Induction of Liquid Crystallinity by Host—Guest Interactions

Johanna L. M. van Nunen, Brigitte F. B. Folmer, and Roeland J. M. Nolte

Contribution from the Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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Abstract: A molecular clip is described which binds aromatic guests by an induced fit mechanism. It contains twelve long aliphatic chains and can evoke liquid-crystalline properties in a variety of molecules, including polymers and porphyrins, by a process of molecular recognition.

Introduction

Supramolecular chemistry involves the design, synthesis, and study of molecular systems and assemblies of molecules held together by relatively weak forces, e.g., hydrogen bonding, electrostatic interactions, Van der Waals forces, etc. In the last two decades attention in supramolecular chemistry has gradually shifted from the host—guest binding of alkali metals in crown ethers to the complexation of neutral molecules in different types of synthetic receptors. Current efforts are directed toward the design of more sophisticated host molecules which can bind guests by an induced fit or allosteric mechanism. Much of this research is inspired by the elegant molecular systems found in nature, which operate by similar mechanisms, leading to efficient catalysis or in a number of cases to the induction of special (materials) properties. A similar incentive underlies the design of more sophisticated host molecules which can bind guests by an induced fit or allosteric mechanism. One of the walls of this research is inspired by the elegant molecular systems found in nature, which operate by similar mechanisms, leading to efficient catalysis or in a number of cases to the induction of special (materials) properties. A similar incentive underlies the design of more sophisticated host molecules which can bind guests by an induced fit or allosteric mechanism.

In this paper we will demonstrate that the idea of making polymers liquid crystalline by clipping molecules of type 1 to them is viable. Furthermore, we will show that the concept is general and can be extended to other host—guest combinations (see Figure 3).

Experimental Section

General Methods. Acetonitrile and CH2Cl2 were distilled from NaH2, diethyl ether and tetrahydrofuran (THF) from LiAlH4, and toluene from sodium. Dimethyl sulfoxide (DMSO) was dried over CaH2. Pyrrole was distilled before use. Methyl 3,5-dihydroxybenzoate (MDB) was a commercial product used without purification. For column chromatography Merck silicagel 60 and for flash column chromatography Merck silicagel 60 were used. Melting points were measured with a Jeneval polarizing microscope connected to a Linkam THMS 600 hot stage. 1H NMR spectra were recorded on Varian EM-390 and Bruker AC-100 spectrometers. Chemical shift values are reported relative to tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin-Elmer 298 infrared spectrophotometer. Mass spectra were obtained with a double focusing VG 7070E spectrometer. Elemental analyses were determined with a Carlo Erba EA 1108 instrument. For the determination of the optical rotations a Perkin Elmer 241 polarimeter was used. A Perkin Elmer 3-5 UV—vis spectrophotometer was used to obtain the UV—vis spectra. Thermograms were recorded at a rate of 10 °C/min using a Perkin Elmer DSC 7 instrument. Samples were prepared in stainless-steel large volume pans (75 mL). Transition temperatures and enthalpies were determined from the second heating and first cooling scans. GPC measurements were performed on a Waters 590 GPC instrument equipped with a PLGEL 352 column using tetrahydrofuran as the eluent and different polystyrenes as standards.

The compound (2, Scheme 1) from which 1 is synthesized has been described previously. Its most important structural features are a concave framework composed of two urea units and two methylene linked aromatic walls. The molecules of...
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Figure 1. (a) Structure of the Gene V protein. (b) Complex of twelve protein molecules and a DNA chain (see ref 6).

Figure 2. Structures of the three conformers of 2.

tetraazapentaleno[1',6':5,6,7:3',4':5',6',7']dicycloocta[1,2-v,3-w,4-l,5-m,6-n,7-o]dihydroxybenzoate (1). Receptor molecule 2 (n mmol) and NaH (10 mmol) were refluxed in THF (10 mL) and after 1 h 3,4,5-tris(dodecyloxy)benzoyl chloride (4.4 equiv) in a mixture of THF/CH2Cl2 (1:1 v/v, 5 mL) was added. The mixture was stirred for 2-24 h and subsequently quenched with a few drops of water. The solvent was evaporated under reduced pressure and the residue was dissolved in CHCl3. The organic layer was extracted (2x) with aqueous 1 N HCl, then with I2O, and dried (MgSO4). The crude product was subjected to flash column chromatography (eluent ethyl acetate-hexane 1:25 v/v). Yield 57%. Kt to I transition at 159-162°C.

