Article Title
Role of cyano groups in the self-assembly of organic molecules on metal surfaces.

Author and Co-author Contact Information
Brian David Baker Cortés, Meike Stöhr
Zernike Institute for Advanced Materials, University of Groningen, The Netherlands
E-mail: m.a.stohr@rug.nl

Abstract
Molecular building blocks substituted with cyano groups have shown to form a myriad of supramolecular architectures on coinage metal substrates upon self-assembly. The flexibility of the polar cyano group to be involved in various bonding motifs such as H-bonding, metal-ligand bonding or dipolar coupling is essential for the formation of these structures. In addition to the intermolecular interactions, the molecule-substrate interactions depended on the structure of and charge distribution within the molecular building blocks have a direct impact on the structure of the organic networks. Here, we discuss the influence of cyano endgroups in the self-assembly of organic molecules on metal surfaces by means of their bonding motifs. Especially, porphyrin and polyphenyl derivatives are excellent candidates for cyano substitution since the number as well as the position of the cyano substituents can be precisely adjusted offering a high degree of both control and variability over the outcome of the self-assembly process.

Keywords
Cyano group
Dipolar coupling
H-bonding
Helicene
Metal-ligand bonding
Molecular self-assembly
Polyphenyls
Porphyrins
Scanning tunneling microscopy
Supramolecular architectures

Glossary
Chirality: A chiral molecule cannot be superimposed on its mirror image. The most often occurring reason is the existence of a stereocenter (a sterogenic atom) around which the attached substituents are asymmetrically distributed.
Dipolar coupling: Electrostatic interaction between permanent charges or dipoles that can be attractive or repulsive depending on the geometrical orientation of the involved species.
Hydrogen bonding: Electrostatic interaction between an electronegative atom and a hydrogen atom bound to another electronegative atom.
Metal-ligand bonding: Bonding motif between a metallic atom and molecules or ions known as ligands that can coordinate around it.
Molecular self-assembly: Spontaneous arrangement without human intervention of molecular building blocks into ordered structures based on non-covalent interactions.
STM: A technique to image conducting surfaces on the nanometer scale. Its lateral resolution is in the range of 1 Å, allowing for imaging of individual molecules and even atoms. The technique is based on the quantum mechanical tunneling effect.

Nomenclature
1D: One-dimensional
2D: Two-dimensional
DFT: Density functional theory
STM: Scanning tunneling microscopy
RT: Room temperature
ML: Monolayer
XAS: X-ray absorption spectroscopy

Body text

Introduction
Over the past two decades, the topic of two-dimensional (2D) supramolecular structures on metal surfaces has seen a change from a niche existence into a vibrant research field. The creation of supramolecular structures is based on molecular self-assembly. A process in which the employed organic molecular building blocks organize spontaneously and reversibly into ordered patterns without human intervention. The self-assembled systems are held together by non-covalent interactions and they are in their global or local equilibrium. In order to build up desired functional structures control over both intermolecular as well as molecule-substrate interactions needs to be gained since their interplay determines the outcome of the self-assembly process. Equipping the molecules with certain functional endgroups to engage in predefined bonding motifs having directionality and specific bonding strength, is a commonly accepted strategy to deliberately steer the self-assembly process towards a desired structure.

A frequently used functional endgroup towards this end is the cyano group (N≡C). Its negatively charged N-atom can interact through different bonding motifs with neighboring molecules. These are the weak interactions single H-bonding, H-bonding in a cyclic trimeric motif and antiparallel dipolar coupling and the substantially stronger interaction metal-ligand bonding. From the mere number of interactions cyano groups can participate in together with the relative weak interaction strength for the first three motifs, it becomes obvious that the rational design of molecular networks as well as the formation of them on surfaces can be quite challenging.

Two prominent classes of molecules, namely porphyrin and polyphenyl derivatives substituted with cyano groups have been frequently studied for the formation of 2D supramolecular architectures. Porphyrins are tetapyrrole macrocycles with a central cavity which can coordinate to a metal ion in the formal +II oxidation state. The porphyrin core – better called porphin - can be substituted with specific molecular endgroups what opens the possibility to tune the structure and bonding strength of the supramolecular networks. Porphyrins play vital roles in nature but they also open the gap for the development of nanoscale electronic devices and applications such as dyes in solar cells or in catalysis. On the other hand, polyphenyls are linear molecular structures of varying length that are composed of a sequence of phenyl rings connected via single C-C bonds to which functional groups can be attached to at each end.

