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# STM observation of 1,3,5-triazines bearing rod-like benzeneazonaphthalene moieties monolayers self-assembled on graphite surface†

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**A series of 1,3,5-triazines incorporating benzeneazonaphthalene moieties have been synthesized and STM observations have clarified the geometrical configuration of the self-assembled molecules on a graphite surface.**

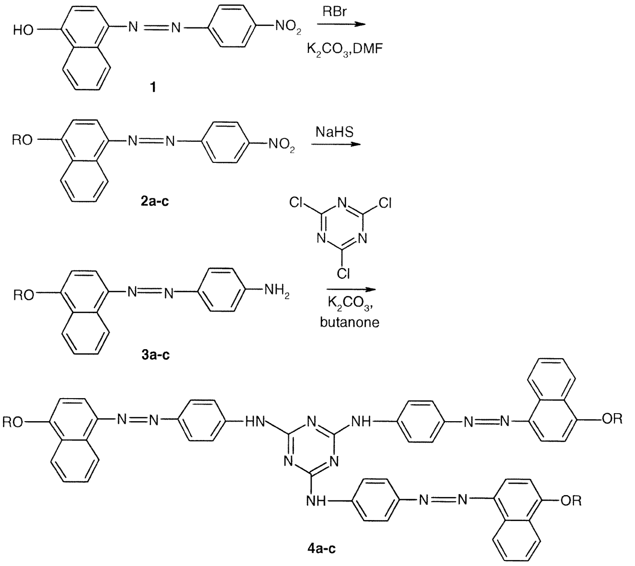
Highly ordered self-assembled organic monolayers adsorbed on solid substrates are of importance in many processes occurring at interfaces such as lubrication, wetting, adhesion, and molecular recognition.[1] Furthermore, the understanding of their structure and properties is critical for applications in fields such as sensors,[2] tribology,[3] and nanofabrication.[4] Scanning tunneling microscopy (STM) can provide direct molecular images of self-assembled monolayers (SAMs) at submolecular scale resolution.[5–7] With the help of STM, it has been found that the stability of SAMs can be appreciably affected by the structure of self-assembled molecules.[8,9] It is thus interesting to explore various effects of molecular structures, such as geometry and functional groups, on the overall assembly structure.

In this paper, we report the liquid crystalline trisazomelamines (TAM) **4** which are threefold substituted *via* amino groups with rod-like benzeneazonaphthalene sub-units. The ability of the incorporated azo moieties of the new 1,3,5-triazines derivatives to be switched by light irradiation makes them promising materials for optical data storage.[10] It has been pointed out that the applications of any azo system will rely on the understanding of the structure of monomolecular layers of azo molecules.[11,12] In the present study we applied STM methods to observe the molecular alignment of the liquid crystalline TAM **4** adsorbed on graphite with submolecular resolution. The study of the self-assembly of the novel thermotropic liquid crystalline 1,3,5-triazines derivatives could help in the development of new materials with novel physical properties for optical information storage.

The synthetic route to the new 1,3,5-triazines **4** bearing three rod-like benzeneazonaphthalene sub-units is shown in Scheme 1. It involves a three-step synthesis. TAM **4** was prepared according to known literature procedures starting from 4-(4-nitrophenylazo)-1-naphthol **1**.[10] The preparation of the alkoxy-substituted intermediates **2** was carried out by the etherification of **1** with alkyl bromides incorporating a different number of methylene groups in the presence of potassium carbonate. Subsequently, the 4-(4-aminophenylazo)-1-alkoxynaphthalenes **3** were obtained by the reduction of the nitro group of the intermediates **2** with an aqueous solution of sodium hydrogen sulfide. To obtain the novel TAM **4**, the anilines **3** were reacted with cyanuric chloride in the presence of potassium carbonate.

The STM samples were dissolved in toluene (HPLC grade, Aldrich Inc.) with a concentration of less than 1%. A droplet of the solution was deposited onto a freshly cleaved surface of highly ordered pyrolytic graphite (HOPG) (quality ZYB, Digital instruments). The substrate was heated at 40 °C for about 40 min and cooled slowly to room temperature. This treatment is employed as a precautionary measure to prepare uniform and stable molecular layers because the molecular weight is relatively high and thus longer time is beneficial for their thermoequilibrium. The experiment was performed with a Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) in ambient conditions. STM tips were mechanically formed Pt–Ir wires (90 : 10). All STM images were recorded using constant current mode of operation. The specific tunneling conditions were given in the figure captions.

Following the above described sample preparation procedure, the as-prepared TAM **4a** samples form large, uniform



**Scheme 1** Synthesis of trisazomelamines **4** (**4a**: R = $C_{18}H_{37}$; **4b**: R = $C_{16}H_{33}$; **4c**: R = $C_{14}H_{29}$).

