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FEATURE ARTICLE

Supramolecular assembly/reassembly processes: molecular motors and dynamers operating at surfaces

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Among the many significant advances within the field of supramolecular chemistry over the past decades, the development of the so-called "dynamers" features a direct relevance to materials science. Defined as "combinatorial dynamic polymers", dynamers are constitutional dynamic systems and materials resulting from the application of the principles of supramolecular chemistry to polymer science. Like supramolecular materials in general, dynamers are reversible dynamic multifunctional architectures, capable of modifying their constitution by exchanging, recombining, incorporating components. They may exhibit a variety of novel properties and behave as adaptive materials. In this review we focus on the design of responsive switchable monolayers, *i.e.* monolayers capable to undergo significant changes in their physical or chemical properties as a result of external stimuli. Scanning tunneling microscopy studies provide direct evidence with a sub-nanometre resolution, on the formation and dynamic response of these self-assembled systems featuring controlled geometries and properties.

1. Introduction

In recent years scientists have demonstrated creativity and considerable skills in the design and construction of complex supramolecular architectures[1] relying on the use of non-covalent interactions to self-assemble chemical entities with a precision on

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the sub-nanometre scale, ultimately forming systems and materials with pre-programmed chemical and physical properties.[2] Supramolecular chemistry[3] offers highest control over the process of molecular self-assembly: due to its unique nature it combines reversibility, directionality, specificity and cooperativity. In the past few years there has been an increasing effort towards the fabrication of functional supramolecular architectures with a nanoscale control over their mechanical movement, aiming at the development of molecular machines[4] and dynamers.[5] The latter may be defined as constitutional dynamic polymers,[5] *i.e.* polymeric entities whose monomeric components are linked through reversible connections and have therefore the capacity to modify their constitution by exchange and re-shuffling of their components. Dynamers are usually formed by self-assembly between recognizable sub-unit sites. Dynamers are by definition dynamic systems: they are able to undergo adaptation and reversible conformational changes under the effect of external physical or chemical stimuli such as light,[6] temperature,[7] an electrical current,[8] microenvironment, or complexation with metal ions.[9] In some cases, a combination of stimuli can be utilized.[10] In addition, the reversibility of connecting events in dynamers, *i.e.* their kinetic liability, confers to systems the capacity to spontaneously undergo self-healing of defects on a time scale that can vary from sub-seconds to the several hours, as it depends on the interplay of molecule–molecule, molecule–solvent, solvent–substrate and molecule–substrate interactions.[1n,11] In contrast, covalently linked, non-labile species can hardly heal spontaneously. Among the known reversible covalent reactions,[5,12] amino/carbonyl condensations to give C=N products such as imines, hydrazones and oximes are particularly attractive in view of the very wide range of structural variations available, the easy synthetic accessibility, the control through conditions of yields, rates and self-healing properties, as well as their role and potential for application in both biological/medicinal[13] and materials sciences.

The need for exploring ordered architectures at the molecular scale has made scanning tunneling microscopy (STM)[14] a widely employed yet extremely powerful tool to study supramolecular materials at interfaces with sub-molecular resolution, providing direct insight into the supramolecular world.[15] The working principle of STM is the tunneling of electrons from a sharp scanning tip to a substrate. Since the tunneling current is roughly proportional to the electron density of the molecule within an energy range,[16] the STM contrast in the so-called "constant (tip) height" mode will appear brighter within electron-rich aromatic molecules than aliphatic groups.[17] This microscopy technique was successfully employed to investigate various phenomena in isolated molecules such as charge-transfer,[18] rectification[19] and switching.[20] The spatial sub-nanometre resolution that can be achieved by STM imaging allows gaining detailed information on molecular interactions; thus it is a crucial tool to assist the design of molecular modules that undergo controlled self-assembly at surfaces at any desired condition (temperature, pressure and concentration) to form the chosen supramolecular structures, and investigate complex functional architectures such as dynamers. Currently molecules adsorbed on conductive substrates can be studied by STM under different experimental conditions including ultra-high vacuum (UHV), atmospheric pressure to image dry films or with the tip immersed into a liquid to investigate the solid–liquid interface, eventually under electrochemical control. The solid–liquid interface provides a particularly interesting environment to carry out the self-assembly experiments and their investigation by STM. Compared to sample preparation and imaging under UHV conditions, the solid–liquid interface has a number of advantages: (1) the experimental approach is straightforward and does not require a complicated or an expensive infrastructure; (2) the dynamic exchange of molecules adsorbed on the surface and the one in the liquid phase promotes self-healing of defects in the self-assembled layers;[21] (3) the solid–liquid interface provides an excellent environment for *in situ* chemical modifications of adsorbed molecules. Working under such condition it is possible to trace the reversible changes in the monolayers structure, upon addition of external chemical stimuli, *e.g.* acidification[9] or coordination of organic molecules to the metallic centers,[9,10d,22] whereas in most of examples of molecular re-organization investigated under UHV conditions is an irreversible change.

Herein, we will discuss the process of supramolecular engineering in the self-assembly of molecular motors and dynamers on various conductive solid substrates as investigated by scanning tunneling microscopy (STM). In the first section (2.1), we will focus on the exploration of systems engineered exclusively to undergo efficient and reversible photochemical reactions between two stable isomers featuring markedly different properties. In the second section (2.2) we will present and discuss systems engineered through the formation of hydrogen-bonds and that are capable of undergoing large conformational changes upon temperature variation. In the third section (2.3) we will describe systems based on metallo–ligand interactions as well as protonation as a way to trigger dynamic processes in dynamers. The final section (2.4) will be addressed to the surface-potential-induced assembly of organic molecules.

2. Dynamic self-assembly

On the nanometre scale (between 1 and 10 nm), molecules are the favorite building blocks to decorate, structure, and functionalize surfaces. Following a bottom-up strategy, supramolecular chemistry provides the guidelines to the design of molecular building blocks that can undergo controlled self-assembly from solution at surfaces. This occurs through a subtle balance between molecule–molecule, molecule–substrate, molecule–solvent, and solvent–substrate interactions leading to the targeted 2D patterns. In particular, the effect of solvent on the formation of 2D supramolecular architectures at the solid–liquid interface has been investigated by many groups in the past two decades.[6c,23] The organic solvents used for performance of STM measurements need to fulfill the following criteria: (i) have a low vapor pressure allowing the performance of measurements in only a drop of solution (*ca.* 5–20 μL), without the need of use of a closed cell, (ii) being electrochemically inert under experimental conditions, (iii) be able to solubilize the investigated compounds, and (iv) possess a low tendency to adsorb on the substrate used in the measurements. One way to tune the molecule–substrate interactions is the use of well-defined atomically flat surfaces, which direct the molecular ordering *via* specific geometric and electronic effects. The most commonly used conductive substrate for measurements is highly oriented pyrolytic graphite (HOPG)

