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ARTICLE TYPE

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

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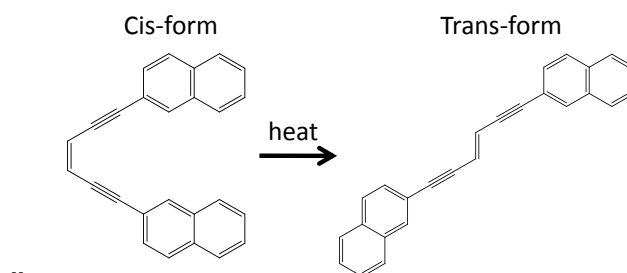
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5 From the interplay of STM imaging and DFT calculations we have investigated the isomerization of an alkene molecule on Cu(110) under ultrahigh vacuum conditions. We show that the on-surface cis-trans isomerization could efficiently occur well below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

In certain biological systems, cis-trans isomerizations of alkenes (i.e. involving carbon-carbon double bond) are 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 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 are mainly performed in solutions to date.^{4,5} 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 bond) have been widely performed and achieved great progress in understanding their isomerization behaviors.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 (shortened as DNHD) on Cu(110) under ultrahigh vacuum (UHV) conditions at the atomic scale. 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 involves 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, 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 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.



Scheme 1 Isomerization of the DNHD molecule.

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-ethynyl-naphthalene under inert atmosphere¹⁸) were deposited by thermal sublimation at ~310K onto a Cu(110) substrate held at ~170 K. The STM measurements were carried out in a temperature range of 100 K–150 K. 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. 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 molecule, and the molecules are distributed on the surface in an isolated way, which was reported in our previous work.^{26,27} Interestingly, when increasing the annealing temperature to ~227 K, besides the majority of heart-

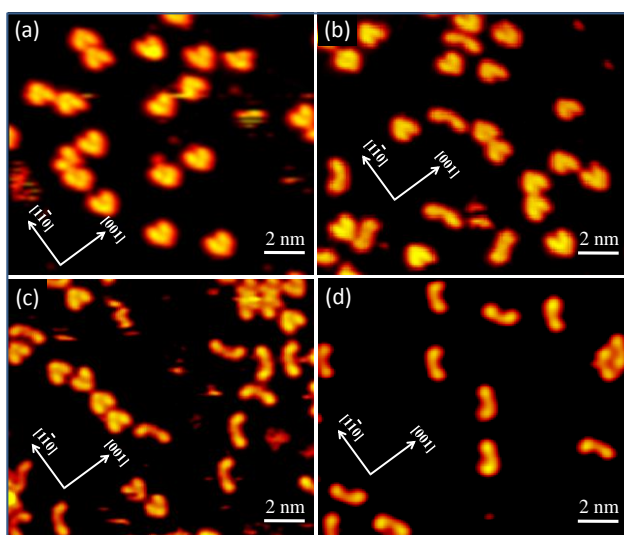


Fig. 1 STM images after annealing the sample with cis-DNHD molecules at (a) 210 K, (b) 227 K, (c) 235 K and (d) 255 K, respectively. Scanning conditions: $I_t = 0.65$ nA, $V_t = -2500$ mV.

