Supramolecular Self-Assembly Initiated by Solid–Solid Wetting

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Abstract: We present a preparation method for self-assembled supra-molecular monolayers of unsubstituted organic semiconductors and pigments on a solid substrate, applicable under ambient conditions. The deposition is based on a solid–solid wetting phenomenon, whereas the subsequent layer growth proceeds according to standard models. Molecular adsorption results from direct contact of the compound in a nanocrystalline state with the solid surface. Based on complementary force field calculations, we propose that molecules disintegrate from the crystalline state and adsorb on the surface because of a gain in binding energy. The preparation method is exemplified by means of a linear hydrogen-bonded system, namely quinacridone (QAC) on graphite. In addition, the chosen system allows us to actively guide the self-assembly after deliberate removal of molecules from a predefined area.

Keywords: adsorption · nanostructures · scanning probe microscopy · self-assembly · semiconductors

Introduction

Whereas conventional microfabrication methods, such as lithographic techniques (top-down approach), encounter principal physical[1] and economical[2] limitations when approaching the length scale of molecules, molecular self-assembly processes[3] have been widely explored for the development of bottom-up approaches for nanoscale structures without such limitations.[4] In contrast to covalent self-assembly[5] (e.g. fullerenes, carbon nanotubes), which is attractive for the growth of inorganic, rigid building blocks with high charge carrier mobility,[6,7] supramolecular self-assem-

bly[5,8–12] is discussed for easy, low-cost fabrication under ambient conditions. Moreover, the reversibility of non-covalent bonds at room temperature offers the possibility of going beyond simple miniaturization by introducing dynamic features to surface-supported devices such as reconfiguration, self-repairing and self-contacting.[13]

For the preparation of surface-supported supramolecular structures, a variety of methods has already been established. Thermally stable compounds can be deposited in a precisely controllable manner by vacuum sublimation, commonly referred to as organic molecular beam epitaxy (OMBE). A clear disadvantage of this method, particularly in the light of future applications, is the enormous instrumental effort. Also, this approach is limited to molecules which are sufficiently stable for sublimation. On the other hand, many alternative techniques are based on dissolving the molecules and utilizing the solution as a carrier to transport molecules to the interface.[14–16] However, this method suffers from a severe disadvantage when the compound of interest is hardly soluble, as for instance many organic semiconductors or pigments. Here we show that these drawbacks can easily be overcome by a simple process applicable under ambient conditions. This novel straightforward preparation method is suitable for a targeted coverage in the monolayer regime. The basic idea is as follows: nanocrystals (pure or suspended within a matrix) of the respective compound are brought into direct contact with the substrate. When the binding energy of the molecule to the substrate, that is, the adsorption energy, exceeds the binding energy of surface

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molecules in the nanoparticle, single molecules detach from the nanoparticle, adsorb on the substrate surface and thus form monolayers. Eventually, combination of thermally activated diffusion and intermolecular forces results in the self-assembly of highly ordered supramolecular structures, if the molecule–substrate interaction is not too strong. In this respect, the behaviour is analogous to the spreading of a liquid on a solid, provided the interface tension exceeds the surface tension. Thus, we refer to the proposed process as "solid–solid wetting initiated self-assembly".

The proposed novel preparation method is exemplified with quinacridone (5,12-dihydro-quino[2,3-b]acridine-7,14-dione) as the supramolecular building block. Its structure is depicted in the inset of Figure 4. Quinacridone (QAC) is an organic semiconductor[8,17,18] and a commercial product of the pigment industry.[19] It is readily available in a nanocrystalline state with an average primary particle size of ≈70 nm in two different polymorphic modifications (β-phase: hydrogen-bonded molecules are interconnected within a plane, γ-phase: hydrogen-bonded molecules form a criss-cross structure).[18] For this chosen model system—QAC on graphite—we find rather interesting properties. Due to the structure of the QAC molecule, self-assembly in linear structures is favoured. These chains are not necessarily straight and neighbouring chains are not densely packed. Kinks within the chains and gaps of various sizes between them give rise to a far more complex structure than just a truly periodic pattern. Thus, the presented system principally offers the prospect to encode information. Moreover, through interaction with an invasive probe, QAC on graphite exhibits another interesting property, the possibility of locally steering the self-assembly, that is, the reassembly after disintegration of the supramolecular structure is guided by the scanning process in a defined manner. For the readsorption, a constant supply of molecules is required, a criterion that cannot be met by standard (O)MBE techniques[20] or the precursor method.[21]

