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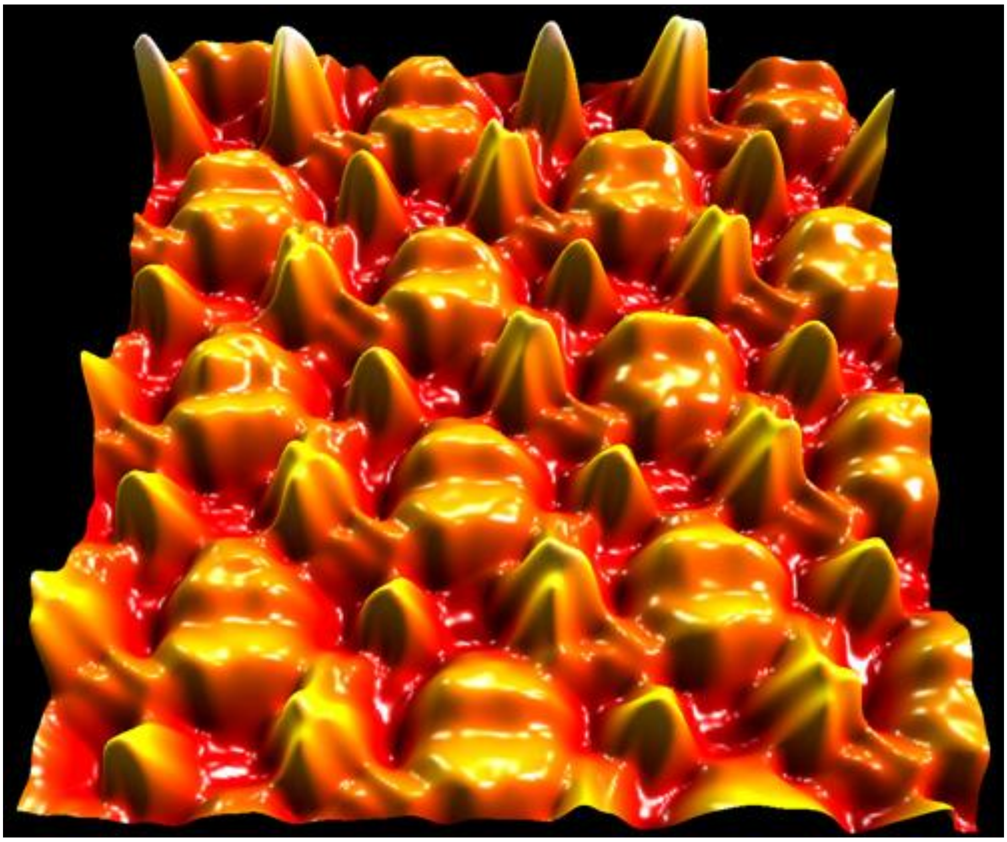

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Cite this: *Chem. Commun.*, 2011, **47**, 10386–10388

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COMMUNICATION

Steering molecular island morphology on an insulator surface by exploiting sequential deposition†

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Received 22nd May 2011, Accepted 2nd August 2011
DOI: 10.1039/c1cc12996a

Depending on the deposition order in coadsorption of C_{60} and SubPc molecules on CaF_2 (111), distinctly different island morphologies can be obtained. We demonstrate that non-equilibrium processes can play a significant role in molecular structure formation and constitute a new route for complex molecular patterning of an insulating surface.

Controlling molecular structure formation on surfaces plays a key role for creating functional surfaces.[1,2] In this context, equilibrium structures have been studied in great detail using molecular self-assembly as a versatile tool for fabricating tailor-made structures.[3] An alternative, while rarely exploited strategy is deliberately employing non-equilibrium processes for increasing structural complexity. A possible approach is to exploit molecular dewetting for steering the growth process, which is different from the well-known growth modes (Volmer–Weber, Stranski–Krastanov, Frank–van der Merwe) as an initially formed wetting layer transforms into thermodynamically stable islands.[4] In this way, unusual island morphologies have been obtained, *e.g.*, upon deposition of C_{60} as well as 3,4,9,10-perylenetetracarboxylic diimide on alkali halide (001) and CaF_2 (111) surfaces.[5–8]

Here, we explore a different strategy namely exploiting the influence of the deposition order in molecular coadsorption to enhance structural complexity. While coadsorption and related phenomena have been studied on metallic surfaces,[9–13] this is a new field for structure formation on insulators.

