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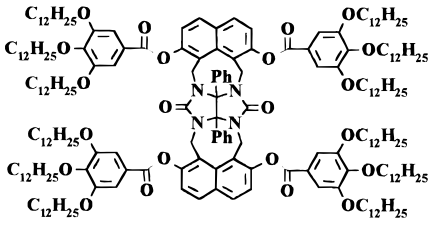
Abstract: A molecular clip is described which binds aromatic guests by an induced fit mechanism. It contains twelve long aliphatic chains and can evoke liquid-crystalline properties in a variety of molecules, including polymers and porphyrins, by a process of molecular recognition.

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.[1] Current efforts are directed toward the design of more sophisticated host molecules which can bind guests by an induced fit or allosteric mechanism.[2−4] 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 work presented in this paper. In a number of recent studies the binding of protein molecules to specific domains of nucleic acid chains has been described.[5] Some of these proteins are dimers having the shape of a super clip or super tweezer, as in the case of the Gene V protein encoded by the bacteriophage M13, which binds to single stranded DNA chains and changes the physical properties of these biomolecules (Figure 1).[6] This particular example from nature inspired us to design a synthetic clip molecule (**1**) which can bind to a polymer chain by an induced fit mechanism. The intention was to change the properties of the polymer, *i.e.* to make it liquid crystalline.[7]



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The compound (**2**, Scheme 1) from which **1** is synthesized has been described previously.[3,4] Its most important structural features are a concave framework composed of two urea units and two methylene linked aromatic walls. The molecules of compound **2** exist in three different conformations (Figure 2): *anti-anti (aa), syn-anti (sa),* and *syn-syn (ss).* The conformers differ in the way the walls are oriented relative to the phenyl groups of the diphenylglucoluril part. The molecules change from one conformation to another by the flipping of one naphthalene wall. Guest molecules can be clamped between the walls and held by $\pi-\pi$ stacking interactions and hydrogen bonding to the urea carbonyl functions. Binding occurs by an induced fit mechanism: one of the walls of **2** flips up to form a cleft which accommodates the guest.[4]

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).[8]

Experimental Section

General Methods. Acetonitrile and CH_2Cl_2 were distilled from CaH_2, diethyl ether and tetrahydrofuran (THF) from $LiAlH_4$, and toluene from sodium. Dimethyl sulfoxide (DMSO) was dried over CaH_2. 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 60H were used. Melting points were measured with a Jeneval polarizing microscope connected to a Linkam THMS 600 hot stage. ^{1}H 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 λ-5 UV−vis photospectrometer 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 μL). 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 PL-GEL 352 column using tetrahydrofuran as the eluent and different polystyrenes as standards.

17b,17c-Dihydro-1,6,10,15-tetrakis(3,4,5-tris(dodecyloxy)benzoyloxy)-17b,17c-diphenyl-7*H*,8*H*,9*H*,16*H*,17*H*,18*H*-7a,8a,16a,17a-

