2D Self-Assembly Monitored by Hydrogen Bonds for Triphenylene-Based Molecules:a New Role for Azobenzenes

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ABSTRACT

A hybrid disk-like/rod-like molecule comprising central triphenylene core symmetrically substituted with six azobenzene moieties (**C-12**) has been adsorbed at the 1,2,4-trichlorobenzene/Au(111) interface, revealing the potential of azobenzene moieties for the control of 2D chiral networks. The **C-12**, which due to its complex molecular structure possesses a relatively large number of degrees of freedom, surprisingly forms monolayers of only one kind of structure, namely a hexagonal network of large period, 3.5 nm. By combining Scanning Tunneling Microscopy (STM) and DFT calculations, we evidence that this specific 2D-ordering is due to cooperative weak hydrogen bonds between neighboring azobenzenes and azobenzene-Au(111) interactions. The crystallographic network is hexagonal, but azobenzene-azobenzene pairing, associated with hydrogen bonding renders the network chiral with a chirality spanning all ranges, from the molecular **C-12** configuration, the configuration of the azobenzene dimers and the rosette-like azobenzene network, to the **C-12** network orientation on Au(111) rotated by ±8° from the main crystallographic direction Au<110>, depending on the handedness of the molecular network. This chiral 2D system thus paves the way for the formation of macroscopic 2D molecular crystals of unique handedness, if additional enantiomeric chiral dopants can be used.

INTRODUCTION

One of the challenging goals within the field of nanoscience and nanotechnology remains the recognition and controllable modification of the adsorption geometries of self-assembled molecules.[1-3] Since the molecular ordering at surfaces is driven by the balance between molecule-substrate and intermolecular interactions, the control of new kinds of interactions leading to self-assemblies bearing specific properties, chiral properties in particular, is highly desirable.[4,5] The main types of interactions responsible for molecular organization on surfaces are van der Waals interactions,[6,7] metal-ligand coordination,[8,9] aromatic interactions,[10] ionic interactions,[11] dipolar interactions[12] and hydrogen bonding.[13] The hydrogen bonding (H-bonding) is based on the interaction of species possessing a hydrogen-containing moiety that is polarizable, together with an atom of high electronegativity - most commonly oxygen or nitrogen.[14] One common feature for all hydrogen bonds is, in comparison to the van der Waals interactions, the definite directionality and increased strength. Due to this directionality the presence of the hydrogen bonding can induce a large number of geometries of self-assemblies,[15-17] including porous molecular networks.[18]

Self-assembly on metallic substrates in the conditions of ultra-high vacuum often results in appearance of chiral phases,[19,20] in particular characterized either by chiral clusters, chiral chains or 2D (extended) chiral domains.[21-23] These chiral assemblies can be stabilized by hydrogen bonding, but the origin of chirality mostly comes from the initial chirality of the molecules themselves. It is in particular the case of polyaromatic and heterocyclic compounds,[24,25] but also of the so-called bio-molecules like amino acids[26] or nucleic acid building blocks[27] which drive the research in the promising areas of biosensors and biomaterials.

An interesting and constantly growing research field comprises the investigation of monolayers composed of molecules which are not chiral in solution, but which result in chiral structures upon the creation of 2D self-assemblies.[4,5] In this frame, the studies of the hydrogen-bonded systems in which chirality is induced by the 2D confinement on a surface were usually concentrated on the organic molecules containing *e.g.* carbonyl or carboxyl groups directly attached to the polyaromatic part of the molecule.[22,28-34] The complexity of the possible output, including frequently appearing polymorphism of self-assemblies, usually renders difficult an accurate study of the balance between hydrogen bonds and molecule-substrate interactions for the determination of the molecular networks. Moreover, besides carboxyl group - the most frequently met functional group bearing the potential for hydrogen bonding formation, there exists interactions defined as weak hydrogen bonding which may involve N atoms in particular.[17,35] It can be inquired if such interactions based on the hydrogen bonding of weak type are capable to induce any specific geometry of self-assemblies. In particular, we are interested if weak hydrogen bonding may induce chiral assemblies of achiral molecules. To answer this question and to get more knowledge about the possible role of molecule-substrate interactions in presence of weak hydrogen bonding on the formation of chiral molecular networks, we have studied the **C-12** molecules at the 1,2,4-trichlorobenzene/Au(111) interface.

EXPERIMENTAL SECTION

STM measurements. The monolayers were investigated using a commercial STM equipped by low current head (Veeco, Digital Instruments, Inc. USA). STM-images recorded in constant current mode with current ranging from 1 to 100 pA and tip bias from ±100 to ±1000 mV were

acquired on different spots of the sample, with different tips and in different sessions to check reproducibility and to ensure that results are free from artifacts. All STM images presented in this work were recorded under ambient conditions without any further image processing. C-12 was dissolved in 1,2,4-trichlorobenzene (Sigma Aldrich, pure >99%, used as received – henceforth called TCB) with a concentration of 0.1 mmol/L. The Au(111) substrates were purchased from Neyco (Structure Probe, Inc.). The raw samples consisted of mica plates of thickness between 50 and 75 μm, onto which thin (~100 nm) layer of gold has been evaporated. A crucial step for ensuring the most favorable conditions for the self-assembly of molecules into the physisorption-driven monolayer is preparation of a high quality surface, *i.e.* composed of atomically flat terraces of large size (100s of nm in 2D). The procedure of preparing of Au(111) consists normally of short (~1 min) flame annealing in a propane gas flame. The gently heated (~60˚C) solution of C-12 has been deposited onto freshly flamed Au/mica sample, straight after the flaming process was ceased. The STM tip, which was mechanically cut from a Pt/Ir wire (90/10 wt%, Goodfellow SARL), was immersed in the droplet of solution during the measurement process.