Usually two-dimensional self-assembly from the liquid results in periodic structures, apart from defects and domain boundaries.[8–10] Normally when molecules are removed from the substrate, these periodic structures just grow back, hence limiting the freedom for actively steering the outcome of the self-assembly process. Here we show that our new approach applied to QAC on graphite opens up a way to steer the self-assembly process in order to deliberately create desired nanostructures.

Results and Discussion

QAC monolayers were generated by direct deposition of nanoparticle powder on the (0001) surface of highly oriented pyrolytic graphite (HOPG) and a subsequent removal of the powder from the HOPG surface. Similar supramolecular structures were also observed when the QAC nanocrystal powder was mixed up with the liquid crystal octylcyanobiphenyl (8CB)[22] and a small amount of the mixture was applied to the graphite surface. Figure 1a presents a high-resolution scanning tunnelling microscopy (STM) image of QAC adsorbate nanostructures. QAC molecules assemble at the graphite base plane into distinct linear chains with a uniform
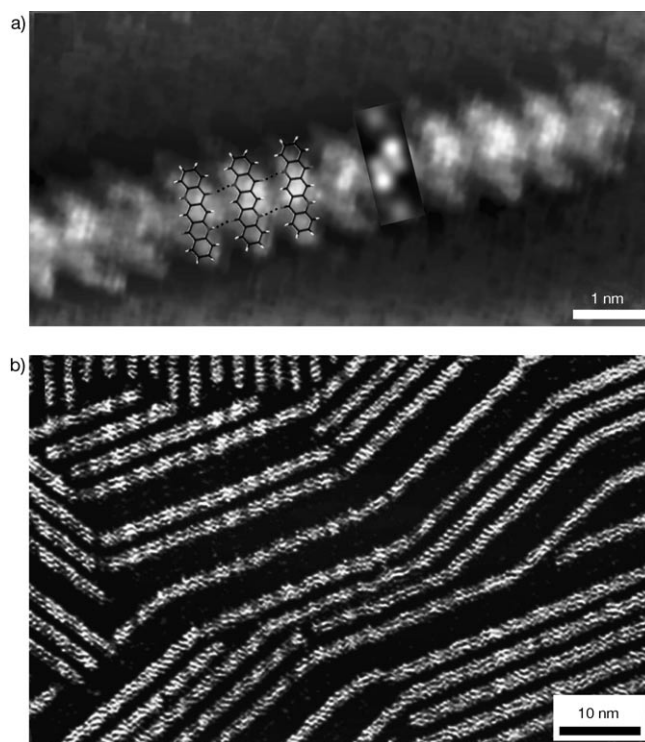

Figure 1. Characterisation of a QAC nanowire. a) High-resolution STM image of a single QAC nanowire adsorbed on a graphite surface. Overlaid on the image is a force-field simulation of adsorbed QAC molecules, dotted lines indicate hydrogen bonds. Inset: image of the LUMO of QAC, as simulated by DFT calculations. The molecular orbital calculation image has been positioned at a site equivalent to the shown molecular models. b) STM image of a QAC nanowire array exhibiting complex features.

