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Substrate tuned reconstructed polymerization of naphthalocyanine on Ag(110)

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The linkage structures between monomers make great influence on the properties of polymers. The synthesis of some special linkage structures can be challenging, which is often overcome by employing special reaction conditions. Here, we build dihydropentalene linkage in poly-naphthalocyanine on Ag(110) surface. Scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) measurements confirm the dihydropentalene linkage structure and a possible formation path with reconstruction steps is proposed. The controlled experiment on Ag(100) surface shows no dihydropentalene structures formed, which indicates the grooved substrate is necessary for the reconstruction. This work provides insights into the surface restricted reactions that can yield special structures in organic polymers.

Keywords: on-surface polymerization, reconstruction, scanning tunneling microscopy, noncontact atomic force microscopy

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1. Introduction

Polymerization is an important chemical process that can synthesize organic chains, ribbons or networks with unique physical and chemical properties^[1,2] which have potential applications in nanodevices. The design of the linkage structures between the monomers in a polymer must be carefully considered as these linkages can greatly influence the properties of the entire polymer.^[3,4] The C–C single or double bonds,^[5–7] C–metal coordinate bonds,^[8,9] and heteroatom bridging^[10,11] have been demonstrated as polymer linkages, which, in the meantime, induce rotatable bonds in the polymer and lead to folded or tangled amorphous morphology that hinders further investigations. Therefore, rigid linkages, such as carbon polygons, are highly desirable to construct robust polymers for better performance in electronic or optical applications.^[3,4,12]

On-surface polymerization can synthesize highly ordered two-dimensional (2D) structures such as graphene nano-ribbons (GNRs)^[13–16] and covalent organic frameworks (COFs),^[17–19] and can be easily tuned with different substrates. We used high-resolution scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) to investigate the mechanism of on-surface polymerization at atomic level,^[20,21] which further promotes the

synthesis of new polymerized structures on surface. As model molecules, phthalocyanine (Pc) and naphthalocyanine (NPc) have been widely studied by STM and AFM for their adsorption,^[22,23] self-assembly,^[22,24–28] and electronic properties.^[29,29–34] The outer periphery of both Pc and NPc is consisted of C–H bonds, which can yield C–C single or double bonds^[35,36] and [4]-radialene like structures^[37] in on-surface polymerization.

In this paper, we report the on-surface synthesis of NPc oligomers with dihydropentalene linkage structure on Ag(110) surface. While most of the polymerization products are single-bond connected, there is also a small portion of 6–5–5 membered ring connecting structure formed on Ag(110). The STM and nc-AFM images unambiguously unveil both of the linkage structures, which indicate the strain induced by the grooves on Ag(110) surface restricts the adsorption orientation of NPc molecules, and leads to the dihydropentalene linkage structure by atom rearrangement. Controlled experiment of NPc on flat surface Ag(100) results in only single-bond connected polymerized products, which further confirms that the dihydropentalene structure is induced by strain on trenched Ag(110) surface.

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2. Results

Two types of linkage structures of polymerized NPC on Ag(110) surface. Ag(110) substrate has grooves along $[1\bar{1}0]$ direction with width of 0.486 nm and depth of 0.289 nm, as shown in Fig. 1(a). The NPC molecules were sublimed at 620 K onto Ag(110) surface that was held at room temperature. The adsorption orientations of the as-deposited NPC molecules are along $[1\bar{1}0]$ direction and 45° to $[1\bar{1}0]$ direction (Fig. 1(b)). After annealing at 710 K for 20 min, some NPC molecules polymerized on the surface with the same adsorption orientations, as indicated in the STM image by red dotted circles in Fig. 1(c).

There are two types of linkage structures in NPC oligomers as highlighted by the green (type I) and red (type II) boxes in the STM overview image (Fig. 2(a)). The type I oligomers (Fig. 2(b)) have larger units than the type II oligomers (Fig. 2(c)) as indicated by the superposed cross-shaped contours with the same size where the two contours overlap for type II oligomers. Figures 2(d) and 2(e) show the center-to-center distance of adjacent monomers in type I and type II oligomers, in which type I is 1.93 nm, while type II is 1.86 nm. The adsorption orientations of type I oligomers

are along $[1\bar{1}0]$ direction and 45° to $[1\bar{1}0]$ direction; while the type II oligomers are only found along $[1\bar{1}0]$ direction.