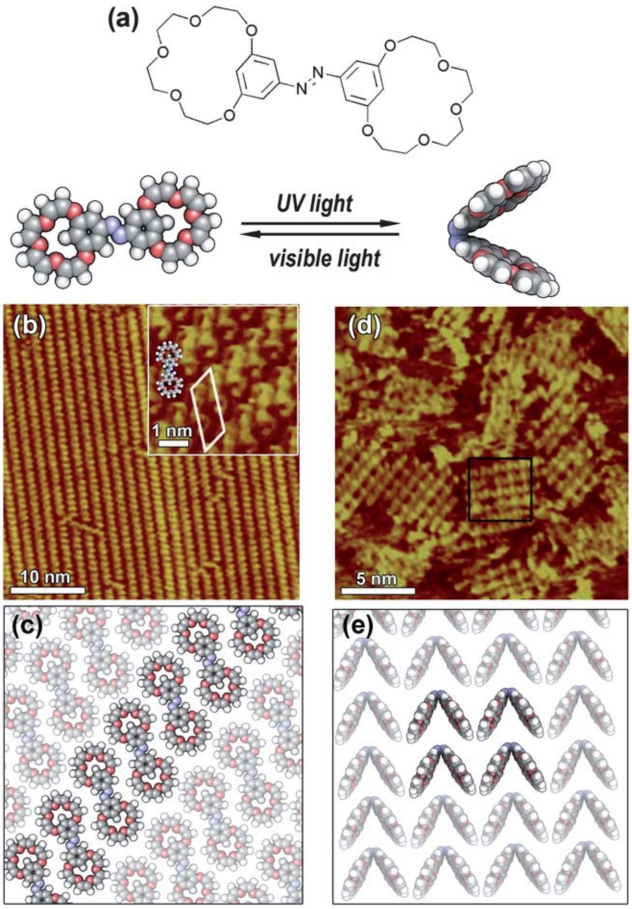

Fig. 1 (a) Schematic representation of azobis-(benzo-15-crown-5) molecule; (b) typical large-scale STM image of *trans*-azobis-(benzo-15-crown-5) molecules on Au(111) surface; (c) proposed molecular packing motif of molecules in their *trans*-conformation; (d) typical large-scale STM image of *cis*-azobis-(benzo-15-crown-5) molecules on Au(111) surface; (e) proposed molecular packing motif of molecules in their *cis*-conformation; images (b) and (d) adapted from ref. 6*a* with permission from the American Chemical Society.

which is a layered structure that can be freshly prepared by simply cleaving its surface with an adhesive tape. Metallic substrates such as copper, silver and gold are typically employed for experiments carried out in ultra-high vacuum (UHV). Another important parameter, which cannot be neglected in processes of supramolecular engineering at surfaces, is entropy, which can be described as a measure of the disorder degree of the system. The impact of entropy can be slightly limited through the proper design of molecular building blocks, for instance by introducing rigid moieties to decrease the degree of flexibility thus limiting the number of accessible conformations.[24] The self-assembly of small organic molecules to form well-defined supramolecular structures under the influence of weak intermolecular forces such as hydrogen bonding, electrostatic interactions, coordination bonding and hydrophobic interactions has been discussed in detail in solution and in three-dimensional (3D) crystals.[25] A substantial number of single- and multi-component self-assembled architectures have already been investigated at various surfaces, including supramolecular discrete assemblies,[23a,26] polygonal structures,[27] 1D supramolecular polymers,[15f,g,28] 2D porous networks,[15k,19b,29] to name a few. Nowadays a great challenge in supramolecular chemistry is the design of molecular systems which can be shown to undergo reversible assembly/reassembly processes, *i.e.* to visualize a dynamer operating at surfaces.

2.1. Photoisomerization

Molecular switches as well as dynamers, when designed ingenuously, can be powered at surface by nature's most abundant and powerful energy source, *i.e.* light. In 1867 Fritzsche[30] discovered the bleaching of an orange colored tetracene solution in daylight that re-colored at night. Since then, small organic molecules, capable of undergoing efficient and reversible photochemical reactions between two stable isomers featuring markedly different properties, continue to impact the materials world. Among all photochromic molecules, azobenzenes have been extensively studied because of their unique photoisomerization.[31]

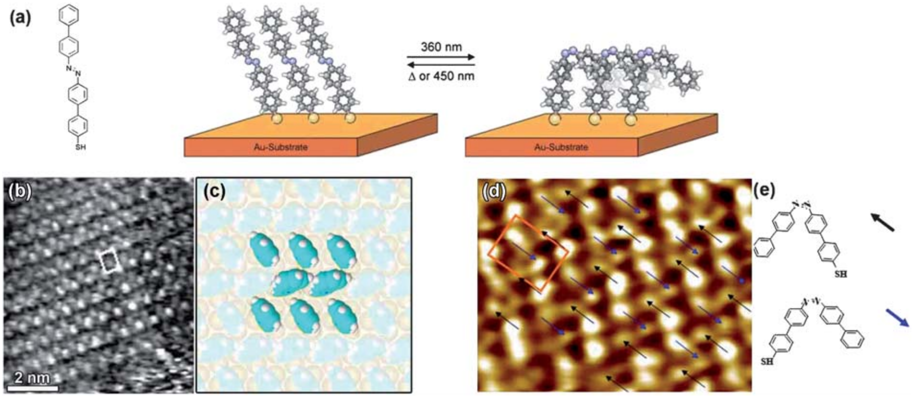

Fig. 2 (a) Chemical structure of the investigated azobenzene derivative and scheme of photoisomerization process; (b) constant-current STM image of *trans*-AZO SAM on Au(111) showing a rectangular unit cell containing two molecules; (c) proposed molecular packing motif of molecules in their herringbone arrangement; (d) STM image showing a *cis* domain of a sample prepared by incubating overnight the Au(111) substrate in solution of AZO molecules under light irradiation at 365 nm. The arrows indicate the direction of the folding during the switch of each molecule in the domain as indicated in (e). Images (b) and (d) adapted from ref. 6*b* with permission from the National Academy of Science of the USA.

The transition from the thermodynamically more stable *trans* to the *cis* conformation can be induced by irradiation with UV light and reversed upon heating or irradiation with visible light.[32] The isomerization occurs at the N═N double bond yielding two different states, identified by the *trans*(*E*)- and the *cis*(*Z*)-isomer. Such photochemical reversible *trans–cis* isomerization of azobenzene was first described by Krollpfeiffer and co-workers,[33] and it has been thoroughly studied in the last decades.[34] While the solution properties are well-established, still much is unknown on the behavior of densely packed assemblies at surfaces of molecules that can undergo isomerization. The preservation of such a dynamic molecule function once adsorbed in a monolayer relies on structural and electronic aspects. The former is due to the availability of sufficient free volume for the functional group to undergo conformational change in terms of both molecule–molecule and molecule–surface interactions. The latter, which is particularly important when working on metal substrates, consists in a (strong) perturbation or even complete quenching of the desired function.[35] The reversible switching of azobenzene derivatives has already been investigated at room temperature at the single molecule level in UHV studies on isolated molecules packed parallel to the basal plane of the substrate,[36] in physisorbed monolayers at the solid–liquid interface,[6c,15b,37] on self-assembled monolayers (SAMs) chemisorbed on Au surface,[6b,38] on Au nanoparticles[39] and as co-adsorbate in a chemisorbed alkanethiol SAM on solid flat substrates.[40]

Hitherto, isomerization of azobenzene containing monolayers on highly oriented pyrolytic graphite (HOPG) has been studied on building blocks physisorbed co-planar to the basal plane of the substrate,[6c,15b,37,41] leading to structural changes primarily in the plane of the graphite. As a result, while the *trans*-isomer based monolayer could be visualized with sub-molecular resolution, the monolayer composed entirely of *cis* isomers could never be observed at the solid–liquid interface, because of the molecular desorption due to the inability of the *cis*-isomer to pack efficiently on graphite.[6c,41] Only one exception was reported thus far.[37] Jiang and co-workers[37] have demonstrated that 4-hydroxy-3′-trifluoromethylazobenzene (FAzoH) molecules physisorbed on HOPG surface can be switched *in situ*, while scanning the surface with STM, from *trans*- to *cis*-conformation upon UV light (365 nm) induced isomerization.

Monolayers of azobenzene derivatives in their *cis* conformation typically feature a low stability and dynamic nature, *i.e.* the tendency to undergo *cis* → *trans* isomerization. Therefore, it is a great challenge to design molecular systems which can allow visualizing by the means of STM the photoisomerization process at the single molecule level.