Molecular modeling. Calculations have been performed using an efficient DFT molecular dynamics technique (FIREBALL).[36] We use optimized minimal basis sets,[37] allowing fast and accurate structural characterization of such a big system. The corresponding cutoff radii of all the elements involved in our calculations are the following: RH(s) = 4.1 a.u., RC(s) = 4.5 a.u., RC(p) = 4.5 a.u., RN(s) = 4.2 a.u., RN(p) = 4.5 a.u. and RAu(s) = 4.5 a.u., RAu(p) = 4.9 a.u., RAu(d) = 4.5 a.u.. The optimization have been performed using (4x4)- and a (8x8)-5 layers slab of Au(111) for azobenzene and azobenzene dimer, respectively. Van der Waals interactions and H-bonds

have been taken into account using specific LCAO-S^2 + vdW formalism based on dipolar approximation and intermolecular perturbation theory.[38]

RESULTS AND DISCUSSION

C-12 self-assembly at the 1,2,4-trichlorobenzene(TCB)/Au(111) interface. The chemical structure of the **C-12** molecule is presented in Figure 1. It consists of a central triphenylene core, which is symmetrically substituted by six 4-dodecyloxyazobenzene units connected with ethylene-ester linkers. Figure 1 shows the molecular conformation of highest symmetry, D_{3h} symmetry group. In such conformation: (1) six carbonyl oxygen atoms point toward themselves creating three pairs of facing oxygens, and (2) azobenzene double bonds (–N=N–) are antiparallely oriented.

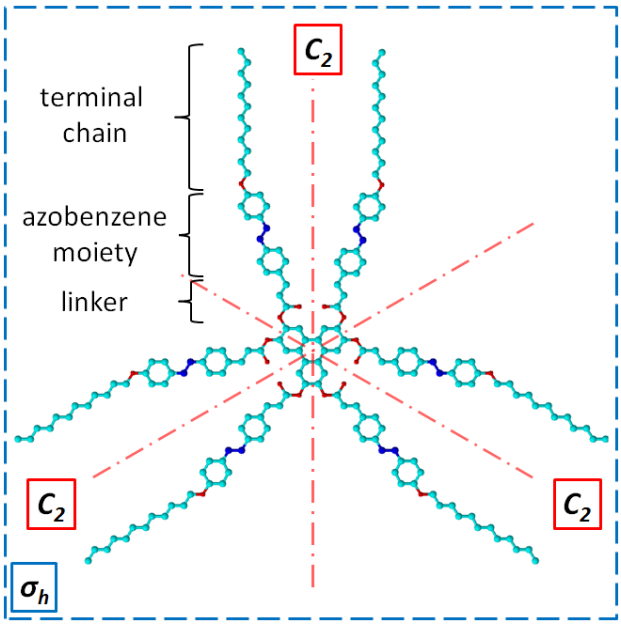

Figure 1. Chemical structure of **C-12** molecule, presented in a D_{3h} symmetry conformation, with some of its symmetry elements indicated. Azure, red and blue balls represent carbon, oxygen and nitrogen atoms, respectively (hydrogen atoms omitted).

C-12 self-assembly at the TCB/Au(111) interface is characterized by a substrate quasi-systematically covered by ordered networks, but with a size for the ordered domains not larger than 300 nm^2. The STM images display regularly spaced bright dots which are packed in a hexagonal way (Figure 2a). Two types of domains were evidenced, henceforth denoted as α and β domains and emphasized by the red and blue color (Figure 2b), and which are locally separated by disordered areas - the fuzzy regions that are noticeable at the edges of domains. From the analysis of drift-corrected images we conclude that the two kinds of hexagonal networks are disoriented by 16 ± 1°, but have a similar lattice parameter $a_{\mathbf{C\text{-}12}/Au}$ = 3.5 ± 0.1 nm. In accordance with the spot shape and size, and the well-known strong contribution of polyaromatic motifs to the STM contrast,[39] we infer those round spots as representing the **C-12** central triphenylene cores which are lying flat on the substrate. Since no visible periodic variations of STM contrast of moiré type are encountered within the monolayers we deduce that the molecules are physisorbed at energetically equal adsorption sites, thus forming commensurate 2D crystals, independently of scanning directions, tip-sample polarities and tunneling current parameters. In contrast with a model triphenylene substituted with no azobenzenes, but just *n*-C_5H_{11} tails,[40] the 23x√3 reconstruction which normally occurs on the Au(111) is never observed, in relation with stronger molecule-substrate interactions for **C-12**/Au(111) system. It should be underlined that the inter-site distance of the molecular network formed by **C-12**, *i.e.* 3.5 nm, confronted with the size of the molecule measured between the ends of the opposite peripheral decyloxy chains (about 6.9 nm) suggests a quite strong interdigitation between the neighboring molecules. In order to obtain firmer insights into the **C-12** geometry on Au(111), we have performed high-resolution STM experiments.

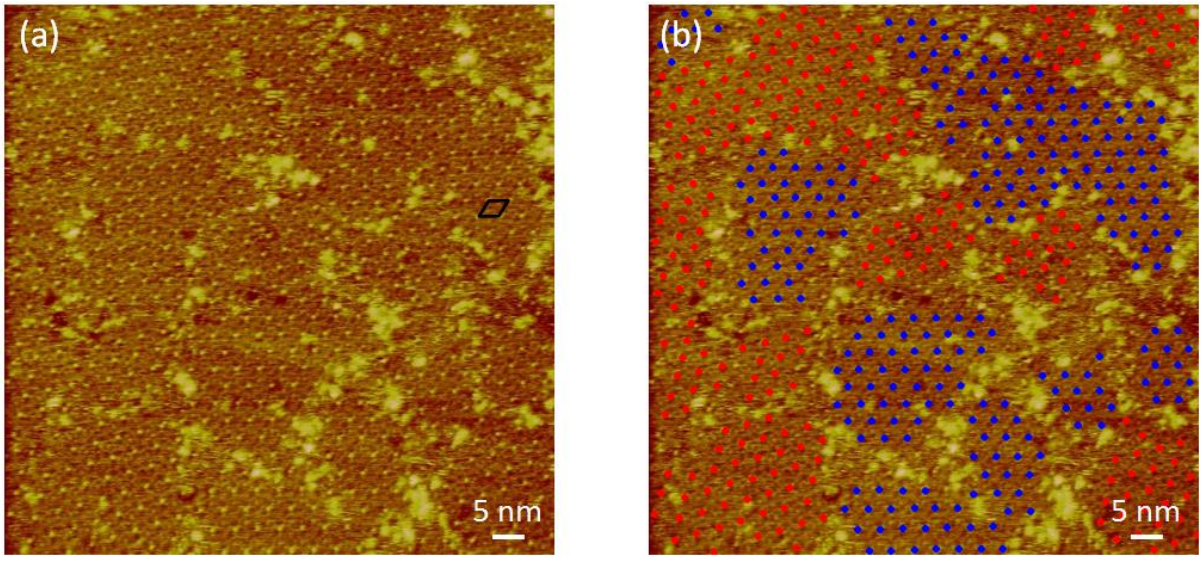

Figure 2. STM constant-current images of **C-12** self-assemblies at the TCB/Au(111) interface. Black diamond on panel (a) represents the primitive unit cell of the 2D crystal comprising the monolayer of **C-12** physisorbed at Au(111). Blue and red dots on panel (b) highlights the two types of hexagonally packed domains which are disoriented by ±16°; I_t = 9 pA, V_t = 150 mV.

