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Active Intramolecular Conformational Dynamics Controlling the Assembly of Azobenzene Derivatives at Surfaces

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Molecular self-assembly at surfaces proceeds through complex selective pathways involving not only the recognition of molecular structures based on lock-and-key interactions, but also the existence of effective methods of dynamical search and trial.^[1] This becomes especially crucial when a mixture of different molecules with immiscible shapes results in the segregation of mesoscopic separated phases. For example, this is the case in the formation of large homochiral phases from a racemic mixture of chiral molecules at surfaces.^[2] Large-scale mass transport through thermally activated diffusion has been proposed as the mechanism leading to phase segregation. However, it is not clear how molecules of one species can move for large distances, in many cases overcoming barriers associated with topological defects such as monoatomic steps.

In solution, the conformational dynamics of molecules with internal flexibility plays an important role in supramolecular assembly. For example, the folding structure of proteins or peptides is governed by dynamical stochastic mapping of multidimensional conformational configurations.^[3] A metal surface represents in turn a rigid object interacting with the molecular adsorbates, in many cases very strongly compared to the magnitude of thermal energy at room temperature. In spite of that, thermally activated conformational changes have been identified at the single-molecule scale,^[4,5] which implies that internal degrees of freedom may also be active during the recognition and growth of molecular thin films at surfaces. Whether they play a crucial role in the mesoscopic ordering and phase separation is not yet clear. Here, we use low-temperature (5 K) scanning tunneling microscopy (STM) to statistically track the different molecular structures of an azobenzene derivative adsorbed on a gold surface. We find that the ratio between different azobenzene rotamers changes in response to an increase in temperature and coverage, thus proving that intramolecular conformational dynamics is an active pathway of molecular recognition during the formation of large-scale molecular assemblies on surfaces.

Our study is performed on 3,3'-di(methoxycarbonyl)azobenzene (CMA)^[6,7] deposited on a Au(111) surface. A gold substrate is employed because it leads to weak molecular adsorption,

thus maximizing the role of intermolecular interactions.^[8] CMA is formed by an azobenzene skeleton functionalized with a carboxymethyl end group at one of the *meta* sites of the phenyl rings (see Figures 1 a and b). The methyl part of the end group

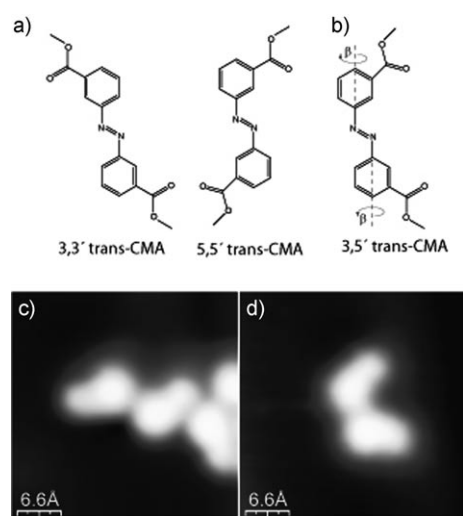


Figure 1. a, b) Lewis structure of the three possible rotamers of *trans*-CMA on a surface. c, d) STM images of the two shapes found on a Au(111) surface. Each pearlike protrusion corresponds to a phenyl ring together with a "bulky" carboxymethyl group; (c) is associated with one of the rotamers shown in (a), whereas (d) corresponds to the rotamer in (b).

can be easily identified in the STM images, while the carboxyl moieties, which are strongly active in the formation of intermolecular H bonds, are in charge of the recognition, selection, and locking of specific molecular shapes in ordered domains. Although azobenzene is a prototype molecular switch, which undergoes a *trans*–*cis* photoisomerization in the gas phase and in solution,^[7,9–11] at the gold surface only the (planar) *trans*-CMA conformer is found.

The *meta* functionalization of phenyl rings does not distinguish between the carbon sites 3 and 5. Both sites are chemically and physically identical and are connected through an internal rotation β of a phenyl ring (Figures 1 a and b). The activation barrier separating both rotamers is small.^[12] At room temperature, the internal β rotation is quasi-free in the gas phase and in solution, whereas in the solid state only the 3,3' conformation is found.^[7]

When CMA is adsorbed on the Au(111) surface the β rotation is frozen, and the molecule is forced to acquire a planar structure. We expect then to encounter three different rotamers depending on the relative orientation of the two phenyl rings.

