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Supramolecular Organization and Chiral Resolution of *p*-Terphenyl-*m*-Dicarbonitrile on the Ag(111) Surface

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Dedicated to Prof. Dr. R. Jürgen Behm on the occasion of his 60th birthday

The supramolecular organization and layer formation of the non-linear, prochiral molecule [1, 1′;4′,1′′]-terphenyl-3,3“-dicarbonitrile adsorbed on the Ag(111) surface is investigated by scanning tunneling microscopy (STM) and near-edge X-ray absorption fine-structure spectroscopy (NEXAFS). Upon two-dimensional confinement the molecules are deconvoluted in three stereoisomers, that is, two mirror-symmetric *trans*- and one *cis*-species. STM measurements reveal large and regular islands following room temperature deposition, whereby NEXAFS confirms a flat adsorption geometry with the electronic π-system parallel to the surface plane. The ordering within the expressed supramolecular arrays reflects a substrate templating effect, steric constraints and the operation of weak lateral interactions mainly originating from the carbonitrile endgroups. High-resolution data at room temperature reveal enantiormorphic characteristics of the molecular packing schemes in different domains of the arrays, indicative of chiral resolution during the 2D molecular self-assembly process. At submonolayer coverage supramolecular islands coexist with a disordered fluid phase of highly mobile molecules. Following thermal quenching (down to 6 K) we find extended supramolecular ribbons stabilised again by attractive and directional noncovalent interactions, the formation of which reflects a chiral resolution of *trans*-species.

1. Introduction

The control of supramolecular self-assembly at interfaces is a promising avenue for the design of low-dimensional nanoscale architectures.[1] A variety of synthesis protocols, using electrostatic interactions,[2] hydrogen bonding[3] or metal–ligand interactions[4] have been explored. In two dimensions, the bonding capabilities of two interacting CN groups were successfully employed to steer the self-assembly of substituted porphyrins on Au(111).[5] Depending on the position of the CN substituents, triangular clusters, tetramers, and supramolecular wires evolve. In different work, the carbonitrile group controlled structure formation by interaction with alkoxy groups.[6] Recently, we employed linear ditopic dicarbonitrilepolyphenyl molecular building blocks and studied their self-assembly on the Ag(111) surface.[7,8] Topologically different supramolecular structures evolve depending on the backbone length. In particular, selecting species containing three to six phenyl groups led to the formation of close-packed layers or different chiral open networks including a kagomé network. All investigated networks turned out to be commensurate with the underlying atomic lattice. Furthermore dicarbonitrile linkers were successfully employed for metal-directed assembly of 2D coordination networks on Ag(111). Hereby we encountered striking differences depending on the symmetry of the linker. When linear species were employed, with the CN moiety at *para* positions, highly regular open nanomeshes with tunable pore sizes were fabricated.[9] The pertaining convergent assembly is in direct contrast to the divergent scenarios leading to random coordination networks when using a linker with CN moieties at *meta* positions.[10] Herein, we focus on the 2D supramolecular assembly of this linker itself. It is depicted in Scheme 1 and consists of three phenyl rings connected via C–C σ-bonds, with two carbonitrile groups in the *meta*-position on the outer side of

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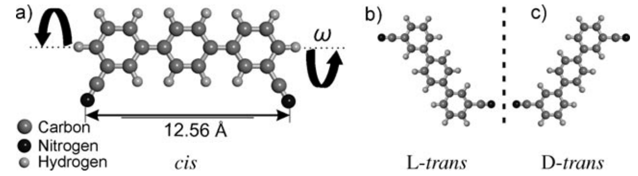

Scheme 1. Molecular model of the [1, 1′;4′,1′′]-terphenyl-3,3“-dicarbonitrile. On the left the *cis* conformation with the rotation angle ω is presented. By rotating the phenyl ring about this angle two mirror-symmetric entities emerge upon surface confinement, pictured on the right (L- and D-*trans*).

the terminating phenyl rings. The angle ω describes the molecule backbone rotation around the σ-bond between the phenyl rings. In the crystal structure for *para*-terphenyl the central phenyl ring is tilted about $\pm 27^\circ$ with respect to both outer phenyl rings, which are parallel.[11]