In the following, the influence of different cyano-substituted molecular building blocks is discussed for the formation of 2D assemblies merely stabilized by hydrogen bonding and dipolar coupling. Additionally, instructive examples for metal-ligand bonding are presented which also cover the effect of the type of metal atom on the created molecular structures. In the last part the usage of cyano groups for controlling chirality on surfaces is detailed. The structural arrangement of the
resulting self-assembled supramolecular architectures is depicted in detail by scanning tunneling microscope images.

[Figure 1]

Self-assembly based on hydrogen bonding and dipolar coupling.

Yokoyama et al. reported the directed self-assembly of surface-supported supramolecular structures for the first time by adequately choosing the functional endgroups – namely cyano groups –, which in turn control the non-covalent interactions of the structure. In Fig. 2a the scanning tunneling microscopy (STM) image of the self-assembly of trans-bis(cyanophenyl)-bis(di-tertiarybutylphenyl) porphyrin (molecule 3 in Fig. 1) on Au(111) displays a linear arrangement in a supramolecular wire-like form stabilized by antiparallel dipolar coupling between the cyanophenyl substituents (Fig. 2d). The bright lobes in Fig. 2a correspond to the tert-butyl substituents, while the cyanophenyl substituents are found in the dimmer mid-region of the elongated structure. The maximum length of the supramolecular wire was reported to be slightly above 100 nm and the estimated length of the methine-cyano (CH…NC) contacts between neighboring cyanophenyl groups is of 2.6 Å, which in turn suggests the additional presence of hydrogen bonding interactions.

A very different scenario happens when this porphyrin derivative is deposited onto Cu(111), as observed in Fig. 2b. An ordered two-dimensional porous networks is arranged by windmill-like structures, each one consisting of six porphyrin molecules. Each windmill structure has a core in its center with a diameter of (18±1) Å, the cores extend throughout the network with a pore-pore distance of (32±1) Å. The bright lobes belong to the tert-butyl substituents once again and each molecule 3 is shared among two windmill structures. Molecules 3 interact via hydrogen bonds arranged in the trimeric cyclic motif between the hydrogen atoms of the cyanophenyl rings and the nitrogen atoms of the cyano end groups as illustrated in Fig. 2e. Comparison of the assembly structures from 3 on Au(111) and Cu(111) indicates that the substrate is a parameter that plays an essential role in the self-assembly of cyano-substituted molecules. In a similar case with the network from molecules 3, a porphyrin derivative with cyanophenyl and alkoxyphenyl substituents at trans meso positions (molecule 6 in Fig. 1) was deposited onto Cu(111) giving again rise to a nanoporous network (Fig. 2c). The network exhibits a pore-pore distance of (48.0±1.4) Å (indicated by a yellow arrow in Fig. 2c), which is significantly larger than the one for the network from molecules 3. This is due to the alkoxyphenyl substituents which directly influence the interaction motif of the cyanophenyl groups: the trimeric motif is varied by replacing one cyanophenyl with an alkoxyphenyl group. In contrast to the previous nanoporous network (Fig. 2b), where one porphyrin unit is shared among two pores, each pore is formed by 6 porphyrin units that are not shared among other pores. Subsequently, this increases the pore-pore distance.

