

## Substrate Templating Guides the Photoinduced Reaction of C<sub>60</sub> on Calcite\*\*

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**Abstract:** A substrate-guided photochemical reaction of C<sub>60</sub> fullerenes on calcite, a bulk insulator, investigated by non-contact atomic force microscopy is presented. The success of the covalent linkage is evident from a shortening of the intermolecular distances, which is clearly expressed by the disappearance of the moiré pattern. Furthermore, UV/Vis spectroscopy and mass spectrometry measurements carried out on thick films demonstrate the ability of our setup for initiating the photoinduced reaction. The irradiation of C<sub>60</sub> results in well-oriented covalently linked domains. The orientation of these domains is dictated by the lattice dimensions of the underlying calcite substrate. Using the lattice mismatch to deliberately steer the direction of the chemical reaction is expected to constitute a general design principle for on-surface synthesis. This work thus provides a strategy for controlled fabrication of oriented, covalent networks on bulk insulators.

**F**abricating functional structures on solid surfaces is of utmost importance in numerous fields, ranging from daily-life applications, such as hydrophobic, self-cleaning, or biocide surfaces, to emerging technologies, such as molecular electronics.<sup>[1]</sup> In this context, molecular self-assembly<sup>[2]</sup> has been identified as an elegant strategy for creating surface functionalization.<sup>[3]</sup>

Molecular self-assembly benefits from the impressive variety and flexibility of organic chemistry, providing tailor-

made building blocks to encode the desired structure and functionality.<sup>[4,5]</sup> However, as molecular self-assembly relies on reversible intermolecular interactions to arrive at the thermodynamic minimum, the resulting structures are inherently instable. To provide stability, on-surface synthesis has been explored as a promising route to create stable structures on surfaces.<sup>[6,7]</sup> Furthermore, on-surface synthesis allows for creating extended conjugated systems that are desired because of their superior electron transport properties, when aiming at electrically conductive structures for molecular electronics.<sup>[8]</sup>

Recently, on-surface synthesis has been demonstrated to provide the possibility to covalently link molecular building blocks on metallic substrates.<sup>[8–14]</sup> An important step towards exploiting the potential of on-surface synthesis for molecular electronics is to extend the range of substrates to bulk insulators, as they provide electronic decoupling of the molecular structures from the underlying support.

Very recently, covalent linking upon thermal activation has been demonstrated on an insulating surface, benefiting from the strong binding of a carboxylic acid moiety to a calcite substrate.<sup>[15]</sup> For many other molecule-insulator systems, however, thermally activated linking fails owing to the typically weak molecule–surface interaction, which results in desorption before the reaction temperature is reached. To overcome this limitation, we follow a novel strategy for insulator-supported systems, where we employ photochemical activation. This approach prevents molecular desorption as often present upon thermal activation.

In this study, we induce non-thermal [2+2] cycloaddition by irradiation of C<sub>60</sub> fullerenes. This well-known reaction has been widely studied in bulk C<sub>60</sub><sup>[16,17]</sup> and in C<sub>60</sub> thin films on metal substrates,<sup>[18,19]</sup> and it is known to result in a two-dimensional hexa-polymer in the bulk. We deposit C<sub>60</sub> molecules onto the (10.4) cleavage plane of calcite (CaCO<sub>3</sub>), which is a bulk insulator.<sup>[20]</sup> The C<sub>60</sub> molecules form ordered islands, wetting the surface.<sup>[21]</sup> Upon irradiation with a laser, we induce covalent linkage. In this work, we provide a detailed picture explaining how the lattice dimensions of calcite dictate the formation of well-oriented covalent networks.

The (10.4) cleavage plane of calcite has a rectangular unit cell of size 0.50 nm × 0.81 nm (Figure 1 a). C<sub>60</sub> forms a hexagonally-ordered monolayer on the calcite surface (Figure 1 b). In drift-corrected<sup>[22]</sup> atomic-force microscopy (AFM) images, we measured the distance between adjacent C<sub>60</sub> molecules, revealing the well-known C<sub>60</sub>–C<sub>60</sub> packing distance of 1 nm, in excellent agreement with previously determined values on calcite,<sup>[21]</sup> alkali halides,<sup>[23]</sup> and in bulk C<sub>60</sub>.<sup>[24]</sup> Besides the

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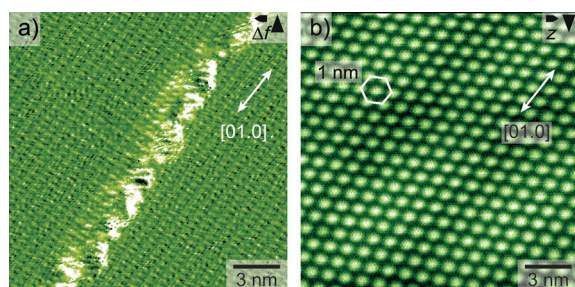
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**Figure 1.** AFM images of the clean calcite (10.4) surface with a step edge (a) and of a monolayer island of  $C_{60}$  on calcite (b).

hexagonal arrangement, a moiré pattern with a periodicity of  $(6.1 \pm 0.5)$  nm is clearly visible in our AFM images (Figure 2a), as evident from alternating bright and dark rows along the [01.0] direction.

