Self-Assembly of Rodlike Hydrogen-Bonded Nanostructures

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The self-assembly of low-molecular-weight building blocks into *noncovalent* polymeric nanostructures has recently attracted considerable interest for applications in nanotechnology as a *bottom-up* approach for the construction of molecular-scale devices.[1] In this paper we describe the preparation of a new class of hydrogen-bonded rodlike polymeric nanostructures $[\mathbf{1}_3 \bullet \mathbf{2}_3]_n$ and their characterization by tapping-mode scanning force microscopy (TM-SFM)[2] and ^{1}H NMR spectroscopy.

Previously, we reported the self-assembly of calix[4]arenes **1** and 5,5-diethylbarbituric acid (DEB) in disklike nanostructures $\mathbf{1}_3 \bullet (\text{DEB})_6$,[3] using the rosette motif developed by Whitesides and co-workers (Figure 1).[4] We anticipated the formation of infinite rodlike stacks by assembling "nonmatching" calix[4]arene dimelamine **1** with calix[4]arene dicyanurate **2**.[5] In this way the "closed" disklike assembly $\mathbf{1}_3 \bullet \mathbf{2}_3$ is prevented, and only the isomeric "open" form, with the top complementary to the bottom, is possible. Noncovalent polymerization of this aggregate will result in linear rodlike nanostructures $[\mathbf{1}_3 \bullet \mathbf{2}_3]_n$.

Dicyanurates **2a** and **2b** were synthesized in 53 and 23% yield, respectively, starting from the corresponding 1,3-dicyanocalix-[4]arenes (for details see Supporting Information). The preparation of dimelamines **1** was described previously.[3b]

Rodlike polymeric nanostructures $[\mathbf{1}_3 \bullet \mathbf{2}_3]_n$ spontaneously form as a result of multiple hydrogen bonding between the monomeric units **1** and **2**. Mixing equimolar solutions of **1a** and **2a** in THF
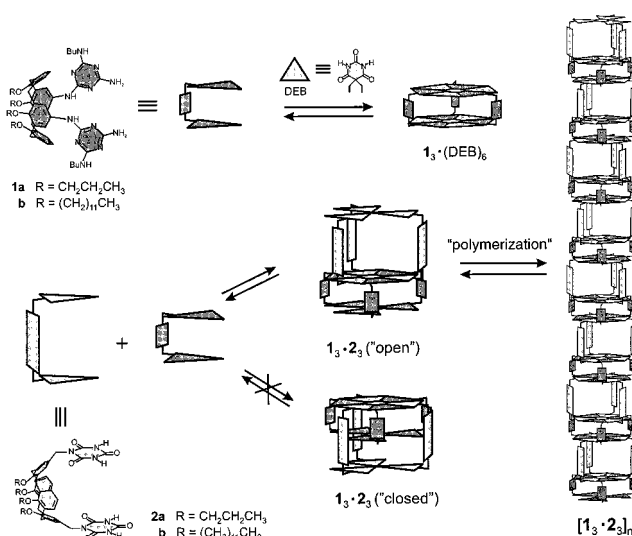

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(2) Zhong, Q.; Inniss, D, Elings, V. B. *Surf. Sci.* **1993**, *290*, L688−L692. (b) Spatz, J. P.; Sheiko, S.; Möller, M.; Winkler, R. G.; Reineker, P.; Marti, O. *Nanotechnology* **1995**, *6*, 40−44. (c) Spatz, J. P.; Sheiko, S.; Winkler, R. G.; Reineker, P.; Marti, O.; Möller, M. *Langmuir* **1997**, *13*, 4699−4703. (d) Winkler, R. G.; Spatz, J. P.; Sheiko, S.; Möller, M.; Reineker, P.; Marti, O. *Phys. Rev. B* **1996**, *54*, 8908−8912.

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(4) For a general overview of this work, see: Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37−44 and references therein.

(5) After submission of this paper, a very similar paper from the Whitesides group was published: Choi, I. S.; Li, X.; Simanek, E. E.; Akaba, R.; Whitesides, G. M. *Chem. Mater.* **1999**, *11*, 684.

