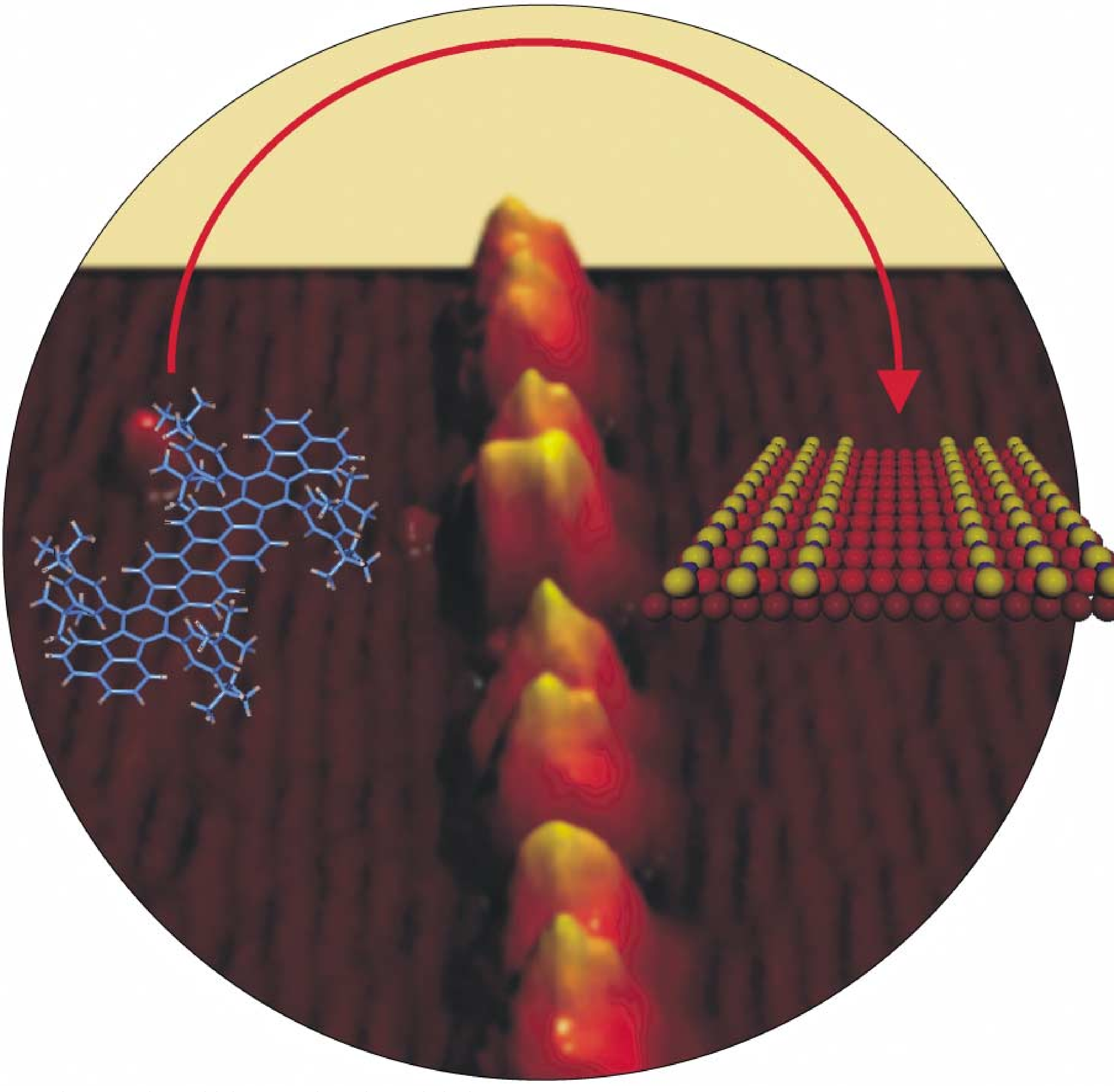
Zuschriften



Das Wachstum einzelner molekularer Baueinheiten lässt sich durch kleine Veränderungen an der Templatoberfläche exakt regulieren. In der Zuschrift von F. Besenbacher et al. auf den folgenden Seiten wird gezeigt, wie die Breite der Streifen eines Cu-Cu/O-Übergitters die Orientierung bestimmt, in der Moleküle auf der Oberfläche adsorbieren.