The structural model in Fig. 2f illustrates the bonding motifs that stabilize this network. Basically, the cyanophenyl substituent acts as a hydrogen bond donor and acceptor. A trimeric bonding motif is formed (central region of the model) by the interaction of the cyano group from one of the cyanophenyl substituents via hydrogen bonding with the hydrogen of the ortho C-H moiety of one of the alkoxy substituents from another porphyrin. Analogously to this interaction, the same cyanophenyl group forms a hydrogen bond between the hydrogen of one of its nearest C-H moieties with the nitrogen of the cyanophenyl substituent of a neighboring porphyrin. Moreover, van der Waals interactions among two or three alkoxy chains of neighboring porphyrins provide further stabilization of the network. Molecules 4 and 5 (Figure 1), which are substituted with different alkoxyphenyl groups compared to molecule 6, also form nanoporous networks (STM images not shown) similar to the one of molecule 6. The pore to pore distance increases from 30.9 to 33.5 Å for the network of molecules 4 and 5, respectively. The pores of both networks are surrounded by alkoxy substituents from six different molecules and each molecule is shared among two pores. In comparison to the network of Fig. 2c, a trimeric bonding motif involving three and not only two
cyanophenyl groups stabilizes the networks of molecules 4 and 5, only the intermolecular interaction is slightly modified. For molecule 4 the trimeric motif is given by interaction between the cyano groups and the β-hydrogen atoms from three neighboring porphyrins. Meanwhile, the trimeric motif of molecule 5 is similar to the one for molecules 3 on Cu(111). The alkoxy groups in terms of size, amount and spatial orientation give access to control the dimensions of the porous networks, such as the pore-to-pore distance.

As shown in Fig. 2, porphyrin derivatives substituted by cyanophenyl groups at trans meso positions display different structural arrangements depending on the metallic substrate they are deposited onto. By either selecting a Au(111) or Cu(111) substrate different structural arrangements of the same molecule can be formed upon self-assembly. Furthermore, by carefully selecting the substituents (as in Fig. 2b and 2c) the intramolecular interactions modify the self-assembly process and provide the formation of a myriad of two-dimensional networks.

[Figure 2]

Varying the substitution pattern from trans to cis for molecule 3 gives rise to molecule 2 in (Fig. 1), i.e. the cyanophenyl and di(tertbutyl)phenyl substituents are located at right angles, results in the formation of tetrameric units on Au(111) (Fig. 3a). The tetramers are stabilized via a combination of antiparallel dipolar coupling of the cyano groups and weak H-bonding between the cyano groups and the CH moieties of the cyanophenyl substituents from neighboring porphyrins. The H-bonding distance is approximately 2.6 Å, which is similar to the distance in the wire-like form in Fig. 2a. Again, the bright lobes observed in the STM image correspond to the tert-butyl substituents. In contrast, Molecule 1 has only 1 cyanophenyl substituent and is responsible for the formation of a cyclic configuration assembled in a trimeric structure (STM image not shown).

Molecule 7 (Fig. 1) is obtained when replacing the cyanophenyl with a cyanobiphenyl group. Deposition of this molecule on Cu(111) resulted in the formation of cyclic oligomeric structures ranging from dimers up to hexamers. This structural diversity is in contrast to the exclusive formation of tetramers from 3 on Au(111). The main reason was assigned to the change in substrate. The Cu(111) substrate is known to generally interact more strongly with organic molecules and thus, the interplay of intermolecular and molecule-substrate interactions is altered with the molecule-substrate interactions becoming more important for the final assembly structure. For the present case, the existence of the latter interactions can be seen by a closer inspection of the STM images displayed in Fig. 3b)-d). The dark bending line originating from the saddle shape conformation of the porphyrin core leads to two conformational isomers labelled as type A and type B. For type A, the bending line separates the cyanobiphenyl from the di(tert-butyl)-phenyl substituents while for type B the bending line is parallel to the symmetry axis of the molecule. The bending line was for all molecules found to be parallel to a principal Cu direction, i.e. the rotational molecular arrangement dictates which types of intermolecular interactions can develop.

The trimer and tetramer shown in Fig. 3b) and d), respectively, are (partly) held together by weak H-bonds between a hydrogen bonded to a sp2-hybridized carbon atom and the nitrogen atom of the cyano group of an adjacent molecule. This bond is weaker than usual hydrogen bonds and lacks directionality. In turn this provides the possibility to adapt to different geometries. For the trimer (Fig. 3b), always consisting of the same conformational isomers, antiparallel CN-CN interactions accompanied by CN-HC H-bonds take place. The rectangular tetrameric structure (Fig. 3c) assembled from alternating conformational isomers is similarly to the trimer stabilized by antiparallel CN-CN bonds and CN-HC H-bonds. Finally, the interaction involved in the all-type A (or B) tetramer is different and is based on non-directional H-bonding.