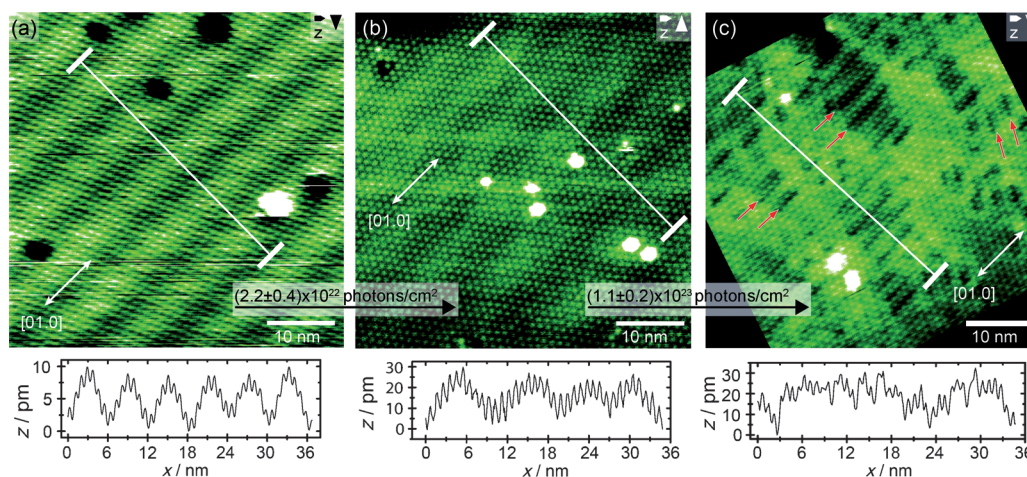
When we irradiate  $C_{60}$ -covered calcite samples with UV light (405 nm), the coverage and the overall distribution of  $C_{60}$  molecules do not notably change. This indicates that the substrate does not heat up significantly during irradiation.<sup>[25]</sup>

In sharp contrast to the large-scale observations, the molecular-scale details change significantly upon irradiation, as shown in Figure 2 (further images are presented in the Supporting Information, Figure S1a,b). A monolayer of  $C_{60}$  was exposed to a total number of  $(2.2 \pm 0.4) \times 10^{22}$  photons  $\text{cm}^{-2}$  (Figure 2b). The most prominent change concerns the aperiodic moiré pattern, clearly indicating that the  $C_{60}$  islands no longer form a perfect periodic superstructure. This is also evident from the extracted line profile, showing an aperiodic modulation perpendicular to the [01.0] substrate direction. After extended irradiation with a total number of  $(1.3 \pm 0.3) \times 10^{23}$  photons  $\text{cm}^{-2}$ , the molecular arrangement changes even more (Figure 2c). The moiré pattern vanished completely, clearly indicating a change in the intermolecular distances. Instead of the moiré pattern, dark lines (indicated by the red arrows in Figure 2c) are identified in the image. These dark lines are gaps between domains of

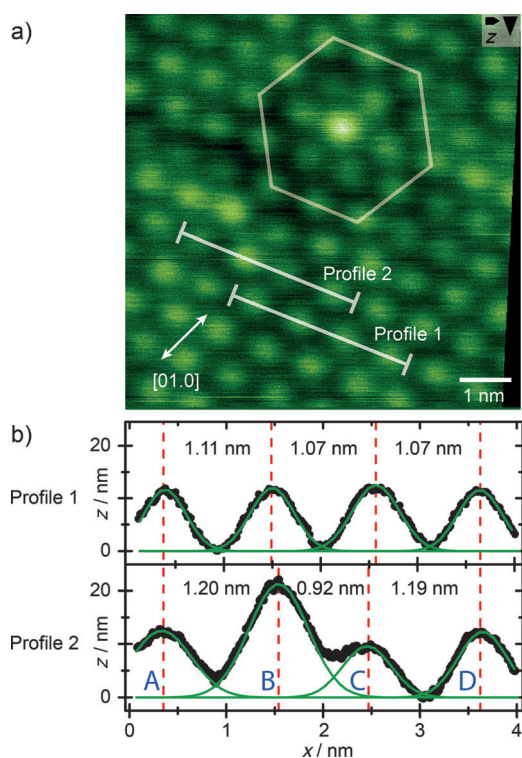
covalently linked  $C_{60}$  molecules, as will be corroborated in the following. As can be seen, the domains are predominantly aligned along the [01.0] substrate direction.

