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### COMMUNICATION

## Modulating the self-assembly of rigid "clicked" dendrimers at the solid–liquid interface by tuning non-covalent interactions between side groups<sup>†</sup>‡

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First generation poly(triazole-phenylene) dendrimers equipped with peripheral alkyl or carboxylic acid groups to engage in van der Waals and hydrogen-bonding interactions, respectively, assemble into distinct two-dimensional nano-structures at the solid–liquid interface as revealed by high resolution STM investigations.

The self-assembly of molecular components into larger supramolecular architectures is ubiquitous in nature and arguably constitutes the most powerful method to fabricate functional nanomaterials from the bottom up. In the confinement of a solid substrate surface this approach can be exploited to generate periodically ordered two-dimensional structures from suitably designed molecular building blocks.<sup>1</sup> Hence, self-assembly at the interface enables the defined positioning of functional entities with sub-nanometre precision over areas of microns and thereby allows for fine tuning of numerous properties of the resulting hybrid nanomaterials<sup>2</sup> for technological applications, in particular in electronics and optics.<sup>3</sup> To allow for structure formation under thermodynamic control, i.e. to warrant equilibration, the use of weak yet multiple non-covalent interactions has proven advantageous. In particular, the combination of van der Waals and hydrogen-bonding interactions constitutes a successful strategy to generate sophisticated two- and three-dimensional architectures as these interactions enable reversibility, directionality, specificity, and even cooperativity in the self-assembly process.<sup>4</sup> Both aliphatic residues as well as hydrogen-bonding sites can be attached to suitable molecular building scaffolds to provide either linear, cyclic or branched arrangements. The latter gives rise to dendritic architectures, which can be tailored to self-assemble into a variety of super-structures in solution and in the bulk.<sup>5</sup> However, due to their commonly rather flexible structure and their typically three-dimensional shape the self-assembly of

dendrimers on surfaces has less frequently been explored. In fact, hitherto dendrimers<sup>6</sup> have been visualized by Scanning Tunneling Microscopy (STM) only under ultrahigh vacuum,<sup>7</sup> in air forming disordered aggregates,<sup>8</sup> and at the solid–liquid interface as non-planar structures.<sup>9</sup>

Here, we report for the first time a sub-molecularly resolved STM study of the first generation of a novel type of dendrimer, physisorbed at the solid–liquid interface into highly ordered monolayers. We have focussed our attention on five derivatives of rigid and fully planar 1,3,5-tris(1-phenyl-1,2,3-triazol-4-yl)benzenes (TPTB, Fig. 1), which constitute the first generation in a series of new shape-persistent poly(triazole-phenylene) dendrimers.<sup>10</sup>

The linking triazole moieties are readily derived *via* Cu-catalyzed 1,3-cycloadditions, *i.e.* the so called "click" reaction.<sup>11</sup> The aim of this investigation was to explore the symmetry mismatch between the graphite substrate and the dendrimer scaffold, due to the presence of the five-membered triazole moieties,<sup>12</sup> in combination with different orientations of the self-recognition groups attached in the periphery of the TPTB. In particular, molecule **1**, equipped with six carboxylic acid moieties in the *meta*-positions of the peripheral phenyl rings, was designed to promote the formation of  $C_6$ -symmetric self-assembled structures linked *via* multiple H-bonds, *i.e.* six carboxylic acid dimers based on di-hapto O–H···O hydrogenbonding. To cast light on the role of such intermolecular



Fig. 1 Chemical formulae of the investigated TPTB derivatives.

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hydrogen-bonding pattern, our study was extended to derivative **2**, which exposes six *n*-hexadecylcarbonyloxy side chains in these *meta*-positions. To finally explore the influence of the orientation of the substituents on the peripheral phenyl rings, regioisomers **3–5**, bearing three *n*-octadecyloxy side chains in their *ortho-*, *meta-*, and *para*-positions of the peripheral phenyl moieties, respectively, were investigated. In the case of compounds **2–5**, the van der Waals interactions between the alkyl side-chains can be expected to play a key role in the self-assembly.

