Chapter 7

Manipulation of HBC derivatives

In this chapter manipulation experiments with HBC molecules and their derivatives are presented. The goal of such investigations is first of all to learn about molecular-substrate, molecular-adsorbate, and molecular-tip interactions.

Furthermore, an important aim of this study is to build well defined molecular nanostructures by means of STM, an important issue for future development of molecular nano-devices. In combination with STM manipulation techniques, the self-ordering properties of the molecules will be used to assemble molecules in defined molecular structures. It has recently been demonstrated by Griessl et al. that C_{60} fullerenes as a guest in a TMA (trimasic acid) matrix can be transferred by means of STM from one cavity to an adjacent one.[139] In such experiments the possibility of building defined molecular structures by STM is combined with the high precision (i.e. defined bond length, defined position and orientation) that is achievable due to molecular self-organisation.

Here it will be shown that molecules can be laterally manipulated between stable positions within the monolayer structure, therefore the final molecular conformation (exact molecular position and orientation) is predefined by the monolayer structure matrix. Moreover, the structures can be modified: On the one hand single molecules can be taken out of a continuous monolayer and on the other hand the conformation of molecules inside the monolayer (in this case the molecular orientation) can be changed. In combination these manipulation

techniques provide the possibility to build human-designed molecular network structures, starting from molecular monolayers.

Furthermore, an example of a single molecular nano-tool performing the task of an atomic assembler under the operation of the STM tip will be shown.

7.1 Manipulation of Isolated Molecules

Manipulation experiments have been performed for all HBC type molecules already described in Chapter 6: HBC, HPB, HB-HBC, and HB-HPB. Molecule-substrate interaction and the diffusion barrier influence the manipulation parameters and thus different manipulation signals are recorded for different molecules. Lateral manipulation experiments have been performed in constant current mode: The tip height is lowered with respect to the imaging mode by increasing the tunnelling current and the feedback loop remains enabled during manipulation. Usually a small voltage, typically 30 mV, is applied during manipulation in order to exclude changes induced by the electric field and electronic or vibrational excitation from tunnelling electrons. The tip height (z) is recorded during the manipulation, serving as manipulation signal. The tip height z can be calibrated with respect to the metallic surface by Eq. (2-22) and by comparing the absolute tip height during the manipulation with the tip height that has been measured on the clean metallic surface, prior to manipulation. For each type of molecule a characteristic maximum tunnelling resistance R_m is determined, which is needed to manipulate the molecule with the STM tip. Note that small resistances R_m reflect small tip heights, i.e. large interaction forces, and vice versa. The value for R_m is estimated by successive manipulation attempts with increasing tunnelling current (decreasing tunnelling resistance), i.e. successive lowering of z, until the molecule is successfully manipulated. The obtained value of R_m is specific for each type of molecule and also depends on the adsorption position, as described later. The error in R_m is rather large, as estimated from the comparison of different experimental runs, probably due to the influence of the tip structure. The experimental error in R_m is about ±1 order of magnitude (i.e. ± 1 Å in tip height).

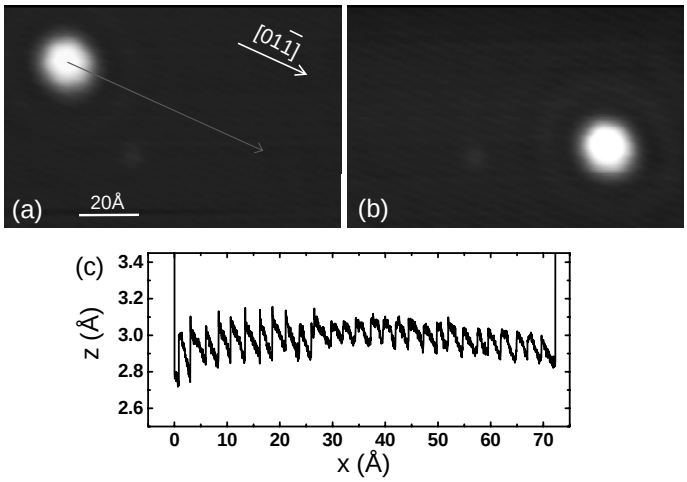

Fig. 7.1. STM images (I = 0.2 nA, V = 200 mV) of a single HBC molecule on Cu(111) prior (a) and after (b) manipulation as indicated by the arrow. Manipulation in constant current mode with $I = 4\times10^{-8}$ A, V = -30 mV. (c) Manipulation signal, i.e. tip height with respect to the contact height on the metallic surface.

