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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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Tunable Supramolecular Structures from a Gluconamide Containing Imidazole

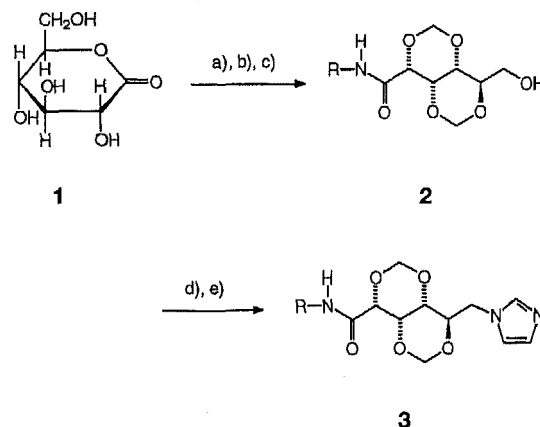
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In recent years, the interest in supramolecular structures has grown steadily. Self-assembling systems have been prepared from a variety of building blocks including surfactants,^[1] polymers,^[2] rodlike,^[3] and disklike mesogens,^[4] etc.^[5] As 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

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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.

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, $\text{H}_2\text{O}/\text{H}^+$ (74%); b) H^+/MeOH (61%); c) excess of octylamine (no additional solvent used, 77%); d) $\text{TsCl}/\text{pyridine}$, 0 °C (87%); e) imidazole, CHCl_3 , 15 kbar, 50 °C (66%). $\text{R} = n\text{-C}_8\text{H}_{17}$.

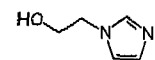
Although the polarity of carbohydrate **2** is decreased due to the methylene bridges, it appears that this compound is soluble in water. However, unlike the unprotected derivative,^[6a,f] it does not form well-defined aggregates, as judged by electron microscopy (EM). Apparently, the amide bond and 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 $\text{p}K_a^*$ value ($\text{p}K_a^*$) of the imidazole group is 6.28.^[10] For comparison, methylimidazole and imidazole were also titrated in this medium and were found to have $\text{p}K_a^*$ 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 $\text{Cu}(\text{ClO}_4)_2$ to a solution of **3** in water led to the appearance of a broad band at approximately $\lambda = 620 \text{ nm}$. Unfortunately, the complex $[\text{Cu}(\text{3})_n]^{2+}$ 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 $\text{Cu}(\text{ClO}_4)_2$, the λ_{max} gradually shifted from 600 to 780 nm when the ratio $[\text{Cu}]/[\text{3}]$ 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.

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).^[14] 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).^[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. 1D).^[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).^[16]



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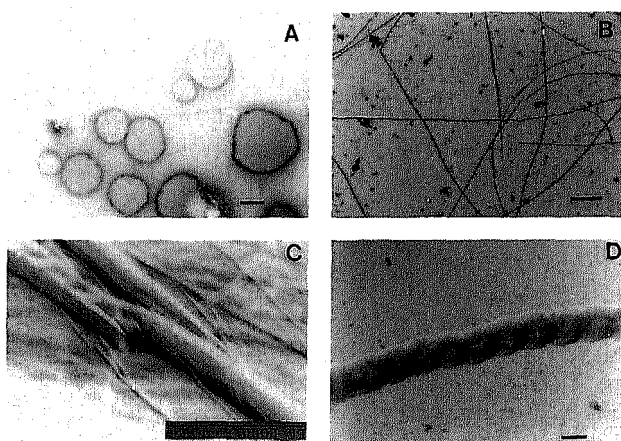


Fig. 1. A: TEM of vesicles of 3 (on a carbon-supported hydrophilic copper grid stained with 2% uranyl acetate; bar is 200 nm). B: TEM of fibers from 3 (Formvar-supported copper grid, stained with 2% uranyl acetate; bar is 5 µm). C: SEM of hollow tubuli and thin fibers of 3 (copper grid from 1 B was sputtered 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(ClO₄)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 (Me₄Sb)₃I₈ and Discrete Triiodide Ions in Me₄AsI₃**

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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 Bu₄Ni₃.^[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(NH₃)₄I₆] are unusual;^[1] in this complex the iodine chains are not discrete, but are linked three-dimensionally by strong coordinative bonds to

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