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The 3,3'- and 5,5'-*trans*-CMA rotamers (Figure 1 a) show both end groups in opposite directions with respect to the inversion center of the azobenzene skeleton. The 3,5'-*trans*-CMA form (Figure 1 b) aligns both end groups to confer a U-like shape to the whole molecule. Additionally, we expect for each rotamer two chiral (mirror-rotated) forms when confined to a two-dimensional (2D) surface (not included in Figure 1).

STM images of CMA single molecules find only two distinct shapes, with either inversion or mirror-like symmetry (Figures 1 c and d). This is because STM can only resolve clearly the relative alignment of the two carboxymethyl end groups, as it is essentially blind to the orientation of the central neck. Therefore, the Z-shaped molecule in Figure 1 c corresponds to either a 3,3' rotamer or its indistinguishable 5,5' form (both called here 3,3'), while 3,5' rotamers are imaged with a U-like shape (Figure 1 d).

When CMA is deposited on a cold Au(111) substrate ($T_s=80$ K), both U-like and Z-like shapes are found with the same probability in the STM images (52% of 3,5' rotamer). At low substrate temperatures, their thermally induced mobility is small, and only molecular islands with disordered structure are found. If CMA is deposited instead on a substrate held at room temperature, the thermal mobility is sufficient to induce molecular self-assembly in two types of characteristic molecular assemblies (Figure 2 a). Interestingly, each type of assembly nucleates only rotamers of one kind, and shows a very different structure as a consequence of the different shape of the 3,3' and 3,5' rotamers. The Z-shaped 3,3' molecules order in highly ordered 2D domains with alternating rows of each of the chiral forms of the 3,3' conformers (Figure 2 b). High-resolution STM images reveal an alignment such that each molecule can form up to eight hydrogen bonds ($O\cdots HC$ and $CH\cdots N$) with its nearest neighbors. The U-shaped 3,5'-CMA molecules are connected in a zipper fashion to form straight molecular chains (Figure 2 c). In these chains we estimate that each molecule is linked by six hydrogen bonds to its neighbors. The different hydrogen-bond patterns of host sites in every domain determine the recognition of each of the rotamers through a lock-and-key strategy.

Both types of structures occupy large surface areas: the 2D domains form defect-free compact regions, while the rows of U-shaped rotamers appear with short lengths, as they are emerging from disordered regions. The massive ordering reveals the existence of an effective mechanism for the phase separation of mesoscopic regions formed by one rotamer. Instead of pure thermal mobility along the surface, we consider here a mechanism based on a stochastic search of multiple conformations by thermal activation of intramolecular dynamics. We note that the transformation between the two rotamers at the surface is possible through the rotation of one phenyl ring. Recently, it has been shown that this transformation can be achieved at the surface via electron-induced excitation.^[13] Such phenyl ring rotational dynamics can also be thermally activated.^[4]

As each of the CMA structures apparently involves a different number of hydrogen bonds, we expect that they require different energies of formation. To probe whether a simple