Figure 3a depicts a zoomed area with seven homeotropically adsorbed **C-12** molecules that form a regular hexagon with one of its dense directions being *quasi*-horizontal. In addition to the central polyaromatic cores (visible on the large-scale images) one may find a peculiar motif between every two neighboring triphenylene moieties, a motif containing four bright protrusions, one of them highlighted by an azure diamond (Figure 3b). In each four-lobe motif, two azobenzenes might be discerned associated with two pairs of spots packed slightly tighter than the remaining two. The Figure 3d (solid frame) shows sections with inter-lobe distance of about 0.73 nm - in good agreement with the data referring to the *trans*-azobenzene in the gas phase, and slightly larger than value in the solid phase.[41]. Figure 3e (dashed frame) shows the alternative sections: with an increased value of the inter-lobe distance, namely of the order of 0.8 nm, and

containing deeper minimum between the lobes. This kind of section is in agreement with intermolecular feature – a distance between centers of phenyl rings of two neighboring azobenzenes. This structure appears in agreement with the known preferred almost planar conformation of azobenzenes with the molecular plane parallel to the surface resulting from the interplay between the Au(111) surface and the π-electrons of the molecules.[42-44]

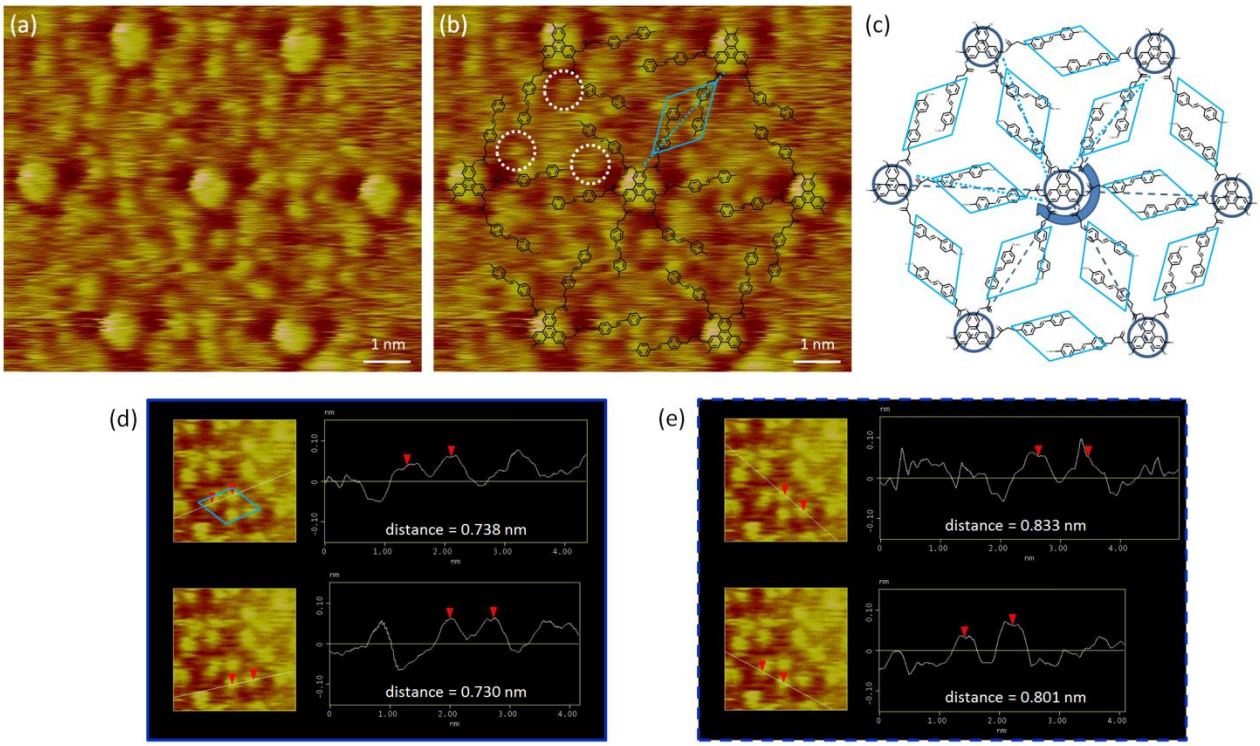

Figure 3. (a) and (b) high-resolution STM images of **C-12** self-assemblies at the TCB/Au(111) interface (I_t = 3.93 pA, V_t = 315.3 mV). In addition to the hexagonally packed triphenylene cores, dumbbell-shaped protrusions represent the azobenzene groups forming intermolecular dimers. (b) shows the same area, with the proposed model of molecular packing, and one of the azobenzene dimers underlined with an azure diamond, and possibly co-adsorbed TCB solvent molecules with white circles. (c) schematical representation of the system highlighting its chirality, with triphenylene moieties (blue circles), and intermolecular azobenzene dimers (azure diamonds)

indicated. (d) and (e) show sections of high-resolution STM images evidencing the difference in the inter-lobe distances, and underlining the azobenzene intramolecular and intermolecular features, respectively.