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†Electronic supplementary information (ESI) available: experimental details for the preparation of compounds **2**–**4**, mass and IR spectra of **3a**–**c** and **4a**–**c**, and $^1$H NMR spectra of **4a**–**c**. See http://www.rsc.org/suppdata/jm/b2/b200043c/

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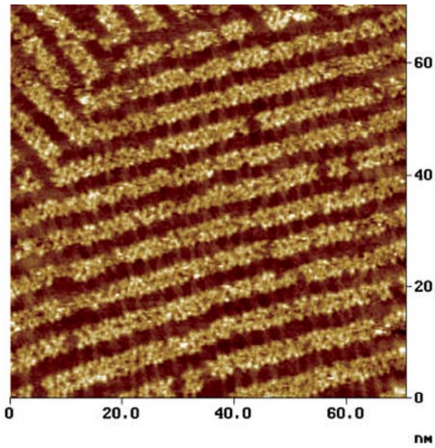

**Fig. 1** STM image of self-assembled monolayer of **4a** on a graphite surface. The scanning area is 70.7 × 70.7 nm. The STM imaging conditions are 600 pA, 700 mV.

regions of molecular arrays with domain sizes ranging from tens to hundreds of nanometres. Fig. 1 shows a large scale STM image of monolayer of TAM **4a** adsorbed on the HOPG surface. The two dimensional array of TAM **4a** molecules is clearly visible as a striped pattern. The angle between the stripes in adjacent domains is about 120°, which indicates that the arrangement of TAM **4a** molecules is commensurate with the graphite surface. Well ordered TAM **4a** molecules form stripe shaped lamellae with a bright band width of *ca.* 3.2 ± 0.3 nm. Although molecular defects were sometimes observed in the monolayer, the two dimensional arrays formed could be reproducibly obtained in large areas, which indicated a high stability of this self-assembled configuration.

The high-resolution image is shown in Fig. 2. It can be seen that the brighter parts can be attributed to the core groups containing conjugated π-electron systems and the darker moieties to the alkyl chains which are interdigitated over the nearly full length of the chains.[13] The length of the alkoxy chains is measured to be 2.30 ± 0.05 nm, which is close to the length obtained by simulation methods (HyperChem software).‡ The striking aspect of this image is that the unit cell of the pattern, as indicated in Fig. 2, contains two distinct fork-like molecules, with antiparallel alignment. The carbon chains of the molecule are divided into two orientation groups and the alkyl chains become parallel to each other, leading to the loss of the original molecular three fold symmetry. The angle of three rod-like azo sub-units should have been 120° with respect to each other in the typical free space configuration, while the measured angle is about 59 ± 2° and 121 ± 2° from the STM image. This antiparallel fork-like arrangement could be due to the requirements for minimization of the free surface area coverage per molecule and unit cell within the monolayer on the graphite surface, resulting in maximum stability. In addition, the nearly fully interdigitated alkyl parts indicate that the 2D crystallization of alkyl parts is important in determining the assembly structure.[14,15] The unit cell as marked in Fig. 2 contains two molecules. The unit cell parameters $a$, $b$ and $\alpha$, as indicated in Fig. 2, are 3.7 ± 0.3 nm, 6.2 ± 0.3 nm, and 75 ± 2°, respectively. On the basis of the observed monolayer structure, an illustrative molecular model (Fig. 3) for the molecular arrangement could be proposed. The proposed model matches well with the unit cell obtained from the STM image.

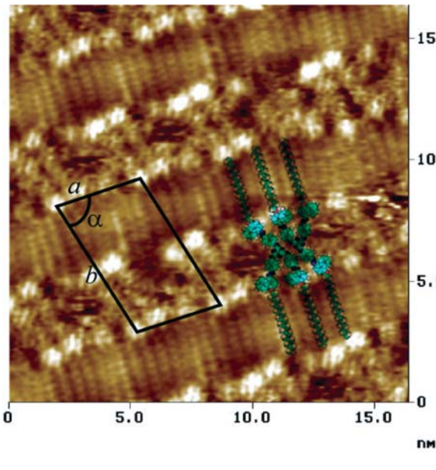

**Fig. 2** A higher resolution STM image of **4a** with superimposed unit cell. The scanning area is 16.4 × 16.4 nm. The imaging conditions are 550 pA, 800 mV.