In order to laterally manipulate single molecules with an HBC core (HBC or HB-HBC) a tunnelling resistance R_m in the order of $10^6\,\Omega$ is needed. An example of the manipulation of a single HBC molecule is shown in Fig. 7.1. The manipulation is performed with constant current and the manipulation signal, i.e. the tip height *z*, reveals the typical form of the pulling mode (see section 2.4). The direction of movement is parallel to the close-packed direction of the sample and the periodicity of the signal corresponds to the nearest neighbour distance, i.e. 2.55 Å. The movement of the molecule can be deduced from the manipulation signal: The molecule jumps from adsorption site to adsorption site following the tip, pulled by van der Waals forces. This is the typical signal and movement of an adsorbate in pulling mode. (Recently, also for pentacene on Cu(111) a similar behaviour upon manipulation has been described by Lagoute et al.[136]). The periodicity of 2.55 Å indicates that the molecule visits only one site inside the surface unit cell. The orientation of the HBC molecules is never changed after the manipulation; molecules are always found with their axis $\vec{m}$ aligned parallel to the $[01\bar{1}]$ direction. The observed manipulation signals in the case of HBC are not surprising, as the molecular adsorption was found to be governed by strong molecule-substrate interactions (see Chapter 6). Moreover, the observation of a

commensurate monolayer structure (i.e. identical positions of all molecules in the monolayer with respect to the substrate) and one fixed molecular orientation with respect to the substrate, indicate a single adsorption conformation in the surface unit cell. In the case of the other derivatives investigated in this work, however, qualitatively different manipulation signals are observed, as described in the following.

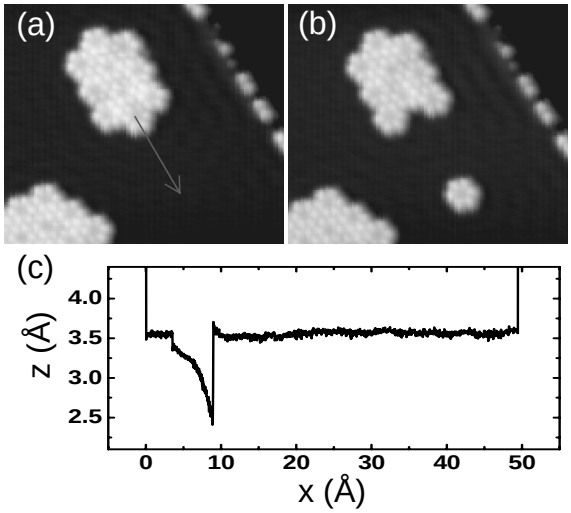

Fig. 7.2. Lateral manipulation of a HB-HBC molecule. Between STM images (a) and (b) (I = 0.2 nA, V = 100 mV, 18×16 nm²) a lateral manipulation has been performed, with the tip movement as indicated by the arrow. The manipulation is performed in const. current mode with $I = 4\times10^{-8}$A, V = -30 mV. The manipulation signal is shown in (c). The tip height is given, with respect to the contact height on the metal surface.

An example of the lateral manipulation of a HB-HBC molecule is shown in Fig. 7.2. The molecule is manipulated from the edge of a molecular island onto the free terrace. The manipulation signal *z* is shown in Fig. 7.2(c). In the first part of the manipulation ($x < 10$ Å) the manipulation signal shows the signature of one molecular jump in pulling mode, corresponding to the detaching of the molecule from the molecular island, with a jump over two lattice constants, i.e. 5.1 Å. In the second part ($x > 10$ Å), i.e. when the molecule has been detached from the island and is moving on the Cu(111) surface, the manipulation signal is almost constant. The flat manipulation signal indicates that the molecule is moved in sliding mode, i.e. the tip-particle interaction is increased strongly (see section

2.4). After manipulation, the molecule is found with its centre at the designated final tip-position of the manipulation path, indicating that the tip remains above the molecular board during the manipulation. On the basis of the tunnelling signal one can try to deduce the molecular movement during the manipulation process: After the onset region, in which the intermolecular bonding between the spacer groups breaks up, the molecule is bound to the tip. Due to the curvature of the tip, the molecular board can be closer to the tip than to the surface, which is separated from the board by the spacer groups. This relatively strong tip-molecule bonding, due to the close approach of the tip to the molecular centre, can explain the observed tunnelling signal, which shows no docking of the molecule to the substrate adsorption positions during manipulation. However, a confirmation of the given interpretation requires detailed MM+ESQC calculations, which are presently performed.