In 2006 Wan and co-workers[6a] have demonstrated that STM can be employed to investigate the photoisomerization of azobis-(benzo-15-crown-5) (Fig. 1a) on Au(111) surface. The STM

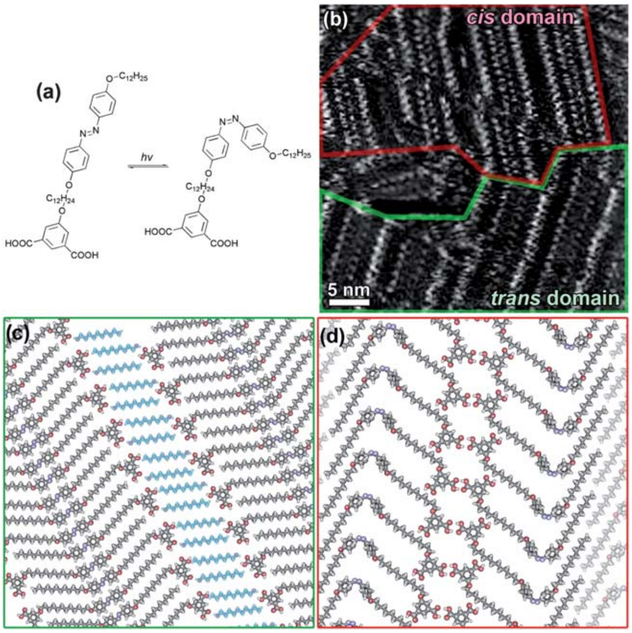

Fig. 3 (a) Chemical structure of 5-[ω-(4′-dodecyloxy-4-azobenzeneoxy)dodecyloxy]isophthalic acid (C_{12}(AZO)C_{12}ISA); (b) STM image of an ordered monolayer consisting two C_{12}(AZO)C_{12}ISA domains of *cis* (marked in red) and *trans* (marked in green) isomers; (c) proposed molecular packing of the *trans* isomer in which solvent co-deposition was observed (1-undecanol molecules are marked in blue); and (d) proposed molecular packing of the *cis* isomer. Image (b) adapted from ref. 6*c* with permission from the American Chemical Society.

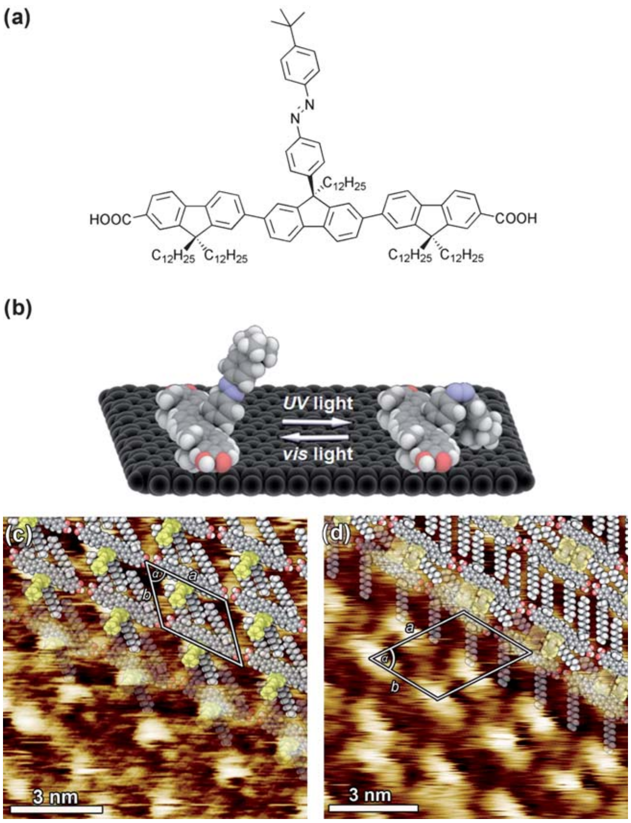

Fig. 4 (a) Chemical formula of *trans*-TAZO. (b) 3D CPK models of *trans*-TAZO and *cis*-TAZO adsorbed on HOPG ($C_{12}H_{25}$ chains are replaced by CH_3 groups for clarity; one minimum structure is shown in which the terfluorene adapts an *anti*,*anti* conformation). STM height image of TAZO at the HOPG–1-phenyloctane interface in its *trans* isomer (c) and *cis* isomer (d) obtained upon UV irradiation (354 nm) of the *trans* monolayer. Unit cell parameters: $a = (2.9 \pm 0.2)$, $b = (2.2 \pm 0.2)$ nm, $\alpha = (50 \pm 2)°$, $A = (4.88 \pm 0.47)$ nm^2 (c), $a = (3.6 \pm 0.2)$ nm, $b = (2.9 \pm 0.2)$ nm, $\alpha = (57 \pm 2)°$, $A = (8.75 \pm 0.63)$ nm^2 (d). Images (a–d) adapted from ref. 49 with permission from Wiley VCH.

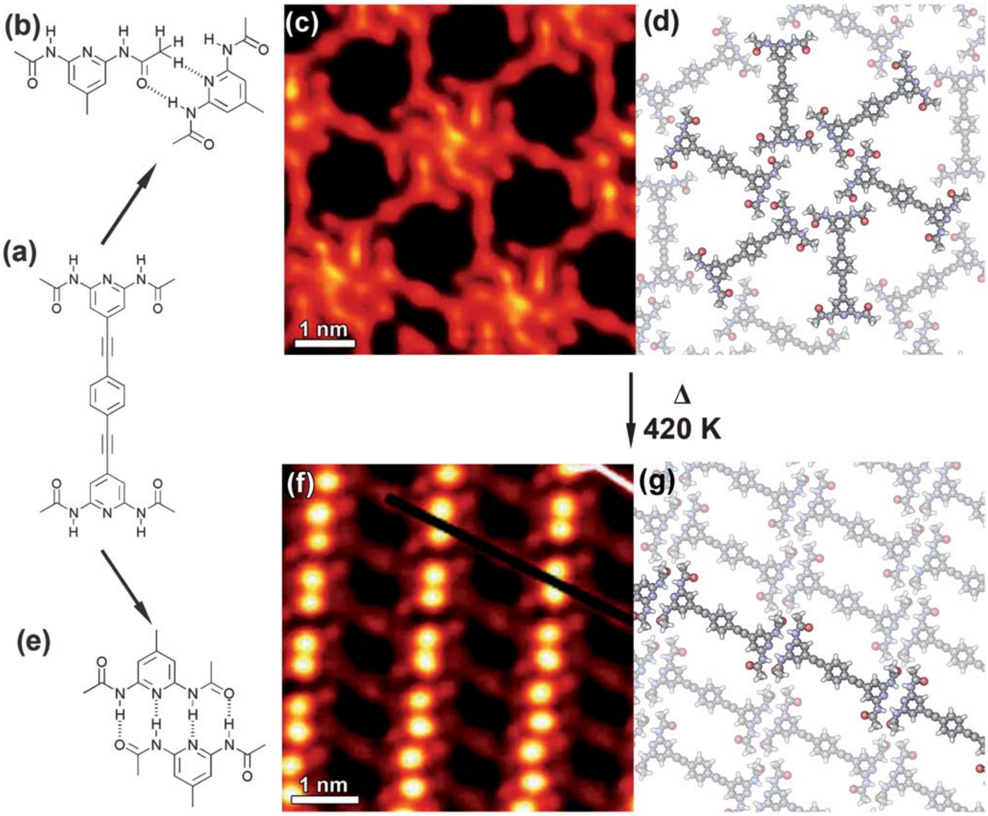

Fig. 5 (a) Schematic representation of 2,6-di(acetylamino)pyridine derivative; (b) H-bonded interaction between molecules in their DAD conformation; (c) STM image of 2D porous hexagonal network on Ag(111) surface, (d) proposed molecular packing motif of molecules in their honeycomb arrangement; (e) H-bonded interaction between molecules in their DADA conformation, (f) STM image of 2D porous hexagonal network on Ag(111) surface, (g) proposed molecular packing motif of molecules in their honeycomb arrangement. Images (c) and (f) adapted from ref. 53*a* with permission from the Royal Society of Chemistry.

image in Fig. 1b revealed that azobis-(benzo-15-crown-5) in their *trans* conformation molecules forming highly ordered array on the flat terrace of Au(111). In the high resolution STM image (Fig. 1b), each molecule appears as a dumbbell shape with two dark depressions. The proposed packing motif features molecules adopting a flat-lying conformation on the Au(111) (Fig. 1c); the dark depressions were assigned to the crown ethers and the bright part connecting the two dark depressions to the azobenzene moiety. Irradiation of the *trans*-monolayer with a high-pressure Hg lamp to induce photochemically the *trans* → *cis* isomerization led to the appearance of many bright clusters on the surface along with the formation of disordered features at the domain boundary. To obtain a monolayer of *cis*-isomer on Au(111), the cleaned electrode was immersed for 1 min in ethanolic solution of azobis-(benzo-15-crown-5) previously illuminated with UV light. The adlayer of *cis*-azobis-(benzo-15-crown-5) exhibits small domains intercalated by numerous defects (Fig. 1d). Each molecule appears as a “V” shape with two elongated spots that can be ascribed to the crown ether moieties (Fig. 1e).