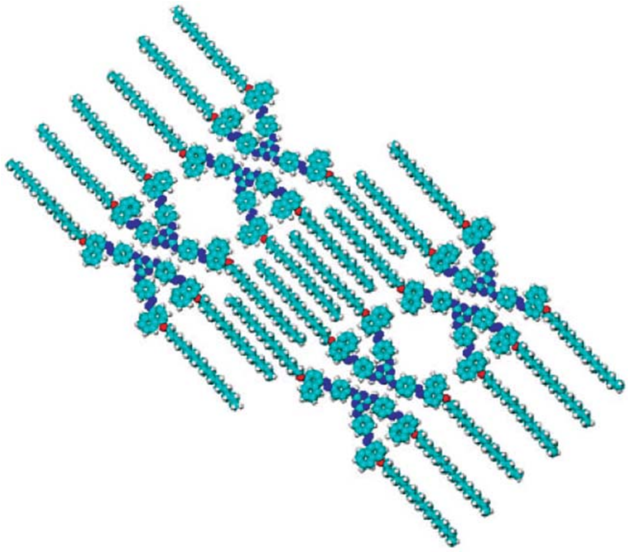

**Fig. 3** Molecular model of the self-assembled monolayer of **4a**.

In order to clarify the effect of the alkyl chain length on the assembling configuration, we also studied samples with decreasing methylene units of the alkyl chain. It is observed that the overall arrangement of the TAM **4b** molecules changes within the large scale. The molecular orientation within the molecular arrays becomes less uniform than that in TAM **4a**. Fig. 4 is the large scale image, with the high-resolution image shown in the insert. The previously observed antiparallel alignment of the molecular cores in the TAM **4a** system

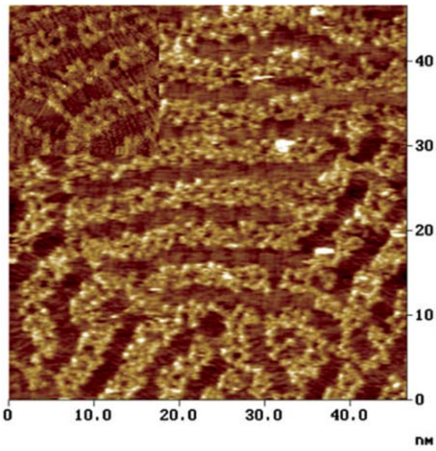

**Fig. 4** STM image of self-assembled monolayer of **4b** on graphite surface. The scanning area is 46.6 × 46.6 nm and the imaging conditions are 539 pA, −555 mV. The inset is a higher resolution STM image of **4b**. The scanning area is 17.6 × 17.6 nm and the imaging conditions are 560 pA, 451 mV.

changes distinctly, and the periodicity of the arrangement disappears along the lamellae. Moreover, it may be difficult to recognize precisely the alignment of the molecular cores in the disordered regions. However, the conformation of a single molecule identified from the STM image is still fork-like, even though part of the fork-like structure is distorted. The observations show that alkyl chain length could exert an appreciable effect on the 2D structure of self-assembled monolayers. This effect is partly attributed to the 2D crystallization energy brought from the regularly arranged alkyl chains and the adsorption potential of alkyl groups parallel to the *a* axis (or *b* axis) of graphite.[14,15] In the present system, the inherent steric hindrance of TAM makes the planar conformation of TAM not an optimal conformation. When TAM **4a** adsorbs on HOPG, the strain of the planar conformation of TAM **4a** is compensated by the relatively large crystallization energy and adsorption potential of the alkyl chains. Hence the whole SAM is uniform and regular. When the alkyl chain length decreases to 16 (TAM **4b**), the crystallization energy and adsorption potential is reduced and thus the planar conformation of the core part of TAM **4b** is less stabilized. The distorted fork-like structure of the core part is a compromise between the steric hindrance of the core part and the adsorption energy from the alkyl part. We would like to note here that the experiments were performed under the same preparation conditions. No apparent improvements were found for the assembly of TAM **4b** with different incubating temperature and concentrations.

When the length of the alkyl chain decreases by an additional two methylene units, the molecular arrangement of the TAM **4c** becomes almost disordered. Even if there are occasionally some regular parts, the features of the core part of molecule cannot be discerned at all. Similarly, we attribute the disordered SAM to the decreasing stability brought from the decreasing alkyl chain length.

In summary, we studied the arrangement of TAM with *n*-carbon side chains ($n = 14, 16, 18$) on the HOPG surface. The STM observations presented have clarified the geometrical configuration of self-assembled TAM molecules where the effect of 2D crystallization of the surrounding alkyl chains in the molecule plays an important role in the molecular alignment. The information on the self-assembling properties of materials obtained from STM investigations could be helpful in studying azo compounds.

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‡The preliminary simulations were performed using the HyperChem software package to model the structure of TAM **4a**.

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