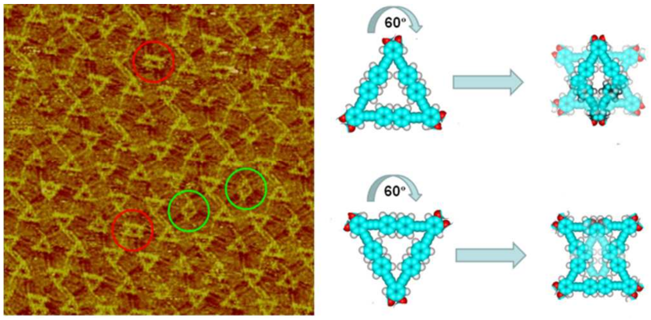


Figure 4. STM image of (36nm × 36 nm, Iset = 472 pA, Vbias = 998 mV) a typical area of **Macrocycle-1** networks. Two special shaped molecules are marked by green and red rings respectively, which attribute to the molecular rotations as shown in right of the image.

Adsorption of **Macrocycle-1** is a spontaneous process and can therefore be characterized by a decrease in the total free energy of the system. In the context of our experiments, we have distinguished four kinds of nanopores in 2D glassy networks. The difference of interaction energy and distribution of nanopores are related to the different free energy G. (The interaction energy between **Macrocycle-1** and the HOPG surface are equal in different nanopores. But the interaction energy of **Macrocycle-1** molecules is different in different kinds of nanopores.) We have simulated the interaction energy of four kinds of nanopores as shown in Figure 2. The 2D glassy can be tiled by the nanopores, so it also can be estimated the interaction energy of glassy networks from the distribution of nanopores. In order to evaluate the difference between glassy and crystal networks, we also simulate a kind of crystal network as shown in Figure 5. Only C and B type nanopores exist in this crystal network, and the arrangement is very orderly. The column of C type nanopores is next to the B type one. The average interaction energy per nanopores in crystal networks is (C+B)/2= -33.72 Kcal/mol. However, the average interaction energy per nanopores in glassy is related to the distribution of nanopores. The distribution and average interaction energy of one nanopore are estimated. The distribution ratios of different nanopores are calculated. (A=0.2%, B=49.7%, C=49.8% and D=0.3%). So the average nanopores energy is about -33.6 Kcal/mol, which approximate to the energy of crystal. This small difference of energy, comparable with the crystal networks in our calculation, highlights the delicate balance required for stabilized randomness in the glassy networks. This can demonstrate that the glassy state exists in networks naturally due to the interaction energy.

Besides the interaction energy reason, the forming of glassy networks can also be attributed to molecular structures. In a general way, larger molecules reorient more slowly than smaller objects. We have simulated three macrocycles with different conjugated core and side groups as shown in Table S1 in SI. The **Macrocycle-1** molecules have the larger conjugated core and longer side groups, which make the molecules adsorb on HOPG surface most stably and more difficult to reorient the molecules configurations.

Our results demonstrate the potential of molecules as model systems for the study of glassy and provide an interesting alternative to the random molecular networks as glassy systems.

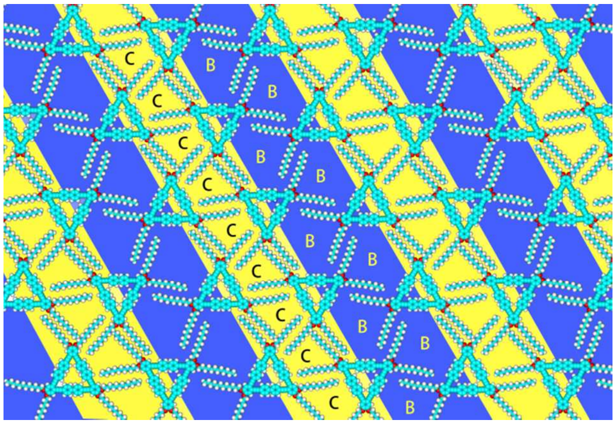


Figure 5. Simulative crystal networks image constructed by **Macrocycle-1** molecules, in which the C and B type nanopores distribute orderly.

Conclusions

Overall, we have reported a new kind of 2D organic glassy networks, which are fabricated by macrocycles molecules via van der Waals force. The larger macrocycles with long side groups would difficultly tune their configurations in 2D structures and form the 2D glassy networks. Besides that, we also observed the molecular rotation phenomenon in the glass structures, which can be regarded as a kind of defect in networks. The exploring of the glasses network can provide novel model systems for the study of random structural arrangements and dynamically arrested materials. Thus, the STM method provides a general methodology to study the glassy systems at the submolecular scale. This new insight may lead to new high-tech applications.

Notes and references

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Electronic Supplementary Information (ESI) available: [details of experimental process and simulations results].

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Abstract figure: In this work, we have reported a new kind of 2D organic glassy networks, which are fabricated by macrocycles molecules via van der Waals force.