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One-Dimensional Assembly and Selective Orientation of Lander Molecules on an O–Cu Template**

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Properly functionalized organic molecules are promising building blocks for nanoscale electronic circuits.[1] A major challenge is to develop a novel technology to assemble such molecular elements in a planar conformation into a predetermined architecture with atomic-scale precision.[2] This requires the ability to create an ordered pattern for the molecular adsorption sites and to steer the adsorption orientation of the molecules into a geometry that will enable the interconnection of the molecules in a circuit. Here we demonstrate that the striped periodic supergrating created by a controlled oxidation of a Cu(110) surface[3] is a suitable nanoscale template for the assembly of individual molecular building blocks, such as the so-called "Lander molecules", into well-ordered arrays of long molecular chains. Furthermore, we show that by controlling the width of the nanotemplate we can select the adsorption orientation of the molecules, and thereby steer their alignment along the specific direction of the template.

The supergrating is created by exposing a clean Cu(110) surface to 4–6 Langmuir ($1\,\mathrm{L}=10^{-6}$ Torr s) of oxygen at 625 K. This procedure leads to a self-organized reconstruction with alternating one-dimensional (1D) bare Cu stripes and (2×1)-O reconstructed regions, consisting of Cu–O added rows, both aligned along the [001] surface direction (Figure 1 a).[3] By controlling the oxidation process, it is possible to adjust the dimensions of the supergrating. For instance, increasing the temperature while keeping the exposure constant leads to an increase in the distance between the stripes, which also become broader, whereas increasing the exposure at the same temperature leads to narrower stripes. The finest nanopattern consists of bare Cu troughs 2.0 ± 0.3 nm wide, separated by Cu–O regions 5 ± 2 nm wide (see Figure 1 b). The Cu–O template exhibits long-range order on the length scale of several hundred nanometers.

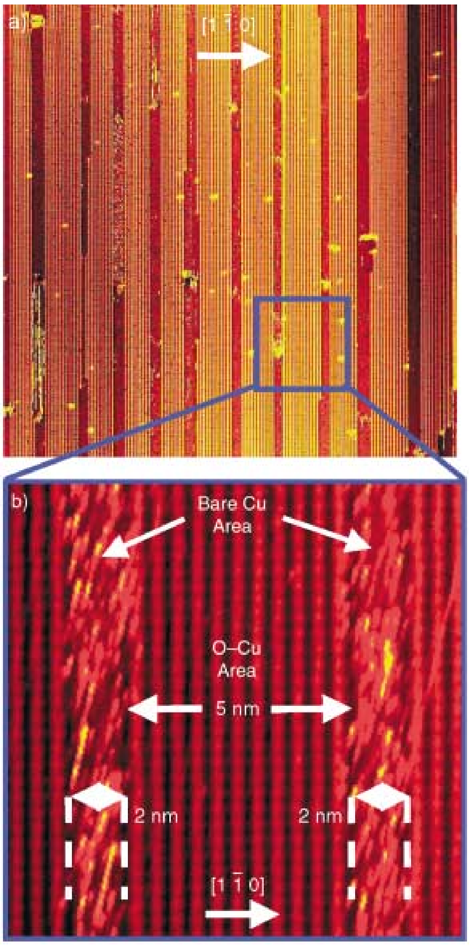

Figure 1. a) 70×70 nm^2 STM image of the Cu–O/Cu periodic nanopattern resulting from O_2 exposure. A certain fraction of the derived image has been added to enhance the resolution; b) 14×14 nm^2 STM image of a partially oxidized Cu(110) surface recorded at room temperature. 2×1 reconstructed oxidized areas can clearly be distinguished, separated by bare Cu stripes running along the [001] direction. The image is rotated so that the [001] direction is vertical. The original scan direction can be easily recognized as the direction of the spike noise originated from the fast diffusion of kink atoms in the Cu–O edges at room temperature.

Onto this alternating Cu–O/Cu template, we have deposited "Single Lander"[4] molecules (SL, $C_{90}H_{98}$). The SLs are composed of a polyaromatic hydrocarbon central board with four lateral 3,5-di-*tert*-butylphenyl substituents acting as

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"spacer legs" as shown in Figure 2a. When adsorbed on a metal surface, high-resolution scanning tunneling microscopy (STM) images under ultraclean conditions reveal that the SL molecules are imaged as four lobes (Figure 2b).[5] From STM images calculated using the elastic-scattering quantum chemistry (ESQC)[6] routine complemented with molecular mechanics (MM2) calculations, we can conclude that each lobe results from the tunneling channels opened by the molecular orbitals of the spacer legs. This analysis also shows that SL molecules on a clean Cu(110) surface adsorb with their board aligned along the [1$\bar{1}$0] direction of the substrate. No ordered molecular structures are observed even at high coverage.[5c]

