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Scanning Tunneling Microscopy-Induced Reversible Phase Transformation in the Two-Dimensional Crystal of a Positively Charged Discotic Polycyclic Aromatic Hydrocarbon

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S *Supporting Information*

ABSTRACT: We report on the observation and manipulation of a two-dimensional crystal formed by a positively charged discotic polycyclic aromatic hydrocarbon at the liquid−solid interface. Using scanning tunneling microscopy (STM) as a tool, the supramolecular scaffolds of charged molecules could be switched between dissimilar polymorphs of different molecular densities. The observed phase transformation was found to be driven by electrical parameters such as magnitude of change of the substrate bias and voltage pulses applied to the STM tip. We conclude that the electrical manipulation of these charged molecules is a result of the creation of large local electric fields that interact with the adsorbed ionic molecules and thus cause molecular rearrangement.

The design of functionalized surfaces that exhibit reversible pattern changes in response to external stimuli has received considerable impetus in recent years due to their potential utility in the fabrication of molecular-scale devices.[1] One of the many ways to dynamically control the properties of a surface is to rely on phase transitions in the self-assembled scaffolds of surface-confined molecules.[2] Supramolecular architectures that can be externally triggered in a controlled fashion are thus expected to become key components in prototype "all-organic" devices.[1e] However, it is not straightforward to obtain reversible switching in densely packed monolayers in view of strong intermolecular as well as molecule−substrate interactions.[3]

In this Communication, we report on the scanning tunneling microscopy (STM)-induced reversible phase transformation in a much more labile and variable medium of charged adsorbate monolayers. The self-assembled system consists of a positively charged polycyclic aromatic hydrocarbon (PAH), namely 9-phenylbenzo[1,2]quinolizino[3,4,5,6-*fed*]phenanthridinylium perchlorate (PQPClO$_4$), physisorbed at the interface of an organic liquid and highly oriented pyrolytic graphite (HOPG). In contrast to the extensively studied self-assembly of neutral alkylated molecules, which is typically dominated by attractive intermolecular and molecule−substrate interactions, the self-assembly of PQPClO$_4$ on the hydrophobic surface of HOPG is expected to be governed by a delicate balance between long-range repulsive (electrostatic) intermolecular interactions and short-range attractive molecule−substrate (van der Waals) interactions.[1f] Such charged molecules are of particular interest for molecular manipulation, as they offer the possibility of coupling an external electric stimulus with the degrees of freedom on the surface.[2c−e] The additional motivation for this endeavor originates from the significance of centrally charged discotic PAHs in the field of supramolecular electronics.[4] The aggregates obtained from the $\pi-\pi$ interactions between PAHs provide charge transport pathways and thus can be used as active materials in electronic and optoelectronic devices.[5] Although the columnar organization of positively charged (hetero)PAHs into one-dimensional superstructures has been demonstrated recently,[4] to the best of our knowledge this is the first report on the two-dimensional (2D) self-assembly and phase transformation of charged PAHs.

Figure 1a shows the molecular structure of PQPClO$_4$. The high-resolution (HR) STM image displayed in Figure 1b shows the existence of a well-ordered compact 2D crystalline monolayer in which the molecules are arranged in a hexagonal motif. Six molecules constitute one hexagon (α phase), with their substituent (noncondensed) phenyl ring pointing toward the center of the hexagon. The monolayer shows long-range order with intermittent defect lines and distorted hexagons. However, the most striking feature of this supramolecular system is its sensitivity to changes in the substrate bias. The molecules often adopt an entirely different structural pattern (Figure 1d, β phase) at a different value of substrate bias. A relatively denser and amorphous supramolecular network appears with the "phenyl lobes" of the molecules now pointing in somewhat random directions. For the sake of comparison, the unit cell presented in Figure 1d,e ignores the absolute orientation of the molecules. Despite the presence of an extra molecule in the (pseudo) unit cell of the β phase, the unit cell vectors of the β phase are only slightly larger than the ones for the α phase due to the random yet efficient packing of the phenyl lobes of the molecules in the former. The counterions could not be visualized in the STM images in this study, probably due to their high in-plane mobility. Despite this fact, one readily expects that the perchlorate anions play a significant role in the process of self-assembly by screening the positive charge and resultant electrostatic repulsions. In order to comprehend the role of counterions, similar experiments were carried out on a very similar species, which however is associated with a bulkier organic counterion (benzene sulfonate,

