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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 azacrown ether derivatives by complexation of metal ions and the engineering of the liquid-crystalline behavior of crown ether containing polymers with the help of alkali metal ions.

Molecular clips derived from diphenylglycoluril (e.g., 1a), can act as host molecules for aromatic guest molecules. Their crown ether derivatives (e.g., 2a) bind dihydroxybenzenes as well as alkali metal and diammonium ions. 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. In CDC13 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 lc in the 'H 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 conformer.

To investigate the effect of acidic or alkali metal salt solutions on the mesomorphic properties 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 lauril chloride. 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 HC1 displayed a K-I transition at 159–164 °C. After supercooling, a 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. Variation of the host-guest ratio gave rise to the appearance of different mesophases covering a wide temperature range as shown in Figure 1.

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.

(7) The binding constant in chloroform was determined by integrating the relevant signals of the different conformers of the receptor molecule by 'H NMR. Solutions of 1.6 mM 1c and 0.1 M NaCl 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 ≈ 5000 M−1.

(8) Thermal transition data, T°(C)[ΔH(J/kmol)]: 0.1 equiv, K(58.8) M 95(1.0) M 144(5.9); 0.2 equiv, K(−150.6) M 84(5.1) M 141(5.3); 0.3 equiv, K(−345.6) M 82(2.1) M 131(3.8); 1.0 equiv, K(−29.5) M 110(3.0).
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. 220 Å² to 160 Å².

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 (see Figure 3). This conformation is less likely for the protonated compound 2e 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 2e 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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