Communication

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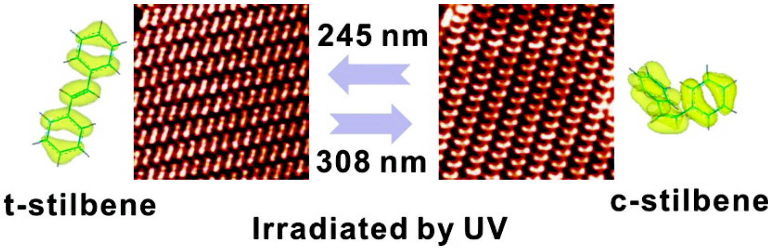

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A Single Molecule View of Bistilbene Photoisomerization on a Surface Using Scanning Tunneling Microscopy

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The absorption of UV light by a molecule can trigger photoisomerization reactions that are mediated by the dynamics occurring on an excited-state potential energy surface.[1] The photoisomerization reaction between *trans*-stilbene (TSB) and *cis*-stilbene (CSB) has served as a prototype for an important reaction class that involves the internal rotation around a carbon−carbon double bond and has been heavily studied in both solution phase and gas phase environments.[2−4] It has been of great interest[2] to study the influence of the molecular environment on its dynamics. In this work, we consider the photoisomerization of stilbene lying flat on a surface to form two-dimensional ordered aggregates. Reaction cannot occur thermally. Unlike the more isotropic solution environment, the absorbed stilbene is expected to exhibit a large steric hindrance to internal rotation that may dramatically increase the barrier to TSB isomerization and, perhaps, induce a barrier to CSB isomerization. There are relatively few studies exploring photoisomerization reactions on surfaces. It should also be noted that on a metallic surface, the excitation may occur either directly through photon absorption or indirectly through interaction with hot electrons from the substrate.

The present work is motivated by our earlier study[5] of the adsorption of TSB on the conductive Ag/Ge(111)−($\sqrt{3}\times\sqrt{3}$)R30° surface (simplified as Ag/Ge(111)−$\sqrt{3}$). Figure 1a displays a scanning tunneling microscopy (STM) image of TSB and CSB molecules co-adsorbed on Ag/Ge(111)−$\sqrt{3}$ at 100 K with a negative bias (−0.17 V). To identify the two isomers, we performed semiempirical calculations (AM1)[6] on the charge distribution of the highest occupied molecular orbital of both molecules (Figure 1b). Their shape and size are clearly mapped out in the STM images. The clear phase separation between co-existing CSB and TSB domains implies a substantial difference in the lateral interaction between the two isomers. The excellent ordering is due, in large part, to the propitious matching between the surface lattice constant and the separation between the two phenyl rings in stilbene, 6.54 Å for TSB.[5] On the basis of STM measurements, we propose a structural model for the system that is illustrated in Figure 1b. The phenyl groups of stilbene are most strongly adsorbed to the 3-fold site at the center of Ag trimers. For TSB, the lattice match between the TSB adsorbate and the substrate allows both phenyl groups to nearly perfectly reside on two alternative Ag trimer sites.[5] The CSB exhibits one phenyl group adsorbed to a 3-fold site, while the other phenyl group lies tilted above the surface. Both TSB and CSB overlayers are consistent with a (2 × 1) registry model, as illustrated in Figure 1b.

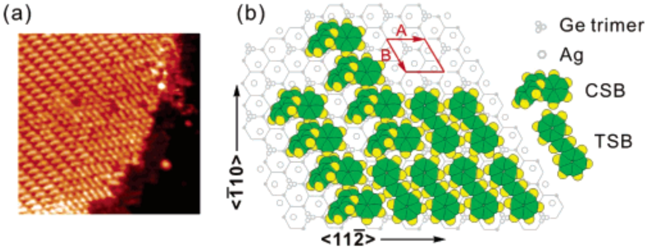

Figure 1. (a) A filled-state STM image (20 nm × 20 nm) of co-existing TSB and CSB domains. (b) Overlayer (2 × 1) structure and registry models.[5] A and B are unit vectors.

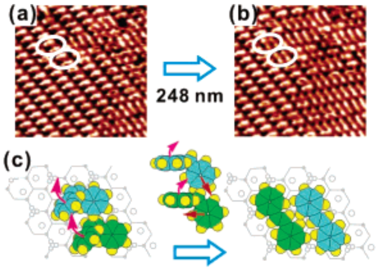

Figure 2. (a) An expanded image of Figure 1a. (b) The image of the same region after exposure to 248 nm UV light (0.07 W/cm^2, 3 min). (c) A conjectured schematic depicting how a CSB pair is transformed to a TSB pair.

The ordered arrays of stilbene offer a unique opportunity to observe the photoisomerization of single molecules in a well-defined chemical environment. In Figure 2a, an STM image of a (dominantly) CSB sample at 100 K is shown before irradiation. The same region is imaged after the sample has been briefly exposed (3 min) to 248 nm UV radiation (Figure 2b), which is known to induce cis−trans conversion in the gas phase. From the careful study of many such images, we find that at a molecular level the isomerization process occurs in a pairwise fashion, with two CSB molecules transforming into two TSB molecules. For example, the two pairs of CSB inside the ellipses in Figure 2a were converted into the two pairs of TSB molecules marked in Figure 2b, while the surrounding molecules did not react. Also, we find that pairwise isomerization occurs predominantly at cis−trans domain boundaries, with relatively few pairs of TSB being created in the interior of ordered CSB domains. Since molecular diffusion is negligible at 100 K, we can conclude that the photoisomerization reaction requires a special molecular environment, such as the domain boundary, to proceed at an observable rate.