1H NMR (CDCl3, ppm) [see Table 1 for uncomplexed host, guest complex: δ host 7.67 (s, 8H, ArH(OR)), 7.44 and 6.99 (2d, 8H, naph-H, J = 8.9 Hz), 7.11-7.05 (m, 6H, ArH), 6.94 (d, 4H, ArH), 5.41 and 4.14 (2d, 8H, NCH2Ar, J = 16.8 Hz, 4.12-3.94 (m, 24H, OCH2), 1.84-1.08 (m, 240H, OCH3)], ppm) and 5.8 (m, 2H, CH-CH2), 4.5 (d, 4H, OC=CH), 1.04-0.80 (m, 36H, CH3), guest (resorcinol) 6.90 (t), 6.21 (dd), 5.75 (br s), 5.49 (s). Anal. (C222H222N2O22)2 C, H, N: calcd 77.37, 10.23, 1.70; found 77.13, 10.56, 1.67.

Phenyl 3,5-Dihydroxybenzoate. This compound was synthesized by an esterification reaction from 3,5-bis(benzyloxy)benzoic acid and phenol. Deprotection of the product was carried out according to a literature procedure.10

Methyl 3,5-Bis(allyloxy)benzoate (3a). A mixture of methyl 3,5-dihydroxybenzoate (1.0 g, 6.0 mmol), allyl bromide (1.0 mL, 12 mmol), and K2CO3 (1.8 g) in acetone (10 mL) was refluxed for 4 h. The solvent was removed under reduced pressure, water was added, and the product was extracted with CH2Cl2. The organic layer was washed with water (2x), dried (MgSO4), and evaporated to dryness under reduced pressure.

After recrystallization from diisopropyl ether the allyl-protected methylbenzoate 3a was obtained in 75% yield. Mp 33°C.

1H NMR (CDCl3, ppm) δ 7.1 (s, 2H, ArH), 6.6 (s, 1H, ArH), 6.2-5.7 (m, 2H, CH=CH2), 5.4-5.1 (m, 4H, CH=CH2), 4.5 (d, 4H, OCH2), J = 6 Hz), 3.9 (s, 3H, OCH3). IR (KBr, cm-1) ν 3150-3050 (arom C-H), 2980-2980 (aliph C-H), 1730 (C=O), 1600 (arom C=C), MS (El, m/z): 248 (M)+, 233 (M - CH3)+, 189 (M - COOH)+, and 41 (allyl). Anal. (C13H13O3) C, H: calcd 75.13, 7.46; found 74.75, 7.39.

3,5-Bis(allylbenzoate)benzoic Acid (4a). A mixture of methyl benzoate (1.0 g, 4.0 mmol) and KOH (0.53 g) in ethanol (15 mL) was refluxed for 2 h. The solvent was evaporated in vacuo and ethyl acetate was added. The organic layer was acidified with an aqueous solution of 1 N HCl to pH 1. The mixture was washed with water (2x) and dried (MgSO4), and the solvent was evaporated. Crystallization from ethanol yielded 60% of the benzonic acid 4a. Mp 71°C.

1H NMR (CDCl3, ppm) δ 7.3 (s, 2H, ArH), 6.8 (s, 1H, ArH), 6.4-5.8 (m, 2H, CH=CH2), 5.6-5.2 (m, 4H, CH=CH2), 4.5 (d, 4H, OCH2), 3.8 (s, 3H, ArOCH3), J = 6 Hz). IR (KBr, cm-1) ν 2900 (COOH), 1690 (C=O), 1600 (arom C=C), MS (El, m/z): 234 (M)+, 189 (M - COOH)+, and 41 (allyl). Anal. (C13H11O3) C, H: calcd 76.66, 60; found 76.63, 60.4.

3,5-Bis(benzyloxy)benzoic Acid (4b). For the synthesis of this compound the same procedure was followed as described for 4a, using 3b (1.6 g, 4.6 mmol) and powdered KOH (0.8 g) in ethanol (60 mL). Yield 94%. Mp 213-218°C.

1H NMR (CDCl3, ppm) δ 7.5-7.1 (m, 12H, ArH), 6.7 (s, 1H, ArH), 5.0 (s, 4H, CH2Ph). IR (KBr, cm-1) ν 2880 (COOH), 1690 (C=O), 1600 (arom C=C), MS (El, m/z): 334 (M)+, 181, and 91 (CH2Ph)+. Anal. (C22H15O3) C, H: calcd 75.43, 5.43; found 75.24, 5.44.

