

# Trimodular Engineering of Linear Supramolecular Miniatures on Ag(111) Surfaces Controlled by Complementary Triple Hydrogen Bonds\*\*

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The basic concept of supramolecular chemistry is rooted in the exploitation of molecular recognition events that take advantage of spontaneous and reversible noncovalent interactions for the assembly of two or more molecules into organized architectures.<sup>[1]</sup> Selective noncovalent interactions have been widely exploited both in solution and in the solid state to prepare extended one- (1D), two- (2D), and three-dimensional (3D) assemblies.<sup>[2]</sup> In this context, linear ordered assemblies, such as supramolecular polymer-like wires,<sup>[3]</sup> are appealing nanostructured systems because of their potential applications as 1D electron-transfer mediators in futuristic molecular-based devices.<sup>[4]</sup> To probe the local properties and functions of the supramolecular assemblies, immobilization on surfaces is a promising approach, as a direct insight into the self-assembly mechanism, the ordering, and the functional properties at the molecular level<sup>[5]</sup> can be obtained by

scanning probe microscopy (SPM) techniques (for example, scanning tunneling microscopy (STM)).<sup>[6]</sup>

A classical approach towards the formation of supramolecular species by the spontaneous self-assembly of precursor building blocks is the use of H bonds.<sup>[7]</sup> The specificity, directionality, dynamics, and complementarity of such interactions can allow for the design of a large library of organic modules bearing H-bond donor (D) and/or acceptor (A) moieties with specific programmed functions and structures that could ultimately lead to the construction of many desired functional assemblies. So far, this method has been successfully employed on solid surfaces for the preparation of extended one-<sup>[8]</sup> and two-component<sup>[9]</sup> assemblies. To the best of our knowledge, no examples of three-component miniaturized H-bonded architectures have yet been described.

Herein we report on the supramolecular engineering of miniaturized assemblies in which three conjugated molecular modules, **1–3** (Figure 1), are linearly assembled through complementary triple H bonds. Specifically, by using low-temperature (LT) STM under ultrahigh vacuum (UHV) conditions we show that modules **1** and **2** form periodic wire-like assemblies [(**1·2**)<sub>n</sub>] on Ag(111) surfaces. The structure and the length of the assembly can be changed by the co-deposition of a molecular stopper (**3**), which terminates the wires governing the formation of linear oligomeric miniatures.

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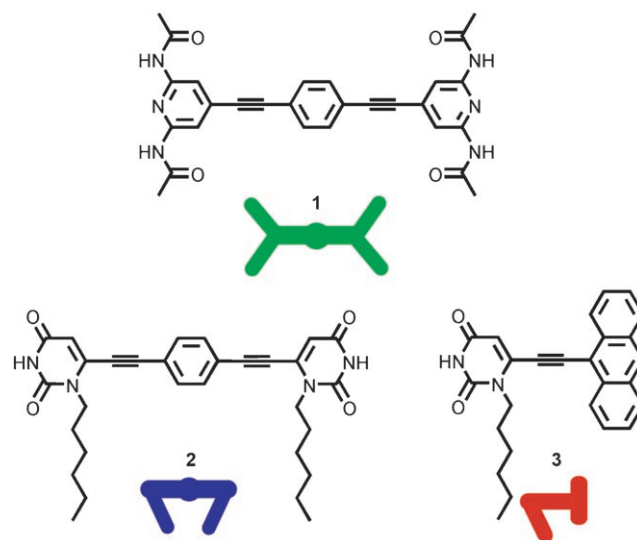
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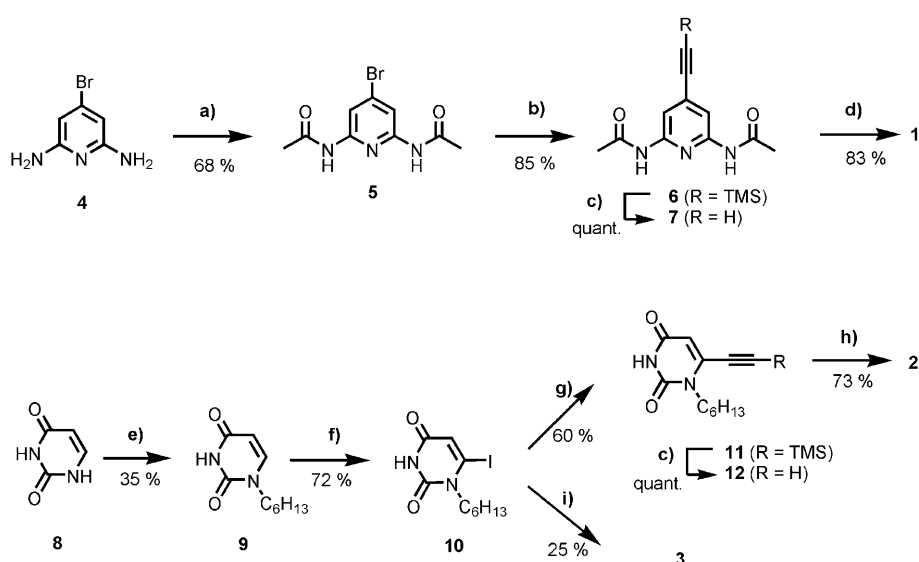