Figure 1. Schematic representation of molecular components **1** and **2** and the hydrogen-bond directed "polymerization" to rodlike nanostructures $[\mathbf{1}_3 \bullet \mathbf{2}_3]_n$.

instantaneously leads to the precipitation of a white solid that is insoluble in any solvent other than DMSO. Although the ^{1}H NMR spectrum in DMSO-d_6 clearly reveals the exact 1:1 stoichiometry of the assembly, only signals for the separate components **1a** and **2a** are observed in this hydrogen-bond breaking solvent. The insolubility of this assembly in CHCl₃ contrasts with the very high solubility of $\mathbf{1}_3 \bullet (\text{DEB})_6$ (>100 mM) or of the many other rosette assemblies that we have obtained and fully characterized.[3] This virtually excludes the formation of "closed" assembly $\mathbf{1}_3 \bullet \mathbf{2}_3$.

The more hydrophobic nanostructure $[\mathbf{1b}_3 \bullet \mathbf{2b}_3]_n$ has sufficient solubility in apolar solvents to be characterized by ^{1}H NMR spectroscopy.[6] The spectrum shows all of the signals characteristic for a rosette-type assembly, i.e., two imide proton resonances at 14.8 and 14.4 ppm and two amine resonances at 9.2 ppm (ArNH) and 8.2 ppm (BuNH).[7] Especially the single set of imide proton signals provides strong evidence for the presence of only one type of hydrogen-bonded assembly. Variable temperature ^{1}H NMR experiments in CDCl₃ and C₂D₂Cl₄ show that the assembly $[\mathbf{1b}_3 \bullet \mathbf{2b}_3]_n$ is stable from −60 up to 140 °C. The signals in the ^{1}H NMR spectrum have the characteristic shape for polymeric structures, i.e., sharp at the top and broad at the bottom.[8]

Characterization of nanostructures $[\mathbf{1}_3 \bullet \mathbf{2}_3]_n$ by TM-SFM was performed by applying a droplet of a dilute equimolar solution of **1** and **2** on a graphite substrate (solvents and concentrations are listed in Table 1). After evaporation of the solvent, perfectly aligned linear strands were observed that form regular patterns across the surface (Figure 2A−C). Formation of these structures was not observed in control experiments with separate solutions of the individual components. Moreover, the formation of these rodlike nanostructures was also not observed on mica substrates. Apparently, the polar, ionic nature of this substrate is not compatible with the hydrogen-bonding interactions and prevents the noncovalent "polymerization" of **1** and **2**. For comparison, we also studied the deposition of assemblies $\mathbf{1a}_3 \bullet (\text{DEB})_6$ and $\mathbf{1b}_3 \bullet (\text{DEB})_6$ (0.01 mg/mL solution in chloroform) on a graphite surface by TM-SFM. Here also the formation of linear rodlike structures

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(6) $[\mathbf{1b}_3 \bullet \mathbf{2b}_3]_n$ was obtained by mixing calix[4]arenes **1b** and **2b** in a 1:1 molar ratio in THF followed by evaporation of the solvent and dissolution in chloroform.

(7) Mathias, J. P.; Simanek, E. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4326−4340.

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Table 1. TM-SFM Data for the Hydrogen-Bonded Rodlike Nanostructures $[1_3 \cdot 2_3]_n$ and $[1_3 \cdot (DEB)_6]_n$

assembly	solvent	conc. (mg/mL)	L^a [nm]	d (calcd)^b [nm]	h (exptl)^c [nm]	n (exptl)^d [nm]
$[1a_3 \cdot 2a_3]_n$	DMSO	0.01	2.9 ± 0.1	3.4 ± 0.1	4.9 ± 0.2	1.5 ± 0.2
$[1b_3 \cdot 2a_3]_n$	THF	0.005	4.8 ± 0.1	5.5 ± 0.1	5.0 ± 0.2	$\sim 0 \, (-0.5)$
$[1b_3 \cdot 2b_3]_n$	CHCl$_3$	0.01	4.8 ± 0.1	5.5 ± 0.1	4.6 ± 0.2	$\sim 0 \, (-0.9)$
$[1a_3 \cdot (DEB)_6]_n$	CHCl$_3$	0.01	2.9 ± 0.1	3.4 ± 0.1	3.8 ± 0.2	0.4 ± 0.2
$[1b_3 \cdot (DEB)_6]_n$	CHCl$_3$	0.01	4.8 ± 0.1	5.5 ± 0.1	5.3 ± 0.2	$\sim 0 \, (-0.2)$