1,4-Bis[3,3-bis(benzyloxy)benzoyloxy]benzene (5). For the synthesis of this compound a procedure described by Hashimoto et al. was...
followed. To a solution of 3.5-bis(benzyloxy)benzoic acid 4a (1.18 g, 5.0 mmol) and hydroquinone (0.25 g, 2.3 mmol) in acetonitrile (3 mL) were subsequently added under an argon atmosphere (CCl₄, 0.52 mL, 5.4 mmol), Et,N (0.69 mL, 5.0 mmol), and PPh₃ (1.39 g, 5.0 mmol). The solution was stirred for 2 days and in addition refluxed for 4 h. The reaction mixture was evaporated to dryness under reduced pressure and the product was dissolved in CHCl₃. The organic layer was extracted with aqueous 1 N HCl (2X), aqueous 1 N NaOH (2X), and water (1X) and dried (MgSO₄). The residue was subjected to column chromatography (eluent: ethyl acetate—hexane 1:9 and subsequently 1:3 v/v). Crystallization from diisopropyl ether yielded 61% of the protected hydroquinone dimer 5. Mp 115 °C.

1H NMR (CDCl₃, ppm) δ 7.36 (d, 4H, (AllylO)ArH, J = 2 Hz), 7.27 (s, 4H, ArH). 6.78 (t, 2H, (AllylO)ArH, J = 2 Hz), 6.22-5.89 (m, 4H, CH=CH₂), 5.52-5.27 (m, 8H, CH=C=CH₂), 4.60 (d, 8H, OCH₂, J = 6 Hz). IR (KBr, cm⁻¹) ν 3150-3050 (arom C—H), 2950-2850 (aliph C—H), 1740 (C=O), 1600 (arom C=C). MS (EI, m/z): 383 (M + 1)+, and 137 (COAr(OH)₂)+. Anal. (C₃₁H₂₆O₁₂) C, H: calcd 64.14, 10.23; found 64.33, 10.10. [α]D²₀ = -32.7° (c 0.7, CHCl₃).

Diacetyl (2R,3R)-O-Bis[3,5-bis(benzyloxy)benzoyl]tartrate (7). This compound was synthesized according to a literature procedure. A solution of 4b (110 mg, 0.3 mmol) and N,N-carbonyldimidazole (67 mg, 0.5 mmol) in dry toluene was stirred overnight at room temperature. Subsequently diacetetyl tartrate (60 mg, 0.16 mmol) was added to this solution. After 6 days the solvent was evaporated and the residue was dissolved in CHCl₃. The organic layer was washed with water (2X), dried (MgSO₄), and concentrated in vacuo. The residue mixture was subjected to flash column chromatography (eluent: ethyl acetate—hexane 1:7 v/v) and the product was obtained as a colorless oil in 81% yield.

1H NMR (CDCl₃, ppm) δ 7.3 (s, 20H, ArH), 7.1 (s, 4H, Ar(C=O)-H), 6.7 (s, 2H, Ar(OBz)₂H), 5.9 (s, 2H, CH(OAc)Ar), 5.0 (s, 8H, CH₂Ph), 4.1 (m, 4H, OCH₂CH₃), 1.8-1.0 (m, 24H, C(CH₃)₂), 0.8 (t, 6H, OCH₃). FAB-MS (m-nitrobenzyl alcohol, m/z): 1006 (M + H)+, 915 (M — CH₂Ph)+, [α]D²₀ = 26.6° (c 0.6, CHCl₃).

Figure 3. Schematic representation of the liquid crystalline complexes that can be obtained from clip molecules I and different types of guest molecules.
concentrated until the crystallization started. In this way white needles carefully added to a suspension of LiAlH₄ (780 mg) in diethyl ether (20 mL) as the solvent. Purification by column chromatography (elucent: ethyl acetate–hexane 1:1 v/v) yielded 88% of compound 14. 

**Scheme 2:**

Copolymer 19. For the synthesis of this polymer the same esterification method was used as described for compound 5. Copolymer 18 (120 mg), 4b (200 mg, 0.60 mmol), CCl₃ (0.16 mL, 1.7 mmol), triethylamine (0.05 mL, 0.36 mmol), and PPh₃ (190 mg, 0.68 mmol) were mixed in acetonitrile (1.5 mL). This mixture was stirred for 3 days at room temperature. The workup procedure was similar to that described for compound 5, except that at the end the residue was dissolved in CHCl₃ and precipitated in methanol. In this way 68% of the esterified copolymer was obtained.