In the frame of a collaboration with Mayor our group has recently demonstrated that a properly designed azobenzene molecule (Fig. 2a)[42] can undergo *cis–trans* photoisomerization in large domains at surfaces.[6b] This switch, which occurs in densely packed single-component SAMs without perturbing the molecular lattice, is complete over thousands of molecules, and it exhibits an ensemble character. The thiol exposing azobenzene chemisorbs on Au(111) forming a highly ordered SAM (Fig. 2b) featuring a herringbone structure (Fig. 2c). By irradiating the monolayer with a UV light (365 nm) the *trans–cis* isomerization is activated. The *cis* domain (Fig. 2d) also adopts a herringbone structure. The *cis* isomer is much more stable on the surface than in solution due to the stabilizing π–π intermolecular interactions. Significantly, in Fig. 2d it is possible to identify the folding direction of the switched molecules, as indicated by the arrows. Inside a *cis*-unit cell, the two “different molecules” isomerize by folding the upper biphenyl moiety in opposite directions. The unidirectional nature of such a switch occurring on adjacent molecules along the direction of the unit cell main axis, together with the opposite orientation of bending in neighboring rows, is caused by the minimization of steric hindrance. Remarkably the binding sites seem to not be disturbed by the switching process. A role of the ensemble in the switching process was previously unexplored and it appears to be widely applicable for switching single component SAMs of intrinsically rigid and tightly packed molecules, to achieve new functions such as cargo-lift. The high yield of the *cis–trans* isomerization on metal substrates opens new perspectives for high-density data storage devices[4c] as well as optically switchable thus multifunctional electronic devices, such as organic field-effect transistors,[43] based on photochromic compounds.

The above examples illustrate how molecular motors[4b,44] based on photo-switches[4f,6d,e] can be used to pattern the surface with a function.[45] Interestingly such molecules can be transformed into the dynamers simply by decorating them with alkyl substituents, which both increase the adsorption of the molecules on surfaces and promote intermolecular interactions *via* interdigitation. Interestingly, alkanes have been reported to have a stronger adsorption capacity on HOPG if compared to aromatics having the same number of carbon atoms.[46] For the sake of example, hexane has a desorption barrier of ∼17 kcal $\mathrm{mol^{-1}}$ on HOPG[47] and slightly lower, ∼13 kcal $\mathrm{mol^{-1}}$, on Au(111).[48] In 1996, De Schryver and co-workers[6c] have employed such a strategy to attempt for the first time the visualization of a dynamer triggered by light irradiation operating at the solid–liquid interface. The authors studied physisorbed monolayers of 5-[ω-(4′-dodecyloxy-4-azobenzeneoxy)dodecyloxy]isophthalic acid ($\mathrm{C_{12}(AZO)C_{12}ISA}$) (Fig. 3a), formed by deposition of $\mathrm{C_{12}(AZO)C_{12}ISA}$ solution in 1-undecanol (under dark) on HOPG. The observed closely packed monolayer consists of *trans*-$\mathrm{C_{12}(AZO)C_{12}ISA}$ molecules co-deposited with 1-undecanol molecules (Fig. 3c). Upon irradiation of $\mathrm{C_{12}(AZO)C_{12}ISA}$ solution at 366 nm, a photostationary mixture with a high *cis* isomer content was obtained. The absorbance of this mixture at 360 nm is strongly reduced owing to the increased concentration of the *cis* isomer. When kept in the dark at room temperature, the *cis* isomer spontaneously converted into the thermodynamically more stable *trans* isomer and the absorbance is restored to its original value. The STM image of a monolayer obtained by physisorption from a photostationary mixture displays two main domains type (Fig. 3b). The molecular packing in the lower domain (marked in green) is identical with the packing observed for the $\mathrm{C_{12}(AZO)C_{12}ISA}$ molecules in their *trans* conformation. The patterns observed in the upper domain (marked in red) can be ascribed to a monolayer of self-assembled *cis* isomers without solvent co-deposition (Fig. 3d). Differently from the case of *trans* domains, the isophthalic acid groups point toward each other and the alkyl chains are not interdigitated. The absence of solvent co-deposition is probably due to the spatial orientation of the acid functions in the molecular arrangement of the *cis* isomer. The co-existence of *cis* and *trans* domains correlates not only with the relative amounts of *cis* and *trans* isomers in the solution but also with the monolayer stability of the isomers at the solid–liquid interface. Similarly, *cis* ↔ *trans* isomerization could be induced and their respective domains be imaged by irradiating *in situ* a droplet of $\mathrm{C_{12}(AZO)C_{12}ISA}$ dissolved in 1-undecanol directly on the HOPG surface. During imaging, the *cis* isomer domains disappear with time. Finally, only *trans* isomer domains could be observed, illustrating the reversible nature of the reaction at the solid–liquid interface.

We recently introduced[49] a platform-based approach to decorate the HOPG surface with upright oriented photoswitchable azobenzene units with a sub-nm precision. The monolayer formed by custom-tailored azobenzene-containing building blocks in the *trans* form can be interconverted to the corresponding *cis* form monolayer leading to substantial and reversible structural reorganization. The target structure TAZO (Fig. 4a) was designed to combine (i) a terfluorene rigid scaffold exposing COOH groups in the α- and ω-positions to promote in-plane intermolecular recognition through H-bonding forming 1D supramolecular nanostructures,[50] (ii) two dodecyl chains in the bridge position of the first and third fluorene moieties to favor physisorption on HOPG and define the spacing between adjacent molecules, (iii) an asymmetric functionalization of the bridge position of the central fluorene with one group having a higher affinity for the HOPG, *i.e.* a dodecyl chain, and a functional group, namely an azobenzene function, which is therefore forced to adopt an edge-on packing at surfaces (Fig. 4b). Such modular approach allows the tuning of the orientation and spacing between adjacent azobenzenes. A bulky