To allow for comparison, all experiments in this study were carried out by applying a drop of solutions of **1–5** in 1-phenyloctane (concentrations up to 2 mM) to the basal plane of freshly cleaved highly oriented pyrolytic graphite (HOPG) surfaces. Studies of TPTB-based systems using different solvents, 1,2,4-trichlorobenzene, tetradecane and 1-heptanoic acid, did not produce any ordered monolayers. The unit cell parameters of the various crystalline patterns were determined *via* peak detection in the Fast Fourier Transform (FFT) on STM images previously corrected for the thermal drift by using the underlying graphite lattice as reference (see ESI<sup>†</sup> for more details on the experimental procedures).

Hexa-acid 1 forms ordered physisorbed monolayers on HOPG. The respective STM current images (Fig. 2a and b) reveal a monocrystalline structure featuring a 2D porous honeycomb-like motif, which topologically coincides with a rhombitrihexagonal tiling. Each unit cell contains four molecules of 1, physisorbed flat on the surface. The hundreds of nm<sup>2</sup> large crystalline domains were found to be stable over tens of minutes. The supramolecular architecture is stabilized by strong (O–H···O) hydrogen-bonds (Fig. 2a and b and S3 in



**Fig. 2** STM images of **1** (a, b) and **2** (c, d) at the solid–liquid interface: (a) survey image, (b–d) small scale image. Images were recorded in (a, b, d) current mode and (c) height mode. Unit cell parameters: (a, b)  $a = (3.12 \pm 0.2)$  nm,  $b = (5.51 \pm 0.2)$  nm,  $\alpha = (87 \pm 2)^{\circ}$ ,  $A = (17.16 \pm 1.26)$  nm<sup>2</sup>,  $A_{mol} = (4.34 \pm 0.32)$  nm<sup>2</sup>, space group *p6nr*; (c, d)  $a = b = (4.15 \pm 0.2)$  nm,  $\alpha = (45 \pm 3)^{\circ}$ ,  $A = (12.17 \pm 0.72)$  nm<sup>2</sup>,  $A_{mol} = (6.09 \pm 0.31)$  nm<sup>2</sup>, space group *cm*; tunneling parameters (a, b): average tunneling current (*I*<sub>t</sub>) = 18 pA, tip bias voltage (*V*<sub>t</sub>) = 600 mV; (c, d): *I*<sub>t</sub> = 15 pA, *V*<sub>t</sub> = 300 mV.

ESI<sup>†</sup>) where each molecule of **1** forms six  $R_2^2(8)^{4c}$  homodimeric H-bonds, i.e. twelve strong O-H...O hydrogen-bonds with neighbouring molecules. Importantly, this 2D motif incorporates two pore types, *i.e.* A and B, with inner voids of 1.5 nm<sup>2</sup> and  $0.65 \text{ nm}^2$ , respectively. The formation of hexameric pores A is a direct consequence of the 120° angle between the two carboxylic functions. Due to the molecular geometry of 1 two of the remaining carboxylic moieties interact via hydrogenbonds with adjacent molecules, forming the second type of pores, i.e. dimeric pores B of smaller size (see ESI<sup>+</sup> for a more detailed explanation and model). From the data it appears that the formed hierarchical pore pattern is dictated by the formation of carboxylic acid dimers via self-complementary hydrogen-bonding interactions. The TPTB scaffold can adapt to the six-fold symmetry of the HOPG by rotating the triazole moieties in one direction only. The difference in contrast between the observed molecules is the result of the Moiré effect (see Fig. S4 in ESI<sup>+</sup>).

Exchanging the hydrogen-bonding interactions for weaker van der Waals interactions leads to formation of rather different self-assembled monolayers in the case of compound 2. The associated STM images (Fig. 2c and d) show a lamellar structure featuring a nanoscale phase segregation between the TPTB cores and the long alkyl side-chains. Within a lamella (marked with a white arrow in Fig. 2c) the cores are arranged in a "head-to-head" and "tail-to-tail" dimeric motif (Fig. 2d). The entire supramolecular architecture is stabilized by the interdigitation of alkyl side chains belonging to adjacent molecules, adsorbed along one of the Miller-Bravais symmetric axes of the underlying HOPG lattice (indicated in the inset of Fig. 2c). For each molecule only four out of six hexadecyl side chains have been detected in the STM image (Fig. 2d). The alkyl side chains belonging to molecules of adjacent lamellae are interdigitated, leading to an interlamellar distance of  $(3.09 \pm 0.22)$  nm. However taking the unit cell parameters and the size of the molecule as obtained by Molecular Mechanics simulations into account, it is more likely that the two remaining side chains are also physisorbed on the HOPG surface but are not imaged due to their high conformational dynamics on the time scale of the STM experiments. By comparing structure formation of 1 and 2, it seems that van der Waals interactions dominate the self-assembly of **2** and lead to a change from a  $C_6$ -symmetric rosette pattern to a linear lamellar structure.