1H NMR (CDCl₃, ppm) δ 7.4—6.2 (br. s, ArH), 5.1 (br. s, OCH₂Ph), 2.2—1.0 (br. s, CH₂Ph—CH₂). IR (KBr, cm⁻¹) ν 3490 (OH), 3020 (arom C-H), 2920 (aliph C-H), 1760 and 1730 (C=O), 1590 (arom C=C), 1150 (C-O ether). GPC (THF): Mₘ = 24000, Mₚ/Mₘ = 2.38. Elemental analysis C, H, N: found 79.60, 6.2, 0.72.

Copolymer 20. Deprotection of copolymer 19 (0.07 g) was performed using a solution of hydrobromic acid in acetic acid (2 mL). The residue was dissolved in acetonitrile and precipitated in water. The copolymer was dried over P₂O₅ under high vacuum. In this way copolymer 20 was obtained as a beige powder in 96% yield.

1H NMR (acetone-d₆, ppm) δ 7.8—6.5 (br. s, ArH), 2.5—1.3 (br. s, CH₂Ph—CH₂). IR (KBr, cm⁻¹) ν 3440 (OH), 3020 (arom C-H), 2920 (aliph C-H), 1730 (C=O), 1600 (arom C=C).

Complex Formation. The 1:1 complexes were prepared by mixing ca. 20 mg of clip molecule (5 × 10⁻⁴ to 10 × 10⁻⁸ mol) and an equimolar amount (between 0.7 and 1.5 mg) of guest (5 × 10⁻⁴ to 10 × 10⁻⁸ mol) in 0.2 mL of CHCl₃. If necessary 1—3 drops of acetone or MeOH was added.²⁰ The solvent was slowly evaporated overnight at 40 °C, and the complexes were dried at room temperature using high vacuum. For the DSC-measurements ca. 10 mg of complex was weighed out in a stainless-steel large volume pan (75 mL). Thermograms were recorded at 10 °C/min. and repeated heating and cooling runs were recorded to study the stability of the complex and all the reproducibility of the measurements. Polarizing microscopy was carried out using the same heating and cooling rates.

Discussion

Synthesis: Receptor Molecule. Clip molecule 1 was synthesized from 2 by an esterification reaction in 57% yield (Scheme 1). Interpretation of the 1H-NMR spectrum of clip 1 was complicated by the fact that this molecule has three conformations (aa, sa, and ss), which interconvert slowly on the NMR time scale. Earlier work performed in our laboratory has shown that the binding of a suitable guest molecule in receptor molecules of type 2 increases the relative amount of the aa conformer, which is the dominant binding conformer.³⁴ We found that upon addition of an excess of resorcinol to a solution of receptor molecule 1, the equilibrium of the conformers was almost completely shifted to the aa conformer. The resonances could be assigned by taking the following points into consideration: (i) the presence of a guest molecule in the cleft will significantly shift the signals, (ii) placing a naphthyl group into the syn orientation will cause a considerable upfield shift of the naphthyl and phenyl signals, due to the ring current effects of these moieties, and (iii) the methylene protons of the sa conformer must give rise to two AX systems with equal intensity.³⁴ The assignments of the most important signals of compound 1 are given in Table 1. These NMR data showed that at 25 °C, 61% of the molecules are in the aa, 33% in the sa, and 6% in the ss conformations. From a 1H NMR titration the association constant for the complex with resorcinol was calculated to be K_d = 400 M⁻¹ and for the complex with methyl 3,5-dihydroxybenzoate (MDB) K_d > 2500 M⁻¹.⁸

Bi- and Tetrafunctional Guest Molecules.⁹ Hydroquinone was used as a spacer in the bifunctional molecule 6 (Scheme 2). This compound was synthesized from 4a and hydroquinone by an esterification reaction using carbon tetrachloride, triphenylphosphine, and triethylamine¹¹ in 61% yield. Removal of the allyl groups yielded 90% of pure guest 6.

