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# A molecular conformational change induced self-assembly: from randomness to order

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From an interplay of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations we reveal how a molecular conformational change induced self-assembly process can result in the conversion from a random molecular phase to the formation of two types of ordered surface nanostructures with different apparent heights.

Bottom-up nano-fabrication strategies on solid surfaces play a vital role in the fields of nanoscience and nanotechnology.<sup>1-4</sup> Selfassembly, directed by non-covalent interactions, has been employed to construct surface supramolecular nanostructures or nanodevices as a typical approach for bottom-up fabrication.<sup>1,4–7</sup> The resulting formation of ordered surface nanostructures through different kinds of non-covalent interactions, e.g. hydrogen bonding,<sup>7-12</sup> van der Waals force,13 dipole-dipole interaction,14 has been reported including fairly complicated systems.<sup>15-18</sup> In nearly all of those studies, phase transition has mainly been determined by the regulation of intermolecular forces. So far the influence of intramolecular conformational changes on the resulting self-assembly process has been scarcely reported. It is generally expected that for those molecules with the possibility of changing their conformations, e.g. from non-planar to planar or vice versa, a self-assembly process may set in. Understanding this process in detail would shed light on designing functional nano-architectures involving smart building blocks such as molecular switches.

In this communication we present a detailed study of the selfassembly process of a photochromic oxazine molecule induced by molecular conformational changes on a Cu(110) surface under UHV conditions. The molecule is a typical spiropyran derivative best known for its use in color changing sun-glasses. These spiropyran derivatives are robust molecular switches that can be converted between two different conformations while adsorbed on a surface by

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Astronomy, Aarhus University, 8000 Aarhus C, Denmark. E-mail: fbe@inano.au.dk <sup>c</sup> Nanophysics and Soft Matter Group, H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, BS8 1TL, UK external stimuli, *e.g.* UV irradiation, heating, or by a STM tip.<sup>19–22</sup> Here we demonstrate, by an interplay of high-resolution STM imaging and DFT calculations, that a self-assembly process is triggered by the molecular conformational change induced by heating. A random distribution of the molecules was initially formed upon deposition on the sample held at room temperature, while triggering the ring-opening reaction by thermal activation resulted in the formation of two types of well-ordered stripe-like surface nanostructures with different apparent heights. The DFT calculations elucidate that the difference between the bright and dark stripe structures results from the different hydrogen bonds involved in these two surface structures. These results indicate that the photochromic molecule may act as a novel prototype, not only for molecular switches or nano-sensors, but also for functional nano-fabrications which may be induced by molecular conformational changes.

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Fig. 1a depicts the schematics for the photochromic ringopening reaction, while Fig. 1b and c present the DFT optimized structures of the closed-form and the open-form molecule adsorbed on the Cu(110) surface. It is well known that in solution the



**Fig. 1** (a) Schematics of the reversible ring-opening reaction of a photochromic oxazine molecule. (b) Side and top views of the DFT optimized structure of the closed-form molecule absorbed on a Cu(110) surface. (c) As in (b), but showing side and top views of the open-form molecule adsorbed on a Cu(110) surface.

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closed-form molecule undergoes a reversible ring-opening reaction (as shown in Fig. 1a), whereas on solid surfaces the closed-form molecule can be easily converted into its open-form isomer irreversibly by cleavage of the spiro C-O bond, which is similar to other spiropyran derivatives used in previous studies.<sup>21,22</sup> The closed-form molecule adsorbed on Cu(110) adopts a non-planar configuration, with the indole ring nearly perpendicular to the Cu(110) surface (cf. Fig. 1b). The binding energy of this structure on Cu(110) was calculated to be only 0.07 eV. Adsorption of the open form on Cu(110) is significantly different from that of the closed form. As shown in Fig. 1c, the adsorbed open-form molecule has a flat-lying configuration, and both the indole and naphthalene rings are parallel to the Cu(110) surface, with the indole ring slightly higher than the naphthalene ring. The calculated binding energy of the open form on Cu(110) is 1.07 eV, which is significantly higher than that of the closed form. This indicates that, when adsorbed on a Cu(110) surface, the open form is thermodynamically more stable than the closed form. These results are in good agreement with previous reports on related molecules adsorbed on solid surfaces in which the open form was found to be energetically more favorable than the closed form.<sup>21,22</sup>

Upon deposition of the closed-form molecule on a Cu(110) surface held at room temperature, randomly distributed molecules are observed on the surface (*cf.* Fig. 2a) and in particular formation of dimers by anti-parallel molecules (mainly *via* weak van der Waals interactions) seems to be a characteristic feature as reflected by the STM image (*cf.* Fig. 2b). No large-scale well-ordered structure was observed during our STM experiments, even at higher surface coverage. From the high-resolution STM image, we can clearly identify the morphology of a single molecule which appears as a bright protrusion with a dark oval lobe (*cf.* Fig. 2b). Comparison with the DFT optimized structure (*cf.* Fig. 1b) suggests that the bright protrusion and the dark oval lobe can be attributed to the indole ring and the naphthalene ring, respectively.