**Figure 1.** Chemical structures of the molecular modules bearing complementary H-bonding recognition sites.

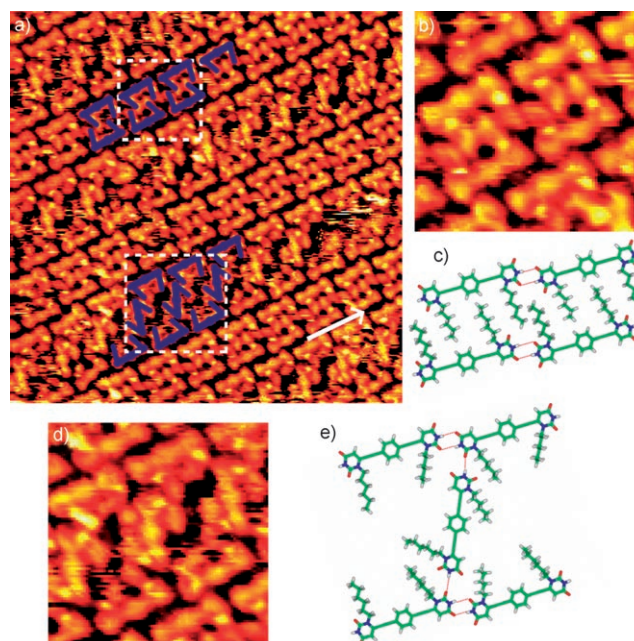
The concept of obtaining linear assemblies by association of monomeric units through noncovalent interactions was first reported by Lehn and co-workers, who prepared helical H-bonded polymers with liquid-crystalline properties.<sup>[10]</sup> Inspired by the wealth of this approach, we prepared modules **1–3**. Molecules **1** and **2** feature two complementary terminal H-bonding sites, namely the 2,6-di(acylamino)pyridyl (DAD, in **1**) and uracil (ADA, in **2**) moieties, which, in both cases, are connected to a central phenyl ring through an ethynyl spacer. Molecule **3**, which is terminated with an anthracyl unit, bears only one uracil moiety and thus can act as a molecular stopper. Linear modules **1** and **2** (also called bis-(DAD) and bis-(ADA) units, respectively) were synthesized by a Sonogashira-type cross-coupling reaction of 1,4-diiodobenzene with the respective ethynyl derivatives **7** and **12**, which bear the H-bonding sites (Scheme 1).