Bifunctional guest 8 was synthesized from tartaric acid (Scheme 2). Reaction of 4b, N,N-carbonyldiimidazole, and L-(+)-dioctyl tartrate in toluene afforded the protected guest 7.
Scheme 3

\[
\begin{align*}
3b & \xrightarrow{\text{LiAlH}_4 \text{ reduction}} 10 \\
& \xrightarrow{\text{Wittig reaction}} 12 \\
& \xrightarrow{\text{H}_2 \text{O}} 11 \\
& \xrightarrow{\text{Wittig reaction}} 13 \\
& \xrightarrow{\text{H}_2 \text{O}} 14 \\
\end{align*}
\]

Scheme 4

\[
\begin{align*}
15 & \xrightarrow{\text{HBr}} 16 \\
& \xrightarrow{\text{AcOH}} 18 \\
\end{align*}
\]

Scheme 5

\[
\begin{align*}
18 & \xrightarrow{\text{CCl}_4, \text{PPh}_3} 19 \\
& \xrightarrow{\text{Et}_3\text{N}} 19 \\
& \xrightarrow{\text{HBr, AcOH}} 20 \\
\end{align*}
\]

in 81% yield.\(^{13}\) Deprotection of the benzyl groups was achieved by catalytic hydrogenolysis in ethanol to give 8 in 86% yield.

The synthesis of 2,6-disubstituted tetrphenylporphyrins has been described in the literature.\(^{14}\) The same synthetic route was used for the preparation of the 3,5-disubstituted derivative 9b. Reaction of 3,5-dimethoxybenzaldehyde and pyrrole in propionic acid gave the protected porphyrin 9a in 53% yield. Deprotection of the methoxy groups with boron tribromide in CH\(_2\)Cl\(_2\) yielded the tetrafunctional guest 9b in 94%.

Polyfunctional Guest Molecules. The polyfunctional guest molecules were synthesized by radical polymerization reactions of styrene derivatives. Since phenol and related hydroxy substituted aromatic compounds are known to be inhibitors or retarders of radical polymerizations, protected styrene derivatives were used.\(^{19}\) Starting from 3b, three steps were necessary to synthesize the disubstituted styrene derivative 12 (Scheme 3). Unfortunately, a selective reduction of 3b with diisobutylaluminum hydride in CH\(_2\)Cl\(_2\) did not result in benzaldehyde 11 but in a mixture of benzyl alcohol 10 and starting material. Compound 3b was, therefore, first reduced to benzyl alcohol 10 with lithium aluminum hydride (81% yield) and the latter compound was subsequently oxidized by a Swern oxidation\(^{16}\) to afford benzaldehyde 11 (74% yield). This benzaldehyde could be transformed into styrene 12 by a Wittig reaction with methyltriphenylphosphonium bromide. Compound 14 was synthesized in two steps, viz. benzyl protection of \(p\)-hydroxybenzaldehyde and conversion of the latter into styrene 14 by the Wittig reaction described above with an overall yield of 69% (Scheme 3).

Copolymerization reactions were carried out using styrene (S) and the benzoxystyrene derivatives 12 and 14 as monomers and azobis(isobutyronitrile) (AIBN) as an initiator in butanone at 80 °C (Scheme 4). The results are presented in Table 2. The reaction of the disubstituted styrene 12 and styrene in a 1.2 to 1 ratio produced copolymer 15. The composition of 15, which corresponded to the monomer feed, was determined by elemental analysis. Copolymerization of monosubstituted styrene 14 with styrene (ratio 14/S = 1.4) resulted in the formation of 17. As can be seen in Table 2, copolymer 17 contains 2.6 repeat units of 14 for every styrene unit. Apparently, styrene derivative 14 is more reactive in the copolymerization reaction than styrene itself. The molecular weight (\(M_w\)) and molecular weight distribution (\(M_w/M_n\)) were determined by gel permeation chromatography (GPC). The results are also given in Table 2. Deprotection of the benzyl groups of the polymers appeared to be very difficult and only starting material was recovered after catalytic hydrogenolysis or reaction with trimethylsilyl iodide. We succeeded in achieving quantitative deprotection by treating copolymers 15 and 17 with HBr in acetic acid. Copolymers 16 and 18 were isolated by precipitation.

Copolymer 18 was esterified with 3,5-bis(benzoxly)benzoic acid derivative 4b using the PPh\(_3\)/CCl\(_4\) method described above for compound 5 (Scheme 5). The yield of the esterification reaction was calculated from the elemental analysis of the resulting polymer 19. It was estimated that 40% of the hydroxyl functions had reacted. Quantitative removal of the benzyl groups of 19 with hydrobromic acid in acetic acid was possible without noticeable hydrolysis of the ester functions in copolymer 20.