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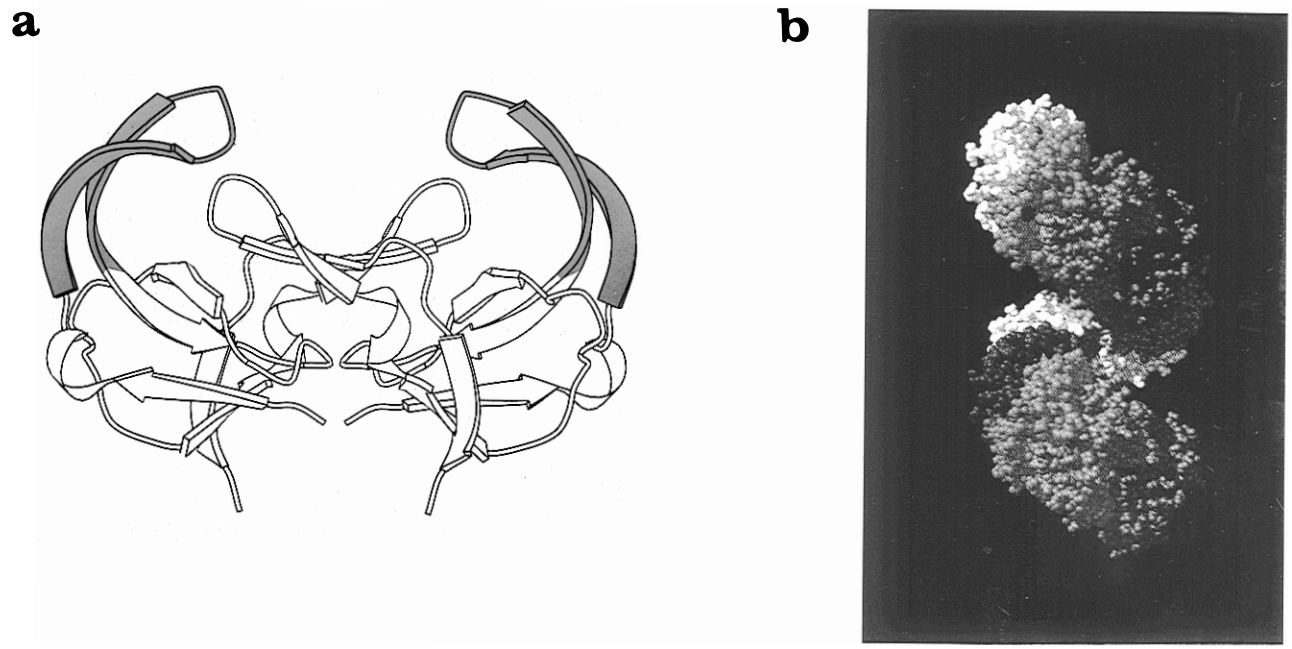

Figure 1. (a) Structure of the Gene V protein. (b) Complex of twelve protein molecules and a DNA chain (see ref 6).

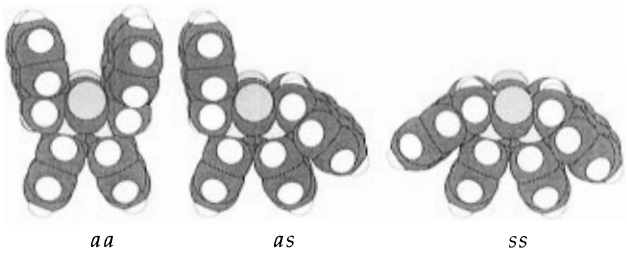

Figure 2. Structures of the three conformers of **2.**

tetraazapentaleno[1″,6″:5,6,7;3″,4″:5′,6′,7′]dicycloocta[1,2,3-*de*:1′,2′,3′-*d*′*e*′]dinaphthalene-8,17-dione (1). Receptor molecule **2**[4] (*n* mmol) and NaH (10*n* mmol) were refluxed in THF (10*n* mL) and after 1 h 3,4,5-tris(dodecyloxy)benzoyl chloride[9] (4.4 equiv) in a mixture of THF/CH_2Cl_2 (1:1 v/v, 5*n* 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 $CHCl_3$. The organic layer was extracted (2×) with aqueous 1 N HCl, then with H_2O, and dried ($MgSO_4$). The crude product was subjected to flash column chromatography (eluent ethyl acetate−hexane 1:25 v/v). Yield 57%. K to I transition at 159−162 °C.

^{1}H NMR ($CDCl_3$, ppm) [see Table 1 for uncomplexed host, host−guest complex]: δ host 7.67 (s, 8H, Ar*H*(OR)$_3$), 7.44 and 6.99 (2d, 8H, naph-*H*, J = 8.9 Hz), 7.11−7.05 (m, 6H, Ar*H*), 6.94 (d, 4H, Ar*H*), 5.41 and 4.14 (2d, 8H, NCH*H*Ar, J = 16.8 Hz), 4.12−3.84 (m, 24H, OCH_2), 1.84−1.08 (m, 240H, OCH$_2$(CH_2)$_{10}$CH$_3$), 1.04−0.80 (m, 36H, CH_3), guest (resorcinol) 6.90 (t), 6.21 (dd), 5.75 (br s), 5.49 (s). Anal. ($C_{212}H_{334}N_4O_{22}$) 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 K_2CO_3 (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 CH_2Cl_2. The organic layer was washed with water (2×), dried ($MgSO_4$), 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.

