

## Inducing All Steps of a Chemical Reaction with the Scanning Tunneling Microscope Tip: Towards Single Molecule Engineering

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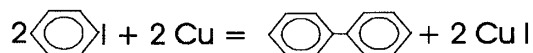
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(Received 25 April 2000)

All elementary steps of a chemical reaction have been successfully induced on individual molecules with a scanning tunneling microscope (STM) in a controlled step-by-step manner utilizing a variety of manipulation techniques. The reaction steps involve the separation of iodine from iodobenzene by using tunneling electrons, bringing together two resultant phenyls mechanically by lateral manipulation and, finally, their chemical association to form a biphenyl molecule mediated by excitation with tunneling electrons. The procedures presented here constitute an important step towards the assembly of individual molecules out of simple building blocks *in situ* on the atomic scale.

PACS numbers: 82.65.Pa, 61.16.Ch, 82.30-b, 85.65.+h

In 1904, Ullmann *et al.* [1] discovered that heating iodobenzene with a copper powder catalyst leads to the formation of biphenyl with high purity. Meanwhile, this reaction has become a textbook case and it is widely used in synthetic chemistry due to its versatility in the association of substituted phenyls to complex biphenyl derivatives. The synthesis of biphenyl out of iodobenzene on copper [1]



essentially consists of three steps (Fig. 1): dissociation of iodobenzene ( $\text{C}_6\text{H}_5\text{I}$ ) to phenyl ( $\text{C}_6\text{H}_5$ ) and iodine, diffusion of phenyl to find another phenyl as a reaction partner, and association to form biphenyl ( $\text{C}_{12}\text{H}_{10}$ ). The dissociation of iodobenzene by thermal activation takes place at  $\sim 180$  K and biphenyl is formed at  $\sim 210$  K for multilayer [2] and  $\sim 300$  K for submonolayer iodobenzene on Cu(111) [3,4]. In recent years the scanning tunneling microscope (STM) has been developed from an imaging instrument to a tool capable of controlled manipulation of single atoms and molecules on surfaces including lateral movement, vertical transfer, and dissociation [5–14]. In this Letter we demonstrate that by employing a suitable combination of several manipulation techniques, the entire chemical reaction process can be induced on single molecules leading to the synthesis of new individual molecules (Fig. 1).

Our experiments were performed with a homebuilt UHV-STM operated at 20 K using electrochemically etched W tips. The Cu(111) surface was cleaned by cycles of sputtering with Ne ions and annealing up to 800 K. The iodobenzene (Aldrich 98%) was first purified by several freeze-pump-thaw cycles with liquid nitrogen and then small amounts were dosed onto a cooled Cu(111) sample through an aperture in the radiation shield of the STM.

STM images (at 20 K) reveal mobility of iodobenzene molecules on the terrace which results in their preferen-

tial anchoring at the lower part of step edges [Fig. 2(a)]. Iodobenzene adsorbs with the  $\pi$  ring approximately parallel to the Cu(111) substrate and binds through substrate interaction of both its iodine atom and  $\pi$  system [4]. High resolution images show two protrusions originating from the  $\pi$  ring and the iodine, respectively [Fig. 3(a)]. Only molecules adsorbed at straight (close-packed) step edges were chosen for the reaction experiments in order to ensure a uniform adsorbate/substrate binding condition.

The first reaction step, iodine abstraction from iodobenzene [Figs. 1(a) and 1(b)], was performed by positioning the STM tip right above the molecule at fixed height and switching the sample bias to 1.5 V for several seconds. Thereby electrons of up to 1.5 eV are injected into the molecule. Simultaneously, the corresponding tunneling

