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Self-assembled monolayers of clamped oligo(phenylene-ethynylenebutadiynylene)s[†][‡]

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Rigid rod oligo(phenylene-ethynylene-butadiynylene)s (oPEBs), "half-rings" of two rigid rods connected *via* a molecular clamp unit, and shape-persistent macrocycles (cyclic "half-ring dimers") are synthesized and their self-assembled monolayers (SAMs) are investigated by scanning tunneling microscopy (STM) at the interface of 1,2,4-trichlorobenzene (TCB)/highly oriented pyrolytic graphite (HOPG). The results are important for the design of molecular building blocks for two-dimensional nanoscale architectures on solid surfaces.

Shape-persistent molecules attract a high level of interest because of their unique structural, electrical, and optical properties, and as building blocks for functional nanostructures. The intramolecular connection of two rigid rods with one or two molecular clamp units leads to half-rings (that can be described as freely rotating chains)¹ or shape-persistent macrocycles, respectively,² that form SAMs on solid substrates.^{3,4} The rigid backbones allow the tailored design of the adsorbate structures, required to achieve predictable surface patterns. SAMs of shape-persistent macrocycles can be applied as templates for the epitaxial codeposition of admolecules, additional guests that otherwise do not adsorb onto solid surfaces.⁵

In a previous study, we have focused on cyclic and acyclic oligomers of shape-persistent rigid rods, connected *via* rotatable oligoarylene corner units.³ The alkoxy substituents define the distances of lamellarly aligned, self-assembled rigid rod units, and the quinquearylene clamps match the width predetermined by the rod–rod distances of hexyloxy substituted oPEB units. In the present work, we maintain the intra- and intermolecular rod–rod spacing and extend the length of the rigid rods systematically to yield structures with an end-to-end distance of up to 12.4 nm. A detailed

description of the synthesis and full characterization of all new compounds can be found in the SI. \ddagger

The rigid rods 1 and 2 are dimers and tetramers of pPE trimers that are connected by butadiynylene units (diacetylene units). Half-ring structures 3 and 4 can be viewed as pairs of rigid rods that are connected *via* a quinquearylene clamp. The ends of 1 and 2, and the rigid rods of 3 and 4 are terminated by acetylene functions. Macrocycles 5 and 6 can be viewed as cyclic dimers of two covalently connected half-rings 3 and 4, respectively (Fig. 1).

1 forms two-dimensional crystalline arrays. The rigid PEB backbones assemble into lamellar rows, so that the flexible alkoxy substituents are adsorbed on the substrate and interdigitate intermolecularly defining the rod-rod distances. From the high-resolution image shown in Fig. 2b, the unit cell (A) is determined to be $a = 4.5 \pm 0.2$ nm, $b = 1.4 \pm 0.1$ nm, and $\gamma(a,b) = 85 \pm 2^{\circ}$ (cf. molecular model in Fig. 2c). The backbones c are aligned along a. The alkoxy side chains are aligned along the HOPG main axis directions (denoted as d_1),⁶ and the backbone-side chain angle $\gamma(c,d_1)$ is 95 \pm 2°. The orientation of the backbones in A' (with the unit cell vectors a' and b'), the enantantiomers of A, is a result of identical direction of the alkoxy side chains along d_1 (as compared to A), and $\gamma(c', d_1) =$ $95 \pm 2^\circ$, explaining the domain angle of $\gamma(b,b') = 20 \pm 2^\circ$ and $\gamma(c,c') = 170 \pm 2^{\circ}$ (cf. Fig. 2c). Contrary, the domain angle $\gamma(b,b'') = 60^{\circ}$ is drawn back on rotation of the molecules (of A),



Fig. 1 Chemical structures of the linear rigid rods 1 and 2, the half-rings 3 and 4, and the macrocycle 5 and 6.

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Fig. 2 STM images, molecular and schematic models of SAMs of (a)–(c) **1**, and (d)–(f) **2** at the TCB/HOPG interface. (a) Large-area STM image of **1** ($V_{\rm S} = -1.0$ V, $I_{\rm t} = 80$ pA, 100 × 100 nm², $c = 10^{-5}$ M); (b) high-resolution image of **1** ($V_{\rm S} = -0.86$ V, $I_{\rm t} = 100$ pA, 24.5 × 24.5 nm², $c = 10^{-5}$ M); (c) molecular model of pattern A and A' of **1** as seen in (a) and (b). (d) Large-area STM image of **2** ($V_{\rm S} = -1.0$ V, $I_{\rm t} = 20$ pA, 86.6 × 86.6 nm², $c = 10^{-4}$ M, thermally annealed to 80 °C for 30 s); (e) high-resolution image of **2** ($V_{\rm S} = -1.0$ V, $I_{\rm t} = 20$ pA, 85.7 × 35.7 nm², $c = 10^{-4}$ M, thermally annealed to 80 °C for 30 s); (f) schematic (left) and molecular (right) model of the pattern observed in (e). The unit cells vectors, HOPG main axis directions, and backbone directions are given in red, white (black) and blue color, respectively.