4-Ethynyl-2,6-diaminopyridine **7** was obtained from 4-bromo-2,6-diaminopyridine.<sup>[11]</sup> Acetylation of **4**, followed by palladium-catalyzed C–C coupling with trimethylsilylacetylene and subsequent cleavage of the trimethylsilyl protecting group with a solution of KOH in MeOH afforded bis-(DAD) unit **7**. Compounds **2** and **3**, which bear the uracil moieties, were prepared in the following way (Scheme 1). Alkylation of **8** with 1-bromohexane afforded **9**, which was then regioselectively iodinated, affording 1-hexyl-6-iodouracil **10**. Sonogashira-type coupling of iododerivative **10** with TMSA, followed by deprotection of the ethynyl moiety with a MeOH/KOH mixture gave the uracil–acetylene conjugate **12**. A second Sonogashira coupling of the product **12** with 1,4-diiodobenzene afforded the bis-ADA unit **2**. Stopper **3** was synthesized by direct Sonogashira-type coupling of **10** with 9-ethynylantracene (synthesized by using a slightly modified procedure than that reported by Dang and Garcia-Garibay<sup>[12]</sup>).

The homomolecular organization of molecule **2** on Ag-(111) surfaces was investigated under UHV conditions at 77 K.<sup>[13]</sup> At submonolayer coverages, di-uracil **2** was found to assemble in well-ordered patterns as depicted in Figure 2. In high-resolution STM images, individual molecules within the ordered pattern can be identified by their characteristic linear shape, defined by three aligned lobes and two bright protrusions at each end of **2**. Each lobe can be attributed to an aromatic core: the central lobe corresponds to the 1,4-disubstituted phenyl moiety, whereas the peripheral lobes correspond to the uracil groups. The two lateral protrusions correspond to the hexyl chains attached to the uracil moieties. Depending on the relative spatial disposition of the hexyl chains, molecule **2** can display two configurations: *cis-2* or



**Scheme 1.** a)  $\text{Ac}_2\text{O}$ , pyridine, RT, 10 h; b)  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $\text{CuI}$ , TMSA,  $\text{NEt}_3$ , THF, reflux, 12 h; c)  $\text{KOH}$ ,  $\text{MeOH}$ , RT, 40 min; d) 1,4-diiodobenzene,  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $\text{CuI}$ ,  $\text{NEt}_3$ , THF, reflux, 12 h; e) 1-bromohexane,  $\text{K}_2\text{CO}_3$ ,  $\text{DMSO}$ ,  $40^\circ\text{C}$ , 20 h; f)  $\text{LDA}$ , THF,  $-78^\circ\text{C}$ , 1.5 h, then  $\text{I}_2$ , 2 h, then  $\text{AcOH}$ , RT, 10 h; g)  $[\text{PdCl}_2(\text{PPh}_3)_2]$ ,  $\text{CuI}$ , TMSA,  $\text{NEt}_3$ , toluene, RT, 12 h; h) 1,4-diiodobenzene,  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $\text{CuI}$ ,  $\text{NEt}_3$ , THF, RT, 12 h; i) 9-ethynylantracene,  $[\text{Pd}(\text{OAc})_2]$ ,  $\text{CuI}$ ,  $\text{PPh}_3$ ,  $i\text{Pr}_2\text{NH}$ , THF, reflux, 12 h. TMSA = trimethylsilylacetylene;  $\text{LDA}$  = lithium diisopropylamide.



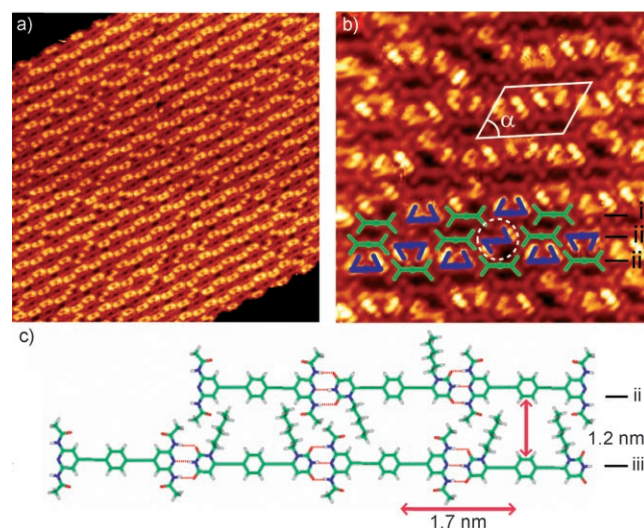
**Figure 2.** a) STM image of **2** on  $\text{Ag}(111)$ . Scan range:  $16 \times 16 \text{ nm}^2$ ,  $V_{\text{bias}} = -0.8 \text{ V}$ ,  $I_t = 20 \text{ pA}$ . b), d) STM images of the two zoomed regions indicated in a). b) scan range:  $4 \times 4 \text{ nm}^2$ ,  $V_{\text{bias}} = -0.8 \text{ V}$ ,  $I_t = 20 \text{ pA}$ , and d) scan range:  $4.5 \times 4.5 \text{ nm}^2$ ,  $V_{\text{bias}} = -0.8 \text{ V}$ ,  $I_t = 20 \text{ pA}$ . c), e) proposed corresponding H-bonding patterns.