width of 1.63 nm and a lattice constant of 0.70 nm along the chain. Based on the STM image contrast and the geometrical dimensions in high resolution images, we conclude adsorption of QAC parallel to the substrate. This is supported by a DFT simulation of the image contrast, as superimposed on the STM image in Figure 1a. The calculation depicts the LUMO of a QAC molecule. The typical S shape and the bright centre appearing in the STM measurements of QAC are well reproduced by the DFT simulation. Within the QAC chains, neighbouring molecules are interconnected by two O⋯N−H hydrogen bonds with each neighbour. The bonding pattern is illustrated by the overlaid model in Figure 1a, representing the minimum energy structure as derived by force-field calculations. Figure 1b provides an overview of the encountered complexity in the self-assembled QAC-wires on HOPG. An individual nanowire can feature kinks of discrete angles while multiwire arrays exhibit discrete, non-equidistant gaps between parallel wires. The distances between adjacent wires were measured to be integer

multiples of the substrate lattice vectors, indicating the existence of an epitaxial relationship. Nevertheless, the observed assemblies are far more complex than ordinary quasi periodic monolayer structures. Crystallographic details of the structure will be published elsewhere.

We propose that the transfer of QAC molecules from the nanoparticle to the substrate occurs as a consequence of direct contact, rather than being mediated through dissolution and diffusion in 8CB. This model is also supported by experiments without the 8CB matrix as described below. A mixture with 1 ppm QAC in 8CB still exhibits sedimentation after heating up to 60°C and subsequent centrifugation, thus a potential actual solubility is definitely below 1 ppm. Molecular coverages as depicted in Figures 1b and 3a were ob-
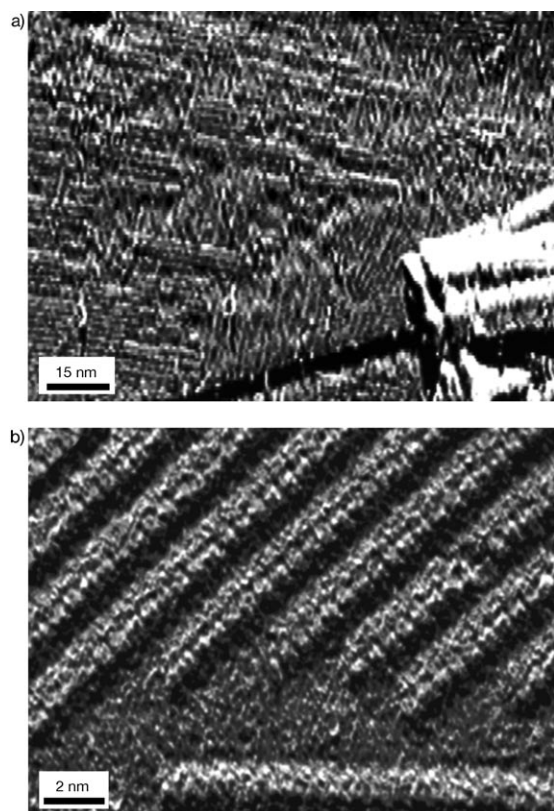

Figure 2. Self-assembly of QAC molecules after direct deposition, that is, without a binder, of nanocrystalline powder on freshly cleaved HOPG. a) Overview scan showing both deposited QAC nanocrystals (bright, large feature in the lower right corner) and adsorbate domains consisting of uniform chains. b) Close-up of a domain, revealing the supramolecular chain structure of QAC assemblies.

tained by applying ≈0.4 mg QAC/8CB mixture per cm^2 on HOPG. In order to provide enough molecules for this coverage (8×10^{13} molecules cm^{-2}), a minimum concentration of ≈100 ppm QAC in 8CB is required. Based on the above mentioned upper boundary for the solubility, the number of potentially dissolved QAC molecules is not sufficient. In order to supply the additionally required molecules, the equilibrium between solution and solid state has to be maintained by dissolution and diffusion of molecules. The report-