The longer diagonal of the azure diamond (azure dotted-line in Figure 3c) is not collinear with the crystallographic axis of the 2D crystal of **C-12** (blue dashed-line in Figure 3c). All azobenzene dimers are unidirectionally rotated by *ca.* 8° leading to a chiral structure of the **C-12** molecular network, underlined by a blue arrow in Figure 3c. Consequently, the conformation of the adsorbed **C-12** molecule is not the achiral D_{3h} conformation presented in Figure 1. Instead, each molecule adopts a modified chiral geometry (Figure 3c). The symmetry breaking of the D_{3h} conformation results in vanishing of three *vertical* reflection planes (which are perpendicular to the plane of the image and contain a C_2 line), and implies the exchange of each of the three C_2 proper symmetry axes into C_1 proper symmetry axes, as compared to Figure 1.

Another constantly occurring STM contrast feature is the dark trigon around the central core, representing the three pairs of facing carbonyl oxygens of the ester linkers between triphenylene and azobenzene subunits. An alternative conformation, when all of the six carbonyl atoms are uniformly oriented, clockwise or counter-clockwise, cannot be definitely excluded, but such conformation is probably sterically forbidden and unfavorable from the viewpoint of the overall dipole moment of **C-12** molecule. The dim areas were previously shown to represent the carbonyl/carboxyl groups.[45-47] Closer look at the apex of each trigon results in finding a bright spot characterized by an average size equal 0.5 ± 0.1 nm, some of them being indicated by white circles in Figure 3b. Those features of increased STM contrast could manifest the co-adsorption

of TCB solvent molecules, previously reported to accompany the self-assembly of several complex aromatic molecules particularly at the TCB/Au(111) interface.[48,49]

Even though *n*-alkanes are well known to readily form self-assemblies on Au(111),[50,51] there is no evidence on the physisorption of the **C-12** peripheral alkyl tails. It is in agreement with the fact that the Au 23x√3 reconstruction plays a critical role in the self-assembly of *n*-alkanes,[52,53] which does not appear on non-reconstructed Au(111), unless an external force (*e.g.* electric field) is applied.[54] Furthermore, the separation of aromatic moieties is found insufficient to accommodate *n*-$C_{12}H_{25}$ alkyl tails on the surface, what is shown in Figure S1. We may thus assume that the peripheral alkyl tails are oriented out of the plane of **C-12** 2D crystal, what is supported by the fact that the energetical restriction of rotation about the ether bond is very low.[55] Such situation is not very common for self-assembled molecular networks, but not unprecedented. For example in the case of naphthalene[56,57] or perylene diimides[58] alkyl tails were evidenced to project above the adsorbate layer. Alternatively, we may also assume that the underlined circles in Figure 3b do not correspond to TCB molecules but to part of the alkyl chains in interaction with Au(111).

Chirality in C-12 domains physisorbed on Au(111). Figure 4a presents simultaneously triphenylene and azobenzene motifs in both α and β networks. In panels (b) and (c) the intermolecular pairing between the azobenzenes in α and β domains is highlighted by the orange and azure diamonds, respectively. Similarly to Figure 3c, direction of the longer diagonal of the azobenzene dimer feature (orange/azure dotted-line) is not collinear with the direction of the corresponding unit cell vector (red/blue dashed-line). Instead, there is an omnipresent rotation of 8 ± 1°, counter-clockwise and clockwise in α and β domains, respectively. The azobenzene dimer

network creates rosette-like superstructures of shape-chirality, as schematically depicted in Figure 4d and Figure 4e.