*trans-2*, in which the alkyl chains lie on the same or on opposite sides of the molecular backbone, respectively.

Along the high-symmetry direction (see white arrow in Figure 2a), the molecules interact with each other through double H bonds, forming linear assemblies which additionally

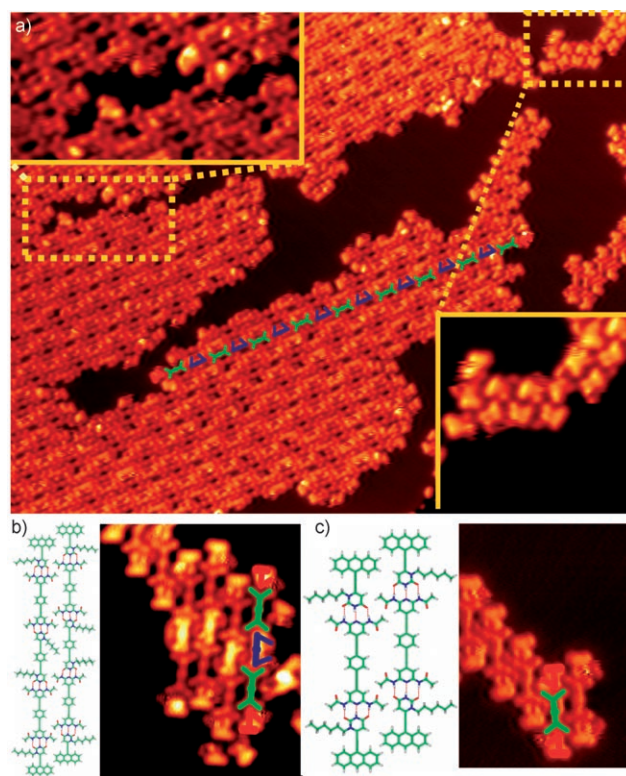
interact between themselves by van der Waals forces. Two different organizational motifs (Figure 2b and d) could be identified within the self-assembled network of **2**. In the first motif (Figure 2b and c), two adjacent rows composed of molecules *cis*-**2** are laterally interacting by van der Waals forces through directional interdigitation of the hexyl chains,<sup>[14]</sup> resulting in double-row wires. In the second one (Figure 2d and e), two lateral rows are linked through sandwiched modules of *trans*-**2**, which are noncovalently interacting through the N–H groups with the free carbonyl groups of *cis*-**2** molecules within the rows.

To probe the recognition properties between the different molecular modules, we have studied the hybrid assemblies resulting from the co-deposition of **2** and **3**, **1** and **2**, and **1**–**3**, respectively. As expected, the uracil-bearing molecules **2** and **3** do not assemble in an ordered layer, but instead form disordered phases consisting of only **3** as well as mixed but disordered assemblies of **2** and **3**.<sup>[13]</sup> In contrast, the subsequent deposition of linear modules **1** and **2** resulted in the formation of extended linear bimolecular wires, [(**1**·**2**)<sub>n</sub>], where the two modules alternate within the linear assembly (Figure 3). As both modules are geometrically symmetric and bear complementary recognition groups (DAD and ADA for **1** and **2**, respectively), the development of the wires unambiguously confirms the formation of the expected intermolecular triple H bonds. The two different molecules can be easily distinguished within the wires as bis-(DAD) **1** is visualized as three aligned lobes and four lateral spokes, the latter corresponding to the acetyl residues, whereas bis-ADA **2** features two lateral protrusions in a *cis* or a *trans*