ed coverages, however, were observed instantaneously after the mixture has been applied to the substrate and did not change during the experiment. As at room temperature the liquid–crystal 8CB is in a smectic-A phase with a layer sliding viscosity of 100 mPa s,[23] relatively fast diffusion of a fairly large molecule such as QAC can be ruled out. Thus mediation of the adsorption through dissolution and diffusion of QAC in the 8CB matrix cannot explain our experimental observations. In addition, confocal Raman microscopy on embedded nanocrystals suggests that QAC remains in its nanocrystalline state upon mixing with 8CB. Spatial mapping of a QAC indicative frequency band reveals aggregation of the pigment in the 8CB matrix: areas with high intensity were found, which originate either from single nanocrystals or aggregations thereof. However, the Raman intensity between those QAC containing areas was virtually zero. Details will be published elsewhere.

Yet, what is the mechanism of the observed self-assembly? Based on the experimental findings described above we propose a different process. Single molecules are transferred from the nanocrystal to the substrate, when the nanoparticle is in direct contact with the surface. Adsorbed monomers diffuse onto the surface and are able to form nuclei for subsequent growth. The main difference between the proposed mechanism and a standard growth process of interfacial monolayers is that building blocks are supplied from a solid rather than solution or gas. Thus we entitle the proposed process "solid–solid wetting initiated self-assembly".

In order to reveal the driving force for this disintegration of the nanocrystal we compared the binding energies of single QAC molecules on graphite with surface molecules of a QAC nanocrystal. Force-field calculations for γ-QAC indicate that the binding energy of an adsorbed molecule on HOPG (1.91 eV) exceeds the binding energy of a molecule within the (010) surface of the nanocrystal (1.77 eV). Hence, purely based on energetic grounds, QAC should exhibit a preference for the graphite substrate. On the other hand, for the organic pigment indigo, the relative magnitude of the binding energies as calculated by force-field methods is reversed and no adsorption was observed with the same preparation method, despite numerous attempts. The adsorption energy of a single indigo molecule on HOPG accounts to 1.56 eV, whereas the lowest binding energy in the solid state was found for the (010) surface with 1.78 eV. Other pigments which we were able to adsorb from a nanoparticle suspension, such as Acridone or PTCDA (perylene-tetracarboxylic-dianhydride) show energy relations comparable to QAC. It is well known that force-field calculations are a simplification and neglect many important interactions, hence absolute energy values are not trustworthy. However, here we calculate binding energies for very similar situations in which van der Waals forces dominate. Hence a relative comparison of binding energies is justified and at least provides qualitative information. Basically, the condition for solid–solid wetting is analogous to the classical case of a liquid spreading on a solid, that is, the adhesion energy be-

tween the surface molecules of the droplet and the substrate surface must exceed the cohesion energy between the molecules of the droplet. So far the occurrence of "solid–solid wetting"[24] has only been reported in the special context of inorganic oxide catalysts in a high temperature regime,[24,25] not for organic molecules.

In order to verify that the 8CB matrix does not trigger the adsorption, the experiment was repeated without any binder for the nanocrystals. After direct deposition of QAC nanocrystal powder on a freshly cleaved HOPG surface and subsequent removal of the nanocrystals, supramolecular chain structures can be detected as shown in Figure 2b. As
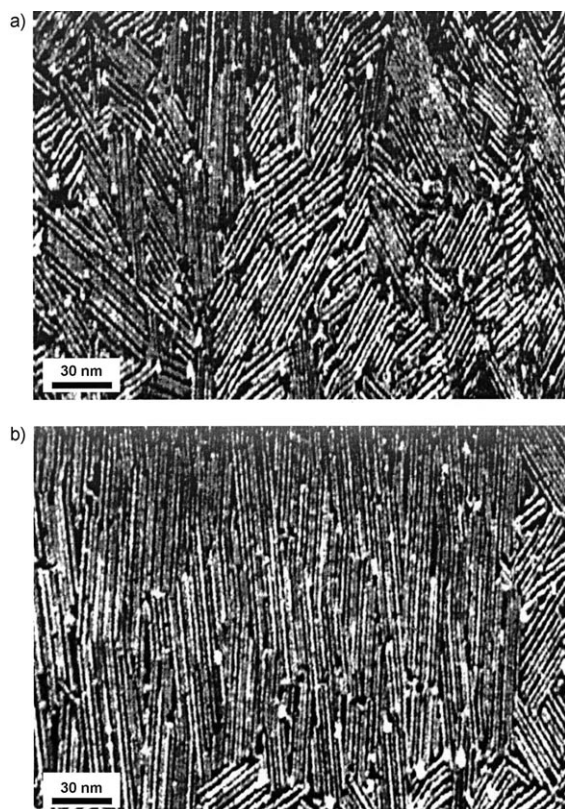