Table 2. Results of Copolymerization Reactions of Styrene and Styrene Derivatives. Composition and Physical Properties of the Copolymers\(^{a}\)

<table>
<thead>
<tr>
<th>comonomer</th>
<th>comonomer ratio (BS:S)</th>
<th>polymer</th>
<th>polymer yield (%)</th>
<th>composition of polymer(^{b}) (X:1–X)</th>
<th>(M_w)</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.55:0.45</td>
<td>15</td>
<td>85</td>
<td>0.55:0.45</td>
<td>35500</td>
<td>2.26</td>
</tr>
<tr>
<td>14</td>
<td>0.58:0.42</td>
<td>17</td>
<td>90</td>
<td>0.72:0.28</td>
<td>22000</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19</td>
<td></td>
<td></td>
<td>24000</td>
<td>2.38</td>
</tr>
</tbody>
</table>

\(^{a}\) S = styrene, BS = benzyl protected styrene derivative. \(^{b}\) Determined by elemental analysis, X = BS. \(^{c}\) Determined by GPC.
of the melting point, whereas a large decrease of the clearing
smectic phases. At higher concentrations of guest only a
change this behavior and to induce reversible liquid-crystalline
crystallization, a monotropic liquid crystalline phase with a
appearance of different mesophases covering a wide temperature
range as shown in Figure 4 and Table 3. At low concentrations
the complexation of mono-, bi-, tetra-, and polyfunctional guest
molecules on the mesogenic properties of receptor molecule
was found to
termination, the hydroquinone spacer in
anisotropic phase. (B) Influence of the host—guest ratio on
the liquid-crystalline behavior of the complex.

**Table 3. Phase Transition Temperatures and Enthalpy Changes of Liquid-Crystalline Complexes of 1 and Different Guest Molecules**

<table>
<thead>
<tr>
<th>guest</th>
<th>host—guest ratio</th>
<th>transition</th>
<th>temp (°C)</th>
<th>ΔH (kJ/mol)</th>
</tr>
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<tbody>
<tr>
<td>MDB</td>
<td>10:1</td>
<td>K → S</td>
<td>0 [−8]</td>
<td>58.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S → S'</td>
<td>95 [86]</td>
<td>1.0</td>
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<tr>
<td></td>
<td></td>
<td>S' → I</td>
<td>144 [136]</td>
<td>5.9</td>
</tr>
<tr>
<td>MDB</td>
<td>10:2</td>
<td>K → S</td>
<td>−1 [−8]</td>
<td>50.6</td>
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<tr>
<td></td>
<td></td>
<td>S → S'</td>
<td>84 [78]</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S' → I</td>
<td>141 [133]</td>
<td>5.3</td>
</tr>
<tr>
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<td>45.6</td>
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<tr>
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<td></td>
<td>S → S'</td>
<td>82 [74]</td>
<td>2.1</td>
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<tr>
<td></td>
<td></td>
<td>S' → I</td>
<td>131 [127]</td>
<td>3.8</td>
</tr>
<tr>
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<td>−4 [−12]</td>
<td>29.5</td>
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<td>6</td>
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<td>K → S</td>
<td>49</td>
<td>123.7</td>
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<tr>
<td></td>
<td></td>
<td>S → S'</td>
<td>90</td>
<td>12.4</td>
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<tr>
<td></td>
<td></td>
<td>S' → I</td>
<td>157</td>
<td>24.8</td>
</tr>
<tr>
<td>8</td>
<td>2:1</td>
<td>K → S</td>
<td>18 [4]</td>
<td>135.5</td>
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<tr>
<td></td>
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<td>S' → I</td>
<td>133 [127]</td>
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<td>1:1</td>
<td>K → S'</td>
<td>12 [−2 ]</td>
<td>66.2</td>
</tr>
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<td></td>
<td></td>
<td>S' → I</td>
<td>114 [99]</td>
<td>6.8</td>
</tr>
<tr>
<td>16</td>
<td>1:2</td>
<td>K → D</td>
<td>21 [10]</td>
<td>73.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D → D'</td>
<td>86 [75]</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D' → I</td>
<td>131 [118]</td>
<td>4.8</td>
</tr>
<tr>
<td>20</td>
<td>1:1</td>
<td>K → D'</td>
<td>30 [19]</td>
<td>75.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D' → I</td>
<td>141 [129]</td>
<td>7.0</td>
</tr>
</tbody>
</table>

* Determined by DSC. K, crystalline phase; S, smectic phase. N, nematic phase. D, discotic phase; I, isotropic phase. The values in
square brackets are obtained from cooling runs. Structural assignments are based on polarizing microscopy measurements.
* Ratio 1/modifed and unmodified 4-HS = 1:1. * Per mole repeating unit (mru) of the polymer that contains one receptor molecule.