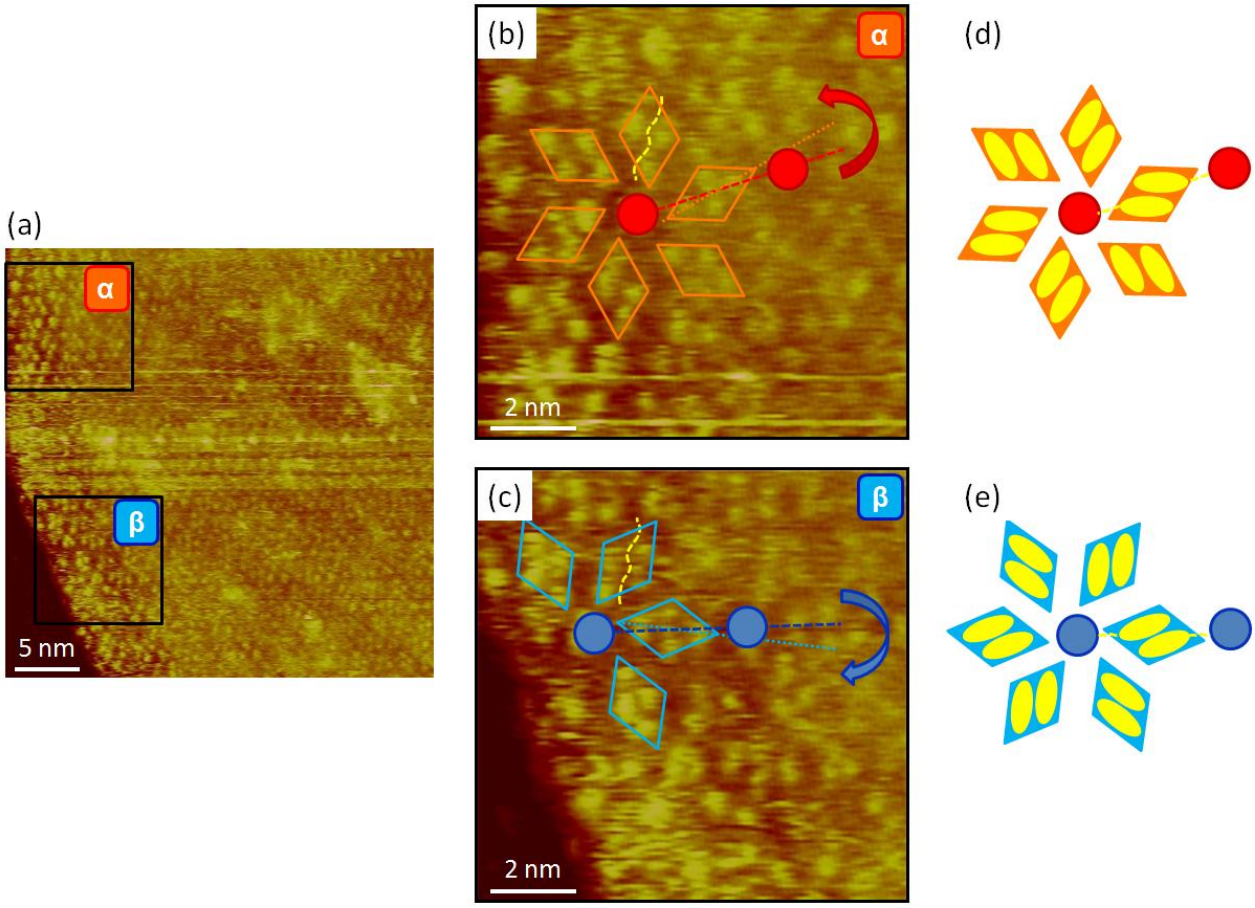

Figure 4. STM images showing well-resolved central triphenylene moieties and azobenzene moieties in both types of domains. (b) and (c) represent close-ups of two regions of (a) with α- and β-type domains, respectively. While in α-type domains, the longer diagonal of azobenzene dimer is rotated counter-clockwise with respect to molecular axis (orange dotted-line), in β-type domains this rotation takes place in the opposite sense. The yellow dashed-line separates the two constituents of the azobenzene dimer, for clarity of concept. I_t = 11 pA, V_t = 250 mV. (d) and (e) schematically show the organization of the azobenzene dimers in α- and β-type domains, respectively.

In order to decipher the origin of the chirality, it appears appropriate to analyze the hypothetical azobenzene pairings which are consistent with STM data. Accordingly, the models of possible arrangements of two azobenzenes are presented in Figure 5. Since STM contrast enables us to localize only the aromatic phenyl rings, the models are based on the center-to-center distances between the phenyl rings. The fact that azobenzene belongs to a C_{2h} symmetry group creates three possibilities of dimers compatible with STM results: two types of *homogenous* dimers and one type of *mixed* dimer. Figure 5a shows a model of molecular arrangement of an azobenzene dimer with the azo bonds (–N=N–) of both azobenzenes adopting similar orientation. The mirror-like orientations for α and β domains are presented on top and bottom parts of the panel, highlighted by orange and azure diamonds, respectively. The distance of hydrogen bonds occurring between hydrogen and nitrogen atoms of neighboring molecules is estimated to be 0.288 nm suggesting that hydrogen bonding may occur,[17,31] in agreement with the fact that the nitrogen atom lies almost at the virtual elongation of the C–H bond, what results in the C–H bond and H···N bond directions being almost collinear.[35] The discrepancy between the two directions, only equals 4°, as illustrated by Figure 5d. The second possibility of a *homogenous* dimer corresponds to the situation presented in Figure 5b, with rotation around the inversion center (i.e. the middle of the –N=N– bond) by 180°. However, as highlighted by the red circles this arrangement appears sterically forbidden, since distance between hydrogen atoms equals 0.06 nm, much less than the sum of the van der Waals radii, r_{H2} = 0.12 nm.[59] The third possibility is a *mixed* configuration, where two azobenzenes constituting a dimer are lying on the two different faces, thus their –N=N– bonds are not collinear (Figure 5c and Figure 5e). The angle between the C–H and H···N bond directions is 22°, implying that the potential hydrogen bond between nitrogen and one of the hydrogens (white dotted-line, Figure 5e) is unlikely to occur. In addition, the restriction coming from the steric reasons cannot be excluded as the hydrogen atoms lies in

the close proximity, the measured intermolecular H···H distance being equal to 0.12 nm (red dotted-line in Figure 5e). Thus, we postulate that the observed rosette-like superstructures are related to the existence of H-bonds between neighboring azobenzenes, pursuant to the model in Figure 5a.

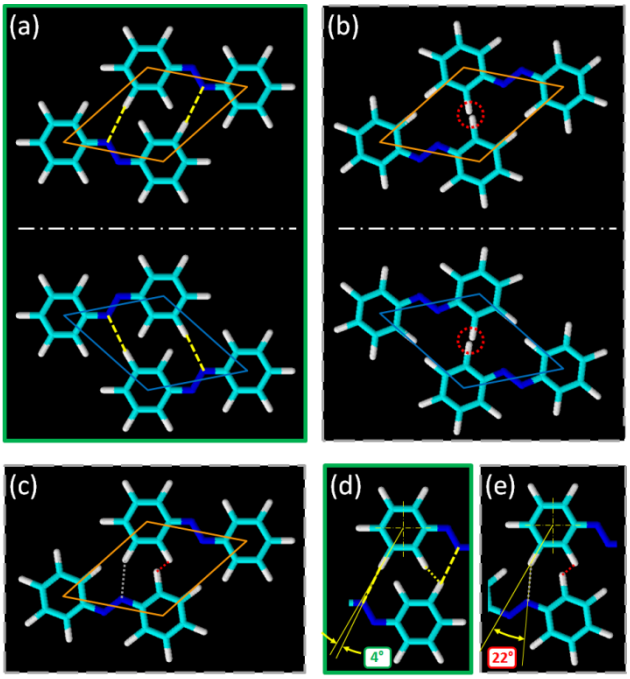

Figure 5. Possible models of the molecular packing of two azobenzene molecules based on STM data. Panels (a) and (b) present two types of *homogeneous* azobenzene dimers. In both cases two surface polymorphs are presented, related to: *left-hand* type dimers in α domains (*orange diamond*, top) and *right-hand* type dimers in β domains (*azure diamond*, bottom). While the arrangement (a) readily promotes the occurrence of intermolecular hydrogen bonding (yellow dashed-lines –panel (d)), molecular packing presented on panel (b) is sterically forbidden due to hydrogen atoms (red circles). Panel (c) shows *mixed* dimer (for the *left-hand* type dimer), with a changed directionality of hypothetical hydrogen bond (22° between the C–H and H···N bond

directions) and potential too close proximity of hydrogen atoms of neighboring phenyl rings. Both factors are highlighted on panel (e).

These results appear in agreement with previous STM studies of azobenzenes on Au(111). In particular, Wang *et al.*[60] have stated that the repulsion between positively charged hydrogen atoms would render azobenzenes of mixed handedness less stable (*cf.* Figure 5c). Kirakosian *et al.*[61] have reported on the formation of supramolecular assemblies of azobenzenes on Au(111) which reveal similar geometry of molecular packing and also duality of orientation of 1D oligomers formed. This latter fact being analogous to the chiral character of **C-12** domains presented here.

