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Surface-assisted *cis*–*trans* isomerization of an alkene molecule on Cu(110)†

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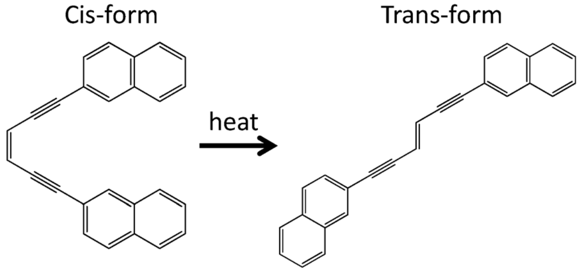
From the interplay of STM imaging and DFT calculations we have investigated the isomerization of an alkene molecule on Cu(110) under ultrahigh vacuum conditions. We show that the on-surface *cis*–*trans* isomerization could efficiently occur well below room temperature, in which the copper surface is speculated to play a key role.



Scheme 1 Isomerization of the DNHD molecule.

In certain biological systems, *cis*–*trans* isomerization of alkenes (*i.e.* involving carbon–carbon double bonds) is important because different isomers often exhibit tremendous differences in physiological activities and pharmacological effects. For example, the *trans*-fatty acid could result in cardiovascular problems while the *cis* state could not,[1,2] and ferrous fumarate (*trans*-butenedioate) has been used to treat iron deficiency anaemia.[3] Due to the intrinsically different properties of isomers, great efforts have been devoted to synthesize geometrically pure alkenes and such studies have been mainly performed in solutions to date.[4,5] The surface has been identified to potentially influence the molecular isomerization behaviors,[6–8] *e.g.*, the stabilities of *cis* and *trans* isomers could be inverted on a surface,[9] and the scanning probe microscopy has proven to be an invaluable tool to explore on-surface isomerization behaviors at the atomic scale. Nowadays, such investigations on azobenzene molecules (*i.e.* involving nitrogen–nitrogen double bonds) are widely performed and great progress in understanding their isomerization behaviors is made.[10–13] However, isomerization of alkene molecules on surfaces has rarely been reported.[14,15] It is therefore generally interesting to investigate the isomerization of alkene molecules on surfaces to supplement the understanding of on-surface molecular isomerization behaviors.

In this communication, we investigate the isomerization of an alkene molecule (denoted as DNHD) on Cu(110) under ultrahigh vacuum (UHV) conditions at the atomic scale. The Cu(110) surface is employed as a platform to heterogeneously catalyze the on-surface *cis*–*trans* isomerization due to its relatively high chemical activity and the well-known 1-D templating effect. As shown in Scheme 1, the DNHD molecule contains a C═C moiety exhibiting potential *cis*–*trans* isomerization capability. From the interplay of high-resolution scanning tunneling microscope (STM) imaging and density functional theory (DFT) calculations, we show that the *cis*-DNHD molecules could be converted to the *trans* form with a rather high yield at unexpectedly low temperatures (∼255 K), in which the copper surface is speculated to play a key role in assisting this isomerization process. Moreover, the kinetic scenario of this process is described and found to follow an Arrhenius dependence on temperature. These novel findings have broadened our knowledge of on-surface molecular isomerization, and such a system may serve as a prototype to efficiently control the isomerization behaviors of alkene molecules, which may further provide theoretical guidance on the production of geometrically pure alkenes.

All the STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature "Aarhus-type" STM,[16,17] a molecular evaporator and standard facilities for sample preparation. After the system was thoroughly degassed, the DNHD molecules (synthesized by Sonogashira coupling reaction between *cis*-1,2-dichloroethene and 2-ethynylnaphthalene under an inert atmosphere[18]) were deposited by thermal sublimation at ∼310 K onto a Cu(110) substrate held at ∼170 K. The STM measurements were carried out in a temperature range of 100–150 K.

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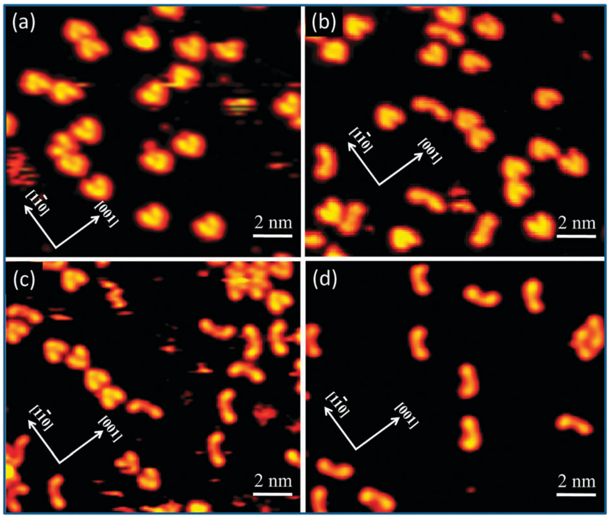

Fig. 1 STM images obtained after annealing the sample with *cis*-DNHD molecules at (a) 210 K, (b) 227 K, (c) 235 K and (d) 255 K, respectively. Scanning conditions: I_t = 0.65 nA, V_t = −2500 mV.