Evidence for the covalent linkage is given by a detailed analysis of the images. To provide independent evidence for the capability of our setup to induce covalent linkage, both UV/Vis spectroscopy as well as mass spectrometry were performed on thick  $C_{60}$  films (Supporting Information, (Figures S3 and S4).

To elucidate the morphological changes in more detail, we analyze drift-corrected images (Figure 3a). We observe two distinct features in this image. First, several  $C_{60}$  molecules appear brighter than the average. Second, some of the  $C_{60}$ - $C_{60}$  distances are changed as evident from an analysis of the spatial separation of the molecules (Figure 3b). Profile 1 reveals the corrugation of four molecules with equidistant intermolecular spacing of  $(1.08 \pm 0.05)$  nm, in good agreement with a row of individual, unreacted molecules. Interestingly, profile 2 differs significantly from profile 1. In profile 2, the two molecules labelled B and C are considerably closer to each other with a distance of only  $(0.93 \pm 0.05)$  nm. Accordingly, the distances towards the two neighboring molecules (A and D) are increased to  $(1.20 \pm 0.05)$  nm and  $(1.19 \pm 0.05)$  nm. This change in distance strongly suggests a successful covalent linking of the two molecules (B and C), as this distance agrees with previously reported values of polymerized  $C_{60}$  in the bulk<sup>[17]</sup> and in thin films.<sup>[19]</sup> The same effect can be seen for a number of  $C_{60}$  molecules in Figure 3a. This finding is particularly obvious when inspecting the group of  $C_{60}$  molecules marked with a hexagon. Six  $C_{60}$  molecules are shifted closer towards the center molecule. To provide further evidence for the change in intermolecular distance, distance histograms before and after irradiation are presented in the Supporting Information (Figure S5a,b), revealing a maximum at a distance of 1.0 nm before reaction. After irradiation, the amount of smaller intermolecular distances at 0.9 nm is notably increased. In Figure 3a, molecules which have reacted with more than one neighbor are imaged brighter



**Figure 2.** A monolayer of  $C_{60}$  on calcite (10.4) before and after irradiation. Line profiles are extracted at the indicated positions, averaged over 60 pixels: a) The pristine film shows a moiré pattern. After irradiation, the moiré pattern becomes aperiodic (b) and eventually vanishes (c). Instead, domains separated by dark lines (red arrows) are observed.

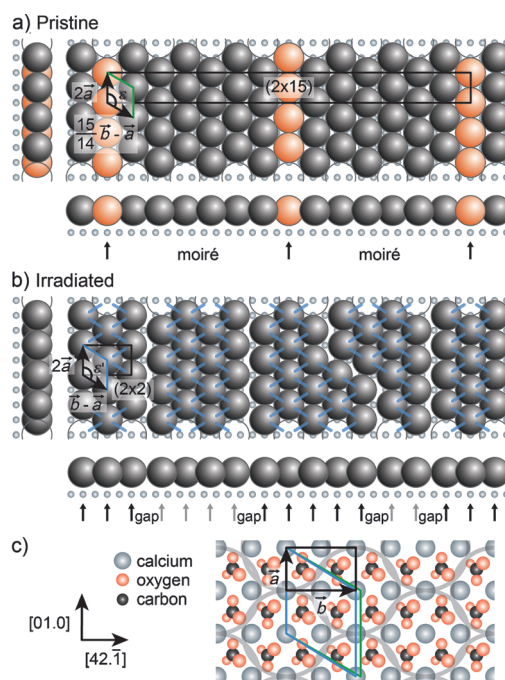


**Figure 3.** a) Image of irradiated  $C_{60}$  on calcite (10.4). A change in brightness of individual  $C_{60}$  molecules can be observed. b) Line profiles from (a) revealing a change in some intermolecular distances.

than others, as demonstrated for molecule B in profile 2 and the center molecule in the hexagon. This leads to an overall heterogeneous appearance of the  $C_{60}$  islands after irradiation.