**Induction of Liquid Crystallinity by Host—Guest Interactions**

Compound 1 displayed, in the first and subsequent heating and cooling runs, a reversible K → I transition at 159–164 °C. Utilizing fast cooling to prevent crystallization, a monotropic liquid crystalline phase with a clearing temperature of 161 °C was observed. The binding of a dihydroxybenzene derivative in the cleft of 1 was found to change this behavior and to induce reversible liquid-crystalline behavior. An enhancement of the stability of the complex could be achieved by introducing a more flexible connection, a chiral spacer derived from 1-(+)-dioctyl tartrate, between the resorcinol

point is observed. Apparently, complexation of guest molecules in the cleft of 1 influences to an appreciable extent the stacking of the rigid central frameworks of the molecules, but has almost no effect on the packing of the alkyl chains, and consequently has almost no influence on the melting point.

**Bifunctional Guest Molecules.** The bifunctional guest 6 contains two resorcinol groups, which are linked by a rigid spacer. A 1:1 complex of this molecule with receptor 1 displayed in the first heating run two smectic phases between 49 and 157 °C (Table 3). During the subsequent cooling and heating runs the complex decomposed and only crystalline material of the uncomplexed host and guest was left. Apparently, the hydroquinone spacer in 6 has an unfavorable influence on the stability of the liquid-crystalline complex. To prove that this instability originates from the rigidity of the spacer rather than from substitution of the phenyl ring itself, a 1:1 complex of 1 and phenyl 3,5-dihydroxybenzoate, the monomeric analogue of 6, was prepared. Two reversible smectic-like phases (birefringent mosaic type textures, T142M1103M2) were observed for this complex by polarizing microscopy.

An enhancement of the stability of the complex could be achieved by introducing a more flexible connection, a chiral spacer derived from 1-(+)-dioctyl tartrate, between the resorcinol
functions in the guest (compound 8). Addition of receptor molecule 1 to 8 in a 2:1 host–guest ratio led to the formation of a complex, which displayed two reversible liquid-crystalline phases: a smectic phase between 18 and 111 °C and another smectic phase of lower order between 111 and 133 °C (Table 3). The objective of using the chiral diocetyl tartrate spacer was to induce chirality at the macroscopic level, but unfortunately, no chiral textures were observed (Figure 5). For this guest molecule we also studied the influence of the host–guest ratio on the liquid-crystalline properties of the complex. The 1:1 complex exhibited only one liquid-crystalline phase between 12 and 114 °C, which corresponds with the lower ordered mesomtic phase of the 2:1 complex. As can be seen from Table 3 and Figure 5 the complexation of more than one molecule of 1 to 8 hardly influences the melting point, whereas the clearing point is strongly affected.

**Tetrafunctional Guest Molecule.** The tetrafunctional guest molecule was a porphyrin modified at the meso positions with 3,5-dihydroxyphenyl groups (9b). When four receptor molecules 1 were bound to porphyrin 9b, two almost identical smectic-like phases were generated, after the first heating and cooling run. These phases were separated by a transition with a small enthalpy change at ca. 127 °C (Table 4). To show that binding in the cleft is necessary for inducing the mesogenic properties we also used a porphyrin modified with 2,6-dihydroxyphenyl groups.11 Because of steric constraints this porphyrin is not able to form hydrogen bonds with the carbonyl functions in the cleft of molecular clip 2. With the 2,6-disubstituted porphyrin no liquid-crystalline behavior could be observed.

We also studied complexes of porphyrin 9b with different equivalents of receptor molecule 1 (Table 4). The 3:1 host–guest complex as well as the 1:1 complex initially displayed a phase transition to the isotropic liquid at ca. 200 °C (ΔH > 50 kJ/mol). In the subsequent cooling and heating runs of the 3:1 complex a similar behavior was observed as for the 4:1 complex (Table 4). In the case of the 1:1 complex more heating runs were required than in the case of the 3:1 complex to achieve this behavior (see Figure 6a–c). The polarizing microscopy results in combination with the large enthalpy changes (Table 4) in DSC suggest that the transitions at 157 and ca. 200 °C are crystal to isotropic liquid transitions. Apparently, crystalline complexes are initially formed, which after repetitive heating and cooling cycles disappear at the expense of the formation of the mesophases of the 4:1 complex and free porphyrin. This suggests that the porphyrin, which is completely surrounded by clip molecules, possesses an enhanced stability. A computer generated drawing of the supramolecular complex is presented in Figure 7.