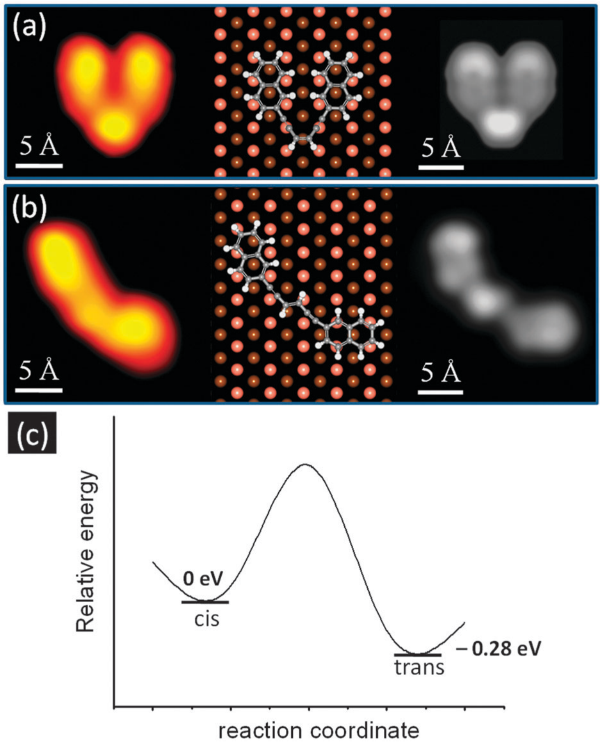

Fig. 2 The high-resolution STM images, DFT-optimized structural models and DFT-based simulated STM images of (a) the *cis*-form DNHD molecule and (b) the *trans*-form DNHD molecule. (c) Schematic diagram of the double-well potential for the isomerization of DNHD molecules on Cu(110). The *trans*-form DNHD molecule is found to be more stable than the *cis* form by 0.28 eV.

All of the calculations were performed in the framework of DFT by using the Vienna *Ab Initio* Simulation Package (VASP).[19,20] The projector augmented wave method was used to describe the interaction between ions and electrons,[21,22] and the PBE generalized gradient approximation exchange–correlation functional was employed,[23] and van der Waals (vdW) interactions were included using the dispersion corrected DFT-D2 method of Grimme.[24] The atomic structures were relaxed until the forces on all unconstrained atoms were ≤ 0.03 eV Å^{-1}. The simulated STM image was obtained using the Tersoff–Hamann method.[25]

As shown in Fig. 1a, after deposition of *cis*-DNHD molecules on Cu(110) at low temperature (∼170 K) and annealing the sample up to ∼210 K, it is seen that nearly all of the molecules are resolved as a uniform heart shape demonstrating the *cis* characteristic of DNHD molecules, and the molecules are distributed on the surface in an isolated way, which was reported in our previous work.[26,27] Interestingly, upon increasing the annealing temperature to ∼227 K, besides the majority of heart-shaped features, some rod-like motifs appear and also adsorb in an isolated way on the surface as shown in Fig. 1b. Upon keeping on increasing the annealing temperature to ∼235 K, more and more heart-shaped features transform to rod-like motifs as shown in Fig. 1c. Finally, when the annealing temperature is up to ∼255 K it is found that nearly all of the heart-shape features transform to rod-like motifs as shown in Fig. 1d. Note that if we anneal the sample with heart-shaped features directly up to 255 K we also find that only rod-like motifs are present on the surface. According to the STM topography and molecular dimension of the rod-like motif we speculate that this motif is very likely to be the *trans*-form DNHD molecule.