7.2 Manipulation within Molecular Structures

The diffusion barrier of single HPB and HB-HPB molecules on the defect free Cu(111) surface is so small that it is not possible to image these molecules without moving them under the influence of the STM tip. The molecules follow the tip, even when the tip is retracted as far as possible without loosing the tunnelling contact. Molecules are still manipulated at tunnelling parameters of $I = 5 \times 10^{-12}$ A and V = 500 mV, i.e. $R_m > 10^{11}$ Ω (corresponding to a tip height of approximately 7 Å). However, when HPB or HB-HPB molecules are embedded in molecular monolayer structures, their adsorption position is stabilized by intermolecular forces. Single molecules can than be manipulated from one position at the border of an molecular island to another position at the edge of an island, as shown in Fig. 7.3. After the manipulation, the molecule is always found in a position according to the molecular structure, i.e. the final position and orientation of the manipulated molecule is defined by the monolayer structure matrix, which is described in the previous chapter (section 6.1.4).

The shape of the manipulation signal (Fig. 7.3(c)) during such manipulations is

similar to the one obtained for HB-HBC, and shows no internal structure (besides noise), indicating a movement in the sliding mode. In contrast to HB-HBC, the tunnel current during manipulation can be chosen several orders of magnitude smaller in the case of HB-HPB, due to its lower diffusion barrier. The noise is most likely produced by instabilities in the tip height, which often arise when large molecules are manipulated with constant current, i.e. with enabled feedback loop. The features at the end of the manipulation signal ($x \approx$ 40 – 60 Å) probably correspond to the arrangement of the molecule into the molecular matrix structure.

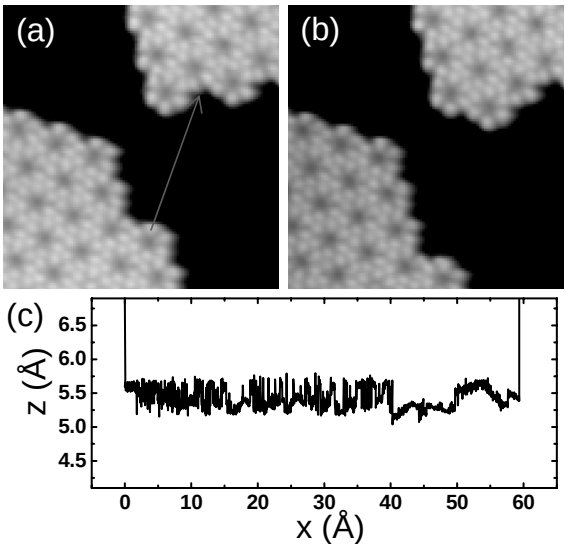

Fig. 7.3. Manipulation of a HB-HPB molecule between two molecular islands. STM images ($I = 8\times10^{-11}$ A, V = 300 mV, 13×13 nm²) before (a) and after (b) manipulation along the path indicated by the arrow. Manipulation in const. current mode with $I = 3\times10^{-10}$ A, V = 30 mV. (c) Tip height during manipulation.

The force and therefore R_m needed to detach a HB-HPB molecule from a molecular island depends on the number of neighbouring molecules. With increasing number of neighbours R_m decreases, thus, the required tip height decreases. $R_m \approx 10^{11}\,\Omega$ for molecules with one neighbour and $R_m \approx 10^{8}\,\Omega$ for molecules with five neighbours. For comparison, the maximum resistance to manipulate a single molecule that has been brought onto the defect-free terrace (no neighbours) is larger than $10^{11}\,\Omega$, as stated before.

The manipulation experiments of HB-HPB molecules between molecular islands indicate that the precision of man-made supramolecular structures by lateral STM manipulation can be greatly enhanced due to the intermolecular self-ordering. While in general the exact final position in STM manipulation experiments of isolated large molecules is hard to define, the precise final position is, in this case, defined by the HB-HPB matrix. Moreover, also the molecular orientation is defined, i.e. it is always in parallel alignment with the other molecules of the molecular island. It is sufficient to manipulate the molecule only roughly (allowing an error of several Å) to the desired position at the border of an molecular island to find the molecule in the exact final position within the molecular matrix. It turned out that two neighbouring molecules are enough to stabilize the position of a molecule against the influence of the STM tip, when operating under typical imaging parameters of 10^{-10} A and 500 mV at 7.5 K. Manipulation of HB-HPB molecules works very reliable and nanostructures of precisely positioned and oriented molecules can be built. Manipulation of HB-HPB molecules has been used to write the letters "Fu" with molecules, as shown in Fig. 7.4. The line width of the letters is two molecules, i.e. 4 nm.