In this work, sequential as well as simultaneous deposition of C_{60} and chloro[subphthalocyaninato]boron(III) (SubPc) on atomically flat terraces[14] of CaF_2 (111) is investigated by non-contact atomic force microscopy imaging.[15]

We first investigate the structures formed after deposition of 0.6 monolayer (ML) SubPc molecules onto the CaF_2 (111) surface, where we observe hillocks as shown in Fig. 1(a). Deposition of pure C_{60} molecules onto CaF_2 (111) results in the coexistence of two-layer high branched hexagonal and triangular islands in a narrow temperature window around room temperature as reported elsewhere.[8]

In a second step, we take the sample with an initial SubPc coverage of 0.6 ML and deposit 0.1 ML C_{60} molecules, yielding results shown in Fig. 1(b). We find islands similar to those observed before, however, they appear larger in area. No structures were observed that can be assigned to pure C_{60} islands.[8] Thus, the preexisting SubPc islands effectively act as nucleation sites for diffusing C_{60} molecules. In Fig. 1(c), a typical island is shown in detail. The island consists of a hillock in the center surrounded by a flat belt. The center nucleus has about the same height as a pure SubPc island, whereas the outer belt exhibits a homogeneous height of approximately 4 nm (see Fig. 1(d)), which is considerably higher than a pure C_{60} island consisting of two C_{60} layers.

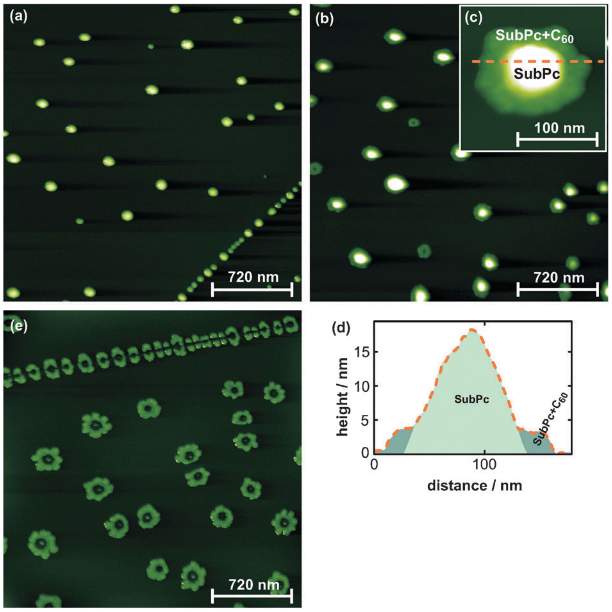

Fig. 1 (a) Image after deposition of 0.6 ML SubPc. Step edges are decorated by molecules as seen in the lower right corner. (b) Image after initial deposition of 0.6 ML SubPc followed by 0.1 ML C_{60}. C_{60} molecules nucleate around the SubPc hillocks. (c) Zoom onto a characteristic island with a SubPc nucleus in the center and an outer belt, consisting of a C_{60}/SubPc intermixed phase. (d) Height profile as indicated in (c). (e) Image after annealing the sample presented in (b) to 505 K for 30 min. In the upper part, a step edge is seen.

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† This article is part of the *ChemComm* 'Molecule-based surface chemistry' web themed issue.

Based on these findings, we tentatively assign the center nucleus of the island to pure SubPc, whereas the outer belt is ascribed to a mixed phase including C_{60} molecules. This assignment is further supported by the annealing experiments presented below. Few smaller islands exist that only consists of an outer belt. These islands are ascribed to originate from initially small SubPc islands, where all SubPc molecules were incorporated into the belt with no molecules remaining for the center hillock.