The chemical bond resolved nc-AFM images obtained with CO-functionalized tips further unveiled the structure of the two kinds of oligomers. In type I oligomer, the linkage is a carbon-carbon single bond connecting the terminal phenyl of two monomers with a bond angle of 120° , as highlighted by the green circles in Fig. 2(f). For type II oligomers, the linkage has a 6-5-5 membered ring structure, which consists of one terminal phenyl of one of the NPC monomer reconstructed into a 5-membered ring, as marked in the red circles in Fig. 2(g). In addition, there is a carbon atom with bright contrast in each pentagon in the nc-AFM image, which indicates stronger repulsion on this carbon atom, most likely due to the out-of-plane C-H bond. Therefore, we could conclude that the type II linkage is a dihydropentalene structure. Since the dihydropentalene linkage can only form along the $[1\bar{1}0]$ direction and is generated through complex reconstruction process, the surface assisted interactions, such as strains induced by the grooves, should play an essential role in the polymerization process.

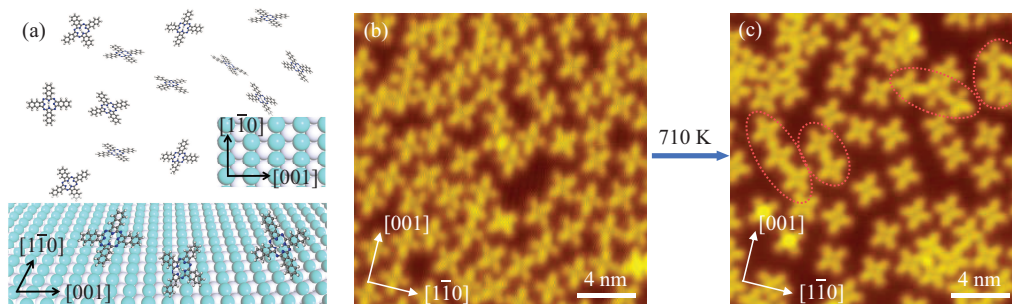


Fig. 1. (a) Sketch of NPC molecules depositing onto Ag(110) surface. The insert shows the enlarged model of grooves on Ag(110). (b), (c) STM topography of as-deposited (b) and after annealing (c) NPC molecules on Ag(110) surface. White arrow shows $[1\bar{1}0]$ and $[001]$ directions. The red dotted circles in (b) highlight the NPC oligomers. Scanning parameters: (a) $V_s = 1.0$ V, $I_t = 100$ pA; (b) $V_s = -0.3$ V, $I_t = 10$ pA.

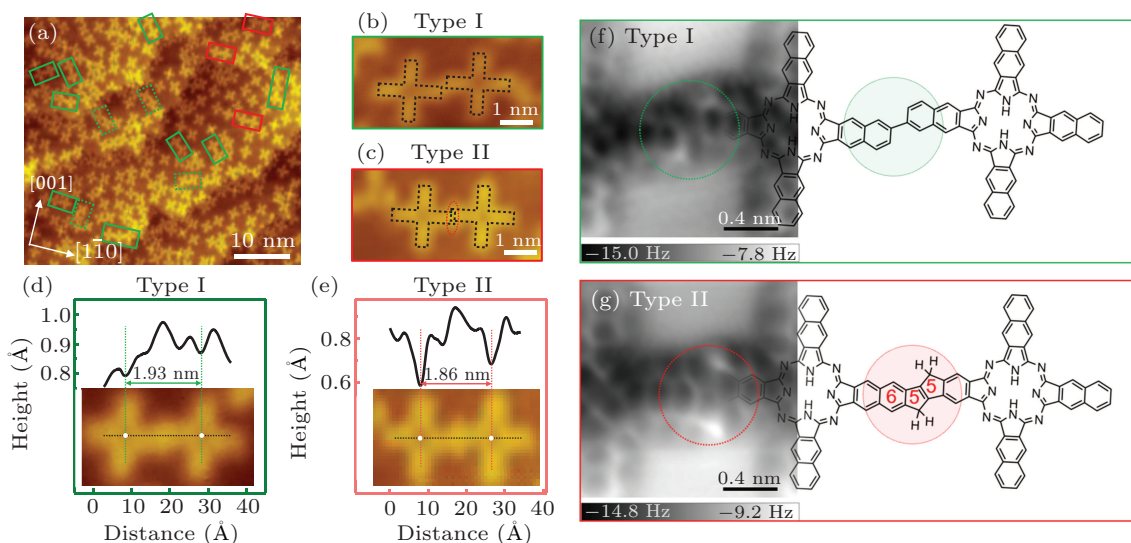


Fig. 2. Two types of polymerized NPC on Ag(110) surface. (a) STM image of NPC oligomers and molecules on Ag(110) after 710 K annealing. Type I and type II NPC oligomers are highlighted by green and red boxes, respectively, in which the solid green boxes mark the single bond linear linkages, while the dotted green boxes mark the angled linkages. The zoom-in STM of these two types of polymerization products are shown in (b) and (c). (d) and (e) STM line profile across the centers of the polymerized NPC oligomers in type I and type II products. (f) and (g) Chemical bond resolved nc-AFM images of type I and type II NPC oligomers. Scanning parameters: (a)–(e) $V_s = -0.3$ V, $I_t = 10$ pA; (f), (g) amplitude = 100 pm.