After deposition of the closed-form molecules on the Cu(110) surface at relatively high coverage a series of annealing experiments were conducted. Interestingly, as observed in the STM images shown in Fig. 3, two distinct well-ordered stripe-like supramolecular surface nanostructures were formed during the annealing experiments. Previous studies on the nitro-spiropyran molecule have demonstrated that the ring-opening reaction proceeds completely and irreversibly in a narrow temperature window just slightly above



**Fig. 2** STM images of the closed-form molecules deposited on Cu(110) at room temperature, imaged at ~150 K. (a) Overview image. (b) High-resolution close-up image showing individual molecules in which the bright protrusion and dark oval correspond to the indole and naphthalene ring respectively. Scanning conditions:  $I_t = 0.61 \text{ nA}$ ,  $V_t = -1250 \text{ mV}$ .



**Fig. 3** STM images obtained after annealing the sample for 10 minutes at 392 K (a), 410 K (b), 438 K (c), and 446 K (d). This sequence shows two distinct stripe-like patterns of which one is more thermodynamically stable. Scanning conditions: (a)  $I_t = 0.37$  nA,  $V_t = -1444$  mV; (b)  $I_t = 0.53$  nA,  $V_t = -1277$  mV; (c)  $I_t = 1.11$  nA,  $V_t = -1250$  mV; (d)  $I_t = 0.48$  nA,  $V_t = -1358$  mV.

room temperature on solid surfaces, and the open-form isomer is energetically more favorable.<sup>21,22</sup> In our experiments, the bright and dark stripes were not formed until the annealing temperature reached 392 K which was high enough to trigger the ring-opening reaction of the closed-form molecules to the open-form. Thus, we suggest that the building blocks of the bright and dark stripes should consist of the open-form molecules attributed to the molecular conformational change induced by thermal activation.

As shown in Fig. 3a, annealing the sample to 392 K led to the formation of the bright and dark stripes as well as some bright oligomers. Upon annealing the sample to 410 K, both the bright and the dark stripes grew more and more ordered and demonstrated different growth phenomena (as shown in Fig. 3b). The bright stripes are much shorter than the dark stripes and prone to getting packed together laterally forming chiral structures. The angle between the two adjacent structures is a fixed value of  $42 \pm 2^{\circ}$  (marked by green lines) implicating a certain effect provided by the substrate. The dark stripes, however, became longer and longer in a quasi-linear manner. Subsequently annealing the sample to temperatures of 438 K, 446 K and finally 453 K, respectively, showed that the initial bright stripes were gradually disrupted into small clusters that were randomly distributed on the surface (cf. Fig. 3c and d). The dark stripes could withstand the thermal treatment up to 446 K indicating that they are thermodynamically more stable than the bright ones. Finally, when the annealing temperature went up to 453 K, the dark stripes were also destroyed into small clusters (not shown).

High-resolution STM images were recorded to gain detailed information on the bright and dark stripes at a single-molecule level. From the close-up STM images (as depicted in Fig. 4), it can be identified that the main difference between the two stripes is that the bright stripes adopt a zigzag arrangement while the dark stripes array in a head-to-head mode. Since we know that at such temperatures



**Fig. 4** High-resolution STM images of the bright stripe (a) and the dark stripe (b) (scanning conditions:  $I_t = 0.49$  nA,  $V_t = -1400$  mV). The DFT calculated molecular models of the bright stripe (c) and the dark stripe (d). The hydrogen bonds are indicated by the dashed lines.

(ca. 400 K) all the closed forms should already be converted into the open forms, the difference in apparent heights between the bright and dark stripes should not be due to the building blocks. To further unravel the mechanism of the formed stripe-like structures, we performed DFT calculations including van der Waals forces. Several possible 2D structures formed by the open-form molecules were proposed from the gas-phase calculations. From a detailed comparison of all the theoretically relaxed structures with the high-resolution STM images we identified two models fitting well with the experimental data as depicted in Fig. 4c and d, respectively. In the model for the bright stripe (cf. Fig. 4c), the molecules are heterochiral and each molecule links to another two via three CH···Cl hydrogen bonds to form a zigzag chain. A weak lateral inter-chain binding provided by the rings of the neighboring molecules contributes to the formation of the bright stripes in 2D. In the model for the dark stripe (cf. Fig. 4d), the molecules are homochiral and two molecules bind to each other via two CH···Cl hydrogen bonds to form a head-to-head dimer first, and then, the dimers are linked together along the stripe via additional hydrogen bonds through CH...O. The two structures were found to have very similar gas-phase stabilities (with a binding energy of 0.24 eV and 0.15 eV per molecule for dark and bright stripes, respectively), and the dark one was slightly more stable than the bright one by 0.09 eV per molecule. Note that the Cl atoms are inevitably involved in the formation process and more difficult to be liberated from the molecule compared to Br and I atoms due to the increased electronegativity; we thus believe that the molecules should be still in open-form and no Ullmann dehalogenation has occurred here. As demonstrated by the DFT calculations, the dark stripe has a different hydrogen bonding configuration from the bright stripe, and moreover, different hydrogen bonding configurations could result in different molecular adsorption geometries as demonstrated by the DFT calculations involving the substrate (discussed elsewhere). We thus speculate that the difference in apparent heights between

the bright and dark stripes observed in the STM experiments could be mainly attributed to the different hydrogen bonding configurations involved in the structures.

In conclusion, we have performed a detailed STM-DFT study of a self-assembly process induced by molecular conformational changes of a prototypical photochromic molecule on a Cu(110) surface. The photochromic molecule used in this work could thus be a good candidate as a switch in organic devices, and the formation of the distinct well-ordered structures induced by external stimuli of such photo-sensitive and/or thermo-sensitive molecules may also provide a new route to the bottom-up fabrication toward involving more and more functionalized components in a sophisticated molecular device.

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