^{a} Measured from X-ray crystal structure or gas-phase minimized (CHARMm 3.3, ABNR, rms < 0.001) structure. ^{b} Calculated according to the relation $d = 2L/(3)^{0.5}$. For definitions of d and L see Figure 3. ^{c} Measured from the TM-SFM images by averaging the distance spanned by 10–15 adjacent strands. ^{d} Calculated according to the relation $h = d + n$. For definitions of h, d and n see text.
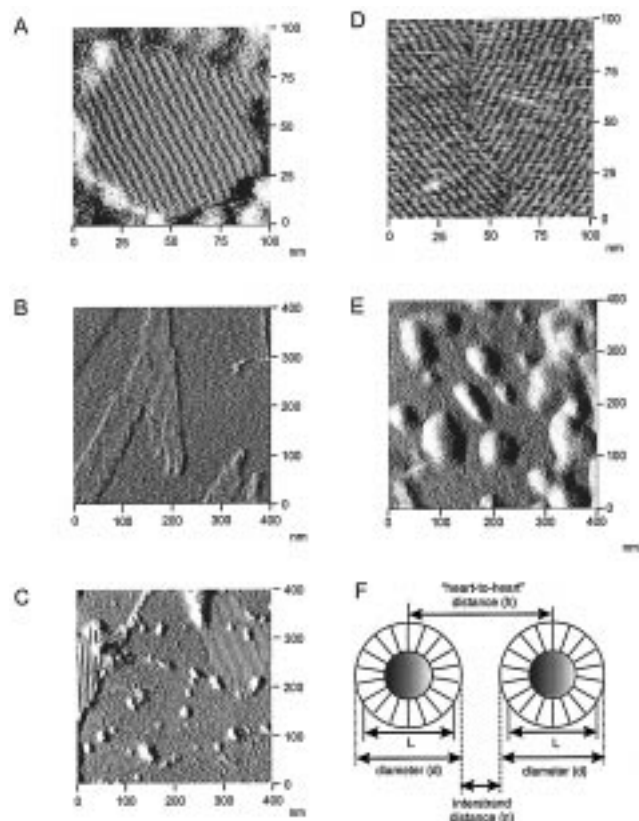

Figure 2. TM-SFM images of rodlike nanostructure $[1_3 \cdot 2_3]_n$ and $[1_3 \cdot (DEB)_6]_n$; (A) structure $[1a_3 \cdot 2a_3]_n$ (DMSO); (B) structure $[1b_3 \cdot 2a_3]_n$ (THF); (C) structure $[1b_3 \cdot 2b_3]_n$ (chloroform); (D) structure $[1a_3 \cdot (DEB)_6]_n$ (chloroform); (E) structure $[1b_3 \cdot (DEB)_6]_n$ (chloroform); (F) schematic front view of the nanostructures indicating the "heart-to-heart" distance (h), the diameter (d), and the interstrand distance (n).

was observed (Figure 2D,E), despite the fact that such rodlike structures are not present at concentrations < 0.1M in chloroform.[9,10] In this case, the rodlike structures cannot be formed by a hydrogen-bonding mediated polymerization process but are most likely formed by the face-to-face arrangement of multiple disklike assemblies $1_3 \cdot (DEB)_6$, a process that is driven by solvophobic interactions.