so that the alkoxy side chains of A'' are oriented along d_2 (Fig. 2a). Conclusively, although the side chains cannot be submolecularly resolved by STM (at r.t.), the alkoxy chain directions and the alkoxy-backbone angles significantly determine the molecular alignment with respect to the HOPG crystallographic directions.⁶

Rigid rods 2 are also aligned in parallel to form quasi-lamellar assemblies (Fig. 2d). However, compared to 1, the lamellae of 2 do not form patterns with two-dimensional order, but appear to be grown into random directions (Fig. 2d). This is a result of the shift of the oligomers in direction of the lamella normal that appears of accidental order and magnitude. At higher resolution (Fig. 2e), a systematic stepping of the aforementioned parallel shift of the oligomers within a lamella is discernable, as schematically visualized in Fig. 2f. Each rod 2, consisting of four butadiynylene-bridged pPE trimers, is shifted in parallel to the rod direction so that the shift distances match multiples of the

intramolecular periodicity of the *p*PE trimer units, 2.3 nm. The shifts reflect the kinetically driven nature of the adsorption process for the longer rods **2** compared to the thermodynamically favored pairwise interaction of adjacent rods.⁷ Nevertheless, defined shift distances keep the energetically favorable alkoxy chain interdigitation degree high. The indexed unit cell, $a = 9.2 \pm 0.2$ nm, $b = 1.4 \pm 0.1$ nm, $\gamma(a,b) = 87 \pm 2^{\circ}$ is consistent with the molecular model proposed in Fig. 2f (right side), and the alkoxy-backbone angles are—similar as observed for $1-\gamma(c,d) = 95 \pm 2^{\circ}$.

STM images of the half-ring structures 3 and 4 at the TCB/HOPG interface are shown in Fig. 3. Two polymorphs are observed for 3 (Fig. 3a-d). In both cases, lamellar patterns are observed where the molecular length axes are tilted with respect to the lamellar normal. The corner unit of each half-ring intercalates asymmetrically into the gaps provided by two half-rings of the neighboring lamella, leading to gaps ("U-gaps", Fig. 3c and d) between the corner units. In polymorph A, both acetylene-terminated ends of the half-rings point toward each other to form O-shaped quasi-dimers. A unit cell of $a_A = 6.0 \pm 0.1$ nm, $b_A = 3.1 \pm 0.1$ nm, $\gamma(a_A, b_A) =$ $101 \pm 2^{\circ}$ is indexed, and the rigid rod parts of the half-rings (pointing in direction c_A) are aligned with $\gamma(b_A, c_A) = 114 \pm 2^\circ$. The alkoxy-backbone angle of **3** is $\gamma(c_A,d) = 103 \pm 3^{\circ}$ (assuming commensurable adsorption of the side chains along the substrate main axis), significantly larger than for 1 and 2 (where alkoxy-backbone angles of $95 \pm 2^{\circ}$ were observed). In polymorph B. the half-rings assemble toward broken sinuous lines, so that the acetylene-termini of each U-shaped molecule point toward the ends of two (different) adjacent molecules. Two of these ends are in contact with each other and determine the packing distance along direction $c_{\rm B}$, while between the two other ends the "I-gap" (Fig. 3d) is formed with $d_{\text{H-H}} = 1.2 \text{ nm}$. A unit cell of $a_{\rm B} = 6.4 \pm 0.1$ nm, $b_{\rm B} = 3.1 \pm 0.1$ nm, and $\gamma(a_{\rm B}, b_{\rm B}) = 90 \pm 2^{\circ}$ is indexed. The alkoxy-backbone angle $\gamma(c_{\rm B},d)$ and the orientation of the rigid rod parts, $\gamma(b_{\rm B},c_{\rm B})$, are the same as determined for polymorph A.