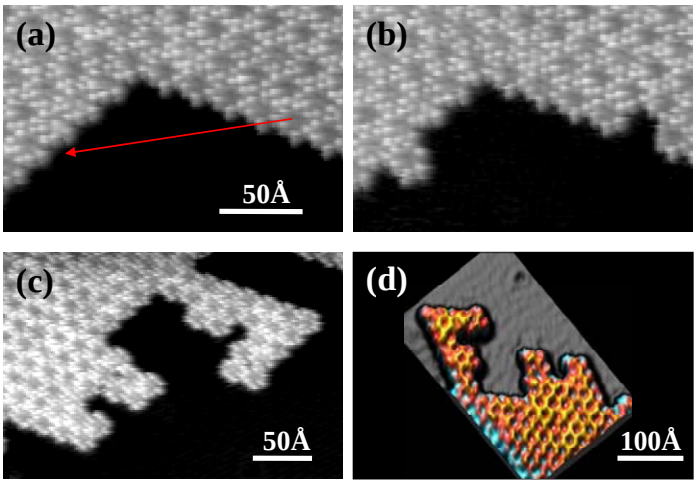

Fig. 7.4. Lateral manipulation of HB-HPB molecules. Before (a) and after (b) lateral manipulation as indicated by the arrow (in const. current mode, R = 1 MΩ). The preferred adsorption site after a manipulation is again in registry with the molecular matrix. After several manipulations of single molecules the letters "Fu" are written (c). The same area is shown in a pseudo 3-dimensional representation (d).

Structures can also be "written" as negative-patterns in molecular monolayers: HB-HPB molecules can be transferred to the STM tip by so-called vertical STM manipulation (see section 2.4). To do that, the tip is first moved to the centre of a molecule in scanning mode. Then the feedback loop is switched off, and the tip height is decreased to approximately $z = 3$ Å with respect to the metal surface underneath (corresponding to a tunnelling resistance of 10^6 Ω in the centre of the molecule). Usually, only a small bias voltage of V = 30 - 50 mV is applied. If the tip approaches the molecule close enough, the molecule is transferred from the surface to the STM tip and when the tip is retracted, the molecule stays on the tip. Often the molecule, which has been transferred to the tip, affects the tunnelling afterwards. In such a case a new tip has to be prepared by controlled tip-sample contact in an uncovered region of the sample (on the bare metal).

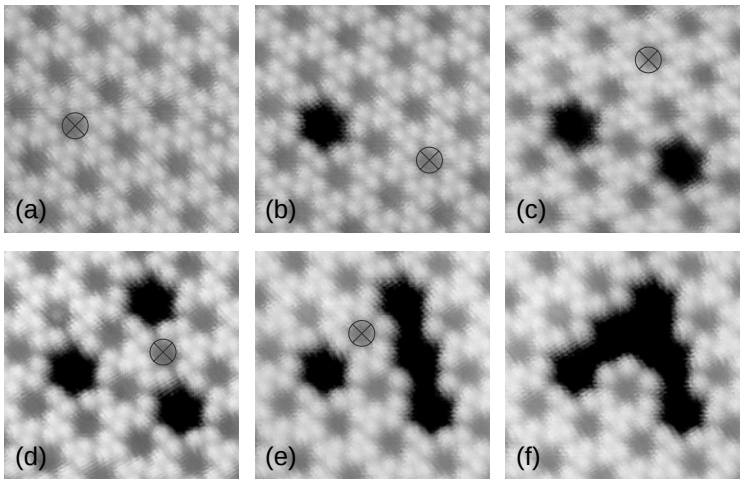

Fig. 7.5. Series of STM images (V = 0.9 V, I = 0.17 nA, size 5×5 nm²). Between two following images a vertical STM manipulation (see text) has been performed at the marked position. HB-HPB molecules are transferred to the STM tip and are extracted from the monolayer by retracting the tip.

Fig. 7.5 shows a series of vertical manipulations of a HB-HPB monolayer. Between each two images one molecule has been transferred to the STM tip by means of the previously described procedure. In this case the molecules are presumably bound to the tip by chemical forces (no dependence on the applied voltage was observed, which would indicate an effect of the electrical field, and the procedure worked down to a few mV).