**Figure 3.** STM images for a mixture of molecules **1** and **2** on Ag(111) after annealing at 383 K: a) scan range: 41.5 × 41.5 nm<sup>2</sup>,  $V_{\text{bias}} = -1.3$  V,  $I_t = 12$  pA; b) scan range: 12 × 12 nm<sup>2</sup>,  $V_{\text{bias}} = -1.3$  V,  $I_t = 12$  pA. The unit cell, which contains four molecules, together with some molecules has been drawn in the STM image. c) Proposed model for the observed [(**1**·**2**)<sub>n</sub>] assembly, in which molecules **1** and **2** are alternately arranged in a linear fashion through triple H bonds. The intra- and inter-row distances between two neighboring central 1,4-disubstituted phenyl rings are (1.7 ± 0.2) nm and (1.2 ± 0.1) nm, respectively. The numbered lines (i–iii) show the different periodic distances between neighboring rows (see text).

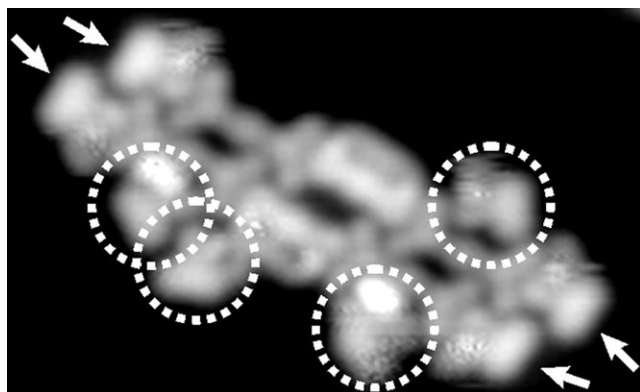
configuration corresponding to the hexyl chains. The large unit cells (3.7 ± 0.4 nm × 2.4 ± 0.2 nm,  $\alpha \approx 58 \pm 4^\circ$ , see also Supporting Information) measured for this arrangement derive from the fact that the distance between the bimolecular wires is alternating (denoted as i, ii, and iii in Figure 3b). In general, molecules adsorbed on surfaces tend to pack as densely as possible, to minimize the occupied area, and thus, to reduce the free surface energy. As a consequence, shorter interwire distances should be preferred. However, as molecule **2** is functionalized with two lateral hexyl chains, densely packed arrangements are limited by the space requirements of such aliphatic chains. Therefore, the observed pattern is a compromise between both requirements. In most cases, the linear module **2** adopts a *cis*-**2** configuration (for example, the hexyl chains of row iii point towards ii), whereas the *trans* configuration, *trans*-**2** (white dotted circle, Figure 3b), is rarely found. Sequential sublimation of molecules **1**, **2**, and **3** on Ag(111) yielded the linear assemblies shown in the STM images of Figure 4. In contrast to the seemingly endless wire-like assemblies [(**1**·**2**)<sub>n</sub>] the length of which is mainly determined by the size of the terraces of the silver substrate



**Figure 4.** STM images of multicomponent submonolayers constructed by a sequential sublimation of molecules **1**, **2**, and **3** on Ag(111) surfaces. a) STM image (scan range: 50 × 40 nm<sup>2</sup>,  $V_{\text{bias}} = -1.7$  V,  $I_t = 20$  pA) of the anthracene-terminated supramolecular wires. The inset in the upper left (13 × 6.5 nm<sup>2</sup>) highlights how molecule **3** interrupts the self-assembly of **1** and **2** while the surroundings still show the closed-packed [(**1**·**2**)<sub>n</sub>] assemblies, thus creating energetically disfavored voids (see text). Inset in the upper right (7.7 × 7.7 nm<sup>2</sup>): aggregate of **3**. b) Left: proposed model for the assembly of pentameric [**3**·**1**·**2**·**1**·**3**] miniatures; Right: zoomed STM image of the assembly. c) Left: proposed model for the assembly of some trimeric [**3**·**1**·**3**] miniatures. Right: zoomed STM image of some trimeric [**3**·**1**·**3**] miniatures.