On noble metal surfaces, such as Ag(111), extended π-systems are well known to preferentially adsorb parallel to the substrate. The carbonitrile groups tends to a metal complexation and acts as an anchoring point for the molecule, enhancing the stability on the sample at ambient temperatures.[11] 2D confinement in a flat geometry furthermore implies the deconvolution in three stereoisomers. Thus, upon 2D confinement the molecule isomerizes into a *cis* and two *trans* enantiomers due to the symmetry breaking effect of the surface and a special 2D chirality scenario is encountered that has not been described so far.[12–14] The natural composition of the pertaining two-dimensional gas can be assumed to be 50% *cis* and 25% for each mirror-symmetric *trans* conformation.[10,15] Our results indicate that the 2D layer formation of these molecules reflects a chiral resolution of these surface enantiomers. Moreover, we investigated the thermal quenching of a fluid phase consisting of highly mobile molecules that coexists with compact islands at 300 K. It notably condensates into extended supramolecular ribbons, representing enantiopure assemblies from the *trans*-species.

2. Results and Discussion

Following deposition with the substrate at room temperature, the molecules self-assemble in well-ordered layer structures. A section of a close-packed island build by the dicarbonitrile linker units is shown in Figure 1 a. The individual molecules are resolved as rod-like protrusions, that is, the imaging is dominated by the carbon backbone. The brick-lined pattern formed shows a high regularity. The islands extend over large areas without defects or an apparent moiré pattern. Even the step edges are covered without formation mismatch. This strongly suggests a commensurate structure, similar to the networks obtained with *para*-polyphenyl–*para*-dicarbonitrile linear analogs.[7,8] However, the superstructure formed with the present *para*-terphenyl–*meta*-dicarbonitrile clearly contrasts that of the *para*-terphenyl–*para*-dicarbonitrile,[7] which fact directly evidences the decisive role of the functional CN endgroups in the pertaining arrangements.

High-resolution STM images and careful data analysis enable us to propose a structural model of the molecular adsorption

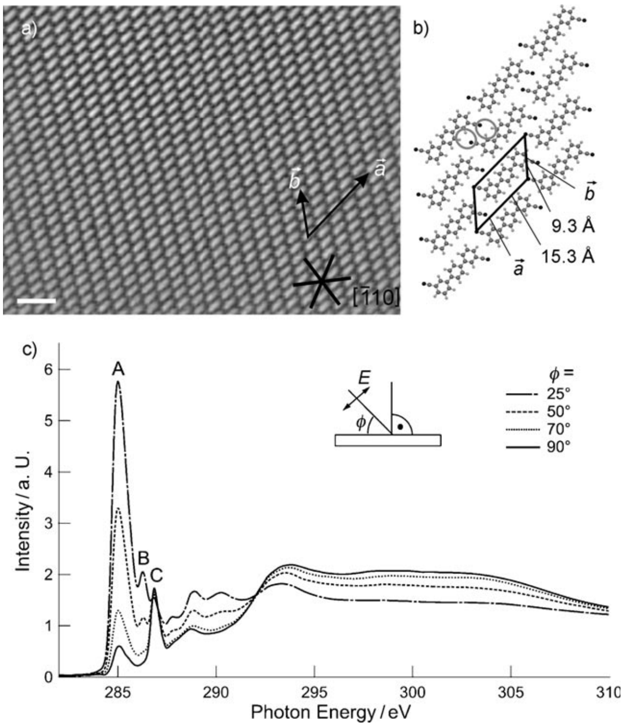

Figure 1. STM overview of a molecular island with a molecular model and X-ray absorption data. a) Overview on a dense packed highly ordered molecular island on the Ag(111) substrate. The atomistic model in (b) gives an insight into the bonding scheme. c) NEXAFS measurements on the C 1s edge demonstrate a strong dichroism indicating a well-ordered monolayer. The angle dependence of the intensities of the different peaks reveal a flat laying π-system (peak A) and carbonitrile groups parallel to the substrate (peaks B and C).

shown in Figure 1 b, despite the fact that generally the placement of the carbonitrile groups can not be unambiguously assigned by STM. The displayed unit cell has a rhombic shape with a edge length of 15.3(±0.5) Å and 9.3(±0.5) Å, respectively, and an implicit angle of 48°. The island structure of the molecules forms a highly regular pattern determined by the vectors ***a*** and ***b*** and the embedded unit cell. The molecular backbone is not perfectly aligned with ***a***, but tilted slightly clockwise by about 5°, most probably due to the steric repulsion of the hydrogens in the *meta* position and the molecular asymmetry. By contrast, for linear 3, 4, 5 and 6 ringed *para*-carbonitrile polyphenyl molecules on the same substrate orientations along high-symmetry substrate directions prevail.[7,8] With respect to the $<$-110$>$ high-symmetry directions of the underlying substrate the molecular main axis is rotated by 15° counter-clockwise.