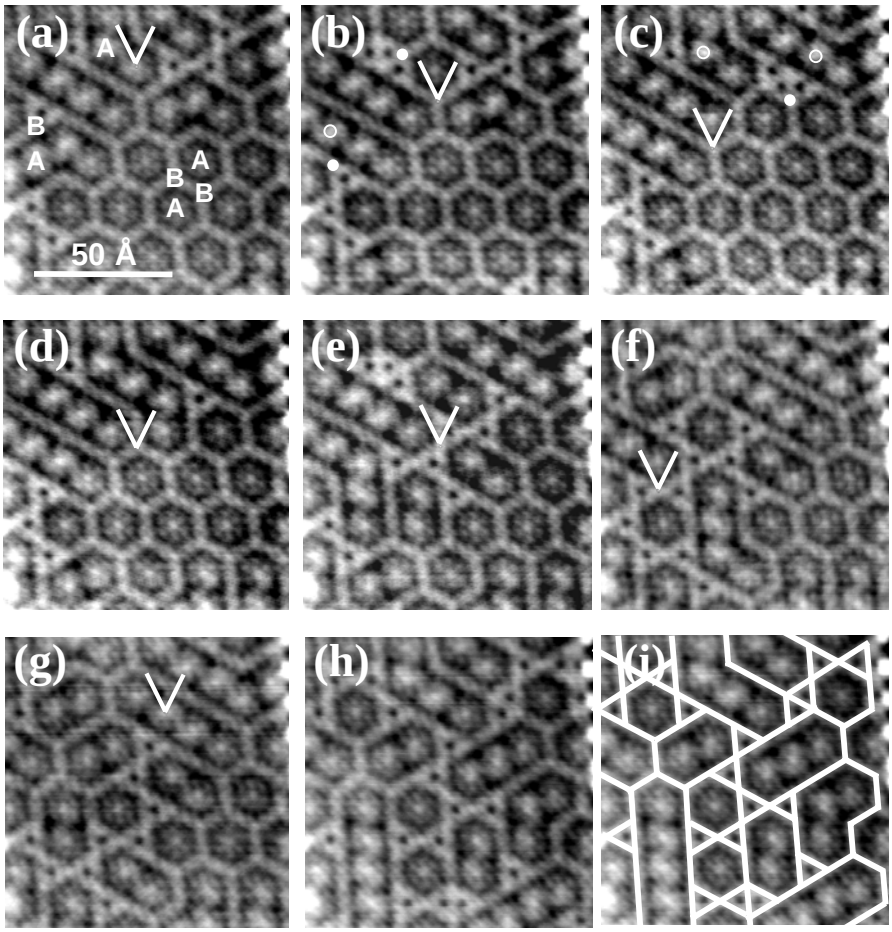

Fig. 7.6. Series of STM images (V = 1500 mV , I = 0.20 nA, 10×10 nm²). After imaging each of the frames (a)-(g) a voltage pulse is applied (Δz = 1 Å, V = +2.6 V) at the position indicated by the tip symbol. The conformations of several molecules change with each applied voltage pulse as can be seen comparing subsequent images. In (a) the conformations A and B are indicated for some molecules. The molecules, which are switched within the first two manipulations, are marked in (b) and (c): The change from A to B is indicated by an open circle and changes from B to A by a dot. In (i) (same measurement as (h)) neighbouring B type molecules are connected by white lines, guiding the eye along the paths of highest LDOS at 1.5 eV above E_F. The changes can be followed concentrating on the patterns formed by these lines.

Another form of STM induced manipulation of molecules inside a monolayer structure has been used for HPB molecules. In this case, it is possible to change the orientation of molecules by STM induced voltage pulses. The monolayer structure of HPB is described in section 6.1.1. As stated before, the HPB molecules are found in two different conformations, i.e. A type ($\vec{m}$ parallel to the

$[01\bar{1}]$ direction) and B type molecules ($\bar{m}$ rotated 30° with respect to $[01\bar{1}]$). By applying voltage pulses of at least 2.5 V between sample and tip, the conformation (i.e. orientations) of molecules in the vicinity of the tip changes randomly. Between two scans of the series of images shown in Fig. 7.6, the tip is moved to the indicated position. Then the feedback loop is disabled, the distance is decreased by $\Delta z = 1$ Å, and a voltage of +2.6 V is applied to the sample for 1 s. In a subsequent scan it can be observed that several molecules have changed their orientation, i.e. conformations have changed between A and B.

However, the induced rotation occurs randomly between A and B and vice versa, and it was also not possible to induce the rotation on only one selected molecule. In most cases several molecules within the vicinity of the chosen molecule change their conformation. It has been checked that molecules are not switched during the imaging mode, i.e. no conformational change is observed without a vertical manipulation between two images. By changing the conformation of single molecules inside the monolayer structure the LDOS of the supramolecular structure changes significantly, as can be observed in Fig. 7.6. While the molecules in conformation A are always imaged equally, showing one central and six surrounding protrusions, reflecting the molecules chemical structure, the image of molecules in conformation B, on the contrary, strongly depends on the conformation of the surrounding molecules: While the apparent height at the position of the side groups pointing into the direction towards other B type molecules is enhanced, the apparent height at side groups pointing towards A type molecules is decreased. (Although the molecular contrast does also depend on the applied bias voltage, this effect is observable over the whole range between -2 V and +2 V). Therefore the LDOS is increased between adjacent B type molecules and is decreased between molecules of different conformation. This effect can not be explained by topological effects alone; presumably the increased LDOS between B type molecules is due to an increased wave-function overlap between their side groups, because of their close proximity, as can be seen in the structure model in Fig. 6.1. As a consequence, paths of increased LDOS are formed between B type molecules, as highlighted in Fig. 7.6(i), and the networks formed by these paths can be changed by the induced conformational changes of the molecules.