(as observed for the mixture of **1** and **2**), in this case the supramolecular structures are terminated with the monouracil conjugate **3**, exposing the anthracenyl moiety as the end point of the assembly  $[3 \cdot 1 \cdot (2 \cdot 1)_m \cdot 3]$ . The structural fingerprints of molecule **3** can be easily distinguished in the STM images of Figure 4a. Each molecule **3** exhibits a characteristic mushroom-like shape with the anthracenyl group as cap and the hexyl chain as lateral protrusion. Conjugate **3** terminates the supramolecular linear assembly  $[(1 \cdot 2)_n]$  by complementary interactions with a **1**-derived free DAD site, ultimately acting as a molecular stopper. Apart from the long oligomers, short linear trimeric and pentameric miniatures have also been observed by STM as displayed in Figure 4b–c. Whereas in the trimeric structure,  $[3 \cdot 1 \cdot 3]$  (Figure 4c), two molecular stoppers are H-bonded to one central bis-(DAD) unit **1**, in the pentameric architecture,  $[3 \cdot 1 \cdot 2 \cdot 1 \cdot 3]$  (Figure 4b and Figure 5), one central bis-(ADA) module **2** axially interacts with two units of **1** through one of their two DAD sites and the other DAD recognition site is H-bonded to molecular stopper **3**.



**Figure 5.** STM image (scan range:  $44 \times 29 \text{ nm}^2$ ,  $V_{\text{bias}} = -1.7 \text{ V}$ ,  $I_t = 20 \text{ pA}$ ) of two pentameric miniatures in which four molecules **3** (dotted circles) have pre-recognized the complementary DAD unit.

Assemblies between **1** and **2** rely on the same H-bonding motif as those between **1** and **3**. Consequently, molecules **2** and **3** are expected to compete equally for binding to the 2,6-di(acylamino)pyridyl sites of molecule **1**. However, long oligomeric  $[3 \cdot 1 \cdot (2 \cdot 1)_m \cdot 3]$  assemblies clearly dominate over the shorter linear miniatures, owing to their tendency to fill empty spaces, minimizing the free surface energy.<sup>[15]</sup> Molecular stopper **3** does not allow such minimization in the occupied area per assembly as effectively as molecule **2**. The reason is that it bears only one uracil unit capable of establishing energetically favored H-bonding contacts. The anthracenyl unit can only originate van der Waals interactions that lead to energetically less-favored assemblies. This assumption is supported by the existence of voids within the intermixed regions (Figure 4a, left dotted rectangle) and the aggregation of molecular stopper **3** in small disordered islands (Figure 4a, right dotted rectangle).

Notably, for the three-component phase, molecular stopper **3** is also often found at junctions of **1** and **2** (Figure 5, dotted circles), most probably interacting through single

H bonds with the carbonyl group of the acetyl residues. This observation could account for a pre-recognition event that organizes the anthracene derivatives at the triply H-bonded **1**–**2** junctions. Consequently, if the molecules obtain enough energy (by thermal annealing, for example) molecule **3** will compete equally with **2** to form a triple H bond with molecule **1**, terminating the long linear assembly.

In summary, the first example of a simultaneous three-component assembly on surfaces mediated by triple H-bonding interactions, which yields the formation of linear supramolecular miniatures, has been studied on Ag(111) surfaces by STM. Two linear modules, **1** and **2**, and an anthracenyl-capped unit **3** (which can act as a molecular stopper) were assembled complementarily, to form discrete linear oligomeric assemblies. Although strict control of the length of the linear assemblies has not yet been achieved, our findings suggest that by controlling the ratio of the molecular modules, as well as the post-annealing treatment of the sample, the preparation of monodisperse auto-assembling architectures on surfaces could be achieved. Additionally, further control over the resulting H-bonded structures could be gained with a slight modification of the molecular building blocks by, for example, varying the length or the chemical nature of the alkyl moieties for **2** and/or **3** or by attaching other functional groups to **1**. This approach would lead to a large library of versatile molecular modules that could be ultimately used as single-molecule devices.

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