[Figure 3]
The self-assembly of linear dicarbonitrile-polyphenyl molecules of varying length on Ag(111) has been intensively investigated by Barth and co-workers. The molecules employed have one cyano group attached to each end (NC-Ph_n-CN for n= 3, 4, 5 and 6) and correspond to molecules 8 to 11 from Fig. 1. The length of the rod-like molecules, which varies from 1.66 to 2.96 nm (N-N distance) for the molecules with n=3, 4, 5 and 6, was found to influence their structural arrangement.

A densely-packed arrangement of molecule 8 is depicted in the STM image of Fig. 4a, the rod-like building blocks align in a V-shape manner or so-called chevron pattern. The overall alignment of the self-assembly clearly shows that the molecules lie in two directions parallel to the [1-10] and [7-3-4] directions of the Ag substrate. In terms of bonding motifs, molecule 8 undergoes two types of interactions, N-N repulsive interactions from the cyano end groups of neighboring molecules and an attractive one given by the cyano end groups and H-atoms of the phenyl groups. Later it was discovered that this type of interaction does not qualify for a classical H-bond and thus, was named PARI (proton acceptor-ring interaction).

If one more phenyl ring is added to the central part of rod-like molecule 8 (molecule 9, Fig. 1), the self-assembly process creates an open rhombic network that comprises a four-fold chiral bonding motif (Fig. 4b) leading to organizational chirality. Similarly to 8, molecule 9 aligns along two Ag directions, namely the [1-10] and [35-8] direction and the molecular arrangement is suggested to be commensurate to the underlying Ag substrate. Due to the increased molecular length combined with the preference for parallel alignment along certain substrate directions, the formation of the chevron pattern is no longer possible. Thus, the molecular patterns are now stabilized by single H-bonds between the cyano groups and phenyl hydrogen atoms. This means the intermolecular interactions adapt to the dominant molecule-substrate interactions.

The 2D kagomé lattice shown in Fig. 4c forms when the even longer rod-like molecule 10 is deposited on Ag(111) (Fig. 1). The nodes of the quasi-hexagonal structure connect four neighboring molecules and small triangular features surrounding each pore can be discerned. This structure is again chiral but much more complex compared to the other two previous ones. The hierarchical ordering levels that the subunits organize in the kagomé lattice, range from linear rod-like building blocks to triangular structures that interconnect in a hexagonal pattern. The terminal phenyl rings are rotated 20° with respect to the molecular axis. For such reason, the kagomé lattice does not lie completely flat on the Ag(111) surface, instead the fourfold nodes exhibit a non-planar geometry. In order to corroborate this assumption X-ray absorption spectroscopy (XAS) measurements were carried out.

Finally, molecule 11 (Fig. 1) self-assembles into three kinds of two-dimensional structures as observed in the STM images shown in Fig. 4d-f. For all three structures, there is a nodal binding motif that connects four molecular units together. The main interaction in between the molecules for all the different arrangements is given by hydrogen bonding in between the cyano groups and the hydrogen atoms from adjacent phenyl rings. The rhombic phase (Fig. 4e) and kagomé network (Fig. 4f) are comparable to the ones obtained from 9 and 10 (Fig. 4b and c), respectively. The main difference is the length of the molecular building block. By taking a closer look at the rhombic network (Fig. 4e), two nodal configurations can be discerned, an open and a compact node. All three phases exhibit organizational chirality and are commensurate to the Ag surface. The H-N bond length in the kagomé lattice for 11 varies from 2.3 to 3.2 Å, compared to the 1.5 Å reported for the kagomé lattice of molecule 10. Summarizing, it can be stated for the self-assembly of cyano-substituted polyphenyls 8 – 11 on Ag(111) that the molecule-substrate interactions prevail and the flexibility of the cyano group to be involved in different intermolecular interactions (H-bonding, dipolar coupling, PARI) is the key for the formation of long-ranged well-ordered architectures.

Self-assemblies based on metal-ligand interactions
The following section focuses on the self-assembly of 2D networks from cyano-substituted molecules stabilized by metal-ligand bonding. Depending on the type of metallic atom, the coordination number, i.e., the number of ligands attached to the atom, can vary resulting in the formation of structurally different assemblies for the same molecular building block. The metal-ligand bonding can be induced either by deposition of metallic atoms onto a previously formed network of molecules or by generating – for example by annealing - native atoms that belong to the metallic substrate.