When deposited on the periodic Cu–O/Cu nanotemplate, the SL molecules are found to adsorb exclusively on the bare Cu regions in between the Cu–O areas, which results in the formation of well-ordered 1D molecular chains (Figure 2c). The driving force for the preference of SL molecules to adsorb exclusively on the bare Cu stripes and not on the (2x1)-O areas of the O–Cu nanotemplate can be understood as follows: From previous studies on the adsorption of SL and related molecules on metal substrates,[5,7] the main interaction between the molecule and the substrate is known to be the van der Waals attractive interaction between the central π board of the SL and the metallic surface. The binding of the SL molecules to the substrate is therefore weaker on the oxidized areas than on the bare Cu stripes, since the oxygen partially withdraws the charge density of the underlying metal; the attractive interaction described above is thereby decreased.

The conformations of the individual SL molecules in the chains can be determined by comparing high-resolution STM images (see Figure 2d) with calculated ESQC images (Figure 2e and f). We find that the conformations of the molecules adsorbed on the bare Cu stripes of the nanotemplate are identical to those found on a virgin Cu(110) surface, with the molecular board aligned along the [1$\bar{1}$0] direction. Thus, the boards of the molecules are perpendicular to the direction of the molecular chain (Figure 2 g and h).

Identifying the driving force for the preference of molecules to adsorb on the bare Cu areas also provides insight into controlling the orientation of the Lander molecules adsorbed on Cu stripes. Since the SL (board length ≈1.7 nm) fits into the bare Cu stripe with its board