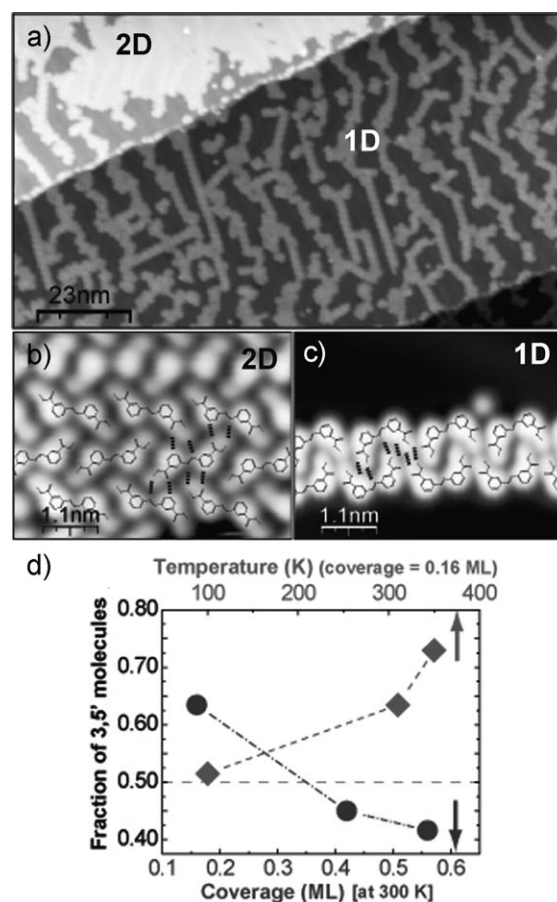


Figure 2. a) STM image of the Au(111) surface covered with 0.42 ML of CMA. CMA was deposited in a vacuum on the gold surface at room temperature with a homemade Knudsen cell. Two distinct regions are identified: the one labeled 2D is a defect-free 2D packing of CMA; 1D indicates molecular rows and disordered regions along the Au(111) reconstruction. b, c) Close-up images in regions similar to the 2D and 1D domains of (a). The images include a proposed model of CMA for the molecular conformation and intermolecular bonding. d) Fraction of the 3,5' rotamer as a function of coverage and annealing temperature, obtained from the analysis of about 10 000 molecules over several statistically representative regions for every coverage and temperature. The fraction of 3,5'-CMA increases with temperature, which indicates a larger stability of this bonding configuration, and decreases with coverage due to its lower packing density. All the results were obtained from STM images after cooling to $T_s=5$ K.

thermally induced conformational transformation between the two rotamers mediates the phase separation and the formation of large CMA domains, we analyzed the fraction of each rotamer at the surface as a function of the substrate temperature. In the limit of low CMA coverage (0.16 monolayers (ML)), an equilibrated mixture of both rotamers (deposited at low T_s) evolves with the annealing temperature towards the exclusive formation of zigzag-like domains of U-shaped molecules. As a consequence, the fraction of 3,5'-CMA molecules increases monotonously with the annealing temperature (Figure 2 d). After annealing to 350 K, 75% of the molecules correspond to the 3,5' conformer. This finding demonstrates that the chains of U-shaped rotamers are indeed the most stable structures, and that their formation involves the internal rotational dynamics of phenyl rings of azobenzene.

At higher CMA coverage, this simple picture breaks down. Molecular density becomes an issue, and the 2D domains of Z-shaped molecules pack CMA more effectively. Correspondingly, at 0.4 ML 19% of the sample is covered by 2D domains of 3,3'-like CMA (at room temperature), and this fraction increases at higher coverages. The formation of 2D structures takes place through an overall decrease in the fraction of 3,5' rotamers in the sample. As shown in Figure 2d, the percentage of these rotamers is reduced to 45% for 0.4 ML and 40% for 0.57 ML. The chain structure, albeit more stable, is less efficient at packing CMA molecules in two dimensions. Thus, at higher coverage the 2D structure becomes gradually more favorable due to its larger packing density. The monotonous change in the fraction of each rotamer at the surface, influenced by temperature and coverage, demonstrates that the large-scale organization of the molecular thin film necessarily involves thermally activated internal rotations of the CMA phenyl ring, and hence the change of its conformation.

The energy required to activate the internal rotational dynamics presumably increases due to the planar interaction of the phenyl rings with the metal surface. However, noncovalent interactions add up when multiple connection points exist between a molecule, which may overcome the adsorption energy and favor three-dimensional (3D) structures.^[8] Thus, we believe that only through the effective mediation of multiple hydrogen bonds (in addition to thermal energy) can the 3D conformational dynamics of CMA at the surface overcome the rigidity imposed by the metal surface.

We have shown that a "flexible" molecule such as azobenzene on a metal surface uses conformational adaptation of its shape through intramolecular rotation of one phenyl ring to fit into host sites within supramolecular assemblies. We envisage that together with the thin-film structure, its functionality and reactivity can be modified through its response to external stimuli.

Experimental Section

The experiments were carried out in a custom-made low-temperature scanning tunneling microscope under ultrahigh vacuum. Cycles of 1.5 keV Ne⁺ ion sputtering and annealing to 800 K led to

an atomically clean Au(111) substrate. CMA molecules were sublimed from a custom-made Knudsen cell at 380 K. The temperature of the Au(111) crystal was adjusted between 80 and 400 K when exposed to a continuous flux of molecules. The sample was then transferred to the microscope where all measurements were performed at 4.8 K.

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