Figure 5 summarizes the various assembly structures observed for metal-coordinated networks from the rod-like polyphenyl derivatives 8 – 11 and different metal atoms. As substrate, Ag(111) was used, except for the combination of 9 and Eu-atoms which was investigated on Au(111) (Fig. 5f). The STM images of Fig. 5a-d have a common 2D arrangement, a honeycomb nanomesh formed by metal-ligand bonding between Co-atoms and the cyano groups of molecules 8 – 11, respectively. The Co-atoms are positioned at the nodes and coordinate to a total of three molecular units (Fig. 5h). The electronegative nitrogen atom of the terminal cyano group interacts via metal-ligand bonding with the Co-atom (orange sphere). The Co-N bond length was reported to be 1.6 Å for the nanomeshes of molecules 8 - 10 and slightly increases to 1.9 Å for the network formed by molecule 11. Density functional theory (DFT) calculations showed a strong hybridization between the Co-atom and the Ag surface suggesting that the Ag substrate takes the role of a fourth ligand. The cavities of the nanomeshes vary in size according to the length of the employed rod-like molecule. For the network of molecule 8 (Fig. 5a) the hexagonal cavity size is approximately 10 nm², meanwhile for molecule 9 through 11 it is 15, 20 and 23.7 nm², respectively.

Replacing the Co-atoms by Ce ones results in a change of the coordination number. Now, exclusively a five-fold coordination is present (Fig. 5e, g). Barth and co-workers gradually varied the ratio between molecules 8 or 9 and Ce-atoms starting with 5:1. For this ratio, only individual pentameric units were formed. Increasing the ratio to 4:1 resulted in the formation of a hexagonal network composed of dodecameric units. In each of these units only 3 molecules are involved with both terminal cyano groups in metal-ligand bonding while the other 9 molecules are only singly coordinated. For a ratio of 5:2 (molecules:Ce) all terminal cyano groups are involved in metal-ligand bonding. Now a surface tessellation consisting of squares and triangles and corresponding to the semiregular Archimedean snub square tiling was formed. The Ce-N bond length for this network was only slightly different for molecules 9 (2.7 Å) compared to molecules 8 (2.4 Å). This indicates, since the linker length has only a marginal influence, that the assembly protocol should be of more general validity.

The metal-organic coordination networks described so far follow a certain degree of periodicity or long-range structural orientation. A completely different scenario happens for co-deposition of 9 and Eu-atoms on Au(111) (Fig. 5f). In dependence of the ratio between molecules and Eu-atoms, the metal-organic coordination networks can even exhibit quasicrystallinity. This is only possible because molecules 9 and Eu-atoms can be involved in four-, five- and six-fold metal-ligand bonding, a prerequisite for the expression of quasicrystallinity.

For a cyano-functionalized triarylamine derivative (molecule 12, Fig. 1) the interplay between molecule-substrate and intermolecular interactions was studied in detail for their adsorption on the (111)-oriented coinage metal surfaces Ag, Au and Cu. Figure 6 summarizes the assembly structures, which were observed with STM on the different surfaces, along with their structural models. The self-assembly of 12 on Au(111) (Fig. 6a) at a coverage of one monolayer (ML) generates a hexagonal close-packed network labeled as phase α. The unit cell of phase α is highlighted with a green rhombus in the tentative structural model on the right of Fig. 6a, with a size of 1.32 x 1.32 nm² and internal angle of 120°. Molecules 12 exhibit two different orientations rotated by 180° with respect to one another what enables their participation in three interaction motifs. These are
antiparallel dipolar coupling given by the interaction between cyano groups from neighboring molecules that align parallel to each other (red oval in the structural model of Fig. 6a), single H-bonding between the N-atom of the cyano group with a H-atom of a neighboring molecule (light blue oval in the structural model) and the trimeric motif governed by cyclic H-bonding (dark blue circle in the structural model). The herringbone reconstruction of the Au(111) surface was unaffected after molecular deposition. However, the molecular orientations were found to exhibit a correlation with the periodicity of the herringbone reconstruction.