Table 1. The ratio of linkage types of naphthalocyanine oligomers on Ag(110) and Ag(100).

Surface	Linkage type		Ratio
Ag(110)	single bond polymerization	linear shaped	76.2 %
		angled shaped	18.6 %
	reconstructed polymerization	5.2 %	
Ag(100)	single bond polymerization	linear shaped	72.9 %
		angled shaped	27.1 %
	reconstructed polymerization	0 %	

In addition, we also observed an angled linkage structure for NPC oligomers as marked by dotted green boxes in Fig. 2(a), which is connected by a C–C single bond with two monomers adsorbed along different directions. The ratio of the two kinds of C–C single bond linkages and the reconstructed dihydropentalene linkage is displayed in Table 1, where the majority of the oligomers have linear shaped single bond linkages (76.2%), 18.6% oligomers are angled linked by single bonds, and only 5.2% have reconstructed into conjugated 6–5–5 membered rings.

Polymerization of NPC on Ag(100) surface. To further confirm the relation between the reconstructed dihydropentalene linkage and the strain from the substrate, a planar surface

of Ag(100) was used for NPC polymerization as a comparison. As displayed in Fig. 3(a), most monomers and oligomers adsorb along the high symmetry directions on the surface, and two kinds of oligomers, linear shaped and angled shaped, are formed on Ag(100), as marked by green and red rectangles. The zoom-in STM and nc-AFM images (Figs. 3(b) and 3(c)) show that both oligomers are linked by single bond between monomers, with the two reacted lobes parallel in the linear shaped oligomers (Fig. 3(d)), and 120° to each other in the angled oligomers (Fig. 3(e)). The ratios of the linear and angled linkages of NPC oligomers on Ag(100) are 72.9% and 27.1%, respectively (Table 1). Notably, there are no naphthalocyanine oligomers formed on Ag(100) surface.

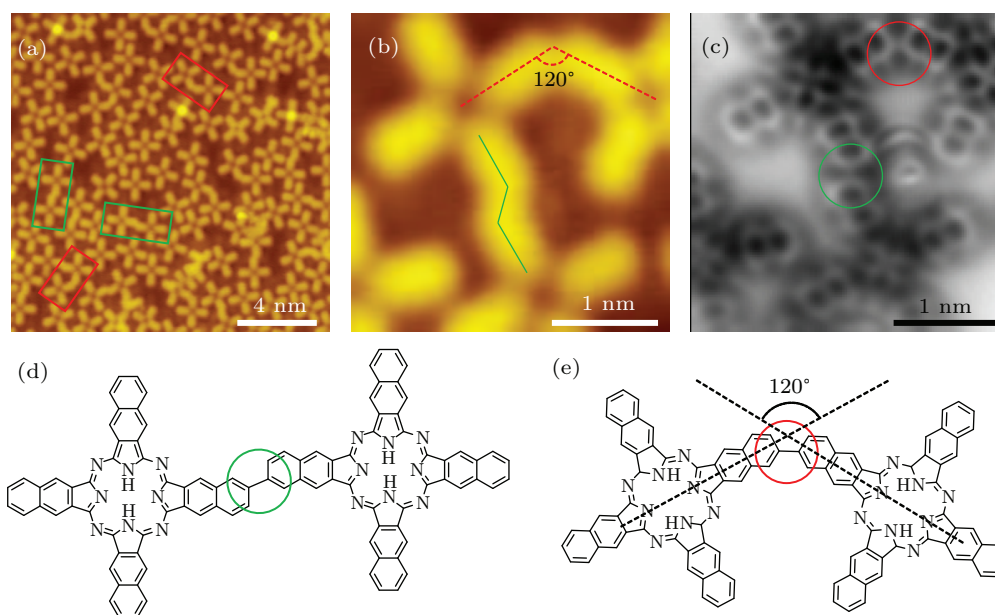


Fig. 3. Polymerized NPC on the Ag(100) surface. (a) STM topography of NPC oligomers and molecules after annealing at 720 K for 20 min on Ag(100) surface. The linear shaped and angled shaped oligomers are highlighted by green and red boxes, respectively. (b), (c) Zoom-in STM image and corresponding nc-AFM image of two kinds of NPC oligomers. (d), (e) Sketches of the two kinds of linkage structures. Scanning parameters: (a) $V_s = -0.3$ V, $I_t = 10$ pA; (b) $V_s = -0.04$ V, $I_t = 10$ pA; (c) amplitude = 100 pm.