In an effort to promote the intermixing of remaining SubPc in the center nucleus, the sample is annealed to 505 K for 30 min and subsequently imaged at room temperature (Fig. 1(e)). Similar to what is observed for the non-annealed sample, the remaining islands consist of a 4 nm high outer belt with a bulky and compact shape. The center part of the island, however, where the former nucleus was situated, is no longer occupied but exhibits a pit, where the bare substrate can be imaged (not shown here). From these results, we can unambiguously conclude that the center phase is different from the belt phase. As pure SubPc is known to desorb at 505 K, we take the removal of the center nucleus as a further support for the assignment that the center part indeed consists of pure SubPc. In the absence of SubPc, however, pure C_{60} molecules are known to exhibit a hexagonal ordering, which should be adopted upon annealing.[8] The fact that the surrounding belt is very different from what we know for pure C_{60} islands, thus, supports the above made conclusion of the belt phase being an intermixed phase.

In a next step, we analyze the reverse deposition order, *i.e.*, deposition of 0.1 ML C_{60} followed by 0.3 ML SubPc with results shown in Fig. 2(a). Comparing Fig. 2(a) with Fig. 1(b) readily reveals a qualitative difference, which is arising from reversing the deposition order. This constitutes a clear indication of non-equilibrium structures being involved in the structure formation, as structures in the thermodynamic equilibrium must be identical regardless of the preparation pathway. Comparing Fig. 2(a) to a sample that is exposed to C_{60} molecules solely, small protrusions appear in addition to the large, two-layer high C_{60} islands. These protrusions are similar in shape to the pure SubPc islands described before. Therefore, these small islands are assigned to pure SubPc clusters. It is evident from Fig. 2(a) and confirmed by a more detailed analysis that the C_{60} islands keep their characteristic shape, lateral dimension and internal holes as observed before the SubPc deposition.[8] Close inspection of the structures, however, reveals a more rough island surface than what is known for pure C_{60} islands as shown in the detailed image in Fig. 2(b). Additionally, the islands are more than two C_{60} layers high (see Fig. 2(c)). Thus, it can be concluded that the C_{60} islands are covered by SubPc molecules. Consequently, the SubPc molecules seem to dewet easily from the substrate surface on top of the preexisting C_{60} island. Dewetted SubPc molecules do not pile up as on bare CaF_2 (111), but form a flat layer on top of the C_{60} islands. As a result, a stack consisting of two layers of C_{60} molecules covered by a SubPc layer is created. The outer shape of the island is governed by the underlying C_{60} layers. Upon further increasing the SubPc coverage, the SubPc layer of the stack exclusively grows in height (not shown here). Thus, the height of the stack can be tuned by the coverage of SubPc without affecting the shape and lateral extension of the island. This indicates a stronger attractive interaction of SubPc molecules towards C_{60} as compared to the substrate surface. Next, we anneal the surface as presented in Fig. 2(a) to 505 K for 30 min to investigate whether intermixing of the phases can be thermally activated. Similar to the SubPc center hillock surrounded by C_{60} molecules as discussed before, pure SubPc islands desorb upon annealing (see Fig. 2(d) to (f)). The C_{60} islands do, in contrast, remain on the surface and preserve their characteristic shape and size. This finding demonstrates that C_{60} molecules do not mix with the SubPc layers on top, indicating a stable C_{60} packing within the two-layer high C_{60} stack.

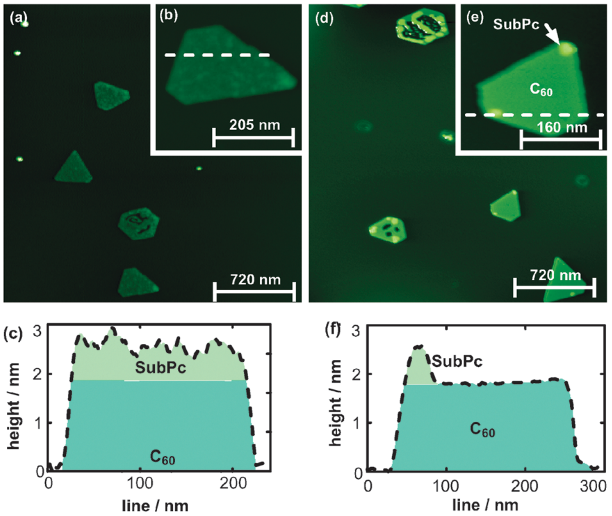

Fig. 2 (a) Image after deposition of 0.1 ML C_{60} followed by 0.3 ML SubPc molecules. Pure SubPc islands can be identified as small hillocks. The flat features exhibit the morphology and lateral extension of C_{60} islands. (b) Zoom onto a SubPc covered C_{60} island. (c) Height profile as indicated in (b). (d) Image after annealing to 505 K for 30 min. (e) Zoom onto a C_{60} island with few residual SubPc molecules. (f) Height profile as indicated in (e).