For a coverage smaller than 1 ML, 12 formed two different phases on Au(111) both exhibiting organizational chirality (Fig. 6b-c). Porous phase α (Fig. 6b) is exclusively stabilized by dipolar coupling and the molecules are alternately rotated by 180°. The second one is the partial porous phase β (Fig. 6c). The pores are arranged by six molecules coupled by dipolar interactions and they interact via metal-ligand bonding between one another (blue circle in the tentative model of Fig. 6c). The metal-ligand bonding is given by one Au-atom coordinating with three cyano groups from different molecules. The unit cell size of phase β (3.77 x 3.77 nm² with an internal angle of 120°) is larger compared to the one of the close-packed phase α.

By replacement of the substrate from Au(111) to Ag(111), a similar hexagonal close-packed pattern is formed for coverages ≤ 1ML of molecule 12 on Ag(111) (Fig. 6d), i.e. only one type of assembly structure was observed. Almost all the molecules are oriented in one direction while only a very few are found that are rotated by 180° (black circles in the STM image in Fig. 6d). The molecules (almost) exclusively interact via the trimeric H-bonding motif what is in contrast to situation on Au(111). The unit cell of this network is 1.32 x 1.32 nm² with an internal angle of 120°. These values overlap to those of the close-packed phase α on Au(111). Despite the very similar lattice constant for Ag(111) and Au(111), the influence of the substrate (with respect to the rotational adsorption position) is large enough to slightly modify the balance between molecule-substrate and intermolecular interactions. This results in the development of different phases on Au(111) because of the flexibility of the cyano group to be involved in different interaction motifs.

The deposition of a submonolayer of molecule 12 on Cu(111) (Fig. 6e) forms a very distinct network in terms of packing and distribution of the molecules compared to the results shown for Au(111) and Ag(111). Only small islands were formed and also some disordered areas where molecules assemble in short-range rows and pores were observed. The disordered parts of the assembly are stabilized by dipolar coupling. Within the ordered close-packed islands (Fig. 6e), the molecules are all aligned in one direction. But this time, they are involved in metal-ligand bonding occurring between the cyano groups and native Cu-atoms. The close-packed islands on Cu(111) have a unit cell (1.4 x 1.4 nm²) larger than the one on Au(111) or Ag(111). Since the molecules point towards each other (different to the cases on Ag and Au) as revealed by the STM image, the repulsion between the electronegative N-atoms would not favor the formation of a network without Cu-atoms incorporated. The missing long-range order evident from the disordered areas and the patches of close-packed structures is a sign for a relatively strong molecule-substrate interaction between 12 and Cu(111), also stronger compared to Au(111) and Ag(111). This can be associated with the lattice mismatch between the Cu(111) unit cell and the one of the regular hexagonal porous network.

The effect of annealing the sample at elevated temperatures was studied for the porphyrin derivative 7 on both Cu(111) and Au(111). For both substrates it is known that raising their temperature results in the creation of adatoms which can be involved in the formation of metal-organic coordination networks.

Annealing 7 adsorbed on Cu(111) above 150°C lead to the formation of dimers (Fig. 7a) while no other oligomeric structures were anymore observed. The cyanobiphenyl substituents flex towards each other forming a 60° angle between them and each cyanobiphenyl substituent bends by 15° (Fig. 7d) to coordinate to one Cu-atom. The saddle-shape conformation of the porphyrin core caused
by the strong interaction between Cu(111) and 12 together with the possibility of bending the single C-C bonds of the cyanobiphenyl substituents by around 5° allows the substituents to become closer. The self-assembly of molecule 7 on Au(111) after annealing at 160°C bears the formation of metal-coordinated 1D flexible polymeric chains (Fig. 7b). Three cyanobiphenyl substituents from three molecules face each other and undergo metal-ligand bonding to a native Au-atom, thereby forming a threefold node. Compared to the dimer of Fig. 7a, the coordination motif is now threefold instead of twofold. The 1D polymer is arranged by a set of threefold nodes as depicted in the structural model of Fig. 7e. Similar to the dimers, the angle between the cyanobiphenyl substituents can deviate from 90° (it can be both larger and smaller). This confers a certain degree of flexibility to the polymer chains as it can be observed in the STM image of Fig. 7b. By increasing the annealing temperature to 210°C a tetrameric bonding motif develops at the step edges of the Au(111) substrate (Fig. 7c). The tetramers are stabilized by a fourfold coordination motif between one native Au-atom and four cyano groups of four neighboring molecules 7 (Fig. 7f). The tert-butyl groups of the porphyrins align directly along the step edge as revealed by the bright lobes in the STM image.