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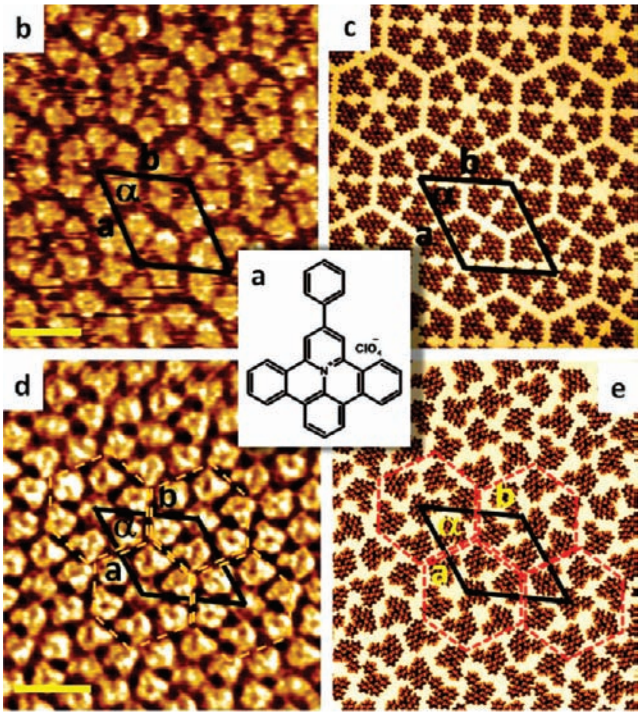

Figure 1. (a) Molecular structure of PQPClO$_4$. (b) HR-STM image of PQPClO$_4$ physisorbed at the octanoic acid/HOPG interface at negative substrate bias. $a = 3.62 \pm 0.05$ nm, $b = 3.64 \pm 0.06$ nm, and $\alpha = 59.8 \pm 1.7°$ (plane group *p6mm*, 6 molecules/unit cell). (c) Tentative molecular model. (d) HR-STM image of PQPClO$_4$ at positive substrate bias. The unit cell drawn in the image ignores the absolute orientation of the molecules. $a = 3.70 \pm 0.04$ nm, $b = 3.71 \pm 0.04$ nm, and $\alpha = 59.1 \pm 1.5°$ (7 molecules/unit cell). (e) Tentative molecular model. Tunneling conditions for panels b and d: (b) $I_t = 0.085$ nA, $V_{bias} = -0.85$ V; (d) $I_t = 0.060$ nA, $V_{bias} = 0.55$ V. The yellow scale bars represent 3 nm.

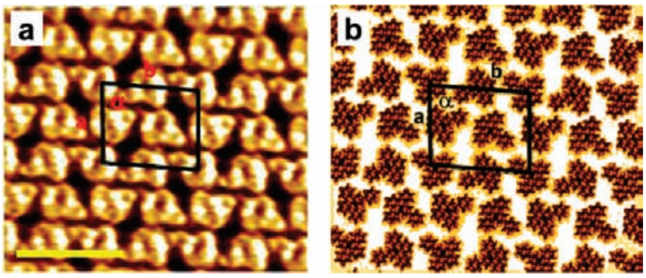

Figure 2. (a) HR-STM image showing the γ phase. The unit cell parameters are $a = 2.54 \pm 0.08$ nm, $b = 2.75 \pm 0.09$ nm, and $\alpha = 86.0 \pm 1.0°$ (plane group *p*2, 4 molecules/unit cell). Imaging conditions: $I_t = 0.09$ nA, $V_{bias} = -0.85$ V. The yellow scale bar represents 3 nm. (b) Tentative molecular model.

PQPBS). Preliminary results (Supporting Information) show that self-assembled networks of PQPBS exhibit behavior similar to that of PQPClO$_4$ with bias-sensitive surface patterns, reminiscent of the cation-driven self-assembly of these molecules. This, however, is rather premature conjecture and needs to be corroborated by screening a number of cation−anion combinations.

Experiments carried out at different tunneling conditions indicate that this supramolecular network is extremely sensitive to electric parameters and could be manipulated by varying the substrate bias as well as by applying momentary voltage pulses to the STM tip. Thus, at a given set of tunneling parameters, either of these two phases could be observed, although the denser and disordered β phase is more preferred. In fact, the β phase survives on the surface for longer times as long as no electric manipulation is carried out. Essentially, a significant change in the substrate bias ($\geq$300 mV) triggers the phase change. The same transformation can also be effected by applying 3.5 V (10 μs) pulses to the STM tip. The switching success rate per tip voltage pulse depends on the detailed configuration of the STM tip apex, and it is rarely 100%. Apart from the two phases mentioned above, a third phase (γ phase, Figure 2a,b) also exists which dynamically transforms into the β phase as a function of time and appears to be driven by an entropic gain. The course of γ-to-β phase transformation could be followed on the surface by recording time-dependent STM images (Supporting Information). Such time-dependent transformation of the γ phase to the β phase is indicative of substantial surface dynamics in this charged monolayer.

