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Modulating Large-Area Self-Assembly at the Solid–Liquid Interface by pH-Mediated Conformational Switching

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Dedicated to Professor Roeland J. M. Nolte on the occasion of his 65th birthday

Nanoscale control over mechanical movement of molecules has been intensely investigated in this decade, aiming at the development of molecular machines that can be implemented in miniaturized systems based on single or few molecules.[1] Molecular movement in such systems can be used directly to create nanocavitands or nanotweezers that can capture/release host molecules[2] or indirectly in order to alter the electronic or optical properties of the systems, for example for the creation of nanoswitches[3] or fluorescence sensors.[4] In this context it is crucial to design molecular systems able to undergo large conformational changes as a result of external stimuli such as light irradiation,[5] metal complexation or change in pH. Among them, pH represents a prototypical biological stimulus and is ideally suited for studies performed in solution or at the solid–liquid interface. A related approach has been already used to trigger conformational switching of molecular grippers[6] that can open or close, or in dynamic chemical devices,[7] where the change of pH can preferentially lead to the complexation or release of metal ions by the system, enabling the reversible contraction/extension of the molecule. However, to exploit such molecular motions the individual building blocks have to be organized into larger functional arrays on meso- and macroscopic length scales at interfaces. This can be accomplished by making use of self-assembly, which is a reliable bottom–up approach for the fabrication of functional surfaces.[8] Nevertheless, in view of the development of future applications, there is a need for developing solutions to integrate such a type of switchable system on a given solid substrate and to achieve control of conformational switching over large areas in order to take advantage of collective effects.[5c,e]

We describe herein the two-dimensional ordering of molecules adsorbed on surfaces at the solid–liquid interface, that are capable to undergo large conformational changes upon the application of an external chemical stimulus, which can be 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 (Scheme 1), which incorporates a tridentate coordination site consisting of two triazole moieties bridged by a central pyridine ring.[9] The BTP core is decorated with three alkoxy side chains providing enhanced solubility as well as improved propensity to physisorption on highly oriented pyrolitic graphite (HOPG) at the solid–liquid interface. We have focused on two BTP derivatives, differing only in the length of their respective alkoxy chains ($R^2 = n\text{-}C_{10}H_{21}$ vs. $n\text{-}C_{18}H_{37}$) to modulate the strength of the interaction with the HOPG surface. Due to favorable electrostatic interactions, the "kinked" *anti*,*anti* 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.[9] This repulsive interaction can be switched into an attractive one by the addition of acids or metal ions to the solution, causing either protonation or metalation of the BTP core followed by a large structural change from the "kinked" to its corresponding "extended" conformation. In this paper we provide the first scanning tunneling microscopy (STM) visualization, recorded on the single molecule

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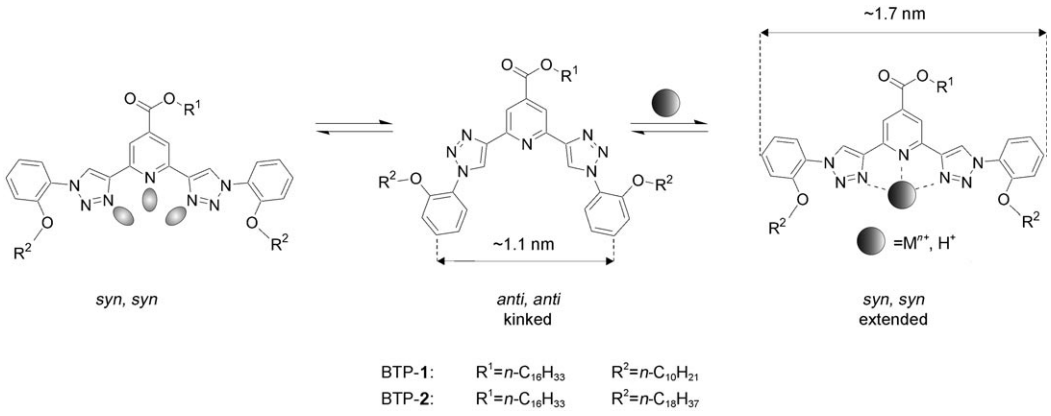

Scheme 1. Conformational switching from the horseshoe-like "kinked" to the linear "extended" conformation of the BTP scaffold upon protonation or metal complexation (the destabilized neutral extended conformation is shown on the left). Distances between terminal 4-C atoms are taken from single crystal structure analyses of several BTP derivatives and complexes.[9a]

level and at the solid–liquid interface, of the conformational changes triggered by protonation. The bistable intramolecular conformational rearrangement in our BTP derivatives, expected to occur in the supernatant solution, was found to induce a collective re-organization of the supramolecular 2D packing motif.