[Figure 7]

Controlling chirality in 2D assemblies

Helicenes are polycyclic aromatic compounds and can be regarded as a prototypical example for a molecular helix. They are chiral without having a stereogenic center. Adsorption of these molecules on surfaces gives basic insight into the transfer of chirality from the molecular level into 2D arrangements. The self-assembly of the cyanosubstituted [7]helicene 13 (Figure 1) was investigated on Cu(111) with respect to the influence of substrate temperature and molecular coverage (Fig. 8). For a racemic mixture (1:1 ratio for (M) and (P) enantiomers) of pristine [7]helicene on Cu(111) no spontaneous resolution into enantiopure domains, i.e. no conglomerate formation was observed. However, when substituting the [7]helicene with cyano groups at almost opposite sides (molecule 13) conglomerate formation was observed for close to 1 ML coverage (Fig. 8a). 13 arranges in a close-packed dimeric structure (a dimer is marked by a filled blue rectangle in Fig. 8a) in which the molecules interact via dipolar coupling between their cyano groups. In other words, the higher lying cyano groups of neighboring 13 interact with each other as well as the lower lying ones. In Fig. 8a two domains can be seen while the upper one consists of (M)-13 and the lower one of (P)-13. That the two domains are mirror domains can be seen from the fact that the rotational angle for the unit cells of the (M)- and (P)- domain is 60° while the one for the dimeric unit is only 21.9°. The conglomerate formation can be explained on the basis of the introduction of the cyano groups: the interactions become more favorable and more directional compared to pristine [7]helicene. The deposition of submonolayer coverage of either (M)- or (P)-13 on Cu(111) held at 90 K prompted the formation of a H-bonded zig-zag chain (Fig. 8b). The H-bond forms between the higher lying cyano group and a H-atom of the higher lying part of a neighboring molecule, likewise for the lower lying part. In this way, chirality is transferred into the bonding pattern. On the other hand, upon annealing at RT for 1 h a transition from a H-bonded chain to a Cu-coordinated linear chain occurs (Fig. 8c). The presence of native Cu-atoms at increasing temperature is evident and triggers the metal-ligand bonding. That both cyano groups can undergo metal-ligand bonding 13 must deform. Now, there is no reason anymore why molecules need to attach either with their higher lying or lower lying part to another molecule in order to optimally adapt the intermolecular interactions. That means no chirality transfer from the molecule into the chain happens.

[Figure 8]

Conclusions.
The self-assembly of cyano-functionalized molecules on coinage metal surfaces under the modification of parameters such as the substrate and molecular coverage was discussed. The variety of bonding motifs cyano groups participate with was illustrated by STM images. For instance, polyphenyl derivatives substituted with cyano groups formed densely-packed arrangements by H-bonding and by deposition of Co-atoms porous-networks stabilized by metal-ligand bonding were formed. Similarly, the influence of the molecule-substrate interaction on the resulting assembly structure was illustrated on the basis of a porphyrin derivative, where dipolar coupling and trimeric bonding motifs were observed on Au(111) and Cu(111). On the basis of the presented examples it becomes clear that cyano-functionalized molecules can undergo a variety of different intermolecular interactions having diverse geometries. Thus, using cyano groups for steering the self-assembly process towards the formation of a specific and predictable supramolecular arrangement can be a challenging endeavor. The reason is that the cyano groups are mainly involved in weak interactions having similar bonding strengths, the exception is metal-ligand bonding. In addition to these weak cyano interactions, molecule-substrate interactions as well as further intermolecular interactions resulting from other functional groups attached to the molecule have to be considered. In order to properly make use of a particular cyano interaction motif for designing supramolecular architectures, all other competing factors have to be carefully evaluated beforehand. Competing factors are the influence of the substrate, molecular coverage, temperature, size and shape of the molecule and if the molecule has further substituents. On the other hand, the flexibility of the cyano group to be involved in different interaction motifs may ensure adaptation of the system to changing environments or external parameters. It is very likely that the system will keep its long-range order based on another cyano interaction motif instead of disintegrating.