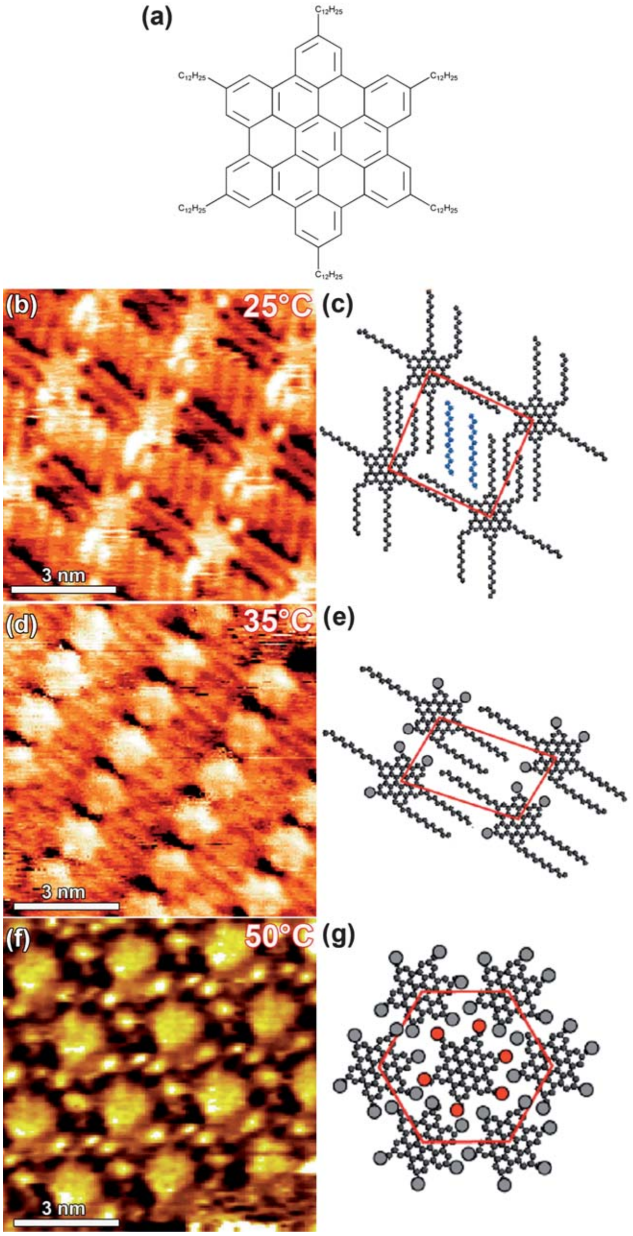

Fig. 6 (a) Chemical structure of hexakis(*n*-dodecyl)-*peri*-hexabenzocoronene (HBC-C_{12}); STM images recorded at 25 °C (b), 35 °C (d) and 50 °C (f). Proposed molecular packing motifs of HBC-C_{12} molecules adsorbed at 25 °C (c)—two co-adsorbed *n*-tetradecane molecules marked in blue, at 35 °C (e)—out-of-plane *n*-dodecyl chains represented as gray circles, and at 50 °C (g)—the six out-of-plane *n*-dodecyl chains of the central molecule are represented as red circles while they appear as gray circles for peripheral molecules. Images (b–g) adapted from ref. 56, with permission from the American Chemical Society.

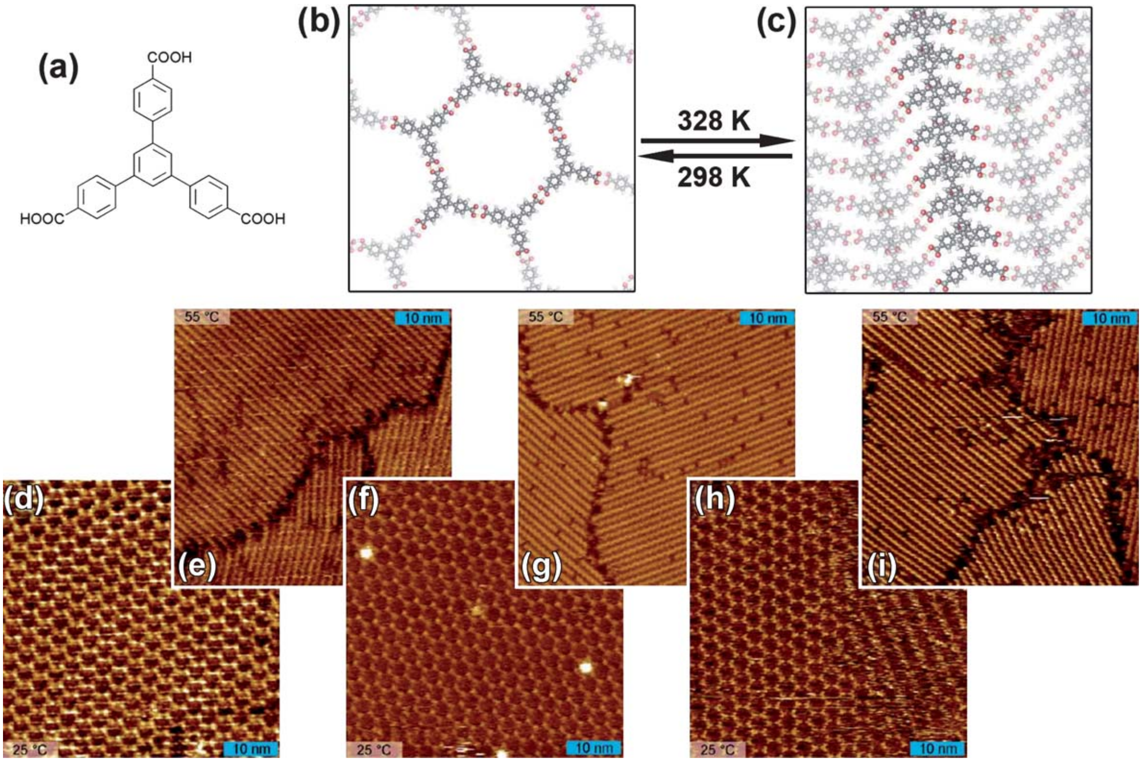

Fig. 7 (a) Chemical structure of 1,3,5-tris(4-carboxyphenyl)benzene (TPB); (b) proposed molecular packing motif of TPB molecules in their chicken-wire arrangement; (c) proposed molecular packing motif of TPB molecules in their lamellar arrangement; (d–i) STM topographs as acquired during repeated heat–cool cycles of saturated TPB in nonanoic acid solutions demonstrating the reversibility of the phase transition. The respective temperature is stated in the lower (upper) left corner of each image. The cycle starts at the lower left image (d) at room temperature and is continued (e) at 55 °C, (f) at 25 °C, (g) at 55 °C, (h) at 25 °C, and (i) at 55 °C. Images (d–i) adapted from ref. 7, with permission from the American Chemical Society.

tert-butyl group attached to the azobenzene terminus further decreases the affinity of the azobenzene for HOPG, inhibiting its face-on packing and therefore promoting its edge-on arrangement. Fig. 4c displays an STM image of the physisorbed monolayer at the solid–liquid interface. It reveals a monocrystalline domain, which is stable over several minutes. Within the 2D crystal it is possible to identify self-assembled 1D H-bonded supramolecular polymers, as a result of the formation of hydrogen bonds between the carboxylic acid groups attached to the terfluorene pedestal. The periodic spots within the monolayer can be assigned to the upright oriented azobenzene moieties of the molecules (marked in yellow in Fig. 4c) emerging as pillars from the flat 2D structure. The STM image after *in situ* irradiation of the monolayer with UV light (354 nm) shows a crystalline pattern featuring different motifs (Fig. 4d), if compared to that in Fig. 4c, exhibits linear supramolecular architectures that can be ascribed to H-bonded supramolecular polymers of *cis*-TAZO. The spacing between two adjacent 1D arrays is in this case not always identical, as found in physisorbed monolayers of *trans*-TAZO. In the *cis* domains, the H-bonded 1D architectures are laterally spaced according to a “dimeric” motif, where two building blocks of adjacent rows are held in close proximity. This more compact packing mode features a different tilt of the aliphatic side chains as well as azobenzene units likely interacting through van der Waals forces. Importantly, the reversible structural reorganization of the monolayer of TAZO from *trans* to *cis* motif could be monitored in real-time over several tens of minutes, taking advantage of the slow nature of the process. Upon irradiation of the *cis*-TAZO monolayer with visible light the *trans* monolayer 2D motif is reformed again, proving the reversible nature of the process.