**Polyfunctional Guest Molecules.** Stimulated by the results obtained with the low molecular weight guest molecules we investigated the possibilities of inducing liquid crystallinity in polymers. The complex of copolymer 20 (21 mol% of 1,3-di­hydroxybenzene functions) with molecular clip 1 (ratio 1/modified and unmodified 4-HS = 1:1) was found to give a very stable liquid-crystalline phase from 30 to 141 °C (Table 3) with a discotic-like (fan-shaped) texture (Figure 8), which was clearly different from the smectic-like (mosaic type) textures of the complexes of 1 with the low molecular weight guests. Complexation to the polymer chains probably induces a change

### Table 4. Phase Transition Temperatures and Enthalpy Changes of Different Host–Guest Complexes of 1 and Porphyrin 9b

<table>
<thead>
<tr>
<th>Host:Guest Ratio</th>
<th>Run</th>
<th>T (°C)</th>
<th>ΔH (kJ/mol)</th>
<th>T (°C)</th>
<th>ΔH (kJ/mol)</th>
<th>T (°C)</th>
<th>ΔH (kJ/mol)</th>
<th>T (°C)</th>
<th>ΔH (kJ/mol)</th>
<th>T (°C)</th>
<th>ΔH (kJ/mol)</th>
<th>T (°C)</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>1</td>
<td>17 [5]</td>
<td>157.4</td>
<td>127 [115]</td>
<td>2.50</td>
<td>149 [132]</td>
<td>27.0</td>
<td>157</td>
<td>74.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>13 [2]</td>
<td>73.9</td>
<td>150 [121]</td>
<td>5.81</td>
<td>197 [136]</td>
<td>8.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>14</td>
<td>53.8</td>
<td>128</td>
<td>0.61</td>
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<td>2.98</td>
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</tbody>
</table>

* Determined by DSC. The values in square brackets are obtained from cooling runs. a K → S transition. b S → S' transition. c S' → I transition. d K → 1 transition.
Figure 8. The discotic-like (fan-shaped) texture observed at 120 °C, viewed under the polarizing microscope during a cooling run from the isotropic liquid (top) and a thermogram of the complex of polymeric guest molecule 20 with clip 1 (bottom), showing the K → D' and the D' → I transitions in the heating (top) trace and the reversed events in the cooling (bottom) trace.

in the conformation of the clip molecules in such a way that their trialkoxybenzoyl groups adopt a more spread out arrangement, resulting in an overall taper-shaped structure for these molecules. The taper-shaped clip molecules may surround the polystyrene chains in a cylindrical fashion.\textsuperscript{21} X-ray studies are underway to further investigate the structure of the complex.

In copolymer 16 the dihydroxybenzene (DHB) moieties are directly attached to the polymer backbone. When receptor molecule 1 was added to polymer 16 in a 1:1 ratio (based on the number of 3,5-dihydroxybenzene units in 16) the DSC thermogram showed the presence of free receptor molecules 1. A 1:2 complex (clip 1: DHB units) was, therefore, prepared, which resulted in the induction of reversible liquid-crystalline phases, \emph{viz.} from 21 to 86 °C and from 86 to 131 °C. The former phase was a more highly ordered one. Its texture resembled a crystalline phase, but the value of the enthalpy change measured by DSC was more in line with a liquid-crystalline phase. The high temperature liquid-crystalline phase displayed a discotic-like texture, similar to the polymer complex described above.

Conclusions

In summary we have shown that molecular recognition can be used as a tool to provide molecules with interesting materials properties. Similar results have been obtained recently by other groups.\textsuperscript{7} The binding of a guest to receptor molecule 1 leads to the induction of liquid crystallinity. Compound 1 consists of a mixture of three conformers. The guest changes the equilibrium of the conformers and, in this way, probably tunes the properties of the material. Experiments with complexes having different ratios of host and guest show that complexation of the guest molecule affects the clearing, but not the melting temperature of the material. This suggests that guest molecules have an effect on the packing of the rigid central frameworks of the host molecules and not on the packing of the alkyl chains. The results described here indicate that the concept of introducing liquid crystalline properties by host–guest interactions is very general and can be applied to both low molecular weight and polymeric guest molecules.