Figure 3. Locally guided growth of QAC chains. a) STM image of the initial configuration. b) Image of the resulting configuration. The alignment was generated by scanning with a decreased tip-sample distance for molecular extraction, and then scanned with an increased distance to enable guided reassembly. The scan area in b) was moved down and to the right by 30 nm relative to a) in order to make the boundaries between non-aligned and aligned areas visible.

graphite is hydrophobic and a solubility of QAC in water is not detectable even at elevated temperatures,[26] it is very unlikely that the under ambient conditions unavoidable interfacial water layer mediates the adsorption; this is supported by the fact that QAC monolayers have not been detected in areas between deposited nanocrystals before their removal from the substrate surface. We conclude that the transfer of molecules from the nanocrystals to the substrate is restricted to the contact area. In a similar experiment of direct deposition and subsequent removal of the nanocrys-

talline powder with indigo, no adsorption could be detected. When QAC monolayers were prepared with the aid of a binder, no nanocrystals were imaged with the STM as in the case of Figure 2a. This indicates that the binder resuspends nanocrystals after their contact with the substrate. Thus the area in which transfer of molecules from the nanocrystal to the substrate has occurred is uncovered and accessible for STM imaging.

Arrangements of QAC nanowires, self-assembled under the conditions of organic solid–solid wetting, can be controlled locally on the nanoscale, as depicted in Figure 3. When the tip-sample gap is reduced and tip-sample interactions are increased,[27] the nanowires within the scan area can be extracted, that is, the QAC molecules desorb from the surface. Readsorption and assembly are initiated simply by restoring the previous scanning conditions. In contrast to the initial, randomly oriented domains, the newly self-assembled wires are aligned nearly parallel to the fast scan direction as shown in Figure 3b. Evidently, the orientation of the wires is still determined by the epitaxial relation to the substrate, rather than just the scan direction. Two slightly different directions are discernible in Figure 3b. The angle between those directions accounts to 9° and the two orientations are bisected by a high symmetry direction of the substrate.

In order to understand the reason for this oriented reassembly we calculated the energy cost of displacing a QAC molecule within a chain for two perpendicular directions by using force-field methods. The results, presented in Figure 4, reveal a highly anisotropic behaviour: displacement along the H-bond axis, that is, compression and extension, requires considerably more force than shearing. This indicates that
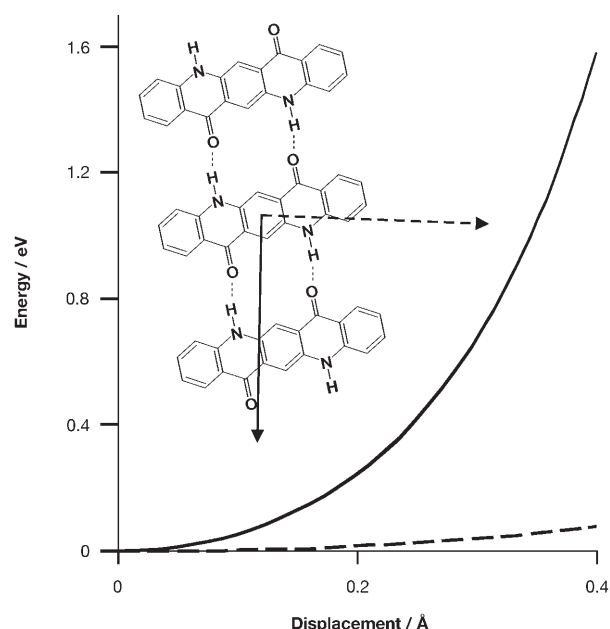