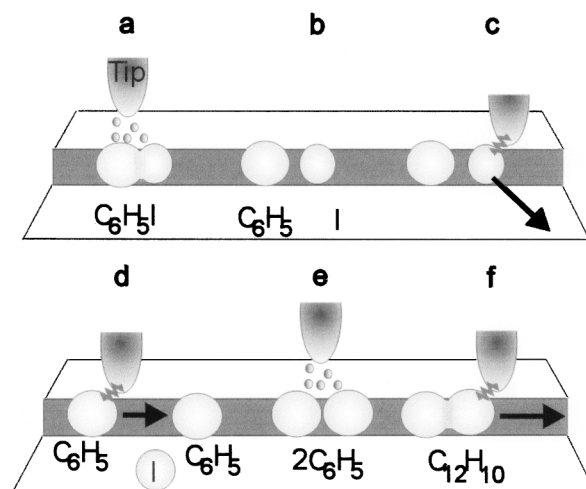


FIG. 1. Schematic illustration of the STM tip-induced synthesis steps of a biphenyl molecule. (a),(b) Electron-induced selective abstraction of iodine from iodobenzene. (c) Removal of the iodine atom to a terrace site by lateral manipulation. (d) Bringing together two phenyls by lateral manipulation. (e) Electron-induced chemical association of the phenyl couple to biphenyl. (f) Pulling the synthesized molecule by its front end with the STM tip to confirm the association.

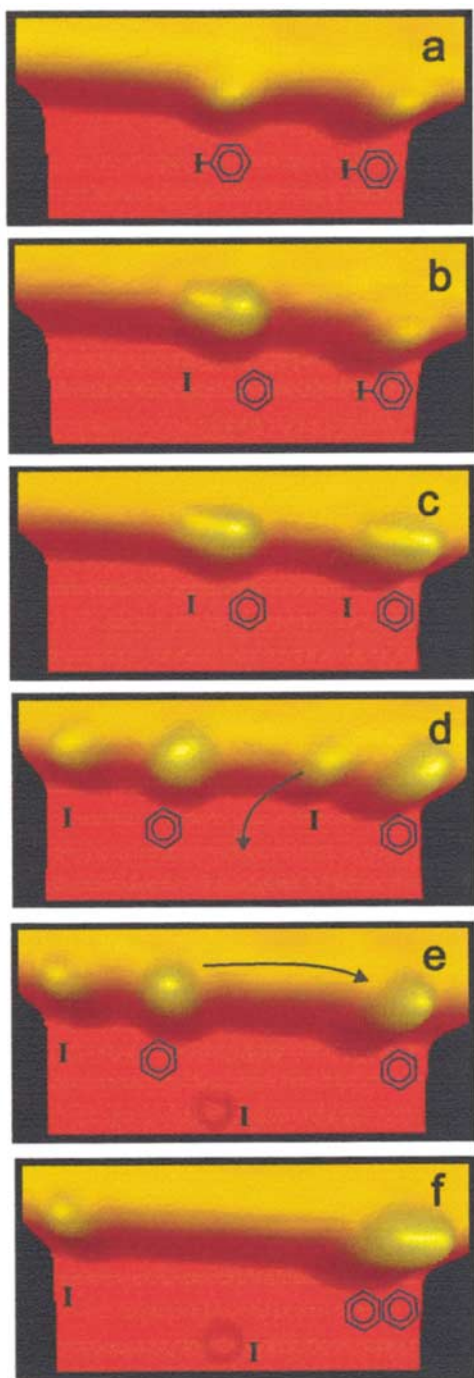


FIG. 2 (color). STM images showing the initial steps of the tip-induced Ullmann synthesis. (a) Two iodobenzene molecules are adsorbed at a Cu(111) step edge. (b),(c) Iodine is abstracted from both molecules using a voltage pulse. (d) Iodine atoms (small protrusions) and phenyl molecules (large) are further separated by lateral manipulation. (e) The iodine atom located between the two phenyls is removed onto the lower terrace to clear the path between the two phenyls. (f) The phenyl molecule at the left side is moved by the STM tip close to the right phenyl to prepare for their association. (Image parameters: +100 mV, 0.53 nA;  $70 \times 30 \text{ \AA}^2$ .)