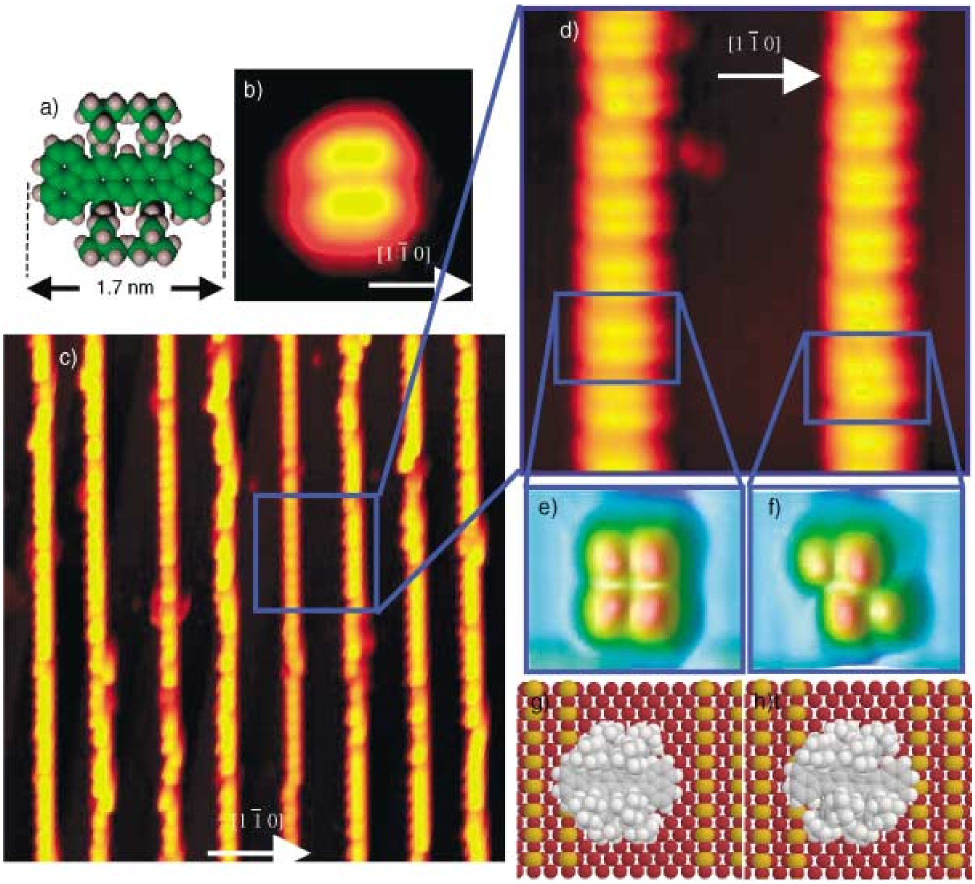

Figure 2. a) Filled-space model of the Single Lander (SL) molecule; b) typical 3×3 nm^2 STM image of the SL molecule on a clean Cu(110) surface revealing the SL as four lobes corresponding to the spacer legs (see text); c) 60×60 nm^2 STM image showing the molecular chains formed after the deposition of SL on the nanopatterned Cu–O surface. The molecules adsorb exclusively on bare Cu stripes; d) 14×14 nm^2 high-resolution STM image. The individual SL molecules can be individually resolved, and their conformation can be extracted thereby; e,f) ESQC-simulated STM images of the SL on the bare Cu stripes, with two different conformations; g,h) ball models of the SL adsorbed on the nanopatterned Cu–O surface from which the simulated STM images e) and f) were extracted. These models show that the SL adsorbs on bare Cu areas with the board perpendicular to the direction of the stripes.

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perpendicular to the direction of the oxygen-induced nanotemplate, no energetic reasons exist for the SL to change its adsorption geometry on the nanotemplate with respect to the one adopted on a virgin Cu(110) surface, that is, aligned along the $[1\bar{1}0]$ direction of the substrate. If, on the other hand, new Lander molecules were synthesized with a board longer than the width of the stripe, and the molecules were still oriented perpendicular to the template, part of the board would be positioned on top of the oxidized area. In this case one would anticipate the Lander molecules to adopt a more energetically favorable orientation in which the board would fit completely within the bare Cu area of the nanotemplate.

To test this hypothesis, we have designed and synthesized another molecule of the Lander family, the "Violet Lander" (VL, $C_{108}H_{104}$).[7b] Figure 3a shows a filled-space model of the VL molecule. Similar to the SL, the VL also consists of a polyaromatic π board with four spacer legs. The VL (board length ≈ 2.5 nm) is however ≈ 0.8 nm longer than the SL.

When deposited on a Cu(110) surface, the VL molecule is also imaged as four lobes corresponding to the tunnel current passing through the spacer legs into the substrate. The VL board is found to be oriented along the $[1\bar{1}0]$ direction (Figure 3b) on the clean Cu surface, as was the case for the SL molecule. From a thorough comparison of high-resolution STM images with calculated ESQC images on the nanopatterned surface, however we find that for the VL molecule the board is now indeed preferentially aligned along the direction of the nanotemplate stripes. For the smallest Cu stripe (1.8 nm or about 3.5 Cu–O rows) all VL molecules in the template Cu areas align their boards along the template (see Figure 3c, e, and g). If the bare Cu stripes are wider, the boards of some VL molecules are found to form an angle of 20° with respect to the [001] direction of the Cu–O rows (see Figure 3d, f, and h). If other Lander molecules were to be synthesized with a longer board than that for the VL, we would expect them to show an even stronger tendency to align along the stripe. In any case, we have shown that the supergrating not only provides specific adsorption sites for the molecules, but it also steers the orientation of the adsorbed molecules, which forces them to align along the preferential direction of the nanotemplate.

The distance between the molecular boards of adjacent VL molecules aligned along the bare Cu stripes can be estimated as the distance between the front legs of one molecule and the rear legs of the next one minus 1.3 nm, which is twice the distance the molecular board extends beyond the position of the spacer legs (see Figure 4a). Although this interboard distance depends on the degree of filling of the bare Cu stripe, it can be as small as 0.3 nm for a Cu stripe fully covered with Lander molecules (see Figure 4b). This interboard separation corresponds to the closest packing distance expected from the van der Waals H–H contact distance (0.24 nm).

In conclusion, by using a self-organized oxygen-induced template, we have succeeded in controlling the parallel fabrication of long one-dimensional molecular nanostructures with a lateral resolution of about 5 nm, which is presently not accessible by conventional lithographic techniques. Furthermore, we have shown that the template is able to steer the Violet Lander molecules to align their boards along the direction of the molecular chain. Unlike other previously reported methods for obtaining 1D molecular chains, our approach does not make use of serial fabrication techniques based on STM manipulations,[2a,f] and it is not based on a weak