Thus, in contrast to the findings of the reverse deposition order, the two molecular species do not mix when SubPc is deposited onto a surface with preexisting C_{60} islands. Rather, the C_{60} molecules form islands that remain stable on the surface even after annealing to 505 K, forming a well-defined interface to the post-deposited SubPc molecules.

Finally, we address the issue of simultaneous deposition of both molecular species. Both molecules are deposited simultaneously, yielding a coverage of 0.2 ML for C_{60} and 1.2 ML for SubPc molecules. The result is shown in Fig. 3. The islands exhibit a flower-like shape, which is similar to the outer shape observed for C_{60}/SubPc intermixed phases. In addition, the apparent island height is about 4 nm, which is in agreement with the height of the previously described islands of the intermixed phase. We conclude that a simultaneous deposition of C_{60} and SubPc molecules on the CaF_2 (111) solely results in intermixed phase islands.

In summary, we find that the structure formation of C_{60} and SubPc on CaF_2 (111) clearly depends on the order of deposition. Sequential deposition of first SubPc and second C_{60} yields belt-like islands surrounding a center hillock. Our data provide evidence for the belt phase being an intermixed phase. In contrast,

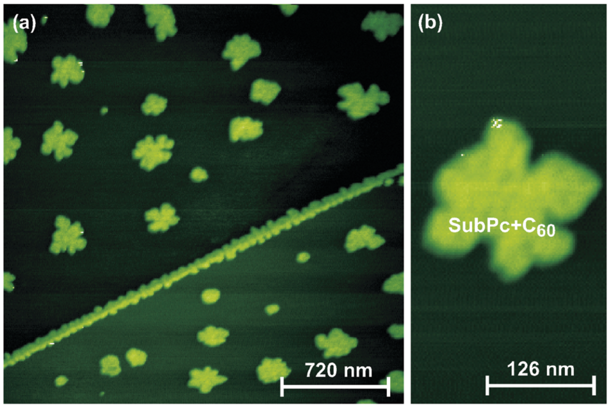

Fig. 3 (a) Two terraces covered by islands formed by simultaneously depositing 1.2 ML SubPc and 0.2 ML C_{60} molecules. The step edge in the center of the image is decorated by molecules. (b) Islands on the flat terraces exhibit a flower-like outer shape.

for the reverse deposition order, no intermixing takes place, but the preexisting C_{60} islands preserve their shape and remain on the surface even after annealing. This is explained by a stable arrangement of C_{60} islands. Simultaneous deposition results in the formation of an intermixed phase, which closely resembles the belt phase observed before. No structures that can be assigned to pure phases are obtained in the case of simultaneous codeposition.

As the main finding we note that the shape of the resulting islands and their thermal stability are steered by the deposition order, indicating that non-equilibrium effects are decisive for the structure formation. A subtle balance between dewetting barrier, interfacial tension and molecular island stability needs to be considered for understanding the complexity in structure formation upon molecular codeposition.

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15 For each experiment, bare CaF_2 (111) surfaces were prepared by cleavage according to a recipe described in ref. 14. All measurements took place at room temperature and were performed with an RHK 750 variable temperature non-contact atomic force microscope under ultra-high vacuum conditions. All images were acquired in the frequency modulation mode using an oscillation amplitude of approximately 10 nm (topography channel of constant frequency shift images). The molecules were deposited onto the substrate kept at room temperature from home-made Knudsen cells, which were calibrated by a quartz crystal microbalance. We choose a rate of approximately 0.3 ML min^{-1} for SubPc and 0.05 ML min^{-1} for C_{60}, corresponding to approximately 450 K (SubPc) and 530 K (C_{60}).