Programming Supramolecular Assembly and Chirality in Two-Dimensional Dicarboxylate Networks on a Cu(100) Surface

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ABSTRACT

We report a comparative study on the 2D self-assembly of two related ditopic benzoic acid species, which have similar shape and endgroups but different backbone symmetry. High-resolution scanning tunneling microscopy data reveal how the symmetry information of molecular building blocks is readily expressed in the resulting chiral or nonchiral supramolecular networks. The underlying square Cu(100) surface steers network orientation and accounts for carboxylate formation, resulting in an unusual intermolecular hydrogen bond motif. Our results demonstrate that symmetry and chiral resolution in 2D supramolecular assembly can be controlled via the design of functional molecules and choice of substrate.

Supramolecular chemistry provides powerful methodologies for the controlled generation of nanostructures following bottom-up fabrication principles.[1-3] Recent studies reveal that surfaces represent platforms to direct the assembly of novel low-dimensional supramolecular architectures using appropriate molecular building blocks.[4,5] These surface-supported systems are attracting increasing attention, since they represent promising materials for potential applications, e.g., in nanopatterning, surface templating, heterogeneous catalysis, and sensing or molecular recognition. The flexibility of the underlying noncovalent interactions facilitates the formation of thermal equilibrium structures, whose functionalities can be either brick-based or emerge as new or altered quality from molecule−surface interactions.[6-9] A particularly interesting feature, frequently occurring in low-dimensional supramolecular assemblies, is the rich variety of chirality phenomena encountered at different levels.[10-14]
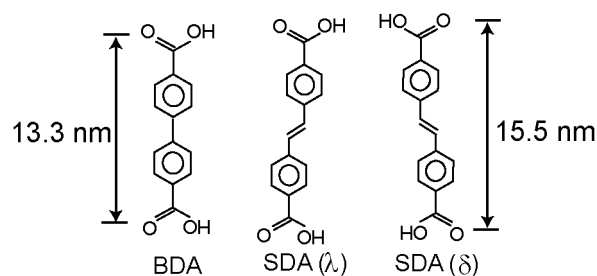
Figure 1. Chemical structure of the molecule **BDA** and both **SDA** 2D enantiomers labeled λ and δ, respectively.

Here we report a comparative scanning tunneling microscopy (STM) study addressing the supramolecular ordering of two related molecular building blocks − 4,4′-biphenyl-dicarboxylic acid (**BDA**) and 4′,4″*trans*-ethene-1,2-diyl-bis-benzoic acid (stilbene dicarboxylic acid, **SDA**) (Figure 1) − at the Cu(100) surface. Although bearing the same functional endgroups, the two dicarboxylic acids have different length (13.3 vs 15.5 nm) and symmetry, with **BDA** belonging to the D_{2h} point group and **SDA** to the C_{2h} point group (assuming symmetric endgroups by deprotonation). This notably implies that two 2D chiral **SDA** configurations exist when the molecules are confined to two dimensions

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(as denoted by δ and λ in Figure 1). As shown previously, deprotonation of carboxylic groups typically occurs on copper surfaces at the conditions employed for the present study.[18−20] Consequently, it is concluded that **BDA** and **SDA** exist as deprotonated dicarboxylate species at the Cu(100) substrate.

Sample preparation and characterization were carried out in a ultrahigh vacuum (UHV) STM apparatus (base pressure $\sim$3 × 10^{-10} mbar) providing well-defined conditions for the experiment.[15] The Cu(100) surface was cleaned by repeated cycles of Ar$^+$ sputtering and annealing at 800 K, which account for an atomically flat and clean surface. **BDA** and **SDA**[16,17] were deposited onto the substrate held at 298 K by organic molecular beam epitaxy (OMBE) from Knudsen-cell type evaporators. To facilitate the self-assembly processes, we used coverages slightly below monolayer saturation. The STM measurements were performed in the constant current mode at room temperature, with 0.5 V bias voltage and 1.0 nA tunneling current.

