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The Bis-urea Motif as a Tool To Functionalize Self-Assembled Nanoribbons

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The formation of well-defined self-assembled structures with nanoscopic dimensions is of importance for a variety of research fields ranging from nanoscience to biomedical engineering.[1] An intriguing approach to such assemblies is the organization of surfactant molecules into highly ordered structures, such as rods, ribbons, tubes, and helices.[2] In many cases, the introduction of strong hydrogen bonding moieties,[3] such as amide or urea groups, has been shown to be instrumental in the structuring and stabilization of these assemblies. To date, these efforts have resulted in the generation of a large variety of functional objects that were demonstrated, for example, to template the deposition of inorganic materials[4] or to have a specific interaction with cell membrane receptors[5] and other biomacromolecules.[6] In addition, the functionalization of solid bilayer membranes by doping additives has been reported.[7]

The incorporation of bis-ureido groups in molecules and polymers gives rise to strong hydrogen bonding interactions that have been used to form stable organo-[8] and hydro-gels,[9] to structure inorganic materials,[10] and more recently also polymeric assemblies.[11] Recently, also, the formation of mixed assemblies of different molecules bearing the same bis-urea unit has been demonstrated through molecular recognition.[11,12]

Here we present a surfactant molecule (**1**) containing an ammonium headgroup, in which a bis-ureido group is incorporated in its hydrocarbon chain. Due to strong hydrogen bonding interactions, **1** forms well-defined highly ordered ribbon-like bilayer aggregates in water. Moreover, we demonstrate that these ribbons can be functionalized via a modular approach through molecular recognition of other bis-urea containing molecules.

Upon heating a 0.5 wt % aqueous dispersion of **1** (for synthesis, see Supporting Information) to 70 °C, a clear solution was obtained, which upon cooling to room temperature yielded a viscous suspension.

Cryogenic transmission electron microscopy (cryo-TEM) revealed that this suspension contained well-defined ribbon-like aggregates, with average widths of 70 ± 20 nm and lengths in the order of micrometers (Figure 1a). The thickness of the ribbons was determined from several twisted aggregates and amounted to 6.0 ± 0.2 nm, which was confirmed by grazing incidence XRD (see Supporting Information). This number, together with the maximum molecular length of 4 nm as estimated from a model, suggests that these ribbons consist of a fully interdigitated bilayer of **1** (Figure 2a).

Polarized transmission IR spectroscopy on a sample of flow-aligned ribbons showed a decrease of the C═O (1616 cm^{-1}) and NH (3321 cm^{-1}) vibrations when the polarization direction was perpendicular to the length of the ribbon (Figure 2b). This indicates that the urea groups of **1** and thus the hydrogen bonds are oriented predominantly in the length direction of the ribbons. The concomitant decrease of the CH-*sym* vibration (2848 cm^{-1}) suggests that in these ribbons also the hydrocarbon chains are highly ordered. Indeed, PXRD showed reflections at 4.5 and 3.9 Å corresponding to a close-packed organization of alkyl chains, with 4.5 Å corresponding to the hydrogen bonding direction (see Supporting Information).

We anticipated that the ribbons might be further functionalized by incorporating other bis-ureido−butylene-modified molecules within the hydrogen bonding arrays formed by the bis-ureido-based amphiphiles (Figure 3a). In a first approach, we explored the incorporation of the azobenzene dye *disperse orange* (**2**) bearing a matching bis-ureido−butylene group. A mixture of **1** containing 6 mol % of **2** was dispersed in water and resulted in a yellow turbid suspension, which contained ribbons, as was confirmed by TEM (see Supporting Information). This dispersion showed a single maximum absorbance (λ_{max}) at 354 nm, which is significantly blue shifted compared to that of a solution of **2** in chloroform or a dispersion of **2** in an aqueous CTAB solution (λ_{max} = 405 nm, Figure 3b). These observations were attributed to the immobilization of the *disperse orange* moiety at the aqueous interface. Polarity studies indicated that the relatively large blue shift was the result of H-aggregation enforced by the tight packing within the ribbon structure (Figure 3a) (see Supporting Information). The selectivity of the molecular recognition process was investigated by incorporating *disperse orange* equipped with a nonmatching bis-ureido−pentylene moiety (**3**). In this case, UV−vis spectra revealed the coexistence of two absorption bands at 340 and 405 nm. As in this case, the bis-ureido unit of the modified dye cannot be effectively incorporated into the hydrogen bonding array, the existence of the weak band at 405 nm was attributed to the partial incorporation of