3. Discussion

For two NPC monomers adsorb on Ag(110) surface, the relative positions of the terminal phenyls can have two configurations. In the first configuration as depicted in Fig. 4(a), the terminal phenyls are corner to corner, and a C–C single bond with a bond angle of 120° to the terminal phenyls can be formed. For the second configuration as depicted in Figs. 4(b) and 4(c), the terminal phenyls are side by side, which results in a C–C single bond of 90° bond angle formed between C1 and

C1'. On the anisotropic Ag(110) substrate, the grooves along $[1\bar{1}0]$ direction restrict the adsorption of the monomers and the phenyl ring cannot rotate freely to release the strain of the 90° bond angle (step 2 in Fig. 4(b)), which may result in the bond cleavage between C1 and C2 with two radicals (step 3). Then, new bonds between C2 and C2', and C1 and C3 would form (step 4) along with H atoms at C2' and C3 transferring to C2 and C6, respectively (step 5). After the rearrangement of electrons and H atoms, the two phenyl rings connecting with a 90° angled C–C bond turn into a 6–5–5 membered ring shaped

dihydropentalene linkage. On the other hand, for polymerization starting from the side-by-side configuration on Ag(100), as shown in Fig. 4(c), the strain of the 90° angled C–C bond

can be released by rotating the monomers due to the small restriction from the substrate, which yields oligomers with linkage of 120° bond angle C–C bonding.

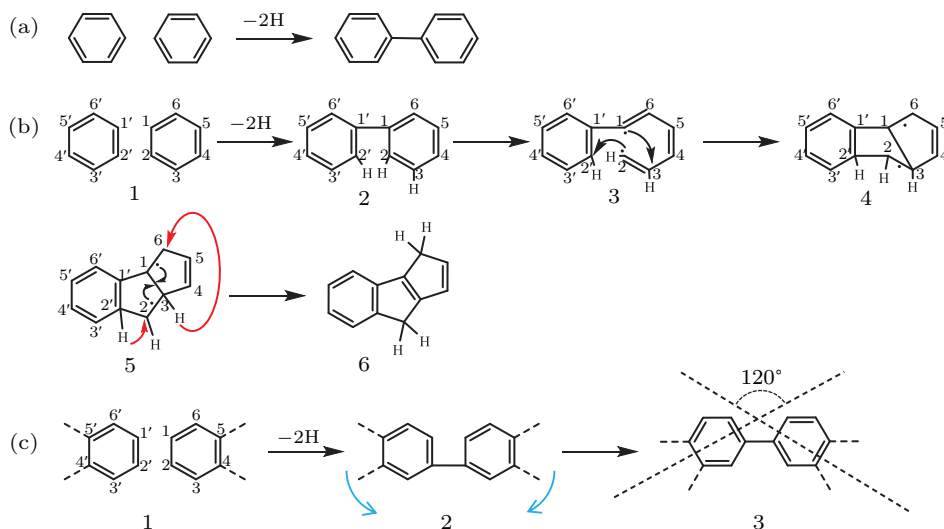


Fig. 4. Schema of the possible reaction routes for NPc polymerization on Ag(110) and Ag(100). (a) Single bond formation with corner configuration of the terminal phenyls. (b) Starting from side by side configuration of the terminal phenyls, the formation of the 6–5-membered ring dihydropentalene linkage structure with reconstructions. (c) Starting from side by side configuration of the terminal phenyls, the formation of the single bond connection with rotation of the phenyl rings.

In conclusion, two kinds of linkage structures in NPc oligomers have been successfully synthesized by annealing at 710 K on Ag(110) surface. STM and nc-AFM images reveal that C–C single bond and dihydropentalene linkage structures can be formed on Ag(110). Some C–C single bonds at the linkage are restricted by the anisotropic substrate to a 90° bond angle between the monomers, which further reconstruct to the dihydropentalene linkage structures to release the strain. Our findings demonstrate strain-induced reconstructed polymerization on anisotropic substrate and provide new insights for on-surface synthesis.

4. Methods

4.1. Sample preparation

The 2,3-naphthalocyanine (NPc, Aldrich, purity >95%) in powder form was purified by a sublimation process with a homemade Knudsen cell (K-cell) evaporator in high vacuum for 5 hours, followed by degassing at 620 K for 60 min in the UHV chamber. The NPc was evaporated at 640 K during the experiment, while the substrate Ag(110) was kept at room temperature.

4.2. STM/nc-AFM measurements

STM and nc-AFM measurements were performed on a combined nc-AFM/STM system (Createc) at LHe temperature with a base pressure better than 2×10^{-10} mbar. All measurements were performed using a qPlus tuning fork sensor in frequency modulation mode with a Pt/Ir tip. The resonance frequency of the sensor is 27.9 kHz, and its stiffness is about

1800 N/m. The STM measurements were performed by the same tuning fork sensor without excitation and the current amplifier is 10^9 up to 1 kHz.

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