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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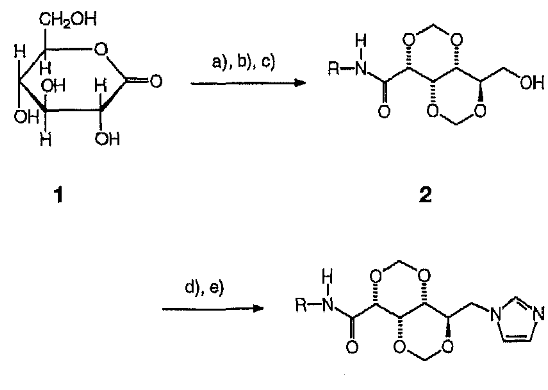
Tunable Supramolecular Structures from a Gluconamide Containing Imidazole

Rudi J. H. Hafkamp, Martinus C. Feiters,* and Roeland J. M. Nolte*

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,[1] polymers,[2] rodlike,[3] and disklike mesogens,[4] etc.[5] 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-D-gluconamide derivative 3, which contains a metal-coordinating imidazole group. Our interest in gluconamides and related carbohydrates was raised by the recent studies of Fuhrhop et al. and others,[6] which indicate that these compounds can form a great variety of nanometer-sized structures in water.

[*] Prof. Dr. R. J. M. Nolte, Dr. M. C. Feiters, R. J. H. Hafkamp
Nijmegen SON Research Center
University of Nijmegen
Toernooiveld, NL-6525 ED Nijmegen (The Netherlands)
Telefax: Int. code + (80) 55 34 50

Compound 3 was synthesized as shown in Scheme 1. 1,5-D-Gluconolactone was hydrolyzed and protected at its secondary hydroxyl functions in a one-step procedure.[7] The resulting product was esterified to give methyl-2,4;3,5-dimethylene-D-gluconate 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).

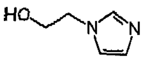


Scheme 1. a) Trioxane, H_2O/H^+ (74%); b) H^+/MeOH (61%); c) excess of octylamine (no additional solvent used, 77%); d) TsCl/pyridine, 0 °C (87%); e) imidazole, $CHCl_3$, 15 kbar, 50 °C (66%). R = n-C_8H_{17}.

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,[6a,f] 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 53 °C, which can be assigned to the disappearance of amide hydrogen bonds. No transition was observed upon cooling.[8] The thermogram of *n*-octyl-D-gluconamide shows two transitions upon heating,[9] 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).[9]

Compound 3 is also soluble in water. From a titration experiment in methanol/water (95/5, v/v), it followed that the apparent pK_a value (pK_a^*) of the imidazole group is 6.28.[10] For comparison, methylimidazole and imidazole were also titrated in this medium and were found to have pK_a^* values of 7.03 and 6.96, respectively, which are comparable to their values in water (6.95 for both compounds[11]).

The copper complexation properties of 3 were investigated by UV/VIS controlled titrations. Addition of $Cu(ClO_4)_2$ to a solution of 3 in water led to the appearance of a broad band at approximately λ = 620 nm. Unfortunately, the complex $[Cu(3)_n]^{2+}$ was not soluble enough in water to carry out an accurate UV/VIS titration. In mixtures of organic solvents such as chloroform/methanol (1/2, v/v), clear solutions were obtained and the complexation behavior of 3 could be determined. During the titrations of 3 with $Cu(ClO_4)_2$, the λ_{max} gradually shifted from 600 to 780 nm when the ratio [Cu]/[3] was increased from 1/4 to 1/1. The titrations revealed that at low copper concentrations a 4/1 ligand-to-copper complex[12] 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 imidazole compound 4[13] and with methylimidazole. In both water and methanol/chloroform mixtures the copper complexation curves of 3, 4, and N-methylimidazole were very similar.



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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. 1 A).[14] In a tris(hydroxymethyl)methylamine (TRIS) buffered solution of pH 8.5 long fibers (Fig. 1 B and C) and hollow tubuli are formed exclusively (Fig. 1 C). The fibers can have a length/width ratio up to 500 (Fig. 1 B, the diameters of these fibers are approximately 100 nm).[15] 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. 1 D).[16] The diameters of these helices are approximately 330 nm; much larger than the ropelike structures formed by N-octyl-D-gluconamide (diameter of 27 nm).[6f]

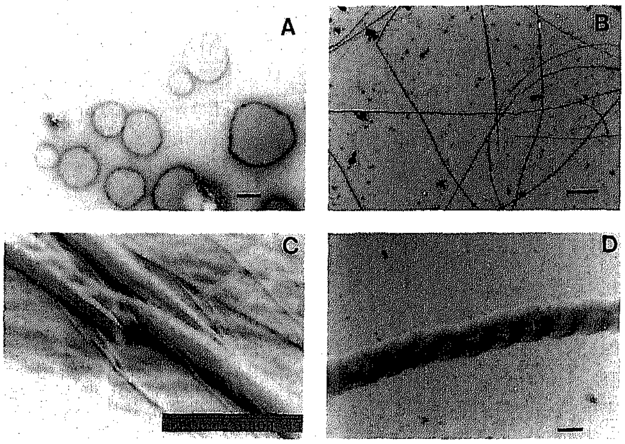

Fig. 1. A: TEM of vesicles of 3 (on a carbon-supported hydrophilic copper grid stained with 2% uranyl acetate; bar is 200 nm). B: TEM of fibers from 3 (Formvar-supported copper gid, stained with 2% uranyl acetate; bar is 5 μm). C: SEM of hollow tubuli and thin fibers of 3 (copper grid from 1 B was sputtered with gold; bar is 10 μm). D: TEM of helices from the copper complex of 3 (Formvar-supported copper grid without staining, bar is 200 nm).

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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[15] For the electron micrographs a hydrophobic Formvar supported grid was used.

[16] To a hot clear solution of 3 (0.5% m/v) in TRIS buffer, 0.25 equiv of $Cu(ClO_4)_2$ was added. The turbid mixture was cooled rapidly to room temperature and allowed to stand for 30 min. No additional staining was used.

Iodine Chains in $(Me_4Sb)_3I_8$ and Discrete Triiodide Ions in Me_4AsI_3**

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

Polyiodides have an extensive structural chemistry,[1] and compounds with discrete iodine chains are of particular interest because of possible unusual electric behavior.[2] Iodine and iodide chains are not rare. They occur, for example, in the iodine–starch complex and in related compounds,[3] in organic metals,[4] in complexes with column structures,[5] and also in saltlike triiodides such as Bu_4NI_3.[6] The iodine chains in these compounds frequently consist of triiodide or iodide ions and iodine molecules.[7] Ordered iodine chains such as in $[Cd(NH_3)_4I_6]$ are unusual;[1] in this complex the iodine chains are not discrete, but are linked three-dimensionally by strong coordinative bonds to

[*] Prof. Dr. H. J. Breunig, M. Denker, K. H. Ebert
Fachbereich 2 der Universität
Postfach 330440, D-28334 Bremen (FRG)
Telefax: Int. code + (421)218-4042
Prof. Dr. U. Behrens
Institut für Anorganische und Angewandte Chemie
der Universität Hamburg (FRG)

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