

Tunable Supramolecular Structures from Clips and Baskets Derived from Glycoluril

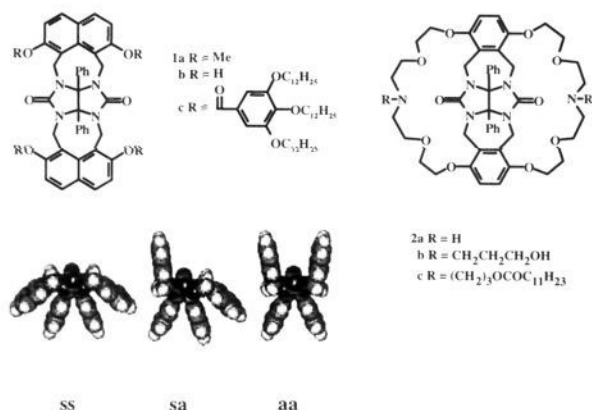
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The development of molecular materials with tunable structures and properties is a topic of great current interest. Recently molecular recognition has been used as a tool to control the architecture of such materials. Examples are the induction of liquid crystallinity in aza-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(dodecyloxy)-benzoyl chloride.⁶ In CDCl_3 solution this compound exists as a mixture of three conformers (designated as *aa*, *sa*, and *ss*), 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 *sa*, 29% in the *aa*, and 5% in the *ss*

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(6) ^1H NMR (CDCl_3 , ppm): δ 5.90 and 5.50 ($\text{CH}_2\text{N sa}$), 5.42 ($\text{CH}_2\text{N aa}$), 5.23 ($\text{CH}_2\text{N ss}$), after adding resorcinol only 5.41 ($\text{CH}_2\text{N aa}$). Anal. ($\text{C}_{212}\text{H}_{334}\text{N}_4\text{O}_{22}$) C, H, N: calcd, 77.37, 10.23, 1.70; found, 77.13, 10.56, 1.67. Experimental details will be published in a full paper.

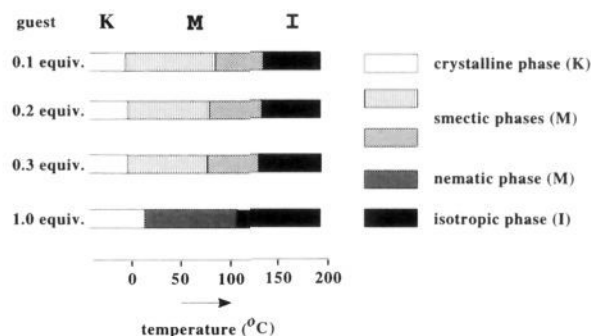


Figure 1. Thermotropic liquid-crystalline behavior of clip **1c** in the presence of different amounts of 3,5-dihydroxybenzoic acid methyl ester.

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.⁶ From a ^1H NMR titration the association constant⁷ for resorcinol was calculated to be $K_a = 400 \pm 60 \text{ M}^{-1}$.

Compound **1c** displayed a K–I 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 lauroyl 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 alkali metal salt solutions in more detail, we carried out monolayer experiments. The isotherms, recorded using different subphases at 20 °C, showed

(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 CHCl_3 could not be accurately measured due to the low solubility of the guest. From studies with other clip molecules we estimate a value $K_a \approx 5000 \text{ M}^{-1}$.

(8) Thermal transition data, T [°C] (ΔH [kJ/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) I.

(9) ^1H NMR (CDCl_3 , ppm): δ 7.07 (s, 10H, ArH), 6.69 (s, 4H, ArH), 5.62 (d, 4H, NCH_2Ar), 4.3–3.5 (m, 32H, NCH_2Ar , CH_2O , CH_2OCO), 2.88 (t, 8H, $\text{NCH}_2\text{CH}_2\text{O}$), 2.69 (t, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.28 (t, 4H, OCOCH_2), 2.0–1.1 (m, 40H, CH_2), 0.8 (t, 6H, CH_3). FAB MS (nitrobenzyl alcohol): m/z 1379 (M + Na)⁺, 1357 (M + 1)⁺. Anal. ($\text{C}_{78}\text{H}_{112}\text{N}_2\text{O}_{14}$) C, H, N: calcd, 69.00, 8.31, 6.19; found, 68.67, 8.44, 6.27.

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

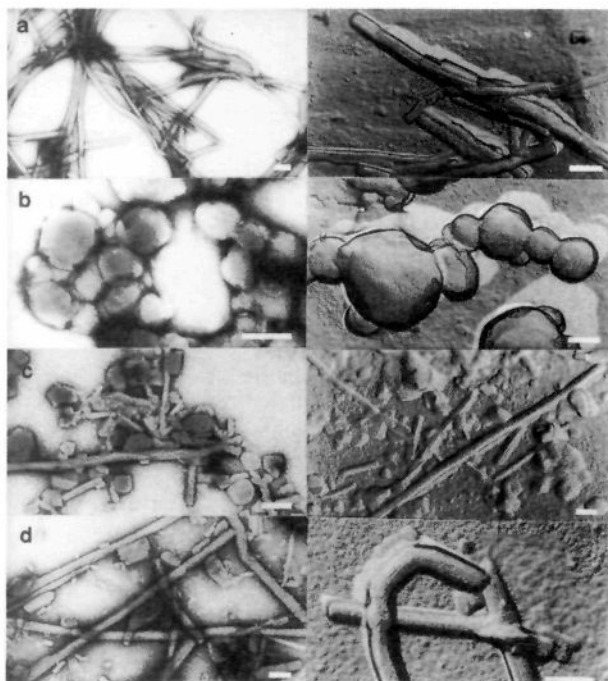


Figure 2. Transmission electron micrographs of dispersions of **2c** (0.2 wt %) in (a) 0.1 N HCl, (b) 0.2 M KCl, (c) 0.02 M RbCl, and (d) 0.02 M CsCl. Bars represent 250 nm. Left: negative staining technique. Right: freeze fracturing technique.

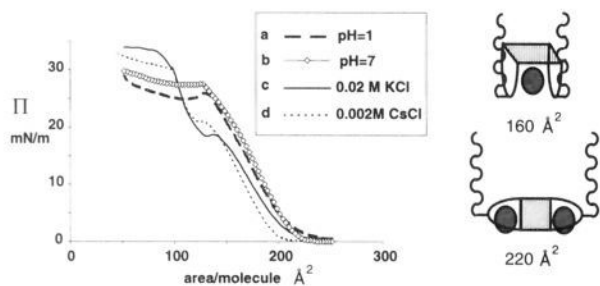


Figure 3. Compression isotherms of compound **2c** on different subphases: (a) pH = 1 (0.1 N HCl), (b) pH = 7, (c) 0.02 M KCl, and (d) 0.002 M CsCl.

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 \AA^2 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 \AA^2 , 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 studies⁵ (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 superstructures. 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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