To furthermore discern the effect of side-chain orientation on self-assembly, high resolution STM images of regioisomers 3-5 were obtained (Fig. 3). The monolayer of ortho-substituted compound 3 exhibits a crystalline structure with a motif similar to the rhombitrihexagonal tiling observed for 1, but incorporating only two molecules within the unit cell (Fig. 3b). It is most likely that the supramolecular architecture is stabilized by weak van der Waals interactions between adjacent molecules. The proposed molecular packing model as well as the unit cell parameters suggests that all n-octadecyloxy side chains of 3 are back-folded into the supernatant solution, which can be ascribed to insufficient van der Waals contacts between the alkoxy chains of adjacent molecules 3. The two domains observed in Fig. 3a exhibit the same packing motif, as proven by their identical cell parameters. Importantly, highly ordered self-assembled structures of 3 were observed only upon use of





**Fig. 3** STM current images of (a, b) **3**, (c) **4** and (d) **5** recorded at the solid–liquid interface. Unit cell parameters: (b)  $a = (3.68 \pm 0.2)$  nm,  $b = (3.70 \pm 0.2)$  nm,  $\alpha = (58 \pm 3)^\circ$ ,  $A = (11.58 \pm 0.67)$  nm<sup>2</sup>,  $A_{mol} = (5.76 \pm 0.33)$  nm<sup>2</sup>, space group *p6m*. Tunneling parameters (a, b):  $I_t = 15$  pA,  $V_t = 900$  mV; (c)  $I_t = 15$  pA,  $V_t = 860$  mV; (d)  $I_t = 15$  pA,  $V_t = 860$  mV.

highly concentrated solutions (c = 2 mM). In strong contrast to compound **3**, its *meta*- and *para*-regioisomers **4** and **5**, respectively, form only unstable and poorly ordered lamellar structures on HOPG, highlighting the high molecular mobility on a timescale faster than the tip scan, thereby hindering high resolution STM mapping. The interlamellar distances for the assembly of molecules **4** and **5** amount to  $(2.98 \pm 0.18)$  nm and  $(2.75 \pm 0.33)$  nm, respectively, providing evidence for a tight molecular packing probably caused by interdigitation of alkyl side chains belonging to molecules of adjacent lamellae.

In summary, we have performed a comparative STM study of the self-assembly of various derivatives of the first generation of new poly(triazole-phenylene) dendrimers at the HOPG-solution interface. All molecules were found to physisorb in a flat adsorption geometry on graphite forming 2D supramolecular structures. Different crystalline nanopatterns were observed, ranging from honevcomb-like networks for compounds 1 and 3 to various lamellar structures of different stability in the case of derivatives 2, 4, and 5. Our results provide unambiguous evidence that subtle modification in the substitution pattern of the TPTB scaffold leads to pronounced effects on its 2D self-assembly at the liquid-solid interface. Two factors seem to be responsible for the variation in the observed structures and their stability: (i) due to the presence of the triazole moieties, the TPTB core cannot completely match the six-fold symmetry of the HOPG substrate, *i.e.* both lattices are not commensurate, and thereby gives rise to an inherent flexibility and thermodynamic instability, and (ii) as a consequence the exact presentation of the alkyl side chains by the TPTB scaffold governs the overall structure formation in the selfassembly process. In general, the capacity of flat dendrimers to pack into highly ordered supramolecular structures at the solid-liquid interface described herein could lead to the design of more complex and multicomponent structures based on dendritic cores.5

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