The molecules in the island layer are assumed to occur in the *trans* conformation. They interact with the next neighbor via the carbonitrile group developing two non-covalent bonds with next-neighbor phenyl moieties, marked with the grey ellipses in Figure 1 b. The N···H distances are about 2.3 Å. Similar binding properties and distance have been reported for CN-terminated adsorbed porphyrins and were supported by ab initio calculations,[16] as well as for adsorbed *para*-dicarbonitrile-polyphenyl species.[7,8] Due to the high electronegativity of the nitrogen, even a dipolar character of the bond is conceivable,[17] similar to related compounds in the gas [18] and crystalline phases.[19] This considerations clearly favours the proposed arrangement of *trans* species, where the orientation of adjacent CN-groups is antiparallel. By contrast with the *cis* species, an energetically unfavorable proximity of nitrogen atoms bearing an electron lone pair and a parallel orientation of adjacent CN-groups would exist.

In order to test our assumption of the geometry of the adsorbed molecules we performed NEXAFS measurements at the C 1s edge, displayed in Figure 1 c. In general, the spectra are similar to benzene spectra with a series of sharp peaks in the π^* region and one peak in the σ^* (294 eV) region.[20] The angle-dependent series exhibits a pronounced dichroism in the whole energy range evidencing a highly ordered adlayer with all molecules in a very similar conformation. From the comparison with the benzene spectra,[20] it becomes clear that peak A (at 285 eV) originates from the lowest phenyl-ring-related π^* resonance and thus comprises information about the average orientation of the phenyl backbone. Furthermore, we attribute the additional peaks B (286.3 eV) and C (286.9 eV), which are not present for benzene, to the two perpendicular π orbitals of the carbonitrile triple bond. Resonance B is shifted to lower energy with respect to resonance C due to the interaction with the phenyl π system.[21] Together the two features allow one to determine the orientation of the CN group independently from the phenyl signals. The decreasing intensity at elevated angle ϕ (the angle between the E-vector of the synchrotron radiation and the surface normal) of peaks A and B as well as the increasing intensity of peak C clearly indicate that the molecules are adsorbed flat on the surface. In more detail, the deviation from the perfect planar conformation assumed in Scheme 1 can be described by a rotation around the σ-bonds of the long molecular axis by approximately 20°, which is a reasonable value for *para*-polyphenyl molecules.[22]

At room temperature, isolated molecules on the Ag(111) surface exhibit a high diffusivity, expressed in a molecular surface fluid at submonolayer coverages. Accordingly, the island boarders are in a dynamic equilibrium with the fluid phase in open terraces, whereas the interior section of the island remains stable. This is shown for both the Ag(111) and Cu(111) surfaces in Figure 2, where on the one hand the fluctuation of an island border at 300 K is clearly discernible, and on the other hand the irregular decoration of island edges with molecules from the fluid following substrate cooling. With the Cu(111) surface, the island patches are smaller than on Ag(111) and even single molecules on steps and defects can be observed. For Ag(111) submonolayer preparations measured at room temperature the mobility zone at the island edges is very extended (10 nm range), which fact is attributed to the weaker surface interactions compared to a copper substrate.

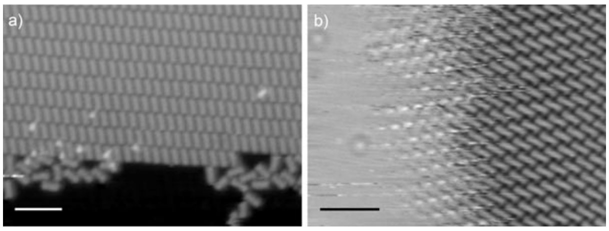

Figure 2. STM images of the island border structure at different temperatures. a) On Ag(111) after room-temperature-assembly and cool-down to 6 K the edge-mobility is frozen and the edge decoration evidences the condensation of mobile species. b) On Cu(111) at 300 K fluctuating edges indicate appreciable mobility of linkers and coexistence with a 2D fluid in open areas. Scale bars 4 nm.

