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Tunable Supramolecular Structures from Clips and Baskets Derived from Glycoluril

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The development of molecular materials with tunable structures and properties is a topic of great current interest. Recently, molecular recognition has been used as a tool to control the architecture of such materials. Examples are the induction of liquid crystallinity in azo–crown ether derivatives by complexation of metal ions1 and the engineering of the liquid–crystalline behavior of crown ether containing polymers with the help of alkali metal ions.2

Molecular clips derived from diphenylglycoluril (e.g., 1a) can act as host molecules for aromatic guest molecules.3 Their crown ether derivatives (e.g., 2a) bind dihydroxybenzenes4 as well as alkali metal and diammonium ions.5 We describe here two novel derivatives of 1 and 2 and report that the thermotropic behavior of compound 1c as well as the lyotropic behavior of compound 2c can be directly influenced by molecular recognition processes.

Clip 1c, containing 12 long hydrocarbon chains, was synthesized from 1b by an esterification reaction with 3,4,5-tris(dodecylxylo)benzoyl chloride.6 In CDC13 solution this compound exists as a mixture of three conformers (designated as ss, sa, and aa), which interconvert slowly on the NMR time scale. This feature is in agreement with the presence of four AX patterns for the methylene protons of 1c in the 1H NMR spectrum, viz., one AX pattern for each of the aa and ss conformers, and two for the less symmetric sa conformer. NMR data show that, at 25 °C, 66% of the molecules are in the ss, 29% in the aa, and 5% in the ss

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(7) The binding constant in chloroform was determined by integrating the relevant signals of the different conformers of the receptor molecule by 1H NMR. Solutions of 1.6 mM 1c and 0–11.9 mM resorcinol were used. The binding constant of 3,5-dihydroxybenzoic acid methyl ester in CHCl3 could not be accurately measured due to the low solubility of the guest. From studies with other clip molecules we estimate a value $K_a = 5000$ M⁻¹.

(8) Thermal transition data, $T^*{\text{[C]}}(\Delta H/K\cdot\text{mol})$; 0.1 equiv, K(58.8) M 95(1.0) M' 144(5.9) I; 0.2 equiv, K−1(50.6) M 84(1.5) M' 141(5.3) I; 0.3 equiv, K−3(45.6) M 82(2.1) M' 131(3.8) I; 1.0 equiv, K−4(29.5) M 110(0.3) M' 66(0.2) I.

(9) Inclusion experiments on vesicles prepared from a similar compound showed that the aggregates have an aqueous interior. Schenken, A. P. H.; de Bruin, B.; Feiters, M. C.; Nolte, R. J. M. Angew. Chem., in press.

Figure 1. Thermotropic liquid-crystalline behavior of clip 1c in the presence of different amounts of 3,5-dihydroxybenzoic acid methyl ester. conformation. By addition of an excess resorcinol the sa conformer was completely converted into the aa conformer, which is the only binding species in solution.8 From a 1H NMR titration the association constant7 for resorcinol was calculated to be $K_a = 400 \pm 60$ M⁻¹.

Compound 1c displayed a K1 transition at 159–164 °C. After supercooling, a monotropic nematic phase with a clearing temperature of 161 °C was observed. A 1:1 complex of 1c and resorcinol showed a smectic phase with a clearing temperature of 110 °C. After repetitive heating and cooling, phase separation was found to take place, indicating that the complex is unstable. In contrast to resorcinol, 3,5-dihydroxybenzoic acid methyl ester formed a stable complex with 1c.7 Variation of the host–guest ratio gave rise to the appearance of different mesophases covering a wide temperature range as shown in Figure 1.8 The nature of the mesophases was derived from the optical textures which are visible under a polarizing microscope and from the magnitude of the enthalpy changes measured by DSC. At low concentrations of guest, two mesophases were present, which were interpreted as being smectic phases (birefringent mosaic type textures). At higher concentrations, only a nematic phase was visible (birefringent texture and small enthalpy changes in DSC). The binding of guest molecules changes the equilibrium of the conformers and, in this way, tunes the properties of the thermotropic liquid-crystalline material.

The basket-shaped compound 2c was obtained by esterification of 2b with lauryl chloride.9 This host molecule showed lyotropic liquid–crystalline behavior in water. The aggregation behavior of 2c was studied by electron microscopy (EM) using both negative staining and freeze fracturing techniques. A 0.2 wt % solution of this compound in 0.1 N aqueous HCl displayed in EM long tubelike structures with a diameter of 100 nm (Figure 2a). In 0.2 M KCl or NaCl solutions 2c aggregated to form vesicles with diameters of 200–500 nm (Figure 2b).10

To investigate the effect of acidic or alkalai metal salt solutions in more detail, we carried out monolayer experiments. The isotherms, recorded using different subphases at 20 °C, showed
interesting differences. Some results are shown in Figure 3. The
isotherms of 2c at pH = 1 (Figure 3, curve a) and pH = 7 (Figure
3, curve b) were nearly identical. From the onset of the curves
a molecular area of 220 Å² can be calculated, suggesting that the
molecules have a stretched-out conformation. Isotherm c (Figure
3) shows the behavior of 2c on a 0.02 M KCl subphase. At a
pressure of 19 mN/m a transition was observed which disappeared
when the concentration of K⁺ ions in the subphase was increased
to 0.2 M. The onset of the curves before and after the transition
points to molecular areas of 220 and 160 Å², respectively. These
numbers suggest that at low pressures and high salt concentrations
2c has a relatively flat structure with two K⁺ ions bound into its
crown ether rings. At high pressure the molecule adopts a
sandwich-like conformation with only one cation bound between
the rings, in agreement with previous studies\(^2\) (see Figure 3).
This conformation is less likely for the protonated compound 2c
because of electrostatic repulsion. On the basis of these results
we tentatively conclude that the tubelike structures seen in 0.1
N aqueous HCl are built up from molecules of 2c in the stretched-
out conformation (Figure 2a). The vesicles (Figure 2b) probably
contain molecules of 2c in the sandwich-like conformation.

To study the influence of the size of the cation on the aggregation
behavior of 2c we also used RbCl and CsCl in our experiments.
Monolayer experiments showed that Rb⁺ and Cs⁺ ions are more
strongly bound than K⁺ ions by 2c. Consequently, it was necessary
to use lower concentrations of these alkali metal ions in the
subphase to achieve a phase transition (see, e.g., Figure 3, curve
d). Addition of 2c (0.2 wt %) to a 0.2 M aqueous solution of
RbCl or CsCl did not result in the formation of well-defined
aggregates (EM). When, however, the concentration of the alkali
metal salt was lowered to 0.02 M, vesicles and small rodlike
aggregates were observed in the case of RbCl (Figure 2c) and
tubelike structures in the case of CsCl (Figure 2d). Apparently
both the occurrence of a phase transition in the monolayer
experiments and the appearance of aggregates in the aqueous
dispersions depend on the concentration of the alkali metal ions.
We believe that the sandwich-like conformation, which is present
at lower concentrations, induces the formation of the super-
structures. Increasing the size of the alkali metal ion, from K⁺
to Rb⁺ to Cs⁺, leads to a decrease in curvature of the aggregates
and hence to a gradual change in aggregate structure, \(viz.,\) from
vesicles to tubes.

In summary, we have shown that molecular recognition
processes can be used to control the properties of molecular
materials. Further studies are in progress in our laboratory.

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