The investigated BTP derivatives were readily synthesized from *n*-hexadecyloxy 2,6-diethynylisonicotinate and the two different 2-(*n*-alkoxy)phenyl azides in almost quantitative yields via click reactions.[10,11]

Figure 1 a–c displays the STM image of the BTP-**1** molecule in a neutral pH 1–phenyloctane solution physisorbed at the solid–liquid interface.[11] It reveals large ordered arrays featuring a "chess-board" 2D packing motif (Figure 1 a). In the high-resolution STM image (Figure 1 b) it is possible to identify the different functionalities of the molecules. Due to the resonant tunneling between the Fermi level of the HOPG and the frontier orbital of the adsorbed molecule,[12] in the STM image the conjugated moieties appear brighter whereas the alkyl chains physisorbed on the surface appear

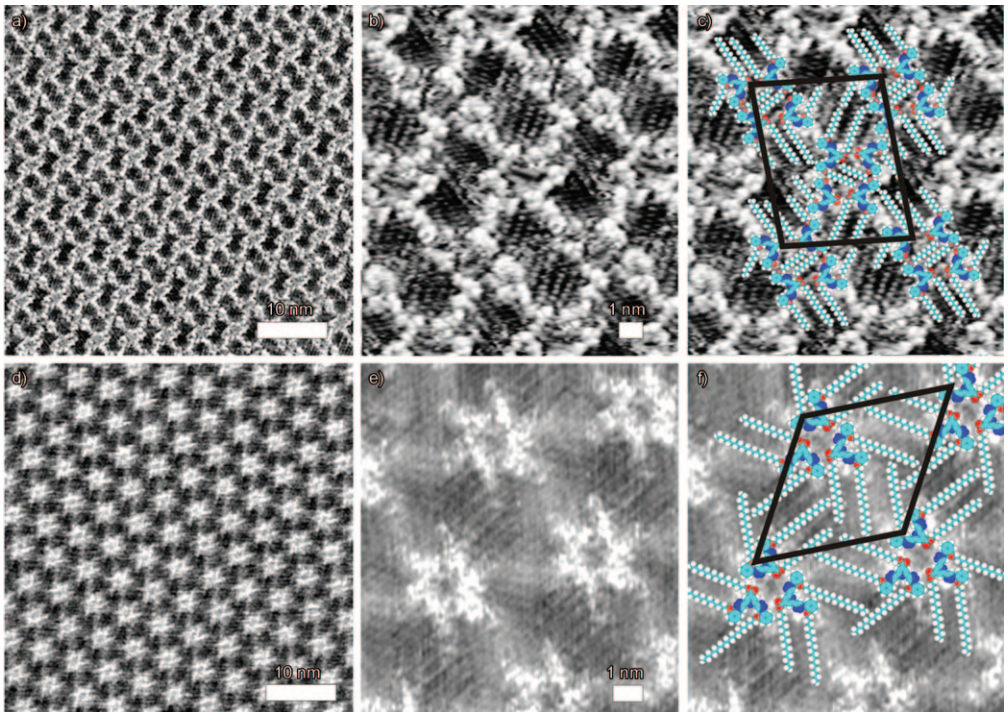

Figure 1. STM images of the self-assembled BTP molecules adopting a "kinked" conformation on HOPG. a)–c) Monolayer of BTP-**1** molecules in their "chess-board" motif and proposed model. Unit cell parameters ($a=5.4\pm0.2$ nm, $b=6.8\pm0.2$ nm, $\gamma=83\pm2°$, area per molecule $=4.6\pm0.4$ nm^2). d)–f) Monolayer of BTP-**2** in their "rosette" motif and proposed model. Unit-cell parameters ($a=5.1\pm0.2$ nm, $b=5.0\pm0.2$ nm, $\gamma=61\pm2°$, area per molecule $=7.4\pm1.1$ nm^2). Tunneling parameters: a) bias voltage $U_t=800$ mV, average tunneling current $I_t=8$ pA. b) $U_t=700$ mV, $I_t=10$ pA. d),e) $U_t=800$ mV, $I_t=5$ pA.