4 adsorbs—similarly to **3**—into tilted lamellar patterns. The ends of the rigid rods are aligned along a continuous line. A unit cell of $a = 11.9 \pm 0.3$ nm, $b = 2.8 \pm 0.1$ nm and $\gamma(a,b) = 83^{\circ}$ is indexed, and the rigid rod parts are aligned along *c* with $\gamma(b,c) = 93 \pm 2^{\circ}$. Assuming commensurate adsorption of the alkoxy substituents along the HOPG main axis *d*, the backbone-alkoxy-angle $\gamma(c,d)$ is $84 \pm 2^{\circ}$. No other polymorph is observed.

Macrocycles 5 assemble in tilted patterns (Fig. 4a). A unit cell of $a = 6.3 \pm 0.2$ nm, $b = 3.0 \pm 0.2$ nm and $\gamma(a,b) = 79 \pm 2^{\circ}$ is indexed, and the rigid rod parts are (on average) aligned along *c* with $\gamma(c,b) = \gamma(c,d) = 90 \pm 2^{\circ}$. The molecular model shown in Fig. 4b is based on an idealized structure of the monomers with rigid rod units aligned in parallel and an alkoxy-backbone-angle of 90°. However, the molecular backbones appear to be significantly deformed, as compared with the half-rings of similar rod length, **4** (Fig. 3a and b), originating from higher sterical demand of the alkoxy chains (see molecular model in Fig. 4c).

Macrocycles 6 assemble—similarly to 5—in tilted patterns of lamellarly aligned backbones (Fig. 4d). A unit cell of $a = 10.9 \pm 0.4$ nm, $b = 2.9 \pm 0.2$ nm and $\gamma(a,b) = 83 \pm 2^{\circ}$



Fig. 3 (a), (b) STM images and (c), (d): Molecular models of a SAM of **3** at the TCB/HOPG interface; (e), (f): STM image and molecular model of a SAM of **4** at the TCB/HOPG interface. (a) Large-area scan ($V_{\rm S} = -1.0$ V, $I_{\rm t} = 5$ pA, 100 × 100 nm², $c = 10^{-5}$ M); (b) high-resolution image ($V_{\rm S} = -0.95$ V, $I_{\rm t} = 10$ pA, 27.6 × 27.6 nm², $c = 10^{-5}$ M); (c) model of polymorph A of **3**, (d) model of polymorph B of **3**. (e) Large-area scan ($V_{\rm S} = -1.0$ V, $I_{\rm t} = 20$ pA, 36.6 × 36.6 nm², $c = 5 \times 10^{-5}$ M, thermally annealed at 60 °C for 30 s). The unit cells vectors, HOPG main axis directions, and backbone directions are given in red, white (black) and blue color, respectively.

is indexed, and the rigid rods are (on average) aligned along c with $\gamma(c,b) = 90 \pm 2^{\circ}$ and $\gamma(c,d) = 84 \pm 2^{\circ}$. The molecular model shown in Fig. 4e is again based on an idealistic alignment of the alkoxy substituents—as compared to the force field geometry-optimized molecular model shown in Fig. 4f. Again sterical requirements of the constrained alkoxy substituents induce deformation of the molecular backbones (Fig. 4f), leading to misalignment of the macrocycles in the monolayer patterns. Most notably, the patterns shown in Fig. 4a and d include backbones (indicated with white arrows) that exhibit 60° bendings from the linear shape, an observation that was not expected for a clamped rod system.⁸

The results prove that the investigated systems behave as rigid rods of defined length—however with unexpected systematic shifts in the lamellar packing of the longer rigid rods. A connection of two rods *via* one or two oligoarylene clamp units has yielded half-rings as well as macrocyclic ring structures, respectively, that form also nanoscale patterns on HOPG.



Fig. 4 (a) STM image of a SAM of **5** at the TCB/HOPG interface. $(V_{\rm S} = -1.0 \text{ V}, I_{\rm t} = 11 \text{ pA}, 41.2 \times 41.2 \text{ nm}^2, c = 10^{-5} \text{ M}$, thermally annealed at 60 °C for 1 min). (b) Idealized molecular packing model. (c) Molecular model of **5** after force field geometry optimization (starting conformation as shown in (b)). (d) STM image of a SAM of **6** at the TCB/HOPG interface ($V_{\rm S} = -1.4 \text{ V}, I_{\rm t} = 10 \text{ pA},$ $65.2 \times 65.2 \text{ nm}^2, c = 10^{-5} \text{ M}$, thermally annealed at 80 °C for 30 s). (e) Idealized molecular packing model. (f) Molecular model of **6** (obtained analogously to (c)). The unit cells vectors, HOPG main axis directions, and backbone directions are given in red, white (black) and blue color, respectively.

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