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Ordering of Dipeptide Chains on Cu Surfaces through 2D Cocystallization

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The fabrication of novel 2D and 3D molecular nanoarchitectures is attracting increasing attention in various research fields ranging from materials science to nanotechnology. Among biomolecules, peptides are very favorable building blocks, owing to the ease of their synthesis, relative stability, and chemical and biological functionality.‡ They have been used for the design and construction of nanostructures for diverse applications, such as templates for the growth of functional networks,† biosensors for monitoring enzymatic reactions,§ and organic catalysts for asymmetric aldol reactions.¶ A large amount of ordered peptide nanostructures with different geometries,¶ including nanotubes, nanospheres and nanofilaments, have been produced in solution or in vacuum. Peptide monolayer structures self-assembled on solid surfaces typically show a strong tendency to form chains.** Two-dimensional (2D) extended arrangements are difficult to produce due to a pronounced anisotropy in the intermolecular interactions.

Here we report on the ordering and interconnection of 1D dipeptide nanoarchitectures. Individual di- phenylalanine molecules (Phe−Phe, Figure 1), only form short isolated chains with a broad length distribution when deposited on Cu substrates. By exploiting 2D cocystallization with the organic linker terephthalic acid (TPA), we show that continuous and highly periodic dipeptide arrangements can be formed on both the anisotropic Cu(110) and the isotropic Cu(100) surface. This approach might be extended to the fabrication of similar peptide-based nanostructures with potential applications in biocompatible functional surfaces.

Scanning tunneling microscopy (STM) measurements of 1,2-Phe−1,2-Phe molecules deposited under ultrahigh vacuum on Cu surfaces reveal a preferential self-organization in the form of 1D chains. On the Cu(110) surface the Phe−Phe chains are typically isolated and characterized by a high density of kinks. On Cu(100) the chains show four possible orientations and are typically shorter, and their distribution is similarly dispersed (see Figure S1 in the Supporting Information).

The formation of isolated chains suggests different intra- and interchain interactions. The binding between Phe−Phe molecules, which results in the development of supramolecular chains, is most probably due to an interaction between the carboxylic group of one molecule and the amino group of the neighboring one.¶ On the other hand, a nonperfect matching of the chain structures with the underlying substrate might cause the frequent kink defects. The same mismatch could also generate a substrate-mediated repulsion among the chains and, similarly to what is observed in other systems,§ result in their separation. Chain−chain repulsion and kink defects are the reasons why extended and ordered structures are never formed, independently of the molecular coverage (see Figure S1).

In order to overcome this limitation, we have co-deposited a molecular linker (TPA) with the aim of connecting the isolated Phe−Phe chains by effectively enhancing their interaction. This kind of multicomponent method is similar to the procedure used in the fabrication of 3D cocrystals,¶ and first attempts have recently been made also in 2D.** Following this approach, it was shown that molecules characterized by a 1D arrangement in their single-component phase are able to form 3D cocrystals stabilized by hydrogen bonds when mixed with specific linker molecules.¶

After co-depositing Phe−Phe and TPA, 2D ordering and extending of supramolecular structures emerge on both copper surfaces. Our STM measurements show that these highly ordered motifs extend over large domains (up to 150 × 150 nm²) and are stable up to temperatures of 540 K. For both substrates the molecules self-organize with a specific stoichiometry of Phe−Phe to TPA (1:1). This ratio is self-selected and is retained even for an excess of the initial Phe−Phe component (see Figure S2). This indicates that these nanoarchitectures are easy to produce, since their formation does not require a precise control of the relative amount of the deposited components. Besides inducing the formation of extended domains, the TPA linker improves the regularity of the Phe−Phe chains by lifting the kink defects. Moreover, on Cu(100) only two main chain orientations are left out of the original four possible directions. Other binary molecular systems produce either segregated monolayers or new motifs presenting a multiphase behavior where the ratio of the components must be carefully controlled.†§ The strength of the 2D cocystallization method

Figure 1. Chemical structure of di-1-phenylalanine (1,1-Phe−1,1-Phe) and terephthalic acid (TPA).

Figure 2. STM images of 2D extended 1-Phe−1-Phe/TPA hybrid motif on Cu(110). Phe−Phe rows appear brighter than TPA rows. The quadrangle in the inset marks one unit of the molecular superlattice. The ellipse and dumbbell indicate TPA and Phe−Phe molecules, respectively. The images are acquired at −2.0 V, 0.5 nA for the large-scale one and at −1.0 V, 0.5 nA for the high-resolution one.
The ability of the TPA linker molecule to order and lengthen the Phe chains on Cu(110) and Cu(100) surfaces. This effect takes place in a single-component phase. Clearly, the effect of the TPA linkers is to combine and extend the isolated dipeptide chains without altering their inherent structure nor modifying the final surface chirality.