darker. The derived packing model (Figure 1c) provides strong evidence that all molecules immobilized on the surface adopt the "kinked" conformation of the conjugated BTP core. Hence, the thermodynamically most stable *anti*,-*anti* conformation at neutral pH in solution is retained upon physisorption on the HOPG surface. A detailed inspection of Figure 1b reveals that the molecules adopt different arrangements on HOPG as determined by the rotation of the terminal alkoxybenzene moieties around the phenyl–triazole C–N single bond. The different orientations of the alkoxybenzene are the result of the interplay of molecule–molecule and molecule–substrate interactions. Surprisingly, the STM images also show that one half of the molecules immobilized on HOPG have at least one alkoxy side-chain not adsorbed on the surface, thus back-folded in the supernatant solution, as previously described for other systems exposing alkoxy side-chains.[13] The resulting rather complex unit cell contains eight molecules.

Interestingly, when considering the rather conservative structural change, that is, extension of the alkoxy side chains by eight methylene units, monolayers of BTP-**2** physisorbed on HOPG from a solution in 1-phenyloctane appear markedly different in the STM images (Figure 1d–f). The BTP-**2** molecules adopt a "rosette" motif resembling a diamond arrangement of cyclic trimers, containing three molecules per unit cell. This nicely illustrates the decisive role that the alkoxy chain length is playing in the packing process. Also in this case, the BTP cores adopt a kinked conformation, but are packed three by three resulting in the formation of the bright 6-legs rosette-like features visible in Figure 1e. The proposed model in Figure 1f reveals that all the alkoxy chains are adsorbed on the surface.

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.[10,13] Figure 2 shows the resulting physisorbed monolayer of BTP-**1** and BTP-**2** obtained after applying the acidified solution. In this acidified environment the resulting structure of BTP-**1** (Figure 2a–c) 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 lamellar domains extend over hundreds of nanometers (see Figure S2 in Supporting Information) and no part of the substrate surface was found to be occupied by molecules adsorbed in the previously described "chess-board" packing. The high resolution image (Figure 2b) reveals that the adsorbed molecules adopt an "extended" conformation, thereby unequivocally confirming the occurrence of protonation. Rows of alkyl chains packed parallel to each other, surrounded by rows of conjugated cores are visible. In contrast to the "chess-board" motif, in the lamellar motif all the BTP molecules carry two alkoxy side-chains, which are not adsorbed on the surface. Importantly, the unit cell drastically changes upon protonation, as highlighted by the variation in symmetry and the number of molecules in the unit cell, that is, two instead of eight. In addition, the area occupied by a single molecule physisorbed on HOPG in the lamellar motif is reduced from 4.6 nm^2 (without TFA) to 3.1 nm^2 (upon TFA addition), as a conse-