2.2. Temperature

Although the temperature is a key parameter for all self-assembly processes,[51] as it directly affects both thermodynamic and kinetic parameters, to date very little is known on its influence in physisorbed monolayers at surfaces.[52] In many cases, molecular ordering at surfaces can be tuned by thermal-annealing, as demonstrated in self-assembled monolayers of organic molecules.[7,53] However, in many reported studies samples are just conditioned at variable temperatures, while measurements are still conducted at room temperature.[54] Furthermore, in most of examples molecular re-organization induced by thermal-annealing is an irreversible change. The temperature usually has a major effect on the rate of a chemical reaction and recognition events. From a thermodynamics perspective, the temperature modulation, being a weighting factor for the enthalpy (H) and entropy (S) contributions to the Gibbs free energy $\Delta G = \Delta H - \Delta(TS)$, allows tailoring intermolecular interactions and free-volume entropy during the formation of supramolecular architectures. The temperature also provides a convenient tool for directing self-assembly of molecules toward desired superstructures. By tuning the temperature as a thermodynamic

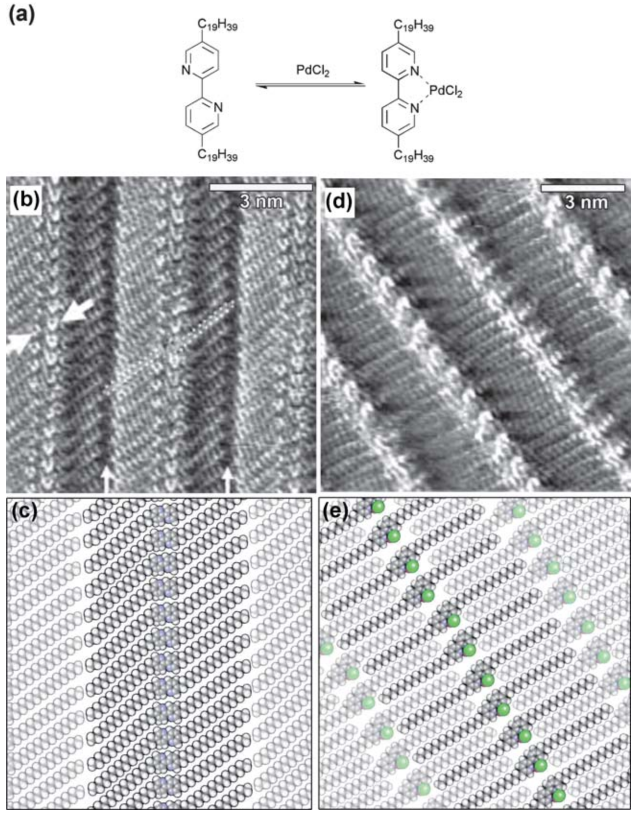

Fig. 8 (a) Chemical structure of 5,5′-dinonadecyl-2,2′-bipyridine; (b) STM image of bipyridine derivative at the solid–liquid interface, (c) proposed molecular packing motif of 5,5′-dinonadecyl-2,2′-bipyridine molecules in their lamellar arrangement; (d) STM image of bipyridine derivative after complexation with PdCl$_2$, (e) proposed molecular packing motif of 5,5′-dinonadecyl-2,2′-bipyridine molecules complexed with Pd ions. Images (b) and (d) adapted from ref. 22, with permission from Wiley VCH.

parameter, the high energy barrier between two energetically different states of supramolecular assemblies can be overcome, leading to the formation of the structures which cannot be observed by working at lower temperatures. However, such a process is irreversible in many cases. Once the supramolecular system was thermally activated to overpass the barrier between the states, its energy in the latter state might be much lower than the former, therefore in order to reverse the process, the system will have to overcome the barrier which is much higher in energy than in the case of the first process. For instance, Bonifazi and co-workers[53a] made use of molecules bearing two terminal 2,6-di(acetylamino)pyridine recognition sites, connected to a 1,4-disubstituted central phenyl ring (Fig. 5a) to generate porous hexagonal networks on Ag(111) surface (Fig. 5). 2,6-Di-(acetylamino)pyridine groups are well-known to be involved in H-bonding interactions featuring a DAD conformation (Fig. 5b).[55] The self-organization of molecules on Ag(111) in sub-monolayer thick films was investigated under ultrahigh vacuum (UHV) conditions. Samples prepared at room temperature exhibit a porous hexagonal network. In the high-resolution STM image in Fig. 5c, each molecule is displayed as three aligned lobes and four terminal spokes that correspond to the aromatic rings and the acetyl residues, respectively. In the proposed model, each 2,6-di(acetylamino)pyridine residue interacts *via* two weak H-bonds with two neighboring moieties, which results in the formation of chiral hexameric units (Fig. 5d). Remarkably, after annealing the sample at 420 K, the hexagonal network was transformed into the close-packed 2D rhombic pattern shown in Fig. 5f. In the proposed model, each molecule interacts with two neighboring modules along the long axis of the unit cell *via* quadruple H-bonds, *i.e.* in a head-to-head fashion over their terminal 2,6-di(acetylamino)pyridine groups (Fig. 5g). This intermolecular interaction is equivalent to the one for the (DADA)$_2$ dimers (Fig. 5e), where the *cis*-conformation adopted by two of the four amidic bonds strongly promotes frontal H-bonding interactions favoring a unidirectional anisotropy.

Fichou and co-workers have demonstrated[56] that the packing density of HBC-C$_{12}$ (Fig. 6a) self-assembled at the Au(111)/*n*-tetradecane interface can be tuned by varying the substrate temperature. Increasing the temperature from 20 to 50 °C induces three successive and irreversible structural transitions accompanied by a 3-fold increase of the HBC-C$_{12}$ packing density. High-resolution STM images reveal that this 2D packing density increase arises from the stepwise desorption of the *n*-dodecyl chains from the gold surface (Fig. 6b–g). Importantly, cooling the samples back to room temperature after a heating experiment is not accompanied by a decrease of the packing density nor by a structural change back to the initial phase.

A temperature triggered supramolecular dynamer operating upon the change of temperature at the solid–liquid interface was obtained from 1,3,5-tris(4-carboxyphenyl)benzene (TPB) (Fig. 7a):[7] an open porous network (Fig. 7b) was re-organized into a non-porous (Fig. 7c), densely packed structure. In order to investigate the reversible nature of the TPB dynamer transition, several heating/cooling cycles were conducted in octanoic and nonanoic acid, while STM images were repeatedly acquired (Fig. 7d–i), allowing the visualization of both supramolecular assemblies of TPB molecules.

2.3. Complexation

Supramolecular architectures combining organic moieties with transition metal ions have been widely employed during the last decades. The interest in such assemblies arises both from their robustness and from their electronic features, leading to the development of applications in various research fields.[57] For instance, monomolecular transistors based on terpyridine–cobalt–terpyridine complexes,[58] as well as dynamic chemical devices undergoing reversible extension/contraction through a pH-triggered complexation of Pb ions[10a] have been reported. Recently, the use of self-assembly processes to generate hybrid molecular arrays with predefined structures on surfaces has been explored by combining metal centers and organic units.[59] STM has been employed to study various self-assembled systems such as metal–organic 2D coordination networks,[60] discrete complexes[22,61] on surfaces or more recently 1D coordination networks based on molecular tectons bridging two coordination poles featuring different denticities.[15g,28a]

In 2004 De Feyter, van Esch and co-workers[22] reported an STM investigation of *in situ* complexation of PdCl$_2$ by a monolayer of an alkylated bipyridine derivative (Fig. 8a) at the 1-phenyloctane/HOPG interface. After the successful imaging of