Figure 3 shows two large-scale chiral L-Phe—L-Phe/TPA hybrid domains with a 90° relative rotation observed on Cu(100). The supramolecular structures can be denoted by the matrices (3 3) and (3 3) relative to the substrate principal [011] and [011] directions. Also here the chains keep the same orientations ([021] and [012]) as in the pure L-Phe—L-Phe phase, resulting in a surface with local chiral symmetry.11

The ability of the TPA linker molecule to order and lengthen the discrete dipeptide chains evidently does not depend on the different substrate geometry. This suggests that also in the 2D case, the cocrystallization approach might be sufficiently robust and of general applicability.

The close packing among the molecules and their orientation indicate that intermolecular H-bonding might be the main driving force for the formation of the final ordered structures.9,10b-g,11 Moreover, the integrity of the Phe—Phe chain motifs indicates that the intrachain binding is stronger than the TPA—chain interaction. However, this latter interaction is evidently strong enough to overcome the original chain—chain repulsion and to avoid the formation of kink defects. This, together with the manifestation of a 2D cocrystallization instead of a phase separation, suggests the following hierarchy in the intermolecular binding strengths: intrachain > chain—TPA > TPA—TPA.

In summary, we have demonstrated the possibility of fabricating extended surface-supported dipeptide architectures by the 2D cocrystallization method. The organic linker TPA was used as a molecular “glue” to bridge isolated Phe—Phe chains and to remarkably improve their regularity. The formation of highly periodic motifs seems to be independent of the specific substrate structure. The characteristics of Phe—Phe molecular chains are successfully transferred to the final structures which, albeit being 2D extended, retain a 1D chiral modulation. Besides acting as nanotemplates, these substrates might therefore be interesting for heterogeneous enantioselective catalysis applications.1 We speculate that the approach presented here might be extended to a wider range of biomolecules with increasing functional groups and could be used for the construction of surface-supported organic cocrystals. Experiments combining different types of polypeptides and linkers are underway.

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Supporting Information Available: Experimental details and STM data of pure Phe—Phe chains on Cu(110) and Cu(100) surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

References
Supporting Information

Experimental details for sample preparation:

The samples were prepared and characterized in an ultra-high vacuum system equipped with a variable-temperature scanning tunneling microscope (STM). Copper was chosen as substrate because of its strong interaction with amino and carboxylic moieties typical of biomolecules. This enhances molecular adsorption and thus facilitates room temperature STM analysis. The single crystal Cu(110) and Cu(100) surfaces were prepared according to the standard scheme of repeated cycles of Ar⁺ ion sputtering (900 eV, 10 µA/cm²) followed by subsequent annealing treatments. Commercially available L-Phe-L-Phe (Bachem AG) and TPA molecules (Fluka) in powder form were outgassed in Knudsen-cell evaporators and then deposited onto the Cu surfaces by organic molecular beam epitaxy. The cells were held at constant temperatures (430 K for Phe-Phe and 445 K for TPA) as measured with K-type thermocouples in direct contact with the cells. Molecular deposition was performed while keeping the substrates at room temperature. All samples were thereafter annealed to 420 K for five minutes. The sample temperature was measured by a K-type thermocouple connected to the back of the Cu crystals. The as-prepared samples were transferred from the preparation chamber (base pressure ~ 2 ×10⁻¹⁰ mbar) to the STM chamber (~ 5 ×10⁻¹¹ mbar). STM measurements were performed at room temperature in the constant current mode.
Figure S1. STM images show a dispersed distribution of supramolecular L-Phe-L-Phe chains on Cu surfaces. (a) and (b) on anisotropic Cu(110), the chain alignment matches with the substrate [\(\bar{T}14\)] direction, which does not coincide with the principal crystallographic [1\(\bar{T}0\)] and [001] directions of Cu(110). The chains are isolated and characterized by a high density of kinks even close to saturation coverage in (b). Only this arrangement is observed on the entire surface, implying that the molecular chirality is successfully transferred to the substrate. Moreover, the chains show a certain mobility on the Cu substrate and their length distribution is quite broad. The ellipse in (a) marks a mobile chain. (c) On the isotropic Cu(100), the L-Phe-L-Phe chains grow along four possible directions. Among these, two main chain orientations can be distinguished along the substrate [021] and [\(0\bar{1}\)2] directions, as illustrated by the dashed lines. This 90° rotational symmetry of the supramolecular arrangements reflects the four-fold symmetry of the Cu(100) surface. The images are recorded at - 2.0 V, 0.5 nA in (a, b) and - 1.4 V, 0.2 nA in (c).

Figure S2. STM image of L-Phe-L-Phe/TPA hybrid motifs on Cu(110) under an excess of the L-Phe-L-Phe component. The data prove that also in this case two components self-organize with a specific 1:1 stoichiometry (alternate Phe-Phe and TPA rows along substrate [\(\bar{T}14\)] direction). The extra Phe-Phe molecules form isolated chains with high density of kinks. Note that the alignment of step edges with the molecular row direction derives from the very high mobility of step edges at room temperature and above. The image is recorded at - 2.0 V, 0.5 A.