A detailed view into the packing schemes of molecular assemblies in different domains and several preparations reveals the occurrence of six orientations of the molecular brick-lined structure, shown in Figure 3. Due to the threefold symmetry of the substrate and the two molecular *trans*-conformations six island formations are expected. We propose that all structure formation is based on the balance between surface epitaxial fit and noncovalent lateral interactions (compare the atomistic model proposed in Figure 1 b). Furthermore the 2D chirality of the molecules needs to be considered, which allows for several bonding motifs because of the different positioning of the reactive CN endgroups. In the upper part of Figure 3 the L-*trans* phases are depicted. The mirrored D-trans islands are each depicted underneath. Every column includes the particular mirror symmetric formation, whereby the mirror axis is given each with one of the crystal high symmetry directions.[13] L-*trans* molecules, exhibiting a clockwise tilt for the molecules and the

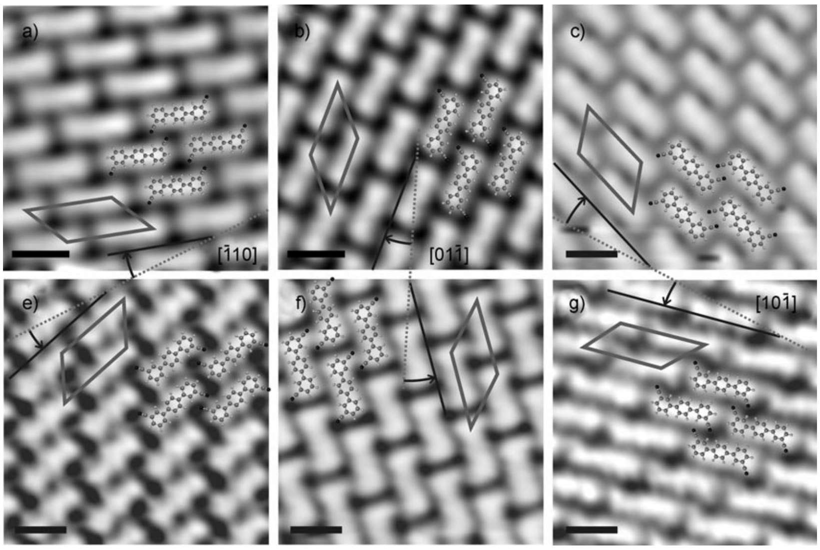

Figure 3. High-resolution STM images of molecular islands at room temperature. Due to the surface threefold symmetry and L- and D-*trans* (upper and lower column, respectively) molecular conformation, six-island orientation can be expected. Following the model in Figure 1, a)–c) are composed of L-trans molecules, whereas images d) and e) consist of D-trans molecules. Scale bars 1 nm.

unit cell, respectively, with respect to the high symmetry direction indicated by an arrow; whereas D-*trans* molecules feature a counter-clockwise tilting. Each island consists of only one conformation and thus represents an enantiomorphic entity due to a 2D chiral resolution.

It should be noted that both intermolecular and molecule–substrate interactions are crucial for the successful self-assembly of the reported structures: The carbonitrile determined packing scheme points to considerable attractive intermolecular forces, while the six orientations of the molecular domains relative to the substrate together with the commensurate island structure (as inferred from the dimensions of the unit cell and a lacking moiré pattern) indicate non-negligible molecule-substrate interactions. Most of the structures investigated displayed a packing scheme that can be explained with these ordering principles implying exclusively the two *trans*-species. However, islands exist with different packing schemes, such as the one in Figure 2 for the Ag(111) surface, that can be better explained with the chaining of *cis*-conformers. Unfortunately the large extension of the islands prevented from a statistical analysis regarding the equal distribution of all island structures and surface stereoisomers.