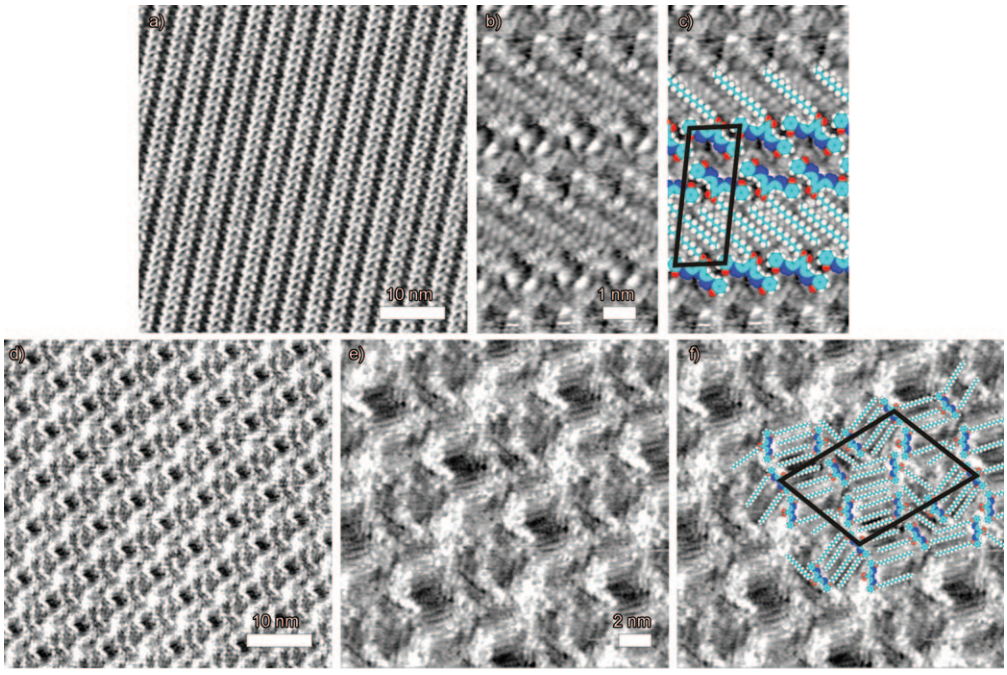

Figure 2. STM images of the packing structure of BTP molecules in their "extended" conformation after the addition of trifluoroacetic acid. a)–c) STM image of the lamellar monolayer of protonated BTP-**1** and proposed model. Unit cell parameter ($a=1.5\pm0.2$ nm, $b=4.1\pm0.1$ nm, $\gamma=81\pm2°$, area per molecule $=3.0\pm0.5$ nm^2). d)–f) Tetragon motif of the protonated BTP-**2** and proposed model. Unit cell parameter ($a=6.2\pm0.2$ nm, $b=8.1\pm0.2$ nm, $\gamma=70\pm1°$, area per molecule $=6.7\pm0.7$ nm^2). a) $U_t=550$ mV, $I_t=5$ pA. b) $U_t=550$ mV, $I_t=5$ pA. d),e) $U_t=800$ mV, $I_t=10$ pA.

quence of both the increased number of non-adsorbed alkoxy side chains as compared to the "chess board" motif and the enhanced density of packing, determined by the registry with the substrate. Interestingly, the same packing motif has been observed in BTP-**1** upon addition of one equivalent of tetrakis(acetonitrile)copper(I) hexafluorophosphate to the solution, leading to the formation of Cu(BTP-**1**)$^+$ complexes (see Figure S5[11]).

Figure 2 d–f shows the packing motif of molecules BTP-**2** after their protonation. Again, major structural changes took place on the surface, that is, from the "rosette" to the "tetragon" motif. The proposed packing model (Figure 2 f), extrapolated from high resolution STM measurements, shows unambiguously that the BTP-**2** cores adopt an "extended" conformation, in line with protonation. Despite their different initial arrangement under neutral pH conditions, both BTP derivatives undergo significant structural transformations of the self-assembled monolayer packing upon protonation. Given that the structure of the unit cell notably changes for both BTP-**1** and BTP-**2** upon protonation, it is most likely that switching takes place in the 3D supernatant solution, through a desorption–readsorption process. Significantly, virtually identical protonation-driven transformations were observed both for ex situ and in situ acidifications.

The real-time conformational switch, and 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 nanometers. The transformation from the "chess-board" to the "lamellar" motif for BTP-**1** based monolayers was found to be too fast for being visualized in real-time with our experimental set-up, due to hardware limitations.[11] Gratifyingly, under the same experimental conditions the structural reorganization of the BTP-**2** monolayer from "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. The observed slower switching kinetics are caused by the longer alkoxy chains of BTP-**2**, providing an increased desorption energy on graphite[14] and hence a partial hindrance towards reorganization of the self-assembled motif. Figure 3 shows a set of measurements where the "rosette" domains are gradually converted into "tetragon" ones in the vicinity of a HOPG step over a time scale of 20 min, the latter "tetragon" packing becoming the more favorable over time. The total coverage of the surface by the "tetragon" assembly is completed a few hours after the deposition of the droplet of the acidified solution. The fuzzy parts on the STM images correspond to areas where the considerable mobility of the molecules, triggered by the protonation process, hinders high resolution STM imaging. Such areas may include solvent molecules as well.