Careful inspection of the STM images reveals the precise molecular picture of the photoisomerization of single CSB molecular pairs. As depicted in Figure 2c, the two tilted phenyl groups exhibit a torsional motion and flip down flat to the surface.

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Accompanying this internal motion within the CSB molecules is a sliding motion along the surface where the molecules move laterally to accommodate to the available adsorption sites. The net result is a 60° rotation of the molecular axis of the TSB pair compared to the CSB pair, and this provides solid evidence for the one-bond-flip mechanism proposed for the stilbene photoisomerization in gas or solution phase.[2-4,7] Of course, from the STM images alone, it is impossible to determine whether these two components of the reactive motion occur sequentially or in a concerted fashion. However, since the reaction is found to proceed mainly at the domain boundaries, it seems very likely that steric hindrance involving neighboring stilbene molecules must have a strong influence on the reaction rate. One expects that near domain boundaries the molecules will have more room to undergo large amplitude reactive motion compared to the more constrained environment of the domain interior. Similar studies were carried out for samples of TSB after brief exposure to 308 nm light, which induces reaction in the gas phase. The molecular level mechanism for this reaction was found to be completely consistent with the reverse of the process depicted in Figure 2c. Samples were also exposed to much longer periods of irradiation, where the reaction had reached steady state and can reach nearly a 100% yield.

It is well-known that excitation of physisorbed molecules can create excitons, which are strongly correlated electron−hole pairs.[8] In the case of stilbenes adsorbed on Ag/Ge(111)−$\sqrt{3}$, Frenkel excitons are formed within individual stilbene molecules since intermolecular interactions are weak.[9] These excitons can migrate to neighboring molecules through Förster[8] and Dexter[10] excitation transfer mechanisms. On the basis of our STM images (Figure 2), the isomerization occurs most readily on domain boundaries, suggesting that exciton migration occurs before the isomerization event occurs. We have estimated the time scale for Förster excitation transfer between neighboring stilbenes on Ag/Ge(111)−$\sqrt{3}$ to be about 10 ps.[8] From Figure 1, the edge distance between neighboring stilbenes is estimated to be far less than 10 Å. At this distance, the Dexter excitation transfer may be even faster than the Förster excitation transfer. Because the average domain size is tens of nanometers,[5] the upper-limit average time for an exciton to migrate from the domain center to the boundary is within 0.5 ns. Realistically, the excitons located closer to the domain boundary are expected to play a more important role in this photoisomerization event because the short migration time would allow them to accumulate on the domain boundary without being quenched by interaction with the substrate. This behavior has been studied in semiconductor systems,[11] where an exciton can couple with another exciton to form an exciton molecule (biexciton)[12] or bind with other entities (such as domain boundary or defects) to form a localized exciton.[9,13]

As presented in Figure 2, surface photoisomerization of stilbenes occurs in pairs, suggesting that biexciton is the precursor of the photoreaction. Assuming only a dipole−dipole coupling mechanism, we have calculated the binding energy (ΔE in Figure 3) of TSB biexciton based on the molecular spacing (Figure 1) and the excited-state dipole moment by semiempirical method AM1.[6] The resultant binding energy (~100 meV) is much larger than the thermal energy of the system at 100 K (~9 meV). It indicates that biexcitons may remain stable without undergoing thermal dissociation during the UV illumination because the induced temperature increase is insignificant. In the case of the CSB biexciton, the estimated binding energy is comparable to that of TSB. The exposition above supports that the bistilbene isomerization phenomenon originates from the formation of biexcitons. The surface area occupied by two adjacent stilbene molecules is large enough to alleviate the steric hindrance constraint imposed by surrounding molecules, allowing two isomerization events to occur simultaneously. The resultant binding biexcitons (Figure 3) presumably reside on a smaller area than their ground-state counterparts due to their intermolecular attraction force, making more space for drastic molecular conformation change during isomerization. Except at defect sites, substrate domain boundaries, and step edges, a more serious steric hindrance is expected for single stilbene isomerization because all of the available neighboring Ag trimer adsorption sites for the flipping phenyl ring have been occupied by other stilbene molecules.

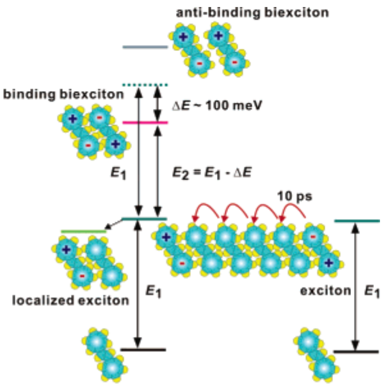

Figure 3. A schematic diagram depicting the exciton propagation and interactions. E_1 is the transition energy between ground state and one-photon excited state; ΔE, binding energy of biexciton.

In summary, we have observed stilbene photoisomerization on the Ag/Ge(111)−$\sqrt{3}$ surface with STM. The direct observation allows us to confirm the microscopic one-bond-flip mechanism in the photoisomerization reaction. A biexciton-assisted photoisomerization model is proposed to explain the finding that the surface photoisomerization reaction occurs in pairs. The unique photochemistry observed here not only is of intrinsic interest but also may prove to be useful in understanding the workings of single-molecule optically activated nanodevices.[14]

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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