All previous findings can be explained with a straightforward model. The adsorption structure of pristine  $C_{60}$  on  $CaCO_3(10.4)$  is depicted in Figure 4a.<sup>[21]</sup> The measured intermolecular distance of 1 nm excellently matches the two-fold substrate periodicity along the [01.0] direction. In contrast, along the other substrate direction, the  $C_{60}$  molecules are out of registry with the surface. The  $C_{60}$ – $C_{60}$  row distance in  $[42.\bar{1}]$  direction equals  $15/14b$ , with  $\vec{b}$  being the calcite unit cell vector in  $[42.\bar{1}]$  direction, resulting in a  $(2 \times 15)$  superstructure. As every seventh row of  $C_{60}$  molecules occupies equivalent adsorption positions on the calcite surface (orange-colored  $C_{60}$  molecules in Figure 4a), the observed moiré pattern has a periodicity of  $7.5b = 6.1$  nm,<sup>[21]</sup> which is exactly the periodicity measured in Figure 2a.

We now extend this model to the molecular arrangement after irradiation. As observed in our experiments, irradiation leads to covalent linkage of  $C_{60}$  and results in reduced intermolecular distances. We do not expect a covalent linkage along [01.0] owing to the excellent match of the intermolecular distance of unreacted  $C_{60}$  with the substrate periodicity. Along the other direction, however, the mismatch between substrate periodicity and intermolecular spacing constitutes a driving force for reaction along the  $[42.\bar{1}]$  direction. As shown in Figure 4b, the projected distance of linked molecules along the  $[42.\bar{1}]$  direction is reduced from 0.88 nm to 0.81 nm, thus now excellently matching the periodicity of the



**Figure 4.** a) Adsorption model of pristine  $C_{60}$  on calcite. b) Model for the formation of covalently linked domains with covalent links marked by blue lines. All  $C_{60}$  molecules with identical adsorption position are marked by small black (gray) arrows. For better visibility, only the  $Ca^{2+}$  ions are shown in (a) and (b). c) Calcite (10.4) surface unit cell (black), and the  $C_{60}$  unit cell before (green) and after (blue) irradiation.

underlying substrate. This clearly explains why the moiré pattern vanishes upon irradiation. As indicated in Figure 2c and further corroborated by a more detailed analysis presented in the Supporting Information, the majority of domains is three molecules wide along the  $[42.\bar{1}]$  direction, which can be understood from the fact that further reaction along the  $[42.\bar{1}]$  direction is unlikely due to the increased  $C_{60}$ – $C_{60}$  distance in the gaps separating the domains (Figure 4b). These gaps are visible as dark lines in our images (Figure 2c). This geometrical constraint thus guides the reaction along specific substrate directions and results in covalently linked domains with a  $(2 \times 2)$  superstructure.

In summary, we demonstrate a substrate-guided photochemical reaction on a bulk insulator. The success of the covalent linkage is evident from a shortening of the intermolecular distances, which is clearly expressed by the disappearance of the moiré pattern. Furthermore, UV/Vis spectroscopy and mass spectrometry measurements carried out on thick films demonstrate the ability of our setup for initiating the photoinduced reaction and, thus, corroborate this assignment. The irradiation of  $C_{60}$  results in well-oriented covalently linked domains. Most importantly, the orientation of these domains is dictated by the lattice dimensions of the underlying calcite substrate. Using the lattice mismatch to deliberately steer the direction of the chemical reaction is expected to constitute a general design principle for on-surface synthesis. Our work thus provides a strategy for controlled fabrication of oriented, covalent networks on bulk insulators.

## Experimental Section

All of the experiments were performed in an ultra-highvacuum chamber with preparation parameters as described previously.<sup>[21]</sup> AFM imaging was carried out with PPP-NCH cantilevers from NanoWorld having an eigenfrequency of typically 300 kHz. The cantilevers were excited to oscillate with an amplitude of typically 10 nm. The crystal orientation of the calcite crystals (Korth Kristalle GmbH, Altenholz, Germany) was obtained by AFM measurements with atomic resolution. For the irradiation process, two laser diodes with a wavelength of 405 nm were used. This wavelength was chosen because it has been proven to provide sufficient energy for C<sub>60</sub> polymerization. The diodes were operated at a voltage of 3 V (8 V) and a current of 0.14 A (0.11 A). The output power was determined to approximately 27 mW (81 mW). As the laser diodes were operated outside the chamber, we assume that only a fraction of the output power reached the sample surface. With a transmission coefficient of the borosilicate glass window of 95% at 405 nm, a spot size of approximately 12 mm<sup>2</sup> (79 mm<sup>2</sup>) and a sample size of 8 mm<sup>2</sup>, the incident power was estimated to be about 16 mW (8 mW), which is comparable to the power densities used in previous experiments.<sup>[19]</sup>

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