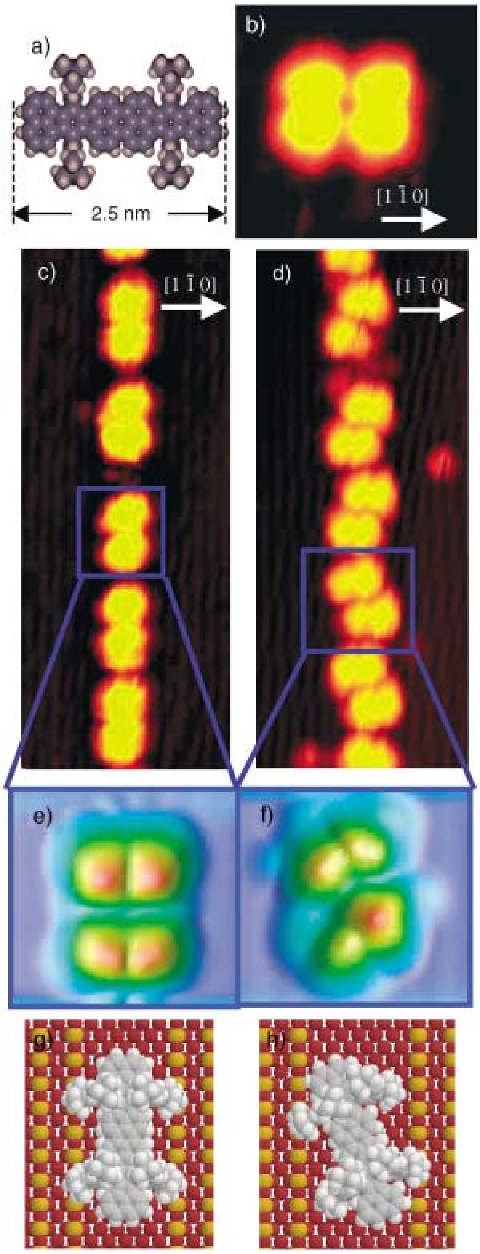

Figure 3. a) Filled-space model of the Violet Lander (VL) molecule; b) typical 3 × 3 nm² STM image of the VL molecule on a clean Cu(110) surface, which reveals the VL as four lobes corresponding to the spacer legs (see text); c,d) 8 × 20 nm² STM images showing the molecular chains formed after the deposition of VL on the nanopatterned O–Cu surface. The molecules adsorb exclusively on bare Cu stripes, but their orientation is no longer perpendicular to the direction of the chain. The molecules are found either perfectly aligned with the direction of the chain (c) or forming an angle of 20° with respect to that direction (d); e,f) ESQC-simulated STM images of the VL on the bare Cu stripes, with two different adsorption geometries; g,h) ball models of the VL adsorbed on the nanopatterned Cu–O surface from which the simulated STM images e) and f) were extracted.

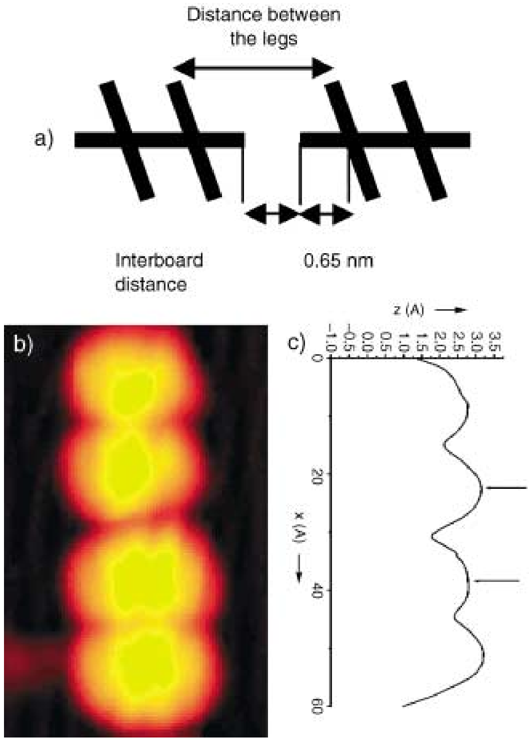

Figure 4. a) Cartoon illustrating how to estimate the interboard distances from the distances between the legs of consecutive VL molecules; b) 3×6 nm^2 STM image showing two VL molecules aligned along the bare Cu stripe in Van der Waals contact, as determined from the interboard distances estimated from the scan line in c); c) scan along the molecular boards of the molecules shown in b).

hydrogen-bond-directed assembly.[2b–d] This greatly enhances the thermal stability of the molecular structures up to temperatures of 350 K. In general, the interplay between self-organized chemical patterning of the substrate and a rational design of molecular structure can be exploited to self-fabricate integrated nanoelectronic devices.

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Keywords: molecular electronics · nanostructures · scanning probe microscopy · self-assembly · surface analysis

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