To verify our hypothesis that the rod-like motif is attributed to the *trans*-form DNHD molecule, we have performed the DFT calculations on the adsorption geometries and simulated STM images of *cis*-form and *trans*-form DNHD molecules on Cu(110) at a bias voltage of the experimental condition as shown in Fig. 2a and b. In comparison with the high-resolution experimental STM image, the DFT-based STM simulation of *trans*-form DNHD molecules shows a quite consistent profile. Moreover, *trans*-form DNHD molecules are found to be more stable than the *cis* form by 0.28 eV on Cu(110) (*cf.* Fig. 2c) implying that this *cis*–*trans* isomerization is an exothermic reaction, which accounts for the formation of *trans*-form DNHD molecules after overcoming the energy barrier. From the above analysis we conclude that the rod-like motif is the *trans*-form DNHD molecule. Note that after further annealing the sample to 400 K the DNHD molecules undergo Bergman cyclization to form 1-D polyphenylene on the surface.[26] Since Bergman cyclization has to occur *via cis*-form DNHD molecules, this experimental result implies that the *cis*–*trans* isomerization is reversible on Cu(110) at higher temperatures.

It is noticeable that most of the isomerization processes of analogous alkene molecules require relatively harsh conditions in solution or gas phase, *e.g.* UV irradiation, high temperature,[28–30] or under ambient conditions with specific catalysts.[4] However, in our case the isomerization of DNHD could occur well below room temperature and no complex catalyst is necessary (only the Cu(110) substrate). Note that we have also studied DNHD molecules on Au(111) and Ag(110) surfaces and, however, no isomerization is found to occur under thermal treatment. It is known from the literature that the isomerization of alkene molecules normally requires a quite high energy barrier of ∼2 eV in gas phase or in solution,[29,30] while in the present study the barrier is significantly reduced to ∼0.59 eV (227 K). The temperature-dependent transformation scenario (*cf.* Fig. 1) indicates that the *cis*–*trans* isomerization

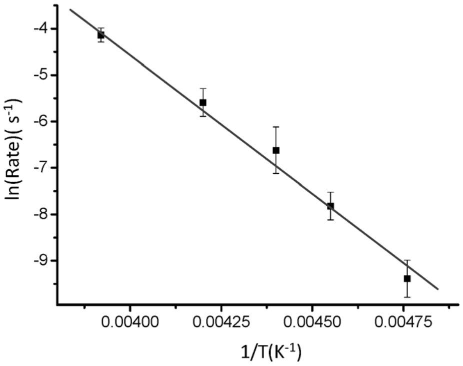

Fig. 3 Arrhenius plot of *cis–trans* isomerization rate of DNHD molecules on Cu(110), which is derived from analysis of the STM data in the temperature range of 210–255 K.

occurs on the copper surface rather than in gas phase during thermal sublimation. We thus speculate that the copper surface plays an important role in this isomerization process.

To get further insight into the isomerization behavior of DNHD molecules on Cu(110), a statistical analysis of the experimental data has also been performed to estimate the isomerization rate for understanding the kinetic characteristics. The isomerization rate R is defined as the *trans*/total ratio within a time interval in the temperature range of 210 K to 255 K. After detailed analysis we find that the isomerization rate obeys the Arrhenius law, *i.e.* $R = A\exp[-E_a/(k_BT)]$, as plotted in Fig. 3. As extracted from the plot, the activation energy E_a is determined to be 0.52 ± 0.03 eV and the prefactor A to be $6.3 \times 10^{8.0\pm0.41}$ s^{-1}. The derived E_a for isomerization of the surface-bound DNHD molecule is nearly reduced by a factor of four as compared to the activation energy for thermal isomerization of stilbene in gas or solution phases,[29,30] which is similar to the case of TBA molecules on the metal surface.[8]

Concerning the mystery of such low activation energy for *cis–trans* isomerization of DNHD molecules on Cu(110), based on the experimental conditions and findings, we propose the following factors which may account for this unpredictable isomerization behavior: (1) surface defects such as step edges are known to be highly active and could somehow facilitate specific surface reactions;[31,32] (2) the Cu(110) substrate is known to supply freely diffusing adatoms even below room temperature,[33,34] such adatoms may serve as catalysts to assist the isomerization process; (3) the charge transfer induced by the surface-mediated effect[35] may affect the physicochemical properties of surface-bound DNHD molecules and lower the activation energy for the isomerization; (4) it is noteworthy that the disperse distribution of DNHD molecules on the surface could also facilitate the isomerization process because the isomerization behaviors were greatly restricted in a densely packed molecular arrangement owing to the steric hindrance.[7,36] Note that the electric field and tunnel current are found to have no influence on this *cis–trans* isomerization.

In conclusion, from the interplay of high-resolution UHV-STM imaging and DFT calculations, we have studied the *cis–trans* isomerization of DNHD molecules on Cu(110). We find that the Cu(110) surface could facilitate the isomerization of surface-bound DNHD molecules by significantly reducing the activation energy barrier, and this novel phenomenon warrants further experimental or theoretical studies on the origin and generality of this unanticipated surface effect on isomerization of alkene molecules.

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