Both molecules assemble readily into well-ordered 2-D supramolecular networks with square unit cells of comparable size. The resolution of the rod-like molecules in the STM data as anisotropic protrusions, $\approx$1 nm in length, reveals that both species adsorb in a flat-lying geometry, in agreement with the bonding of related large aromatic species at metal surfaces.[6−15,18−20] The lateral intermolecular coupling is mediated by a rather unusual hydrogen bonding between carboxylate moieties and aromatic rings (cf. discussion below). However, the structural information of the higher symmetry **BDA** molecule is expressed in a single phase with C_4 symmetry (Figure 2a), whereas the self-assembly of the lower symmetry **SDA** species goes along with the formation of two enantiomorphic arrangements with $p4$ symmetry (Figure 2b). Note that the molecular arrangement, bonding length and observed orientation excludes a Cu adatom mediated coupling of the molecules, which was encountered with related systems.[5,19]

The long axes of the **BDA** molecules align with one of the two high-symmetry directions of the square Cu(100) substrate ([011] and [01−1]). Adjacent **BDA** molecules are perpendicular to each other, with each endgroup pointing to the center of the next neighbor. This accounts for a quadratic motif with C_4 symmetry. The corresponding unit cell is marked by the square in Figure 2a, which has a side length of 1.45 nm and runs along the substrate [001] direction (marked in Figure 2a). Following conventional surface science notation, this is a c($4\sqrt{2} \times 4\sqrt{2}$) superstructure. The arrangement shown in Figure 2a is the only phase observed on the entire sample, and it may cover entire terraces with widths as large as 100 nm.

In contrast, the reduced symmetry of the **SDA** molecule is reflected in two distinct network phases as shown in the left and right parts of Figure 2b, respectively. Similar to **BDA**, adjacent **SDA** molecules are oriented orthogonally. However, the **SDA** endgroups do not point exactly to the center of the neighboring molecules. This dissymmetric arrangement produces two types of voids, large and small ones, as represented by the yellow and red squares in Figure
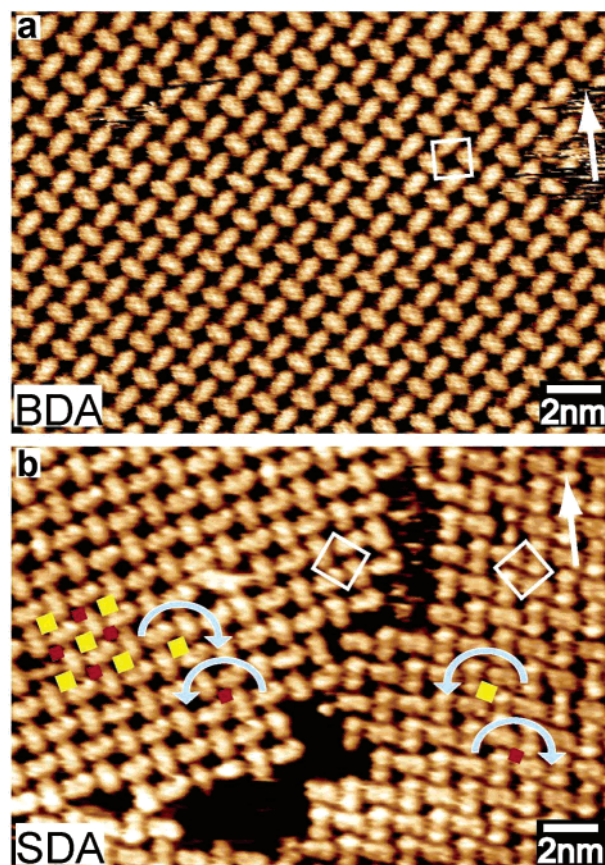

Figure 2. STM topographs of 2D dicarboxylate networks: (a) **BDA**; (b) **SDA**. White arrows mark the [001] direction of the Cu-(100) substrate. Square frames show the unit cells of the supramolecular motifs. Blue arrows in (b) mark **SDA** folding; the yellow and red squares represent the large and the small voids, respectively.