Figure 4. Displacement energies of a single QAC molecule within a wire for the direction parallel (——) and perpendicular (-----) to the hydrogen bonds as calculated by force-field simulations. The exact directions of the displacement are indicated in the inset.

wire-nuclei with the H-bond direction aligned nearly parallel to the scan direction are more resistant against disruption by the scanning probe, and thus can continue to grow, whilst non-parallel nuclei are extracted and replaced. We therefore propose that—in contrast to STM tip-induced mechanical reorientations of already adsorbed wires—the rearrangement is the result of readsorption and direction selective growth of nanowires, and hence can be described as a locally guided supramolecular self-assembly. As the growth is actually influenced by the probe, its time constant must be in the same order as the scanning process. Monomers for the readsorption are again supplied by the nanocrystals, which are still present or molecules might originate directly from the tip, a situation reminiscent of dip-pen lithography.

The effect of guided self-assembly was also observed on smaller length scales down to the regime of ≈10 nm as illustrated by the series of subsequent STM images shown in Figure 5a–c. The initial defect was generated by moving the STM tip in 0.1 s along the path indicated by the dashed line with reduced gap resistance. The manipulation was done in the constant current mode, that is, the feed-back remained active, and the tip-sample distance was decreased by ≈0.5 nm with respect to the imaging mode. After the extraction of the molecules, the area was repeatedly scanned under normal tunnelling conditions. Likewise, the result of this manipulation can be described as guided self-assembly: Figure 5b shows that the STM tip generates a gap in the nanowire assembly along the manipulation path. The fuzzy features within the gap can be explained by molecules which are still mobile and in the process of diffusion and self-assembly during the scan. The orientation of the eventually regrown and stabilised self-assembled wires is clearly related to the scanning direction (Figure 5c).

Conclusion

It has been shown that polyaromatic molecules can be transferred from a nanocrystal, which serves as a precursor, to a solid substrate, just by establishing mechanical contact. Molecules deposited in this way then form self-assembled supramolecular structures according to their structure and functional groups for hydrogen bonding. The method was demonstrated by means of QAC on graphite, a system which also offers the opportunity for rearrangement by guiding the self-assembly process through interaction with the scanning probe.