The influence of the substrate is also obvious when the low-coverage system is thermally quenched to low temperatures (6 K), where entities from the molecular fluid deduced above condense notably into molecular ribbons. Because these assemblies are not perfectly ordered they represent metastable configurations due to kinetic limitations in the 2D aggregation processes. The formed ribbons are oriented along the three high symmetry orientations of the substrate (marked with the black star in the lower right corner in Figure 4a). They can extend up to more than 100 nm, whereby for each direction two different chiralities are observed. In the shown STM image a mirror-symmetry axis (white line) demonstrates the two opposite molecular conformations of D-*trans* and L-*trans*. Thus altogether six dominating structural orientations are visible. Besides this, defect structures are observed in rare cases, which are interpreted as interconnections between the stable 1D ribbons. They are significantly shorter and may be an indication for the flexibility of entire chain segments.

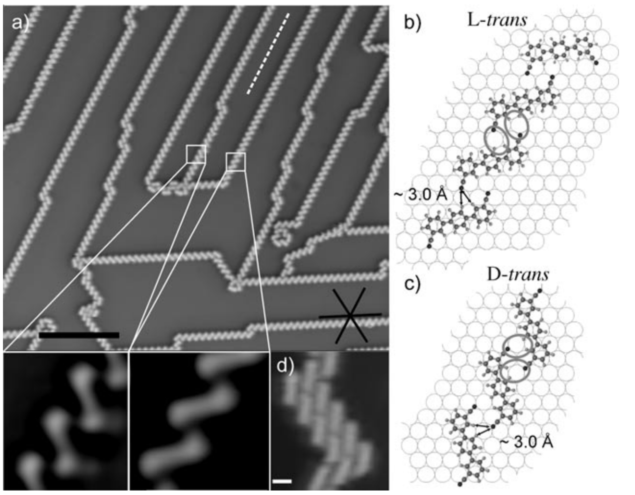

Figure 4. Set of STM images and atomistic structure model: a) high-resolution image of linker molecules assembled in a linear structure imaged at 8 K on Ag(111) with a coverage of 0.1 ML. A mirror axis (white line) helps to visualize the chirality of the assembled ribbons. The high symmetry orientations of the substrate are marked in the bottom right corner. Scale bar: 14 nm. b) Structural model of the linear phase with interatomic distances. c) Island patches evolve with increasing molecular coverage. Scale bar: 1 nm.

High-resolution images have been recorded to clarify the bonding scheme in the linear structure. The periodicity of the ribbon is 11.5 Å, that is, similar to the one in the island formation. The data allow us to propose an atomistic model of L-*trans* conformation lines featuring planar molecules like in the island structure that is displayed in Figure 4b. The carbonitrile groups point towards phenyl hydrogens of the neighboring molecule. The pertaining N···H distance is slightly above 3 Å, which is consistent with a recent analysis of nanoporous network structures consisting of sexiphenyl with two carbonitrile groups in the *meta* position.[8] The atomistic model features the position of the nitrogen in the hollow site of the substrate achieving commensurate assembly consistent with the measured molecular orientation and distances. Our model is in agreement for D- and L-*trans* conformation, whereas the molecular backbone of the L-*trans* is tilted clockwise by ca. 12° from the propagation direction of the 1D ribbon and the D-*trans* counter-clockwise, respectively. Only rarely are *cis* species incorporated in the ribbon structures. Their presence in characteristic defects where lateral shifts occur is modeled in Figure 4b.

Thus the condensation of the molecular fluid upon thermal quenching and the pertaining 2D self-assembly is a chiroselective process. In the fluid phase, where the density is low and molecules are rarely in contact with each other, it must be assumed that a thermal equilibrium distribution with equal proportion of *cis* and *trans* species prevails.[10] However, during the condensation the intermolecular interactions might render the *trans* conformation more favorable. Note that the expression of the ribbons points to a limited mass transport in the assembly. It implies on the one hand a chiral resolution of the two different *trans* species. Hereby the coexistence of mirror-symmetric ribbons from both *trans* species in large terraces excludes a self-replication process in their formation, which contrasts findings with related systems.[23] On the other hand, the minor proportion of *cis* species that could be identified can be understood as a hint that during the self-assembly a dynamic chiral switching process is possible, that is, the rotation of a cyanophenyl moiety about the molecular axis occurs driving a *cis*–*trans* transformation. This is in agreement with previous observations of complex adsorbed organic molecules where chiral switching could be correlated with spontaneous conformational changes.[14] Furthermore on close-packed noble metal surfaces the interaction between phenyl rings and the substrate is relatively weak, such that reorientations of rotatable phenyl moieties are possible.[24] Note that a lift from the surface in cluster formation was already demonstrated in ab initio calculations for adsorbed benzonitrile.[16]