7.3 Manipulation of Atoms with Molecules

Besides the imbedding of molecules in the matrix of molecular islands, another possibility of anchoring HB-HPB molecules on the Cu(111) surface is given by the adsorption of the molecules on defects or adatoms. While imaging of HB-HPB molecules on the defect-free surface was not possible without moving them under the influence of the STM tip, the molecules can be manipulated on Cu adatoms, thus increasing the diffusion barrier of the molecules and therefore allowing imaging with the STM. To produce adatoms, the tip is indented a few nm into the substrate at applied bias voltages between +4 and +8 V.[140] Thereafter, adatoms are found in the vicinity (several ten nm) of the tip crash. These tip crashes are less deep than the ones performed for the creation of dislocation steps, where the tip was crashed several 10 nm into the surface (see section 5.4).

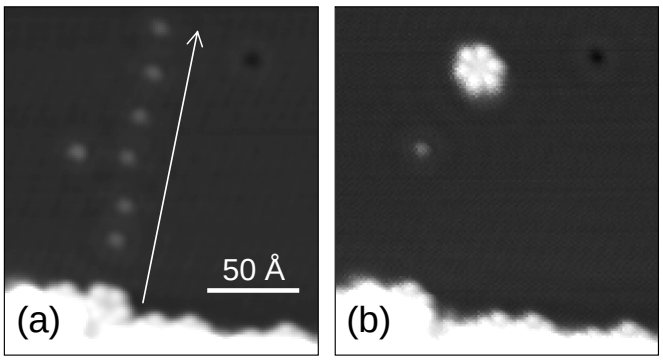

Fig. 7.7. STM images (I = 0.2 nA, V = 100 mV), before (a) and after (b) the manipulation of a single HB-HBP molecule across 6 Cu adatoms. The adatoms have been brought into a line before by atomic manipulation.

A HB-HPB molecule can be manipulated on a surface containing adatoms, thereby all adatoms along the manipulation path will be accumulated under the molecule, up to a maximum number of six atoms. An example is shown in Fig. 7.7, where a molecule is manipulated along a line of six adatoms. The atoms have been aligned before by atomic STM induced manipulation. They are collected by the molecule during its manipulation. After absorption of the atoms, the molecule is stabilized on the surface, allowing the imaging with a tunnelling current of 0.1 nA, without moving the molecule.

In Fig. 7.8 several single adatoms have been collected by the molecule one at a time. The diffusion barrier increases with the number of adatoms that are absorbed by the molecule, as can be concluded by comparing the maximum tunnelling resistances, needed to manipulate the molecules for the different cases. For molecules with one absorbed atom R_m is in the order of 10^{10} Ω, while the tip height has to be further reduced, i.e. R_m has to be decreased to 10^7 Ω, to move a molecule with five absorbed atoms. It is not possible to manipulate a molecule with six absorbed atoms with 10^7 Ω and a further reduced tunnelling resistance results in destruction of the molecule.