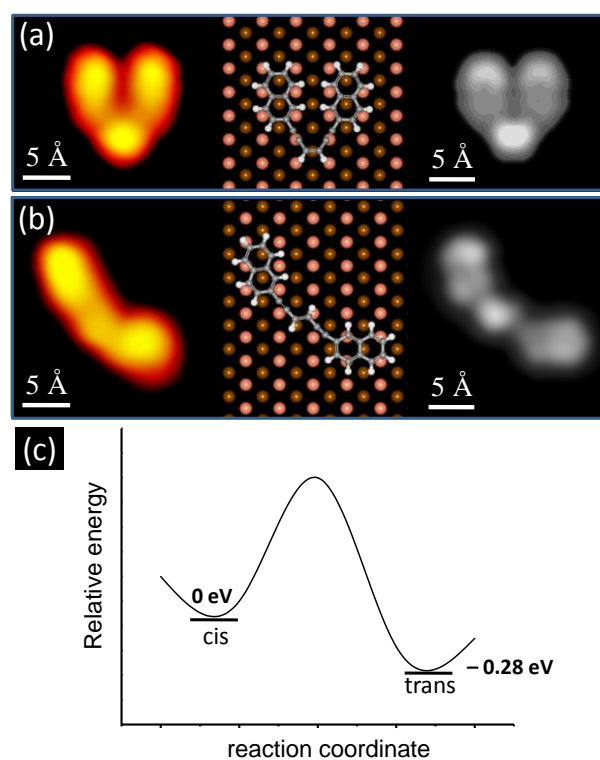


Fig. 2 The high-resolution STM images, DFT-optimized structural models and DFT-based simulated STM images of (a) the cis-form DNHD molecule and (b) the trans-form DNHD molecule. (c) Schematic diagram of the double-well potential for the isomerization of DNHD molecule on Cu(110). The trans-form DNHD molecule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

shaped features some rod-like motifs appear and also adsorb in an isolated way on the surface as shown in Fig. 1b. When 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 2b. In comparison with the high-resolution experimental STM image, the DFT-based STM simulation of trans-form DNHD molecule shows a quite consistent profile. Moreover, trans-form DNHD molecules is calculated 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 400K 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, thus 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 analogue 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 molecule on Au(111) and Ag(110) surfaces and, however, no isomerization is found to occur under thermal treatment. It is known from the literatures 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 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 molecule 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. $R = A \exp[-E_a/(k_B T)]$, 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 $6.3 \times 10^{8.0 \pm 0.41} \text{ s}^{-1}$. 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 molecule on the metal surface.^[8]

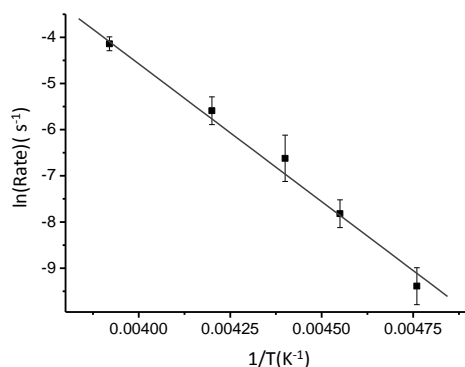


Fig. 3 Arrhenius plot of cis-trans isomerization rate of DNHD molecules on Cu(110), which is derived from analysis of the STM data in a temperature range of 210 K–255 K.

Concerning the mystery of such low activation energy for cis-trans isomerization of DNHD molecule 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 the catalyst to assist the isomerization process; (3) the charge transfer induced by the surface-mediated effect³⁵ may affect the physicochemical properties of surface-bound DNHD molecule 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 molecule by significantly reducing the activation energy barrier, and this novel phenomenon warrants further experimental or theoretical studies into the origin and generality of this unanticipated surface effect on isomerization of alkene molecules.

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Notes and references

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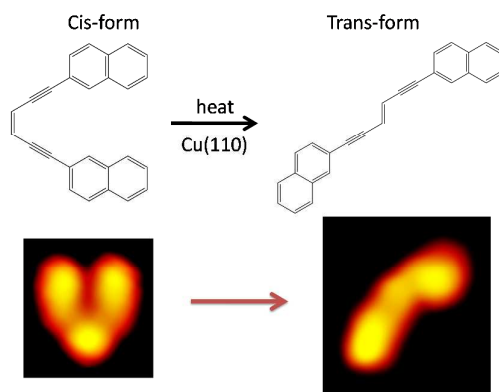
[†] Authors contributed equally to this work

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TOC

Surface-assisted Cis-trans Isomerization of an Alkene Molecule on Cu(110)

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Interplay of STM imaging and DFT calculations demonstrates 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 surface is speculated to play a key role in assisting this isomerization process.