In Figure 4a the coverage is about 0.1 ML. By increasing the coverage at first small islands can be found which seem to evolve from two adjoining ribbons. In Figure 4d the transition from a one-dimensional to a two-dimensional structure is depicted. Nevertheless, the direction of the molecular main axis is not exactly the same as in the linear structure, presumably due to the interaction with the neighboring ribbons. Hence the island is different from the linear structure. Further molecules exhibiting a *cis* conformation occur especially on the step edges and on unusual/border positions, such as the outer right and left molecule in Figures 4 b,d.

Both enantiomers of the *trans* specimen were found to assemble in the typical linear 1D chiral structures. At intersections of 1D ribbons with the same chirality, 2D chiral nodal motifs arise. In Figure 5 a the D-*trans* conformation resembles a counter-clockwise rotating "windmill" structure at the intersections marked with white arrows. The nodes in these 2D structures consist of two different binding motifs, as illustrated in the inset. The positioning of two of the CN groups suggests a dipole interaction with an antiparallel orientation (marked with a grey circle). The second bonding motif is more hydrogen-bridge-like, similar to the ribbon and island formation. A dominant orientation resulting in the dipolar bond was not observed.

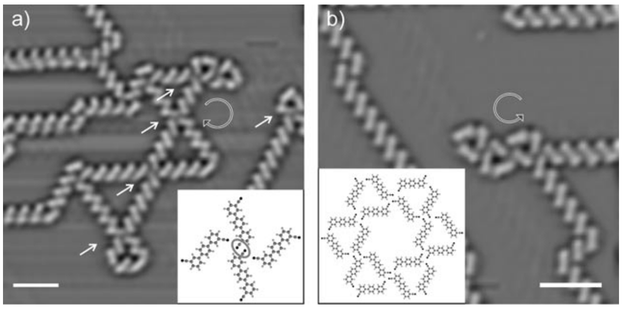

Figure 5. Supramolecular structures, exhibiting chiral nodal motifs. a) At intersections of the ribbons, chiral structures with a counter clockwise rotation can be found (marked with the white arrows). In (b) a similar bond motif is displayed with a clockwise rotation. The motifs resembles those identified in the kagomè like superstructure with linear building blocks (see refs. [7, 8]), which could be assembled as depicted in the inset with the molecules used herein. Scale bar: 4 nm.

Figure 5 b features the windmill motif as well. However, being composed of L-*trans* molecules, the sense of rotation is inverted. By merging several equally oriented windmill motives more complex structures can be created (inset of Figure 5 b). Three windmill motifs are connected forming a sector of a circular structure. This motif is alike a structure formed by five and six phenyl dicarbonitrile molecules on Ag(111) where they form regular kagomè-like structures over wide areas.[7,8] Furthermore in the island structure as well as in the 1D ribbon formation, the D-*trans* molecule is rotated clockwise and the L-*trans* counter clockwise, respectively. In combination with the initial state of island formation (Figure 4 d) the depicted atomistic model for the island formation is corroborated. Hence over wide areas a racemic distribution of molecular arrangement by means of the island pattern could be evidenced.