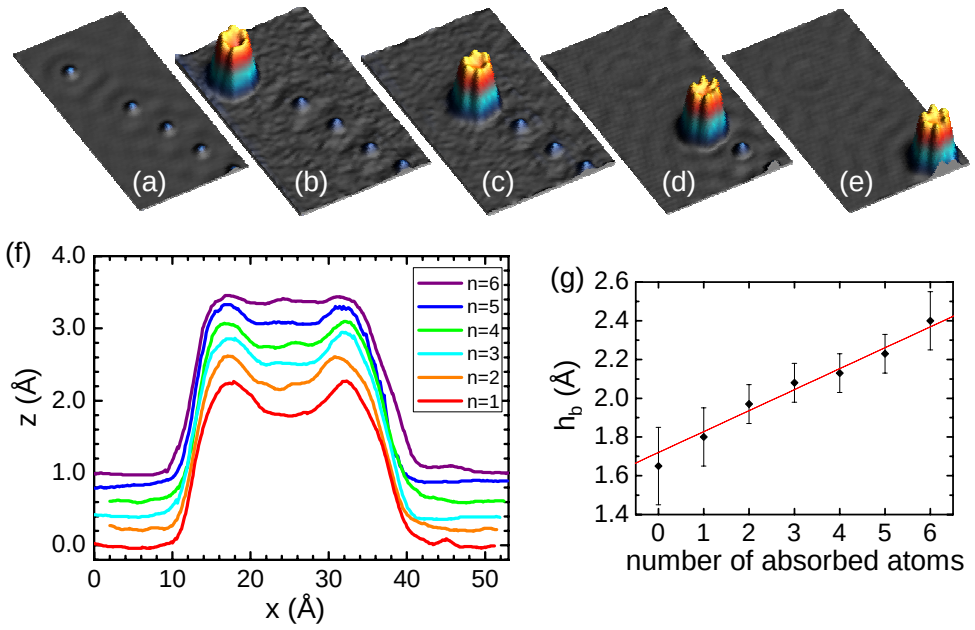

Fig. 7.8. (a)-(e) Series of pseudo 3-dimensional images of a single HB-HPB molecule. By manipulating the molecule to the adsorption positions of the adatoms, four single Cu atoms are absorbed by the molecule, one at a time. All images are recorded with identical bias, V = 100 mV, but with different currents: (a), (d) and (e) with a current of I = 0.1 nA, while the tunnelling current had to be reduced to I = 5 pA in (b) and (c), due to the low diffusion barrier of the molecule with one or two absorbed atoms. (f) Line profiles of the molecule with 1 to 6 adsorbed atoms. Profiles are taken across molecular centre and two opposite legs, the heights are shifted for better visibility. (g) Averaged apparent molecular board height (h_b) in dependence on the number of atoms absorbed under the molecular core (at a bias of V = 100 mV).

Moreover, the appearance of the molecular board is also influenced by the absorbed adatoms. The apparent height of the molecular board increases with the number of absorbed adatoms. Line profiles of molecules with one to six absorbed atoms are shown in Fig. 7.8(f). In Fig. 7.8(g) the apparent averaged board height h_b is plotted against the number of adatoms absorbed by the molecule (n). The average board height h_b has been determined by taking the mean value of the apparent height in the area of the molecular board, averaging over several (~10) STM measurements. Since the board height shows some dependence on the tunnelling bias, all measurements reported in Fig. 7.8 have been performed at identical bias, V = 100 mV. As one can see, the apparent board height increases linearly with the number of absorbed adatoms, by about (0.11 ± 0.03) Å per atom absorbed by the molecule. The appearance of the molecular legs is not affected by the adsorption of adatoms, leading to the conclusion that the collected atoms are located under the molecular board. Such behaviour is similar to the thermally activated restructurings that have been observed in case of the Lander molecule, where metal adatoms are also found under the planar aromatic molecular board[96].

In the case of HB-HPB on Cu(111), the molecule has to be manipulated vertically to reveal the atomic structure formed under the molecule. Transferring HB-HPB molecules to the STM tip is possible, as has been described in the previous section 7.2. If the HB-HPB molecule is transferred to the tip by vertical manipulation, the collected atoms remain on the surface and form a cluster at the former position of the molecular board.

In the series of images shown in Fig. 7.9, two adatoms have first been collected under the molecule. Then the whole metal-organic complex of (HB-HPB + 2Cu) is laterally moved with the STM tip. In the last stage, the molecule is transferred to the STM tip, leaving the two Cu atoms on the surface. The adsorbate remaining on the surface in Fig. 7.9(e) can be clearly identified as a Cu dimer by the apparent height of 0.6 Å (in contrast to the 0.4 Å of a single Cu) and by the characteristic fuzzy shape in STM images (the appearance of a Cu dimer on Cu(111) is fuzzy, since the two adatoms oscillate between adjacent hexagonal close-packed (hcp) and face centred cubic (fcc) sites as pointed out by Repp et al.[83, 141]).