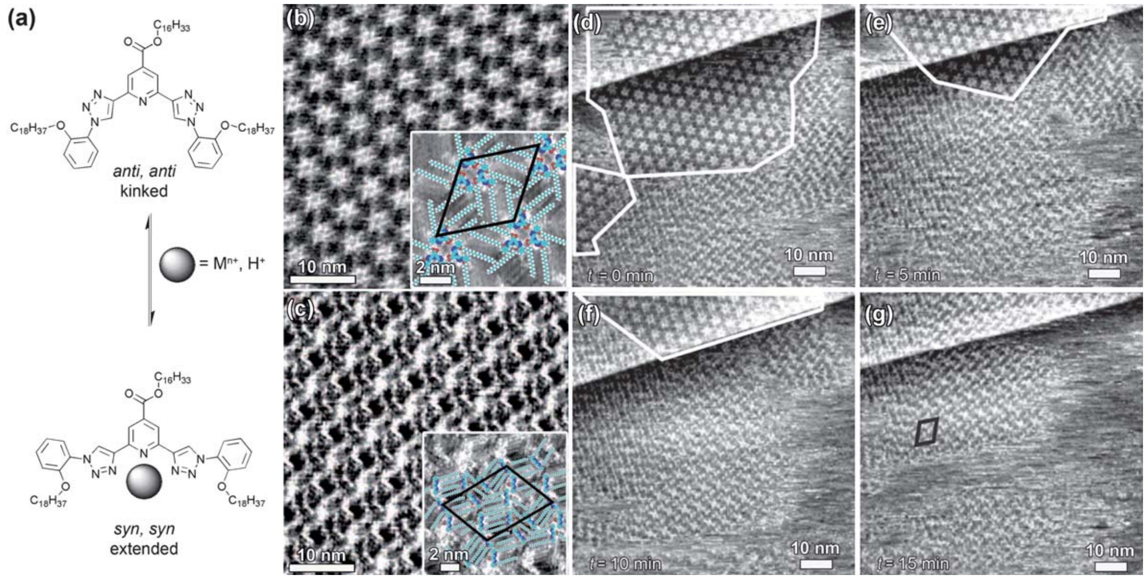

Fig. 9 (a) Chemical structure of 2,6-bis(1-aryl-1,2,3-triazol-4-yl)pyridine (BTP); STM images of the self-assembled BTP molecules adopting (b) a "kinked" and (c) "extended" conformation on HOPG. (d–f) Consecutive STM images showing the structural evolution of a monolayer of BTP over 20 min after the addition of *ca.* 10 μL TFA. The evolution of the shape of the domain containing the molecules in the rosette packing is highlighted in white. (d) Image taken right after the addition of TFA, (e) after 5 min, (f) after 10 min, and (g) after 15 min. Images (d–i) adapted from ref. 9, with permission from the Wiley VCH.

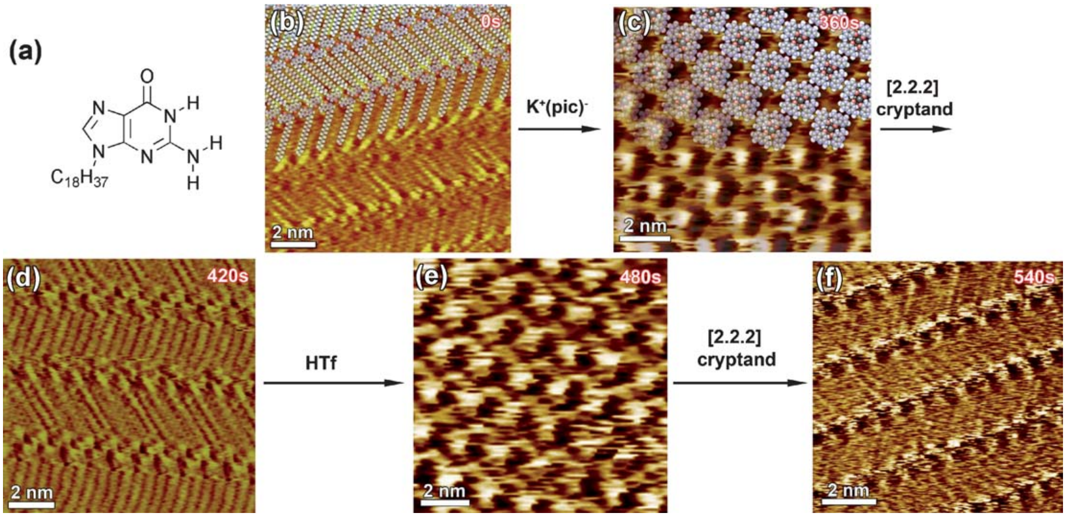

Fig. 10 (a) Chemical structure of octadecyl guanine; (b–f) consecutive STM images showing the structural evolution of a monolayer of 1 over a 9 min time scale (time range displays in the upper right part of the images correspond to the time that was needed to reach the equilibrium after addition of reacting agents). Images (b), (d), and (f) show ribbon-like structure, whereas (c) and (e) exhibit G4-based architectures. Images (b–f) adapted from ref. 10*d*, with permission from Wiley-VCH.

the 5,5′-dinonadecyl-2,2′-bipyridine monolayers at the solution–HOPG interface (Fig. 8b) which revealed a lamellar arrangement (Fig. 8c), a drop of $PdCl_2$ in 1-phenyloctane was applied. Suddenly the monolayer re-organized into a different lamellar motif (Fig. 8d and e).

We have recently demonstrated[9] extended 2D assemblies at the solid–liquid interface that are capable to undergo large conformational changes upon either a change of pH or the addition of metal ions. As a model system we have chosen a 2,6-bis(1-aryl-1,2,3-triazol-4-yl)pyridine (BTP) derivative, which incorporates a tridentate coordination site consisting of two triazole moieties bridged by a central pyridine ring. The BTP core is decorated with three alkoxy side chains providing enhanced solubility as well as improved propensity to physisorption on HOPG at the solid–liquid interface. Due to favorable electrostatic interactions, the "kinked" *anti*,*anti* (Fig. 9a) conformation of the BTP core dominates in solution at neutral pH, whereas the repulsive interactions between the lone pair of the nitrogen atoms destabilize the alternative "extended" *syn*,*syn* conformation (Fig. 9a). This repulsive interaction can be switched into an attractive one by the addition of metal ions or acid to the solution, causing either metal complexation or protonation of the BTP core followed by a large structural change from the "kinked" to its corresponding "extended" conformation.[62] In order to trigger the switching of the BTP molecules from the "kinked" to the "extended" conformation, a small amount of trifluoroacetic acid (0.75 vol% TFA) was added to the solution covering the already formed monolayers on the surface.[63] Fig. 8c displays a markedly different 2D architecture consisting of a lamellar-like motif, which appeared on the surface 5–10 min after the deposition of the acidified solution. The real-time conformational switch and the related reorganization of the self-assembled pattern, occurring at the solid–liquid interface, have been monitored *in situ* on the scale of several tens of nanometres. The transformation from the "rosette" to "tetragon" motif could be monitored in real-time on the timescale of several tens of minutes, taking advantage of the slower nature of the process (Fig. 9d–g).

As a building block for the fabrication of dynamers, we studied lipophilic guanosines,[64] and guanine derivatives,[65] because of their versatility: depending on the experimental conditions they can undergo different self-assembly pathways, leading to the formation of either H-bonded ribbons or quartet-based columnar structures. Given the possibility to functionalize the guanosines in the side-chains they appear as ideal building blocks for the fabrication of complex architectures with a controlled high rigidity, thus paving the way towards their future use for scaffolding, *i.e.* to locate functional units in pre-programmed positions.[66] Recently we have provided direct evidence on the sub-nanometre scale metal-templated reversible assembly/reassembly process of an octadecyl substituted guanine into highly ordered quartets (G_4) and ribbons[10d] (Fig. 10a). The self-assembly of octadecyl guanines alone on HOPG has been studied, and, upon subsequent addition of [2.2.2]cryptand, potassium picrate ($K^+(pic)^-$), and trifluoromethanesulfonic acid (HTf), the reversible interconversion between two different highly ordered supramolecular motifs was triggered. In the absence of metal ions, the obtained monolayer shows a crystalline structure consisting of ribbon-like architectures (Fig. 10b). This self-assembly behavior is in good agreement with previous observations on guanosine derivatives.[64] Upon *in situ* addition of 10 mM potassium picrate solution in TCB to the initial ribbon-like motif in Fig. 10b, the G_4 supramolecular motif was obtained (Fig. 10c). Upon subsequent *in situ* addition of a 10 mM solution of [2.2.2]cryptand in TCB to the G_4 supramolecular architectures on HOPG, the guanine reassembled into the original ribbon (Fig. 10d). By adding a 10 mM solution of trifluoromethanesulfonic acid (HTf) in TCB, the potassium ions were released from the cryptate and the G_4 assembly was regenerated (Fig. 10e). Upon further addition of a [2.2.2]cryptand solution, the ribbon structure was regenerated (Fig. 10f).