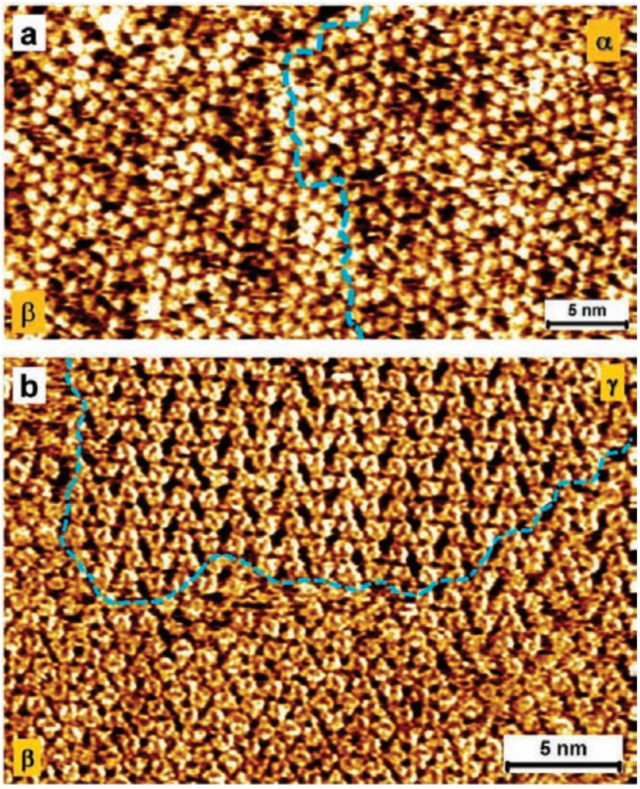

Figure 3. STM images showing the coexistence of (a) the α and β and (b) the β and γ networks. The disordered arrangement of molecules in both panels essentially represents the β phase. Dashed blue lines represent the domain boundaries. Additional images are provided in the Supporting Information.

It must be noted at this juncture that the electrical parameters used to stimulate the reversible interconversion between α and β phases can lead to substantial changes in the STM imaging mechanism.[6] Thus, considering the fact that the lattice parameters for the unit cells represented in Figure 1 are somewhat identical, the results presented here could be alternatively interpreted as simply a change in the STM imaging mechanism upon electric manipulation. One of the ways to rule out this possibility and to separate out the existence of the different phases from the effect of changes in the STM contrast is to obtain STM topographs showing the coexistence of the different molecular networks. Figure 3 shows such a case wherein domains of the two ordered networks (α and γ) could be visualized coexisting with the disordered β phase, thus unambiguously proving the presence of all of the three different types of packing described earlier.

Having established their existence, we begin to understand the relative stabilities of the three phases as follows. The relative occurrence of the three phases on the surface of HOPG reflects that the β network of molecules is the most preferred arrangement, followed by the α phase, whereas the γ phase is a metastable phase. It must be noted at this juncture that both α and γ phases consist of ordered arrays of molecules, which is entropically unfavorable. In contrast, the β network is rather disordered and hence entropically favored. On the other hand, the calculated packing densities of α, β, and γ phases are 0.52, 0.61, and 0.58 molecules/nm^2, respectively. On the basis of the molecular densities, the binding enthalpy is expected to be highest for the β phase. Thus, considering both the enthalpic and entropic contributions, the preference for the β phase appears to be reasonable. However, one should also consider the contribution from the long-range electrostatic interactions in the self-assembly of these charged molecules. Such repulsive interactions will prevent the molecules from coming too close to each other. As a consequence, it is not unreasonable to expect a lower surface density phase to survive on the surface, which readily explains the stability of the α phase. In a nutshell, the preference for the β phase arises due to a complex interplay between long-range electrostatic interactions, packing density, and entropic considerations.

Experimental evidence suggests that switching is possible at positive as well as negative bias, and the threshold voltage is not a constant value. The parameter that drives the transformation is the "magnitude of change" in the substrate bias. The larger the change, the greater is the probability of initiating the phase transformation. Thus, a large variation in the electric field surrounding the adsorbed ions acts as a "trigger" to induce molecular motion, and thus the molecules then adsorb in one of the possible configurations. Voltage pulses applied to the STM tip reduce the energy barrier between the two supramolecular configurations, or they may directly provide enough energy to the molecules to cross over the barrier. In both modes of switching, there exists an intriguing possibility of a 2D structural rearrangement which transpires on the surface. Although it is usually not straightforward to prove the 2D nature of the transformation, some STM images (Supporting Information) do indicate that this is an instantaneous process and might take place on the surface. Thus, considering the prevalence of substantial surface dynamics in this system, once the transformation is induced locally, it is probably transmitted via a cooperative mechanism similar to what has been observed in numerous ionic self-assembly processes.[7] However, taking into account the delicate balance between the attractive and repulsive forces that stabilize the self-assembled network in the present case, one cannot entirely rule out the desorption of molecules followed by readsorption.[2e]

In conclusion, we illustrate that the supramolecular network of a charged PAH could be visualized and manipulated in a number of ways on HOPG surface by using STM. A subtle balance between attractive and repulsive interactions enables the realization of such reversible interconversion between different phases of dissimilar molecular densities on the surface. This strategy also opens up doors to large-scale adsorbate manipulation with a bottom-up perspective.

ASSOCIATED CONTENT

Supporting Information. Additional STM images of the three phases; STM images depicting the instantaneous nature of the phase transformation as well as time -dependent transformation of the γ phase to the β phase; synthesis and characterization of $PQPClO_4$; experimental details of the STM measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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