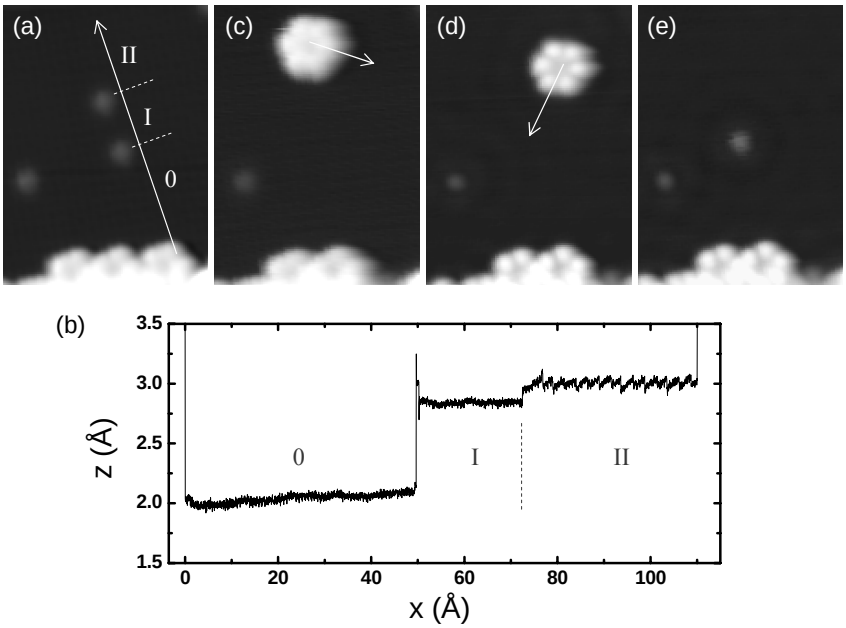

Fig. 7.9. Moving atoms with molecules. Between each STM image (a-d) (I = 0.2 nA, V = 100 mV, 8×13 nm²) a lateral manipulation has been performed, in the direction as indicated by the arrows. A HB-HPB molecule is manipulated across two single Cu adatoms (a). The manipulation is performed in constant current mode with $I = 4\times10^{-8}$ A, V = -30 mV. The manipulation signal, i.e. tip height is shown in (b). It can be divided in three different parts, corresponding to manipulation of the molecule with no (0), one (I), and two (II) Cu atoms underneath. The atoms are absorbed by the molecule, and both, molecule and adatoms are moved to the final position (c). Molecule and atoms can be moved together (d). When the molecule is transferred to the tip (occurring at the end of the lateral manipulation indicated in (d)), the two adatoms are left on the surface, in the formation of a dimer (e).

The manipulation signal shown in Fig. 7.9(b) corresponds to the constant current manipulation between images (a) and (c) during which the two atoms have been picked up. The tip height increases by about 0.8 Å when the molecule reaches the adsorption site of the first atom and further increases by another 0.2 Å after the movement of the molecule across the adsorption site of the second adatom. This height increase corresponds to an increased tunnelling conductance due to the absorbed atoms. Furthermore, the internal structure of the signal abruptly changes after the second atom has been picked up (in region II). Before that point (in region 0 and region I) no internal structure of the signal is visible (besides noise), probably corresponding to a manipulation in sliding mode, as described before.

However, when the second atom is located under the molecule (region II), a clear pushing signal is visible, similar to the signal obtained for the manipulation of a single atom (see Fig. 2.4). The signal shows that with two atoms underneath the molecule, the diffusion barrier is increased so far that the whole complex of atoms and molecule hops between specific adsorption sites during the manipulation (as is typical for pulling). Contrary, with none or one absorbed atom the corrugation of the surface potential is so small compared to the tip-adsorbate interaction that the tip-sample distance remains unaffected by the surface corrugation during manipulation.

7.4 Conclusions

HBC and HPB derivatives, described in section 3.3.2, have been laterally manipulated on Cu(111). Manipulation signals have been compared, showing characteristic differences in the movement of the molecules. These differences could be explained by the different molecule bonding due to its chemical structure to the tip on the one hand and to the sample on the other hand (see also section 6.2).

The HB-HPB system was investigated in detail, finding that molecular self-organisation could be combined with STM manipulation techniques to produce atomically defined man-made structures. On the one hand, the lateral and vertical manipulation of HB-HBP molecules allowed to assemble molecules in the matrix of the molecular monolayer structure, thus increasing the precision and reproducibility of man-made supramolecular structures fabricated by STM induced manipulation of large molecules. In this context molecular self-ordering is employed in lateral manipulation experiments, which causes the molecules to lock-in once they have been manipulated to the edge of a molecular island. This is a remarkable result, taking into account that all experiments have been performed at cryogenic temperatures where molecular diffusion processes are frozen in.

In the case of HPB, the induced change of conformation of molecules inside a

monolayer structure has been shown, thereby changing the LDOS between the adsorption sites of molecules. Techniques as these, which guarantee a defined geometry of the connected molecules by molecular self-organisation, but allow STM induced modifications of the structure and thereby also of the electronic properties, are of high interest for the future build-up of molecular electronic devices.

Moreover, it has been demonstrated that single HB-HBP molecules can be utilized, in combination with the STM, to move and aggregate adatoms. In particular, when single HB-HPB molecules are laterally manipulated to the adsorption sites of adatoms, the following observations are made:

- The diffusion barrier of the molecules increases with the number of adatoms underneath the molecule.
- The atoms stay under the molecule when the molecule is laterally manipulated.
- A maximum number of 6 adatoms can be accumulated under the core of a single HB-HPB molecule.

The situation shows similarities to the induced restructurings that have been found for the Lander molecules [96, 100](see section 4.2), in all cases atoms are rearranged under the aromatic molecular board, allowing an increased overlap between electronic states of the metal and delocalized π-states of the molecules.