Although some restrictions apply for the solid–solid wetting to occur, namely, the adsorption energy of the molecule on the substrate has to exceed the binding energy on the surface of the initial nanocrystals, it is still applicable to a wide range of interesting compounds. In addition, the ease of preparation renders this novel extremely economic preparation method highly interesting for future applications. The fact that computationally inexpensive force-field simulations appear to predict the applicability of the method for a given system correctly certainly helps to pave the road for a new
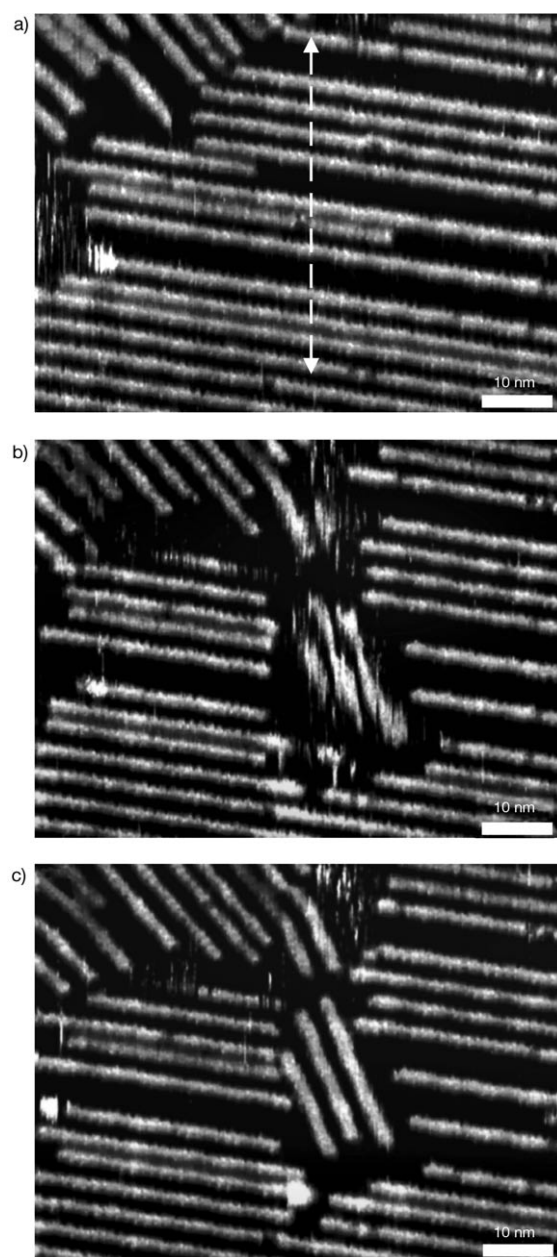

Figure 5. Nanoscale reconfiguration by tip-influenced reassembly. a) STM image of the initial array. After this image was recorded, the scan was stopped and the STM tip moved with a reduced tip-sample distance six times along a vertical vector (dashed arrow) with a frequency of 53 Hz. b) The process of reassembly within the produced monolayer gap. c) Re-established new wires within the gap.

preparation technique for self-assembled molecular monolayers.

Experimental Section

HOPG surface (Figure 2a,b). Monolayers were also generated by mixing up QAC powder with the liquid crystal octylcyanobiphenyl (8CB)[22] in molar ratios of QAC/8CB ranging from 1:3 to 1:20 (Figures 1, 3 and 5). Various mixing ratios, however, had no measurable influence on the reported results. As discussed above, 8CB does not dissolve QAC, but merely serves as a matrix (binder) and carrier for the suspended QAC nanocrystals. To verify that no specific properties of 8CB account for the observed effect, experiments were performed in various other liquids such as alkyd resins and vitamin K1 with similar outcome. The spontaneous self-assembly of QAC nanostructures at the surface of freshly cleaved highly oriented pyrolytic graphite (HOPG) was initiated by applying a small amount of the mixture to the (0001) surface of HOPG.

STM: The supramolecular assemblies were investigated in situ with a home-built scanning tunnelling microscope (STM) under ambient conditions at room temperature, that is, without removing the excessive 8CB/QAC mixture. Electrochemically etched tungsten tips served as probes. STM measurements were performed in the constant current mode of operation with a typical line frequency of 14 Hz, tunnelling currents ≈ 0.5 nA and voltages $\approx +1.0$ V (with respect to the tip). In order to perform molecular extractions, the tip-sample gap was decreased by ≈ 0.5 nm with respect to the imaging mode by reducing the tunnelling resistance (changing the tunnelling voltage from $+1.0$ to $+0.1$ V).

Simulations: For a profound understanding of the intermolecular QAC hydrogen bonds and to explain the anisotropy in growth and properties, force-field calculations were conducted. Geometrical constraints were derived from STM measurements and applied to these simulations to estimate the binding energies of various polyaromates in their crystalline state and on graphite, respectively. The calculations were performed with the Cerius2 software package employing a Dreiding II force-field,[28] which contains an explicit term for hydrogen bonding. DFT calculations within the generalised gradient approximation[29] were performed with the Vienna ab initio simulation package (VASP).[30] The DFT simulated STM image was calculated within the Tersoff–Hamann picture.[31]

Acknowledgements

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