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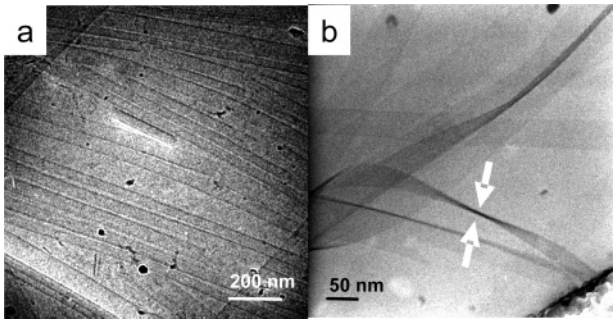

Figure 1. Cryo-TEM image of an aqueous dispersion of **1** (0.5 wt %) showing (a) ribbons with a homogeneous width distribution and (b) a twist point (arrows) from which the thickness of the ribbon was determined.

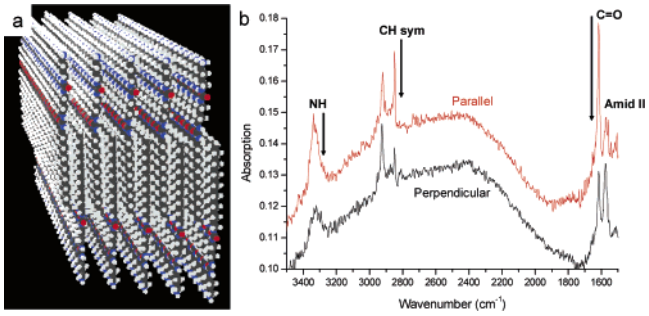

Figure 2. (a) Molecular model of the ribbon, showing full interdigitation of the alkyl tails and hydrogen bonds running in the length direction. (b) Polarized transmission IR spectra on aligned ribbons with the polarization direction parallel and perpendicular to the length direction of the ribbons.

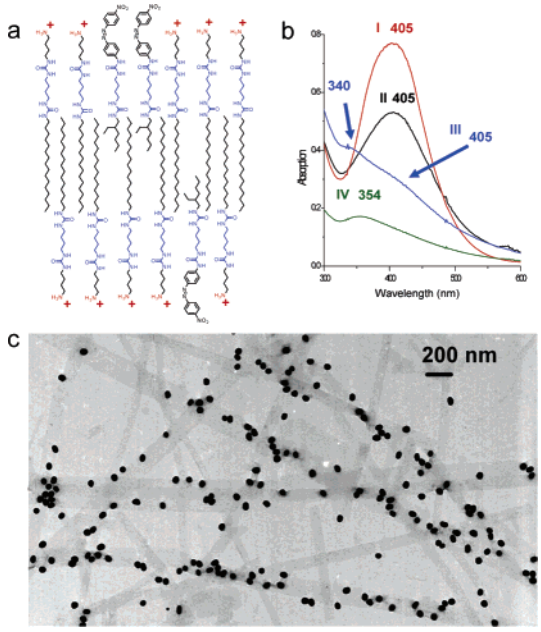

Figure 3. (a) Schematic representation of **2** incorporated into the ribbon structure. (b) UV−vis spectra of **2** (I) dissolved in chloroform, (II) dissolved in an aqueous CTAB solution, (IV) incorporated in a ribbon suspension, and (III) of **3** incorporated in a ribbon suspension. (c) TEM image of biotin functionalized ribbons with 25 nm gold-labeled streptavidin selectively bound to the pendant biotin groups.

3 into the hydrocarbon interior of the surfactant bilayer, in which the *disperse orange* experiences a similar environment as in the CTAB micelles. The band at 340 nm was attributed to phase separation of **3** at the ribbon surface due to ineffective anchoring within the ribbon lattice, causing more effective H-aggregation and a larger shift (cf. 354 nm for **2**).

To demonstrate the possibility of functionalizing these ribbons with molecules of biological origin, biotin was coupled to a ureido−butylene moiety via a PEG spacer (**4**). Using the procedure described above, 10 mol % of **4** was incorporated into aggregates of **1**. TEM analysis of the resulting dispersion showed also in this case the formation of ribbons. Incubation of the biotin-containing ribbons with gold-labeled streptavidin led to the selective decoration of the ribbons with these biomacromolecules (Figure 3c). Nonspecific binding was excluded by incubation of ribbons containing only **1** with the gold-labeled streptavidin, which yielded only a very low amount of ribbon-bound gold particles.

In summary, we have demonstrated that the new bis-ureido surfactant reported here organizes into well-defined ribbon-like aggregates directed by strong hydrogen bonding. The anchoring of different functionalities in a modular approach proved to be possible using the molecular recognition capabilities of the bis-ureido moiety, thereby opening possibilities to a wide range of applications.

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Supporting Information Available: Experimental details and spectroscopic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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