3. Conclusions

We presented a study addressing the supramolecular organization and layer formation of the non-linear, prochiral molecule [1, 1′;4′,1′′]-terphenyl-3,3′′-dicarbonitrile adsorbed on the Ag(111) surface. Our combined STM and NEXAFS investigations provide novel insights in the 2D self-assembly of this prochiral species that upon surface confinement deconvolutes in three stereoisomers, that is, two mirror-symmetric *trans*- and one *cis*-species. STM measurements reveal large and regular islands following room temperature deposition, whereby NEXAFS confirms a flat adsorption geometry with the electronic π-system and functional CN end groups parallel to the surface plane. The ordering within the densely packed supramolecular arrays reflects a substrate templating effect, steric constraints, and the operation of weak lateral interactions between the functional end groups. The expressed bonding motifs suggest both mutual interactions between carbonitrile and phenyl moieties. Chiral resolution processes in the self-assembly lead to enantiormophic characteristics of the molecular packing schemes in different domains of the arrays. Notably a set of six brick-lined arrangements could be identified comprising rotational domains of three *trans* species with two mirror-symmetric configurations each. At submonolayer coverage supramolecular islands coexist with a disordered fluid phase of highly mobile molecules. Following thermal quenching, we find extended supramolecular ribbons stabilized again by attractive and directional noncovalent interactions driven by CN endgroups. The ribbon formation reflects an exclusive chiral resolution of *trans* species.

Experimental Section

The STM experiments were performed on a Ag(111) single crystal in ultrahigh vacuum providing well-defined conditions. Before running the experiments, the sample was cleaned thoroughly by repeated Ar$^+$ sputtering cycles with an energy of 1.0 keV and a typical sputter current of 10 μA for 15 min. The sputtering was followed by annealing at 770 K for 10 min. Subsequently the molecules have been deposited by organic molecular beam epitaxy (OMBE) from a quartz crucible held at 500 K after prudent degassing, while the sample was kept at room temperature. The pressure during evaporation never exceeded 1×10^{-9} mbar. The molecular flow was about 0.14 ML min^{-1}, as derived from the STM measurements to be. The cooling rate for the low-temperature experiments was approximately 1 K s^{-1}in the decisive temperature interval 300–100 K.

The synthesis of the rod-like *m*NC-*p*Ph$_3$-*m*CN molecule was developed according the published procedure by coupling of bis(iodobenzene) and two equivalents of 3-phenylboronic acid under typical Suzuki conditions with 10 mol% Pd(^{0}).[25] The geometry of the free molecule was calculated in the semi-empirical AM1 framework.

Room-temperature STM measurements were performed in a custom-designed ultrahigh vacuum apparatus equipped with a commercially available Aarhus 150 variable temperature STM (cf. www. specs.de) and standard tools for in situ sample preparation. All measurements were carried out at a base pressure below

5×10^{-10} mbar. STM topographic images were obtained with an electrochemically etched tungsten tip and bias voltages between -1.5 and $+1.5$ V applied to the sample. Data was recorded in constant-current imaging mode. Low-temperature STM measurements were performed with a Besocke-type low-temperature (LT) STM from Createc (cf. www.createc.de and[26]) at ca. 6 K, housed in a custom-designed ultra-high vacuum chamber with a base pressure lower than 2×10^{-10} mbar.[27] Similar scanning parameters, as in the Aarhus STM, have been applied. All presented STM topographic images were processed with the WSXM SPM program.[28] The images presented in Figures 2b and 3 were measured with the Aarhus-type STM. Figures 2a, 4 and 5 comprise micrographs recorded with the LT-STM.

The near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy measurements were carried out at the HE-SGM beam line located at BESSY II in Berlin providing highly monochromatic light with a linear polarization of 82%. Molecules were deposited at room temperature after verifying surface cleanness by repeated NEXAFS spectra recorded at the C1s and N K edge. To minimize X-ray mediated damage to the molecules the sample was cooled down to 110 K for the measurement.[29]

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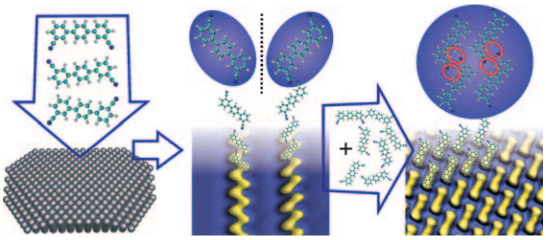

The supramolecular organization and layer formation of a non-linear, prochiral molecule adsorbed on the Ag(111) surface is investigated. Upon 2D confinement the molecules are deconvoluted in three stereoisomers. The ordering within the expressed supramolecular arrays reflects a substrate templating effect, steric constraints and the operation of weak lateral interactions (see picture).

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Supramolecular Organization and Chiral Resolution of *p*-Terphenyl-*m*-Dicarbonitrile on the Ag(111) Surface