Intermolecular interactions: DFT simulations of azobenzene dimer and dynamics. The stabilization of the azobenzene dimers in a *homogenous* geometry shown in Figure 5a is confirmed by DFT calculations of the equilibrium structure of an azobenzene dimer. In Figure 6a, we present the interaction energy between two azobenzene molecules as a function of N-N interatomic distance, taking into account the weak intermolecular interactions.[38] This curve reveals two minima: a less favorable one at 6.6 Å, and a global minimum at 8.2 Å. The first minimum corresponds to a dimer presented in Figure 6b, very close to the geometry extracted from STM data (Figure 5). This first minimum is associated with a very compacted geometry and a gear-like interlocking of four hydrogen atoms, moreover with both azobenzenes restricted in one plane. The balance between the strong repulsion forces and attractive H-bonds resulting from the close proximity of the molecules is manifested by the narrowness of the respective interaction energy well. The distance between the two phenyl rings of each azobenzene is around 0.66 nm

according to DFT calculations. This result is expected to be in agreement with experiments ±10%.[38] It is close to the experimental 0.73 nm, related to STM data (Figure 4), also close to the center-to-center spacing of phenyl rings in crystalline *trans*-azobenzene equal to 0.63 nm.[41] However, the distance between the centers of phenyl rings of neighboring azobenzenes constituting a dimer is slightly smaller for DFT calculations (Figure 6b) with respect to STM data (Figure 5a), 0.66 nm to be compared to 0.8 nm. In contrast the distance between the centers of phenyl rings of neighboring azobenzenes for the second dimmer, 0.82 nm, is closer to the experimental value. However the corresponding dimer geometry of this second minimum (not shown) is very different from the experimentally evidenced dimmer geometry (Fig. 5a). As a result we have excluded it, considering that the first minimum was stabilized due to the specific azobenzene-Au(111) interactions, in relation with the observed commensurability on Au(111) and a possible induced molecular density increasing on the surface.

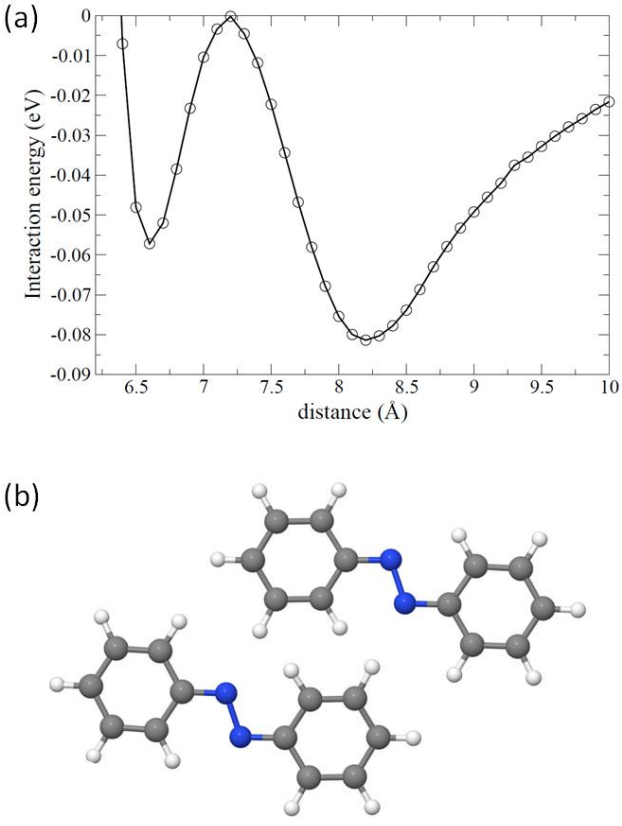

Figure 6. (a) Interaction energy for a homogenous azobenzene dimer as a function of N-N distance between the two equivalent nitrogen atoms. Two minima are obtained: the short-distance minimum at 6.6 Å and a global minimum at around 8.2 Å. (b) The geometry of the azobenzene dimer corresponding to the first minimum, with highly intercalated molecules close to the model constructed on a basis of STM data (Figure 5a).

Finally, the occurrence of specific interactions between azobenzenes in each dimer, is also confirmed by the observation of occasional dynamical events, as the one shown in Figure 7. Figure 7a depicts two **C-12** molecules in which both of them initially reveal STM contrast of darker trigon pointing 'down'. However, further scanning (Figure 7b) evidences a rotation of the left **C-12** molecule by 60°, leading to the STM contrast change from 'down' to 'up'. As a result, the STM contrast, corresponding to the area occupied by the azobenzene dimer, *i.e.* between the left and right triphenylene cores (red parallelogram in Figure 7), becomes fuzzy in relation with some motion of the two facing azobenzenes. In panel (c) the STM contrast features of the 'top' azobenzene belonging to the left **C-12** molecule, disappears (as indicted by the orange parallelogram). After several steps when the quality of STM contrast decreased, in the area of the azobenzene dimer, the left molecule undergoes another rotation and returns back to its initial 'down' position (Figure 7f). The original clearness of the STM contrast is recovered. This shows that when the orientation between neighboring azobenzenes is appropriate (parallel **C-12** molecules, evidenced by the 'down'-'down' contrast), the azobenzenes in the dimer are stabilized, in agreement with highly directional interactions between neighboring azobenzenes, like H-bonds.