2.4 Electrochemistry

Electrified surfaces offer a further dimension to influence the molecule–surface interactions by controlling the electrochemical potential of the substrate when immersed in aqueous electrolyte. Electrochemical scanning tunneling microcopy (EC-STM) is the technique of choice to unravel with submolecular resolution the ordering of small organic molecules induced by a potential applied to the surface.[67] Details of the packing arrangement and even the internal structure for adlayers of various organic molecules such as benzene, naphthalene, anthracene, water soluble porphyrins and polythiophenes can be obtained in aqueous solutions.[68] Highly ordered H_2TMPyP (Fig. 11a) layers on an iodide modified Cu(111) electrode surface have been investigated by Wandelt and co-workers.[67f] A change of these electrostatic forces, obtained by modulating the electrode potential from −400 mV to −300 mV, resulted in structural transition from the motif shown in Fig. 11b to a slightly less dense packing displayed in Fig. 11d. The results demonstrate that

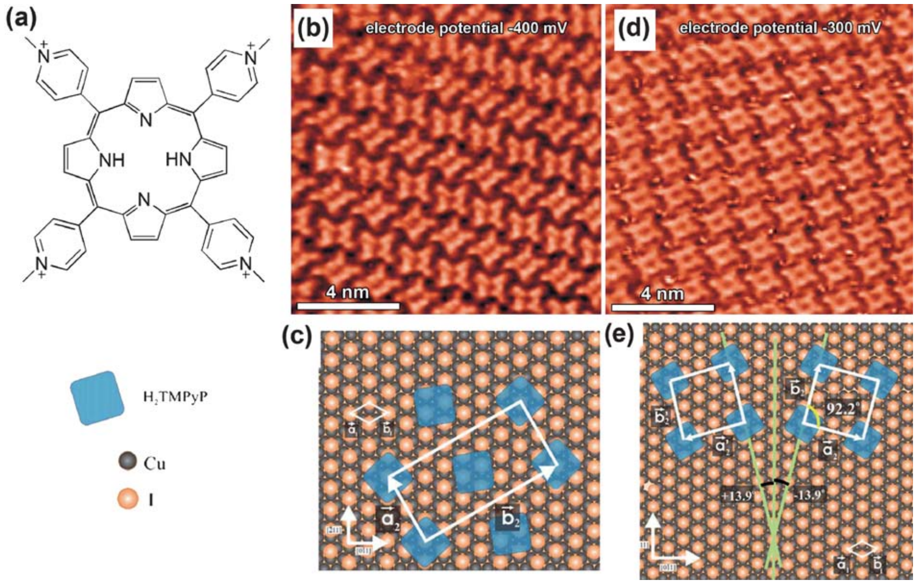

Fig. 11 (a) Chemical structure of *meso*-tetra(*N*-methyl-4-pyridyl) porphyrine tetratosylat (H_2TMPyP); (b) STM image of the self-assembled H_2TMPyP molecules adsorbed on an iodide modified Cu(111) surface—electrode potential −400 mV, and the proposed molecular packing of H_2TMPyP molecules (c); (d) STM image and proposed molecular arrangement of H_2TMPyP molecules adsorbed on iodide lattice—electrode potential −300 mV. Images (b–e) adapted from ref. 67*f*, with permission from Elsevier B. V.

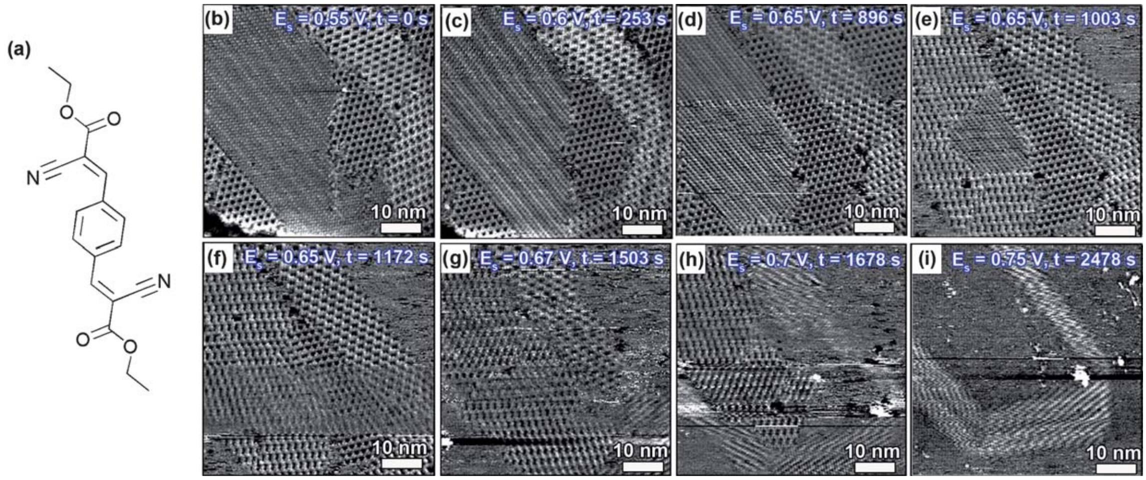

Fig. 12 (a) Chemical structure of *p*-phenylenedi(α-cyanoacrylicacid)di-*n*-ethyl ester (*p*-CPAEt); (b–i) potential-dependent series of STM images of *p*-CPAEt molecules adsorbed on Au(111) surface—electrode potential from $E_s = 0.55$ V to $E_s = 0.75$ V. Images (b–e) adapted from ref. 67*i*, with permission from the American Chemical Society.

it is possible to modulate the self-assembled behavior of organic molecules on a suitably modified metal surface from solution by controlling the electrochemical potential of the electrode.

Molecular chirality and phase transition of *p*-phenylenedi(rcyanoacrylicacid)di-*n*-ethyl ester (*p*-CPAEt) (Fig. 12a) assembled on Au(111) surface have been studied by Su and co-workers.[67*i*] At 0.65 V < E_s < 0.8 V, the closely packed chiral stripe architectures have been observed on a Au(111) surface. At a more negatively charged electrode surface, *i.e.* with the potential range 0.2 V < $E_s \leq 0.65$ V, chiral 2D network has been visualised. Time-dependent sequences of dynamic phase transition of chiral supramolecular nanostructures formed by *p*-CPAEt molecules (Fig. 12b–i) show that a stripe pattern could be transformed into a network structure. Furthermore, if the electrode potential was scanned at a more positively charged electrode until the region of the thermodynamic stability of the stripe pattern, the network nanostructure dissolved and the stripe pattern re-appeared again. These dynamic processes, in combination with electrochemical cyclic voltammetry, showed that the transformation from the chiral stripe nanostructure to the chiral network structure was purely potential-dependent and reversible, meaning that the chiral supramolecular nanostructure could be controlled by tuning the electrode potential in the electrochemical environment.

3. Conclusions and general remarks

In summary, the proper design of single molecular motors and dynamers makes it possible to self-organize molecules into 2D supramolecular responsive crystalline materials. The labile character of dynamic supramolecular polymers, *i.e.* dynamers, makes these materials also of much value for the development of dynamic films coatings, as well as for "dynamic formulation", allowing slow release of active ingredients in pharmaceutical chemistry and medicine. Increasing complexity of molecular motors and dynamers, being one of the greatest challenges in materials science, can be pursued through self-assembly by exploiting interactions which act in a hierarchical manner, governing at distinct scales, to achieve a high degree of order on both molecular and mesoscopic dimensions. This leads to the elaboration of smart responsive materials as well as meta-materials. With the help of scanning tunneling microscopy, the adsorption of molecular motors and dynamers on surfaces and their response to photoisomerization, changes in temperature, complexation with metal ions and protonation have been unraveled at the sub-nanometre scale. By identifying the structural transition which dynamers and molecular motors undergo in the response of external physical or chemical triggers, detailed information about the reaction process on the surface has been obtained. The features of light responsive dynamic molecules on the surface open new pathways for the fabrication photo-responsive functional molecular devices operating on surfaces.[43] We have shown here these early attempts of *pre-programming* self-assembly of molecules forming dynamers which can function at surfaces, as a predecessor of surface templated 3D supramolecular *engineering* of responsive materials, laying the foundations for an atomistic 3D bottom-up assembly of smart architectures.

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