current is recorded as a function of time. The separation of iodine [15] is accompanied by a sudden and easily measurable change of the tunneling current, which

allows one to determine the dissociation rate. Altogether 175 molecules were dissociated at four different tunneling currents of 0.01, 0.02, 0.03, and 0.6 nA, respectively. The linear dependence of the dissociation rate on the tunneling current [Fig. 4(a)] shows that the energy transfer from a single electron causes the breaking of the C-I bond [12,13]. It is not possible to break the C-H and C-C bonds with a single electron process at this voltage [14], especially as their bond energies are about 2 and 3 times higher than the C-I bond [16]. Upon dissociation, resultant species change their positions from the original location under the tip [17]. This effectively terminates tunneling through the fragments (as observed in the drop of the tunneling current); no further dissociation of the C-H and C-C bonds was observed.

After dissociation, the iodine and phenyl are spaced at distances of “ $(n + 1/2)a_0$ ” ( $n = 2, 3, \text{ or } 4$ ;  $a_0 = 2.55 \text{ \AA}$  denoting the Cu nearest-neighbor distance) along the step edge [Figs. 2(b) and 2(c)]. The phenyl appears larger in the STM images and can be dissociated further into smaller fragments using biases  $\geq 3 \text{ V}$  and high currents [14,17,18]. This is in good agreement with experiments on benzene on Cu(001) [14] where the C-H bonds can be broken only with tunneling voltages  $\geq 2.9 \pm 0.1 \text{ V}$ . Because of the high bias requirement to decompose both phenyl and benzene, dehydrogenation does not occur during the initial iodine abstraction process.

High resolution STM images—acquired with the tip sharpened by a deliberate transfer of an iodine atom onto its apex [19,20]—display phenyl with an approximately triangular shape exhibiting a maximum at its center [Fig. 3(b)]; this shape resembles the calculated STM image of a hollow site bound benzene on Pt(111) [21]. Figure 3(c) shows a model based on this shape where the phenyl is lying with its  $\pi$  ring on the terrace while one of its C atoms is pointing toward a step edge Cu atom. This adsorption geometry allows for  $\pi$  interaction with the terrace and  $\sigma$  bonding to a Cu step edge atom. It is also consistent with the observed  $(n + 1/2)a_0$  distance along the step between the iodine atom adsorbed at the highly coordinated site [22] and the phenyl being  $\sigma$ -bonded [3,4] to a step edge Cu atom [Fig. 3(c)].

After having prepared the phenyl reactants, we proceeded to the second reaction step, namely, migration of one phenyl close to another phenyl. We employed the “soft” lateral manipulation technique, which uses only tip-adsorbate forces [10,11] [Fig. 1(d)]. First we chose the manipulation path for phenyl along the Cu(111) straight step edge. This path has the advantage that due to the higher binding energy and well defined geometry of the step edge as compared to the plane surface, it is more convenient to move the adsorbates along the step with the STM tip without losing them.

To perform lateral manipulation, we first surveyed the initial and final locations of the phenyl to be moved by scanning the STM tip along the chosen path with a tunneling current of 0.53 nA at +70 mV sample bias. The actual