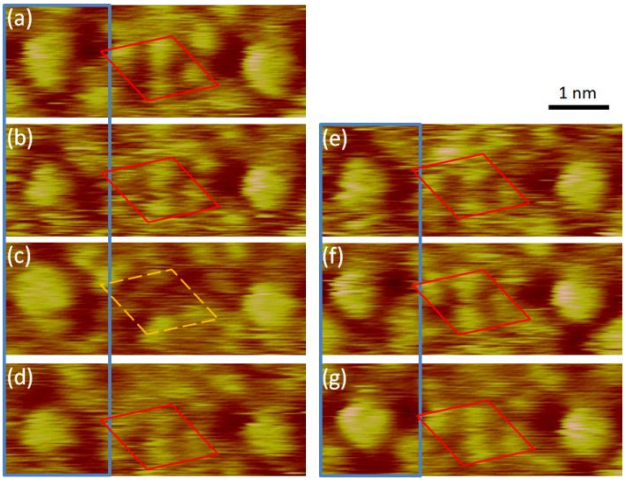

Figure 7. Sequence of STM images showing dynamic behavior of **C-12**/Au(111) system. The molecule on the left rotates by 60°, as evidenced by the change of the STM contrast in the area around the central triphenylene core. Change from 'down' to 'up' conformation occurs between the (a) and (b) frames. This event is associated with a decrease (or even disappearing – panel (c)) of the STM contrast of the azobenzene dimer between neighboring triphenylenes. The return to the initial state observed on frames (f) and (g) suggests that a 'down'-'down' conformation is necessary for a stabilization of interacting azobenzenes of neighboring molecules. Time interval between subsequent frames equals 15 s. I_t = 3.93 pA, V_t = 315 mV.

Specificity of the C-12 network orientation: azobenzene-Au interactions. It is however not obvious that only H-bonds stabilize the **C-12** network. Calculated interactions between azobenzenes within a dimer are very small, around 80 meV, as shown in Figure 6a. The second step towards understanding of the self-assembly of **C-12** is thus related to the analysis of the role of the Au(111) substrate. Even if the two types of handedness of the molecular network are assumed according to the model depicted in Figure 5a, an arbitrary number of orientations with respect to the underlying substrate can be expected. It is indeed very common that the role

of the substrate is ignored in the studies of 2D assemblies originating from the hydrogen bonding interactions.[18,29,62] Nevertheless, our observations evidence solely two orientations of ordered **C-12** networks (Figure 2), associated with a fixed disorientation between α and β domains, equal to 16°. This suggests that the molecule-substrate interactions are not negligible and only one particular orientation for each of the mirror domain is stabilized.

In order to determine the crystallographic orientations of α and β domains, we have considered all the possible symmetric molecular networks which are commensurate with the underlying Au(111). The assumption of commensurability is supported by the lack of any STM contrast modulation of moiré type, and also by the non-appearance of the Au 23x√3 reconstruction. The mirror-like character of α and β domains, with respect to the main crystallographic directions: Au<110> or Au<112>, is supported by their identical lattice parameters, their omnipresent co-existence, including the similar numerousness of molecular sites of both types of domains (Figure S2, 50.01% and 49.99%, for α and β domains, respectively). Taking into account geometrical factors: the lattice parameter and the inter-domain rotation, only one commensurate solution for mirror-like α and β domains can be found. It corresponds to the superstructures (√147 x √147)*R*-8.21° and (√147 x √147)*R*8.21°, in Wood's notation, where the negative sign corresponds to a counter-clockwise rotation.

The corresponding molecular packing is presented in Figure 8, with the hexagonal mesh of lattice parameter a_{model} = 3.49 nm, and the dense direction of packing rotated by ±8.21° from Au<110>. The orientation of the triphenylene cores in both domains remains such that the symmetry axes of the core are collinear with Au<112> crystallographic direction, as schematically depicted by red/blue trigons in Figure 8. This orientation of the central part of **C-12** is not favorable according to the previous results obtained on the model alkyl-substituted

triphenylene analogue.[40] Since we neglect interaction between alkyl chains and Au substrate, the concerted behavior of the six azobenzenes of the **C-12** molecule dominates the system and imposes the molecular orientation of **C-12** on Au(111), through strong interactions with Au(111). Undisputedly it is connected with the hexagonal symmetry of Au(111), which allows similar interaction for the six azobenzenes of one given **C-12** molecule with Au(111).

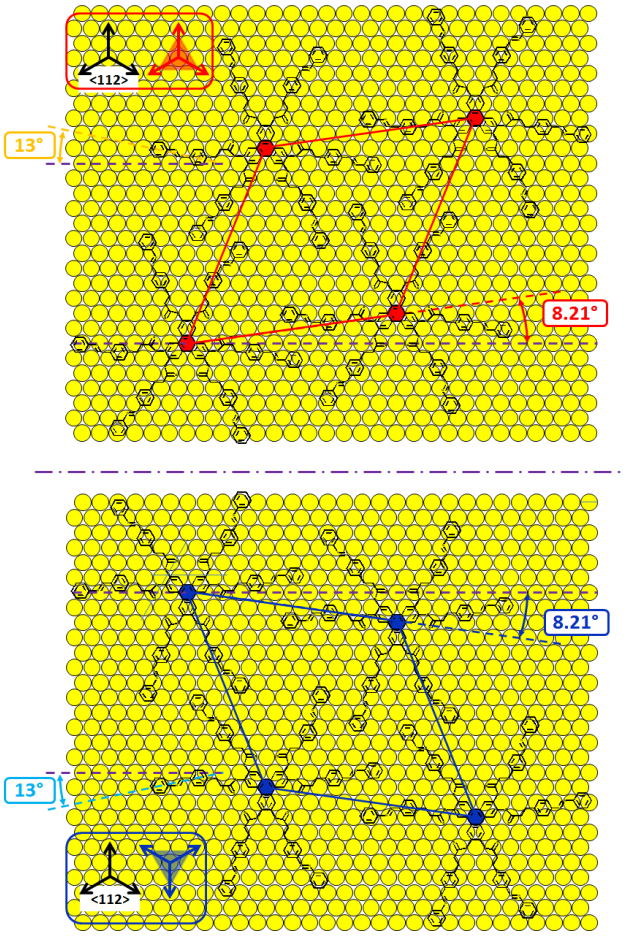

Figure 8. Proposed models of molecular packing of **C-12** molecules in α domains (*top*) and β domains (*bottom*). Rotation between the dense direction of molecular packing and Au<110> equals theoretically 8.21°. It is counter-clockwise and clockwise, for α domain and β domain, respectively. Terminal alkyl tails (assumed to point out of the plane) are omitted for clarity.