The observed molecular switch occurring in a dynamic scenario, that is, at the solid–liquid interface, differs from previous STM evidences of pH-mediated conformational switching for physisorbed organic systems that were detected on dry films.[15]

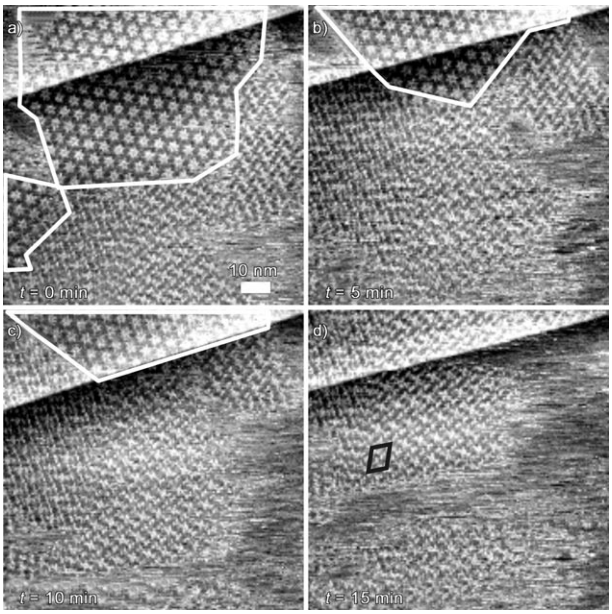

Figure 3. Consecutive STM images showing the structural evolution of a monolayer of BTP-**2** over 20 min after the addition of ca. 10 μL TFA. The evolution of the shape of the domain containing the molecules in the rosette packing is highlighted in white. a) Image taken right after the addition of TFA b) After 5 min c) After 10 min d) After 15 min. The unit-cell found for the new packing corresponds exactly to the one of the tetragon structure. Tunneling parameters: $U_t = 500$ mV, $I_t = 10$ pA.

In summary, for the first time we have utilized STM to visualize large conformational changes of a responsive molecular building block resulting in its dramatically altered self-assembly behavior at the solid–liquid interface. Protonation can successfully be used to overcome the repulsive interaction between the adjacent N atoms present in the neutral "kinked" heteroaromatic BTP molecule and result in the formation of an "extended" conformation on a HOPG surface. This represents the first yet crucial step towards the development of reversible pH triggered switches at the solid-liquid interface. Furthermore, more sophisticated, functionalized (macro)molecules are being synthesized in order to control the adsorption conformation of extended foldamers on solid substrate surfaces[16] and to switch beneficial physico-chemical properties of the monolayer, in particular fluorescence[4] and conductivity.[3,9]

Experimental Section

Scanning tunneling microscopy (STM) measurements at the solid–liquid interface have been carried out both in constant height and constant current mode using a DI Multimode microscope. The STM tips have been mechanically cut from a Pt/Ir (80:20) wire. Samples have been prepared by applying a droplet of solution on freshly cleaved highly oriented pyrolytic graphite (HOPG). The molecules were dissolved in 1-phenyloctane with an approximate concentration of 1 mmol L^{-1}. The protonation of the molecules was performed ex situ, by addition of trifluoroacetic acid (TFA) to the solution containing the molecules before the deposition, and in situ, that is, when an acidified solution of 1-phenyloctane was de-

posited on top of the already formed monolayers, under the STM tip. It is important to note that the ex situ and in situ protonation of the molecules led to the same effects on the monolayers. The raw STM data have been processed by the application of background flattening and the drift has been corrected using the underlying graphite lattice as a reference. The latter lattice is imaged underneath the molecules by lowering the bias voltage to 20 mV and raising the current to 65 pA.

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Keywords: clickamers · molecular switches · self-assembly · solid–liquid interfaces · scanning probe microscopy

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