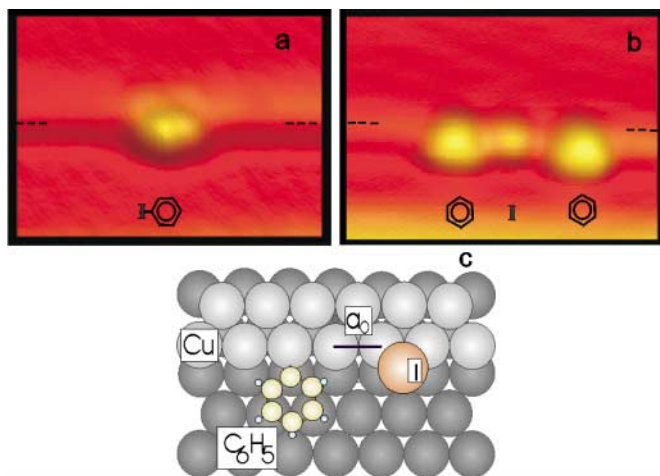


FIG. 3 (color). Adsorption and geometry of reactants. (a) A STM image of step edge bound iodobenzene shows a larger protrusion on the left side indicating the iodine position (image size:  $60 \times 42 \text{ \AA}^2$ ). (b) The STM image shows two phenyls (triangular shape) and an iodine atom (center) adsorbed at a (100)-type step edge after tip-induced dissociation of two iodobenzene molecules. The other iodine was deliberately transferred to the tip apex to improve the image resolution [19]. The approximate triangular shape with a maximum in the center is typical for phenyl/benzene adsorbed at a hollow site with three of its C atoms positioned on top of three substrate atoms [21]. The dashes indicate the location of the step (image size:  $45 \times 31 \text{ \AA}^2$ ). (c) A sphere model of the chemical constituents illustrates the adsorption sites of phenyl and iodine in (b).

movement was accomplished by increasing the tunneling current by a factor of 200 at its initial site to reduce the tip-phenyl separation. Then the tip was moved along the predetermined path in constant current mode. The corresponding tip height curves during manipulation [Fig. 4(b)] show typical pulling behavior [11] with hops equal to  $a_0$  or  $2a_0$  along the step edges. Stronger tip-adsorbate forces (lower tunneling gap resistance) are necessary to move a phenyl compared to an iodobenzene. We attribute this to the  $\sigma_{\text{C-Cu}}$  bonding of phenyl to the step edge in addition to its  $\pi$  interaction with the terrace.

If necessary, the iodine atoms were also pulled by the tip to further separate them from the phenyls [Fig. 2(d)] and to clear the manipulation path [Figs. 2(e) and 1(c)]. Lateral manipulation was continued until two phenyls were located close to each other [Figs. 2(f) and 1(e)]. The shortest achievable distance between the centers of two phenyls is  $3.9 \pm 0.1 \text{ \AA}$ , as determined from the STM images. We emphasize that even though the two phenyls are brought together spatially they do not join at our working temperature (20 K) unless further measures are taken: In attempts to laterally manipulate the phenyl couple, the two phenyls are always separated again. Therefore we assume that both phenyls are still bound to the step edge via their  $\sigma_{\text{C-Cu}}$  bonds at this stage.

To induce the last reaction step, association, we used molecular excitation by inelastic tunneling. Figure 4(c) visualizes the chemical association of two phenyls brought

to the closest approach. The upper half of this image was acquired before association. Right above the center of the phenyl couple the tip was stopped and the bias was raised to 500 mV for 10 s. Then the voltage was reduced to its original value of 100 mV and the STM tip continued scanning the lower half of the image, which corresponds to the postassociation stage. The distance between the phenyl centers changes upon association with  $4.4 \pm 0.05 \text{ \AA}$  [see Fig. 4(c), inset] which is consistent with the distance of  $4.3 \text{ \AA}$  between the two centers of the  $\pi$  rings in gas-phase biphenyl [23]. It is known that biphenyl binds with both  $\pi$  rings parallel to the Cu(111) terrace at low temperatures and interacts through its  $\pi$  orbitals with the substrate [4].

We suggest the following explanation for the association process: Since the two adjacent phenyls are initially tied up to the step edge, both of their  $\sigma_{\text{C-Cu}}$  bonds are pointing towards it. If the phenyls are activated by the tunneling current, this can also lead to their in-plane rotation. A slight rotation points the reactive C- atoms out of the step edge normal. As Zheng *et al.* [24] explained, this can lead to the formation of a  $\sigma_{\text{C-C}}$  bond, if the initial rotation is sufficiently energetic. By exposing the phenyls to the 500 meV electrons of the tunneling current the necessary activation energy is supplied. The observed process can be initiated only by using voltages  $\geq 0.5 \text{ V}$ . Since the bias necessary for association is as small as 0.5 V, dehydrogenation during the association process can be ruled out.

