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Dinitium ion, the long-wavelength band disappears. Our long-term goal with these investigations is to be able to enantioselectively control not only the spectroscopic behavior but also the reactivity of prochiral guest molecules.

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Tunable Supramolecular Structures from a Glucanamide Containing Imidazole

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In recent years, the interest in supramolecular structures has grown steadily. Self-assembling systems have been prepared from a variety of building blocks including surfactants,14 polymers,15 rodlike16 and disklike mesogens,3 etc. As part of our program aimed at the development of novel chiral matrices for catalytic applications, we report here on the synthesis and self-assembling properties of the n-octyl-N-glucanamide derivative 3, which contains a metal-coordinating imidazole group. Our interest in glucanamides and related carbohydrates was raised by the recent studies of Fuhrhop et al. and others,17 which indicate that these compounds can form a great variety of nanometer-sized structures in water.

Compound 3 was synthesized as shown in Scheme 1. 1,5-D-Glucanolactone was hydrolyzed and protected at its secondary hydroxyl functions in a one-step procedure.17 The resulting product was esterified to give methyl-2,4,3,5-dimethyleneglucanate which was aminolyzed with octylamine to give the amide 2. The latter compound was tosylated and subsequently converted into 3 by reaction with imidazole in an autoclave at high pressure (15 Kbar).

Although the polarity of carbohydrate 2 is decreased due to the methylene bridges, it appears that this compound is soluble in water. However, unlike the unprotected derivative,3,10 it does not form well-defined aggregates, as judged by electron microscopy (EM). Apparently, the amide bond and the primary hydroxyl function in 2 cannot form hydrogen bonds leading to stable supramolecular structures in water. The DSC studies (DSC = differential scanning calorimetry) of an aqueous solution of 2 showed only one transition near 43 °C, which can be assigned to the disappearance of amide hydrogen bonds. No transition was observed upon cooling.18 The thermogram of n-octyl-N-glucanamide shows two transitions upon heating,19 which are attributed to the breaking of a network of intermolecular hydrogen bonds between the hydroxyl groups (at 61 °C), and between the amide hydrogen bonds (at 70 °C).20

Compound 3 is also soluble in water. From a titration experiment in methanol/water (95/5, v/v), it followed that the apparent $p_K$ value (pK$^+$) of the imidazole group is 6.28.21 For comparison, methylimidazole and imidazole were also titrated in this stable suprastructure in water. The DSC studies (DSC = differential scanning calorimetry) of an aqueous solution of 2 showed only one transition near 43 °C, which can be assigned to the disappearance of amide hydrogen bonds. No transition was observed upon cooling.22 The thermogram of n-octyl-N-glucanamide shows two transitions upon heating, which are attributed to the breaking of a network of intermolecular hydrogen bonds between the hydroxyl groups (at 61 °C), and between the amide hydrogen bonds (at 70 °C).23

As part of our program aimed at the development of novel chiral matrices for catalytic applications, we report here on the synthesis and self-assembling properties of the n-octyl-N-glucanamide derivative 3, which contains a metal-coordinating imidazole group. Our interest in glucanamides and related carbohydrates was raised by the recent studies of Fuhrhop et al. and others, which indicate that these compounds can form a great variety of nanometer-sized structures in water.
from 1/4 to 1/1. The titrations revealed that at low copper concentrations a 4/1 ligand-to-copper complex is present, whereas at high copper concentrations other complexes, for example \([3][Cu] = 3, 2, 1, 1\) prevail. For comparison, titrations were also carried out with the non-amiophilic imidazole compound and with methyldimazole. In both water and methanol/chloroform mixtures the copper complexation curves of 3, 4, and \(N\)-methyldimazole were very similar. The types of aggregates formed by 3 in water were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). In a NaOAc/HOAc buffer of pH 4.5, protonated 3 self-assembly to give interesting supramolecular structures which can have a length/width ratio up to 500 (Fig. 1B, the diameters of these fibers are approximately 100 nm). Freeze fracture experiments showed that these fibers are composed of multilayers (not shown). The hollow tubuli have diameters of approximately 3 μm. In a TRIS buffered solution, (pH 8.5), the 1:4 copper complex of amphiphile 3 forms helices (100%, Fig. 1D). The diameters of these helices are approximately 330 nm; much larger than the ropelike structures formed by \(N\)-octyl-d-glucamide (diameter of 27 nm) (14).

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**Iodine Chains in (Me₄Sb)₃I₈ and Discrete Triiodide Ions in Me₄AsI₃**

Ulrich Behrens, Hans Joachim Breunig, Michael Denker, and Klaus Heinz Ebert

Polyiodides have an extensive structural chemistry and compounds with discrete iodine chains are of particular interest because of possible unusual electric behavior. Iodine and iodide chains are not rare. They occur, for example, in the iodine-starch complex and in related compounds in organic metal, in complexes with column structures, and also in saltlike triiodides such as Bu₄N₄I₈. The iodine chains in these compounds consist of triiodide or iodide ions and iodine molecules. Ordered iodine chains such as in \([Cd(NH₃)₄I₆] \) are unusual; in this complex the iodine chains are not discrete, but are linked three-dimensionally by strong coordinative bonds to...