2b, respectively. The corresponding unit cell has a size of 1.54 nm, which is slightly larger than that of the **BDA** phase and consistent with **SDA** being the longer molecule. Moreover, the unit cell is oriented 54° counterclockwise off the [001] direction and all large voids (yellow) are enclosed by four clockwise folding **SDA** molecules, while the small voids (red) by counterclockwise folding **SDA** (marked by blue arrows). This arrangement accounts for a $p4$ symmetry, which implies that the motif cannot be superimposed on its mirror image by 2D translation or rotation and that the **SDA** network is enantiomorphic. The chiral counterpart is found as a coexisting domain, resolved in the right part of Figure 2b, where the large voids are surrounded by counterclockwise folding **SDA** and the small voids by clockwise folding **SDA**. This structure has a unit cell of the same size but rotated 54 degrees clockwise off the [001] direction, i.e., the two phases are mirror images with respect to [001]. The two superstructures are described as [6, 1/−1, 6] and [1, 6/−6, 1] in matrix notation, respectively. The different orientations of the molecular networks are associated with the different lengths and shapes of the molecular building blocks. Moreover, unlike the relatively large and perfect **BDA** networks, in the case of **SDA** defects and domain boundaries are encountered frequently and the network domain size is typically below 30 nm.
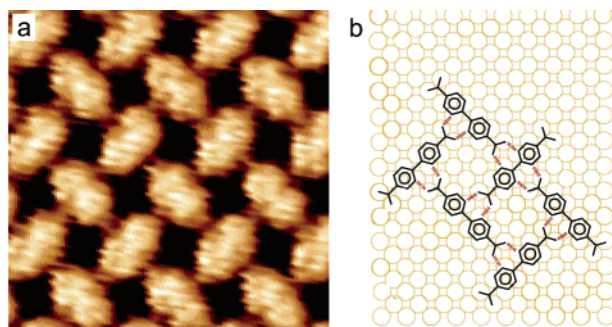
Figure 3. (a) High-resolution STM data of the **BDA** supramolecular motifs. (b) Tentative model. The red dashed lines indicate lateral hydrogen bonds. The symmetric rod-like species bind centrally to the adjacent molecules via hydrogen bonds between carboxylato groups and phenyl rings. Image size: 4.4 nm × 4.2 nm.
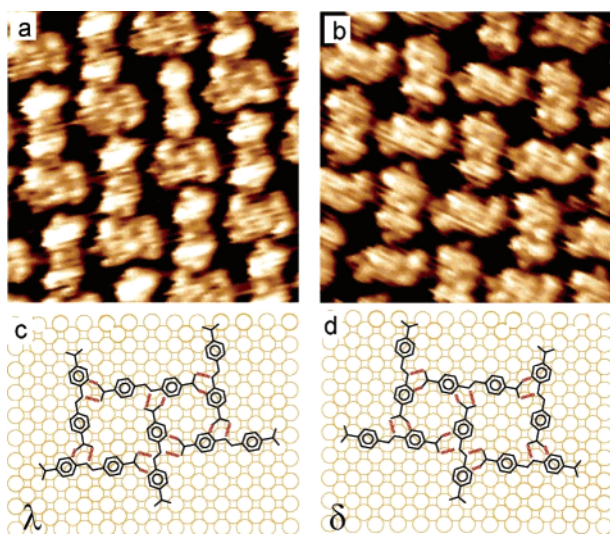
Figure 4. (a,b) High-resolution STM data of two enantiomorphic networks of **SDA** reveal chiral resolution of the 2D chiral (δ, λ) species. (c, d) Tentative models. The intermolecular hydrogen bonds reflect dissymmetric coupling (red dashed lines) of carboxylato to both phenyl and ethenylene moieties. Image size: 4.4 nm × 4.2 nm.