In order to understand if the orientation of the **C-12** molecules is imposed by specific interactions between azobenzene and Au(111), we performed DFT calculations of the equilibrium structure and energy of a single azobenzene on Au(111). The results are presented in Figure 9 and clearly show that the equilibrium structure of the single azobenzene corresponds well to the orientation of each of the azobenzenes in the model shown in Figure 8. Its geometry appears to be characterized by a quasi-parallel orientation of the –N=N– bond with respect to the Au<100> direction, confirming that the orientation of **C-12** molecules is imposed by the interaction between the azobenzenes and the substrate. As a result, only two possible orientations for the chiral molecular assemblies are present on Au(111), one for each handedness. Moreover the azobenzene-Au(111) interaction is large, around 900 meV for one single azobenzene associated with roughly ½ *e* of charge transfer. The presence of this charge transfer may slightly modify the electrostatic interactions between azobenzenes regarding the DFT calculations presented in Figure 6, which were performed without the presence of Au(111) substrate. This may partially explain the discrepancy between the experimental and calculated distances between neighboring azobenzenes, but most probably the observed difference between measured and calculated distances of neighbouring azobenzenes is due to the imposed commensurability associated with strong molecule-substrate interactions. The fact that the azobenzene-Au(111) interaction is definitely larger than the azobenzene-azobenzene interaction, calculated in the absence of Au(111) (Figure 6a), suggests that H-bonds involving nitrogen atoms, in order to stabilize a network, need to be promoted by the favorable molecule-substrate interactions. We confirm it by the comparative studies of **C-12** at the interface of TCB and highly oriented pyrolytic graphite (HOPG) (Figure S3a,b), which showed a lower tendency to form self-

assemblies associated with a decreased stability of the infrequently formed monolayers. Moreover, comparing to TCB/Au(111) system the period of the occasionally formed monolayers was found much larger, equal 4.3 nm. This distance is too large to allow formation of H-bonds between neighboring azobenzenes analogical to TCB/Au(111) interface, as shown in Figure S3c,d.

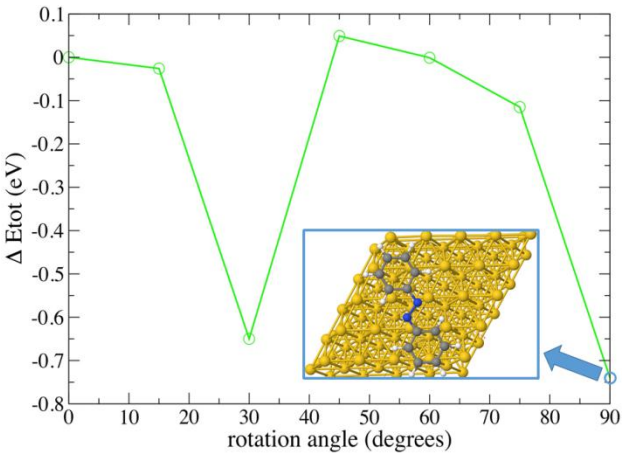

Figure 9. Energy of an azobenzene molecule on Au(111) surface, calculated for various orientations. The inset shows the minimum 90°-rotation, which geometry fits well into the molecular packing model from Figure 8.

It is remarkable that self-assemblies of molecule of such complex structure present only one chiral organization, with only two surface enantiomers coexisting on Au(111), whereas it is common for molecules of much simpler molecular structures than **C-12**, to form numerous types of self-assemblies,[40] including porous and dense networks.[13,29] Hexagonal symmetry of packing is also not very common for molecules with such high aspect ratio. For example all hexaalkoxy-triphenylenes with substituents $–C_{11}H_{23}$ and longer, tend to form row-like self-assemblies.[63] This is most probably the cooperative influence of H-bonds between neighboring azobenzenes and

azobenzene-substrate interactions which allows for the stabilization of this hexagonal network, in addition associated with a chirality revealed at all levels, from the molecular configuration to the molecular network configuration. This suggests in particular, that if one specific handedness could be favored, for example using a chiral solvent together with a single crystal of Au(111), we may obtain macroscopic 2D chiral monolayers.

CONCLUSIONS

In this article we present a detailed description of the self-assembly of **C-12**, a molecule composed of a central triphenylene core decorated with six azobenzene moieties. By using the scanning tunneling microscopy at the liquid/solid interface, we evidence that **C-12** forms well-ordered domains of hexagonal symmetry of packing. Upon self-assembly, the **C-12** molecules lose the highest symmetry configuration (D_{3h}) and adopt a rosette-like configuration. This configuration is in turn transmitted to the ordered network, with azobenzene dimers being rotated either clockwise or counter-clockwise, leading to the formation of domains of opposite handedness. The 2D chiral specificity of the **C-12** monolayer is demonstrated, the chirality spanning all ranges, from the molecular configuration, the rosette-like configuration of the azobenzene dimers to the network orientation on Au(111). As shown by a careful analysis of STM data supported by DFT calculations, the chirality appears to be related to cooperative H-bonds between neighboring azobenzenes and strong azobenzene/Au(111) interactions. The latter interactions being specific and necessary for the **C-12** network stabilization, as it was confirmed by a different hexagonal network being observed on HOPG, also far less stable than on Au(111). Specificity of azobenzene-azobenzene interactions on Au(111) should pave a way for the analysis

of similar behavior of those molecular motifs on different metallic substrates, to study whether similar strong interactions between azobenzene and substrate can as well stabilize this kind of chiral structure. In a longer perspective an azobenzene building block may be found as a useful motif for programmable monolayers for specific systems. Despite the expected large number of degrees of freedom of **C-12**, originating from the incorporation of the azobenzenes into molecular structure, rather surprisingly the monolayers exhibit a single type of structure, namely a chiral hexagonal network of handedness which could become unique if chiral solvent was used. The next step will consist of irradiation of the **C-12** monolayers in order to test if the *trans-cis* photoisomerization of the azobenzenes is possible. The close proximity of **C-12** to the metallic substrate, associated with the strong interaction that has been revealed in this paper, may result in quenching of the switching property of the molecule. Otherwise, it could allow for a control of chiral monolayer ordering by UV-irradiation.

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Supporting Information Available: model of C-12 molecular packing excluding the physisorption of terminal alkyl tails, statistics of α and β domains and STM images of C-12 at

TCB/HOPG interface. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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