References


**Further Reading**

**Figures**

**Figure 1.** Summary of the chemical structures of each cyano-terminated molecule discussed herein.
Figure 2. Top: STM images of the self-assembly of trans-cyano substituted porphyrin derivatives. a) Supramolecular aggregation in a wire-like form of molecule 3 on Au(111) (scan area= 5.3 x 5.3 nm²). Nanoporous network of: b) molecule 3 on Cu(111) (scan area= 12.5 x 12.5 nm²) and c) molecule 6 on Cu(111) (scan area= 15 x 15 nm²). Bottom d), e) and f): Respective tentative structural models of each network displaying the bonding motifs involved. Figures adapted with permission from: a) Macmillan Publishers Ltd: [Nature](4), copyright (2001); b) ref. 5. Copyright 2007 Wiley; c) ref. 6. Copyright 2008 Wiley.

Figure 3. Top: STM images of the self-assembly of cis-cyano-substituted porphyrin derivatives. a) Tetramer of molecule 2 on Au(111) (scan area= 5.3 x 5.3 nm²). Molecule 7 on Cu(111): b) All-type A trimer (scan area= 6.3 x 6.3 nm²), c) tetramer formed by both conformational isomers (A and B) (scan area= 6.4 x 6.4 nm²) and d) all-type B tetramer (scan area= 6.2 x 6.2 nm²). Bottom: Respective tentative structural models of each arrangement displaying the bonding motifs involved. Figures
Figure 4. STM images of linear ditopic dicarbonitrile-polyphenyl molecules on Ag(111). Top: a) Molecule 8 aligned in a densely-packed fashion, b) molecule 9 assembled in an open rhombic network and c) molecule 10 arranged as a kagomé network. Bottom: Assembly of molecule 11 in a d) rectangular, e) rhombic and f) Kāgōmē network (scale bars are displayed within the images). Figures adapted with permission from: a)-c) (JACS). Copyright (2008) American Chemical Society; d)-f) (JPCC). Copyright (2009) American Chemical Society.
Figure 6. STM images of the self-assembly of molecule 12 on coinage metal substrates. Self-assembly on Au(111) (scan area= 7 x 7 nm²): a) Close-packed phase α, b) porous phase α, c) phase β, d) close-packed arrangement on Ag(111) (scan area= 25 x 25 nm²) and e) close-packed islands on Cu(111) (scan area= 20 x 20 nm²). Right column: Tentative structural models for each network with the unit cells highlighted in green and the bonding motifs marked by circles and ovals. Figures adapted with permission from ref 15. Copyright 2016 Wiley.
Figure 7. STM images of the self-assembly of molecule 7 at different experimental conditions. a) Self-assembled dimer structure coordinated by native Cu-atoms on Cu (111) after annealing at 150 °C (scan area= 5.7 x 2.7 nm²), b) Metal-coordinated 1D molecular chain on Au(111) after annealing at 160 °C (scan area= 16 x 10 nm²) and c) 1D molecular chain formed upon annealing at 210 °C on Au(111) (scan area= 25 x 12.4 nm²). Bottom d), e) and f): Tentative structural models for each molecular arrangement shown in a), b) and c), respectively. Figure a) and d) adapted with permission from ref. 7. Copyright 2009 Wiley.

Figure 8. STM image of the self-assembly of molecule 13 on Cu(111) in dependence of the molecular coverage. a) Dimer formation from a racemic mixture of molecule 13 with two mirror images (scan area= 20 x 20 nm²), b) (M)-13 forms H-bonded chains (scan area= 5.4 x 3.2 nm²) and c) Cu-coordinated chains of enantiomer (M)-13 (scan area= 5.4 x 3.2 nm²). d) and e) DFT models for b) and c), respectively. Figures adapted with permission from: a) ref. 18. Copyright 2011 Wiley; b)-e) (JACS). Copyright (2013) American Chemical Society.