The high-resolution data shown in Figure 3a provide further insight into the **BDA** supramolecular assemblies. The symmetric rod-like shape of **BDA** is clearly resolved. A tentative model is depicted in Figure 3b (because substrate atomic structure and adsorbed molecules could not be resolved simultaneously, we assume for simplicity that the **BDA** phenyl rings reside at substrate hollow sites). The lateral coupling of the **BDA** molecules is associated with two equivalent hydrogen bonds between the carboxylato oxygens and the phenyl groups of the adjacent molecules symmetrically (cf. red dashed lines in Figure 3b). Assuming that the adsorbed molecules do not undergo structural relaxations, the O··H−C distance is approximately 2.7 Å, falling in the typical range of hydrogen bonds.

The STM topography of the **SDA** molecules in Figures 4a and b evidences an asymmetric shape, reflecting the crooked molecular backbone due to the ethenylene bridge. Because the molecules are confined flat to two dimensions, the ethenylene bridge accounts for 2D chirality. The chirality

signature of the individual molecules can be determined unambiguously from the submolecular resolution images shown in Figures 4a and b, where the flection must be associated with the shape of the ethenylene bridge. Figures 4a and b reveal that each of the two **SDA** phases consists of single enantiomers and hence is homochiral. Consequently, chiral segregation has occurred in the assembly process and the molecular chirality is expressed in the supramolecular motifs. With the tentative models in Figures 4c,d the observed structures can be rationalized: the carboxylato groups point to the C−C single bonds, forming hydrogen bonds to a phenyl hydrogen and an ethenylene hydrogen (O··H−C distances are estimated to 2.5 and 3.2 Å, respectively; note that this coupling and the molecular geometry imply that the molecules do not match as well with the substrate as in the case of the biphenyl species described above). This nicely explains the distinct large and small voids. Moreover, the smaller **SDA** network domain size can be attributed to the mass transport required for chiral resolution.

It is interesting to put the present reults into perspective with earlier findings for the rod-like species 4-[*trans*-2-(pyrid-4-yl-vinyl)]benzoic acid (PVBA) and 4-[(pyrid-4-yl-ethynyl)]benzoic acid (PEBA), where intriguing 2D chiral supramolecular ordering phenomena were encountered on the close-packed Ag(111) substrate.[10,21,22] In all cases, the matching of the molecular dimensions with the substrate atomic lattice proved to be an important factor for the orientation of the molecules and the supramolecular assemblies. However, for the Ag(111) substrate, the carboxylic acid moieties remain unaffected and H-bonds that could be similarly expected in 3D are decisive for the self-assembly scenario. By contrast, for the case of Cu(100) the substrate modifies the chemical nature of the molecular building blocks. This accounts for carboxylate-mediated intermolecular coupling, whence a H-bond motif rarely encountered in 3D drives the network organization. This emphasizes the important role of the substrate chemical activity in steering the organization and chiral signature of 2D supramolecular assemblies.

In conclusion, we have demonstrated that two related molecular building blocks, **BDA** and **SDA**, readily assemble into 2D supramolecular networks with the carboxylato moieties acting as active lateral bonding sites. Moreover, the symmetry content of both molecules is differently expressed in distinct supramolecular domains comprising different H-bond configurations. The breaking of the molecular backbone symmetry is associated with a symmetry reduction of the supramolecular motifs. Whereas the symmetric **BDA** molecules organize in networks with C_4 symmetry, the 2D chiral **SDA** molecules undergo mesoscopic chiral resolution and assemble in enantiomorphic domains with $p4$ symmetry motifs. The findings indicate that in general supramolecular assembly and chiral organization of 2D dicarboxylate networks can be programmed with the adequate choice of the molecular building blocks and substrate chemical properties.

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