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dinium 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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[7] Trioxane, H2O/H+ (97%); b) H+ /MeOH (61%); c) excess of octylamine (no additional solvent used, 77%); d) Toulonpyridine, 0°C (87%); e) imidazole, CHCl3, 15 kbar, 50°C (65%). R = n-C4H9.

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, 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 suprastructures 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. The thermogram of n-octyl-D-glucosamidine shows two transitions upon heating, which are attributed to the breaking of a network of intramolecular hydrogen bonds between the hydroxyl groups (at 61°C), and between the amide hydrogen bonds (at 70°C).

Compound 3 is also soluble in water. From a titration experiment in methanol/water (95/5, v/v), it followed that the apparent pKw value (pKw) of the imidazole group is 6.28. For comparison, methylimidazole and imidazole were also titrated in this stable suprastructures 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. The thermogram of n-octyl-D-glucosamidine shows two transitions upon heating, which are attributed to the breaking of a network of intramolecular hydrogen bonds between the hydroxyl groups (at 61°C), and between the amide hydrogen bonds (at 70°C).

Compound 3 was synthesized as shown in Scheme 1. 1,5-D-Gluconolactone was hydrolyzed and protected at its secondary hydroxyl function in a one-step procedure. The resulting product was esterified to give methyl-2,4,3,5-dimethyl-2-glucosaminate which was amorphous 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).

Scheme 1. a) Trioxane, H2O/H+ (97%); b) H+ /MeOH (61%); c) excess of octylamine (no additional solvent used, 77%); d) Toulonpyridine, 0°C (87%); e) imidazole, CHCl3, 15 kbar, 50°C (65%). R = n-C4H9.
from 1/4 to 1/1. The titrations revealed that at low copper concentrations a 4/1 ligand-to-copper complex\(^ {112}\) is present, whereas at high copper concentrations other complexes, for example [3][Cu] = 3, 2, or 1 prevail. For comparison, titrations were also carried out with the non-amphiphilic imidazolide compound 4\(^ {113}\) and with methylimidazole. In both water and methanol/chloroform mixtures the copper complexation curves of 3, 4, and N-methylimidazole 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-assembles to yield vesicles (100%) with diameters ranging from 160 to 780 nm (Fig. 1A).\(^ {114}\) In a tris(hydroxymethyl)methylamine (TRIS) buffered solution of pH 8.5 long fibers (Fig. 1B and C) and hollow tubuli are formed exclusively (Fig. 1C). The fibers can have a length/width ratio up to 500 (Fig. 1B, the diameters of these fibers are approximately 100 nm).\(^ {115}\) 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).\(^ {116}\) The diameters of these helices are approximately 330 nm; much larger than the ropelike structures formed by N-octyl-D-glucosamine (diameter of 27 nm).\(^ {110}\)

In conclusion, we have shown that gluconamide 3 can self-assemble to give interesting supramolecular structures which can be tuned by changing the pH or by adding metal ions.

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[8] DSC analysis was carried out on a Perkin Elmer DSC 7 using a 4.9% (w/v) aqueous dispersion in a sealed pan, heating and cooling down rate was 5 K min\(^ {−1}\).


[10] a) The titration was carried out under a nitrogen atmosphere and the electrode was calibrated with a sodium succinate/succinic acid and an ammonium ex­­citate/oxalate acid buffer. D. Perrin, B. Demay. Buffers for pH and Metal Ion Control, Wiley, London, 1974.


[14] a) Vesicle samples for EM were prepared by cooling a hot clear solution of 3 in NaOAc/HOAc buffer of pH 4.5 to room temperature. Subsequently, a drop of this solution was placed on a hydrophilic Formvar supported grid. The vesicles were stained with uranyl acetate (2%).

[15] To a hot clear solution of 3 (0.5% m/v) in TRIS buffer, 0.25 equiv of Cu(C2O4)2 was added. The turbid mixture was cooled rapidly to room temperature and then allowed to stand for 30 min. No additional staining was used.

Iodine Chains in (Me4Sb)3I4 and Discrete Triiodide Ions in Me4AsI3**
Ulrich Behrens, Hans Joachim Breunig,* Michael Denker, and Klaus Heinz Ebert

Polyiodides have an extensive structural chemistry,\(^ {11}\) and compounds with discrete iodine chains are of particular interest because of possible unusual electric behavior.\(^ {11}\) Iodine and iso­diode chains are not rare. They occur, for example, in the iodine­starch complex and in related compounds,\(^ {11}\) in organic,\(^ {11}\) and in complex crystals, mainly in column structures,\(^ {11}\) and also in saltlike triiodides such as Bu4N3I.\(^ {11}\) The iodine chains in these compounds frequently consist of triiodide or iodide ions and iodine molecules.\(^ {11}\) Ordered iodine chains such as in [Cd(NH3)4]I2 are unusual;\(^ {11}\) in this complex the iodine chains are not discrete, but are linked three-dimensionally by strong coordinative bonds to

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