The TM-SFM data were analyzed according to the model presented in Figure 2F. The "heart-to-heart" distance (h) is experimentally determined from the SFM images by averaging the distance spanned by 10–15 adjacent strands. This parameter is related to the others via $h = d + n$. The diameter of the strands (d) is calculated either from the crystal structure of $1a_3 \cdot (DEB)_6$ (see ref 3b) or from the simulated structure $1b_3 \cdot (DEB)_6$ (see ref 11) via the relation: $d = 2L/(3)^{0.5}$. These calculations assume that stacking occurs "randomly", i.e., the alkyl chains are organized in a circular fashion around the structure. The diameters calculated for the disklike assemblies $1_3 \cdot (DEB)_6$ are also used to describe the dimensions of the corresponding rodlike nanostructures $[1_3 \cdot 2_3]_n$.[12]

Analysis of the TM-SFM data using the model described above demonstrates that there is a good correlation (<20% difference) between the experimentally determined and calculated parameters for four of the five nanostructures (Table 1). The best correlation was found for assemblies $[1_3 \cdot (DEB)_6]_n$ (<10%), which is most likely the result of the densely packed structure. For nanostructures with C$_{12}$ side chains (either from **1b** or **2b**) it was found that *h is always smaller than d*, whereas for those with only C$_3$ side chains it was found that *h is always larger than d*. This can be rationalized by taking into account that the structures with C$_{12}$ side chains have the possibility to interdigitate. In addition, nanostructures $[1b_3 \cdot 2a_3]_n$ and $[1b_3 \cdot 2b_3]_n$ have a much higher tendency to interdigitate ($-n = 0.5$–0.9 nm) compared to $[1b_3 \cdot (DEB)_6]_n$ ($-n = 0.2$ nm). This effect is most probably related to the more "open" structure of these assemblies.[13] Finally, it is remarkable that for assembly $[1a_3 \cdot 2a_3]_n$, the only one that is formed from the polar solvent DMSO, a significant interstrand distance ($n = \sim 1.5$ nm) is observed. These values suggest that the nature of the solvent (high boiling point) certainly plays a role here.

On the basis of these results we conclude that rodlike noncovalent nanostructures with dimensions between 3.5 and 5.5 nm can be prepared by self-assembly of small molecular components. Such structures have a hydrophobic outer shell and a polar core. In most cases the dimensions of the structures show good correlations with model calculations, indicating that the structures are densely packed on the substrate. We are currently investigating structural modifications of these systems for possible applications, e.g., as molecular wires.

Supporting Information Available: Synthetic scheme, schematic representations of the nanostructures $[1_3 \cdot 2_3]_n$ and $[1_3 \cdot (DEB)_6]_n$, and experimental details for the preparation of calix[4]arenes **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(9) Dilution studies of $1a_3 \cdot (DEB)_6$ in chloroform showed no significant shifts of the ^{1}H NMR signals over a concentration range of 100–0.1 mM. Assembly $1a_3 \cdot (DEB)_6$ formed large crystals ($\sim 3 \times 3$ mm in size) from a variety of solvent systems, but none of these crystals gave diffraction data good enough for structure determinations.

(10) Differential scanning calorimetry (DSC) experiments indicated that the crystallization of calix[4]arenes **1b** and the corresponding hydrogen-bonded assemblies were rather hindered. For example, for calix[4]arene **1b**, which melts at 145–147 °C during the first heating run, no transitions were observed when the material was cooled and heated again. The corresponding disklike assembly $1b_3 \cdot (DEB)_6$ only showed a broad endotherm around 200 °C (which is much higher than the melting temperatures of the separate components) probably indicating the disintegration of the hydrogen-bonded assembly.

(11) The simulation of assembly $1b_3 \cdot (DEB)_6$ was based on the X-ray crystal of assembly $1a_3 \cdot (DEB)_6$, and was performed by manual substitution of the propyl for dodecyl (all-trans configuration) side chains followed by a gas-phase minimization (CHARMm 3.3, ABNR, rms < 0.001).

(12) Model calculations showed that also in the rodlike nanostructures $[1_3 \cdot 2_3]_n$ the alkyl chains of component **1** mainly determine the lateral dimensions of the strands.

(13) Molecular modeling studies show that the distance between adjacent units **1** in nanostructure $[1_3 \cdot (DEB)_6]_n$ is 3–4 Å, whereas in nanostructure $[1_3 \cdot 2_3]_n$ these units are at least 10 Å apart.