Successful chemical association is verified by pulling the synthesized molecule by its front end with the STM tip [11] [Figs. 5(a), 5(b), and 1(f)]. The corresponding

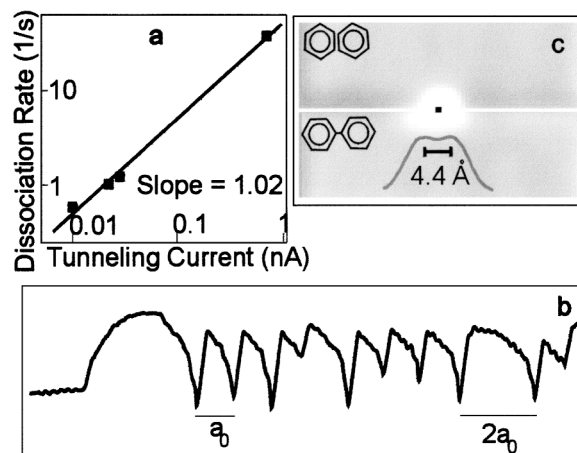


FIG. 4. Investigations concerning the mechanisms of dissociation, manipulation, and association. (a) A double logarithmic plot of the dissociation rate of iodobenzene versus the tunneling current shows a slope close to unity indicating a single electron process. (b) Tip height curve during lateral movement of a phenyl corresponding to Figs. 2(e) and 2(f). During pulling adsite hops of distances  $a_0$  and  $2a_0$  can be observed. (c) A background subtracted STM image with a phenyl couple in its center. The upper and lower parts correspond to the stages before and after the chemical association. The tip height profile across the centers of the synthesized biphenyl molecule is indicated. (Image parameters: +100 mV, 1.3 nA;  $24 \times 7 \text{ \AA}^2$ .)

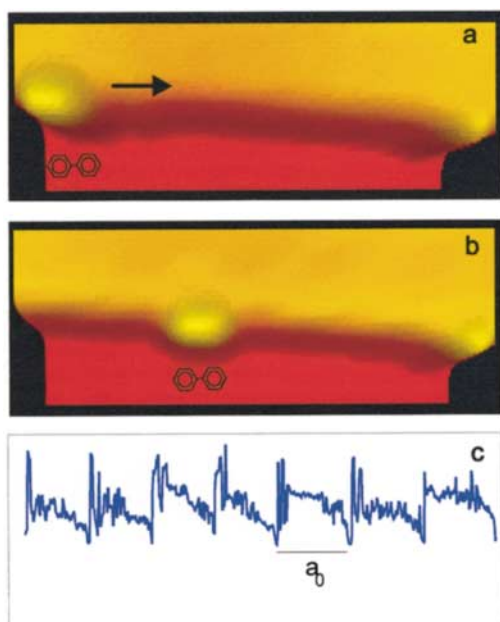


FIG. 5 (color). Verification of successful chemical association of two phenyls. (a),(b) The synthesized biphenyl molecule is pulled by the STM tip from the left part of the image to the middle. (c) The corresponding tip height curve reveals characteristic pulling behavior with the entire molecule trailing the STM tip for a distance of  $7a_0$ . (Image parameters: +100 mV, 1.3 nA;  $60 \times 20 \text{ \AA}^2$ .)

tip-height curve [Fig. 5(c)] shows single adsite hops of the molecule along the step edge. The entire species following the tip illustrates that the two phenyls have joined together to a new single molecule. The lack of fragments at the initial site and along the pulling path indicates the clean transfer of the phenyls to biphenyl and the stability of the product.

In conclusion, we have demonstrated that by employing the STM tip as an engineering tool on the atomic scale all steps of a chemical reaction can be induced: Chemical reactants can be prepared, brought together mechanically, and finally welded together chemically. These processes open up new fascinating routes to the individual assembly of novel man-designed molecules or construction of nanoscale molecular-electronic and molecular-mechanical devices from a variety of building blocks which might also be prepared *in situ*.

We acknowledge valuable discussions with G. Ertl, P. Weiss, and E. Borrs. This work was supported by DFG, Sfb 290, and Academia Leopoldina.

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