^{1}H NMR ($CDCl_3$, ppm) δ 7.1 (s, 2H, Ar*H*), 6.6 (s, 1H, Ar*H*), 6.2−5.7 (m, 2H, C*H*═CH$_2$), 5.4−5.1 (m, 4H, CH═CH_2), 4.5 (d, 4H, OCH_2, J = 6 Hz), 3.9 (s, 3H, OCH_3). IR (KBr, cm^{-1}) ν 3150−3050 (arom C−H), 2980−2880 (aliph C−H), 1730 (C═O), 1600 (arom C═C). MS (EI, *m*/*z*): 248 (M)$^+$, 233 (M − CH$_3$)$^+$, 189 (M − COOCH$_3$)$^+$, and 41 (allyl)$^+$. Anal. ($C_{14}H_{16}O_4$) C, H: calcd 67.73, 6.50; found 67.74, 6.44.

Methyl 3,5-Bis(benzyloxy)benzoate (3b). A mixture of methyl 3,5-dihydroxybenzoate (5.0 g, 30 mmol), benzyl bromide (15.2 g, 89 mmol), and K_2CO_3 (11.7 g) in acetone (50 mL) was refluxed overnight. The inorganic salts were filtered off and washed with $CHCl_3$. The solution and the $CHCl_3$ extracts were combined and evaporated to dryness. The residue was crystallized from diisopropyl ether to give the methyl benzoate **3b** in 97% yield. Mp 70 °C.

^{1}H NMR ($CDCl_3$, ppm) δ 7.50−7.22 (m, 12H, Ar*H*), 6.80 (t, 1H, Ar*H*, J = 2 Hz), 5.06 (s, 4H, CH_2Ph), 3.90 (s, 3H, OCH_3). IR (KBr, cm^{-1}) ν 3120−2980 (arom C−H), 2980−2800 (aliph C−H), 1715 (C═O), 1600 (arom C═C). MS (EI, *m*/*z*): 348 (M)$^+$, 317 (M − OCH$_3$)$^+$, 181, and 91 (CH$_2$Ph)$^+$. Anal. ($C_{22}H_{20}O_4$) C, H: calcd 75.85, 5.79; found 75.65, 5.75.

3,5-Bis(allyloxy)benzoic Acid (4a). A mixture of methyl benzoate **3a** (1.0 g, 4.0 mmol) and powdered 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 (2×) and dried ($MgSO_4$), and the solvent was evaporated. Crystallization from ethanol yielded 60% of the benzoic acid **4a**. Mp 71 °C.

^{1}H NMR ($CDCl_3$, ppm) δ 7.3 (s, 2H, Ar*H*), 6.8 (s, 1H, Ar*H*), 6.4−5.8 (m, 2H, C*H*═CH$_2$), 5.6−5.2 (m, 4H, CH═CH_2), 4.5 (d, 4H, OCH_2, J = 6 Hz). IR (KBr, cm^{-1}) ν 2900 (COOH), 1690 (C═O), 1600 (arom C═C). MS (EI, *m*/*z*): 234 (M)$^+$, 189 (M − COOH)$^+$, and 41 (allyl)$^+$. Anal. ($C_{13}H_{14}O_4$) C, H: calcd 66.66, 6.02; found 66.73, 6.04.

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.

^{1}H NMR ($CDCl_3$ + CD_3OD, ppm) δ 7.5−7.1 (m, 12H, Ar*H*), 6.7 (s, 1H, Ar*H*), 5.0 (s, 4H, CH_2Ph). IR (KBr, cm^{-1}) ν 2880 (COOH), 1690 (C═O), 1600 (arom C═C). MS (EI, *m*/*z*): 334 (M)$^+$, 181, and 91 (CH$_2$Ph)$^+$. Anal. ($C_{22}H_{20}O_2$) C, H: calcd 75.43, 5.43; found 75.24, 5.44.

1,4-Bis[3,5-bis(allyloxy)benzoyloxy]benzene (5). For the synthesis of this compound a procedure described by Hashimoto *et al.* was

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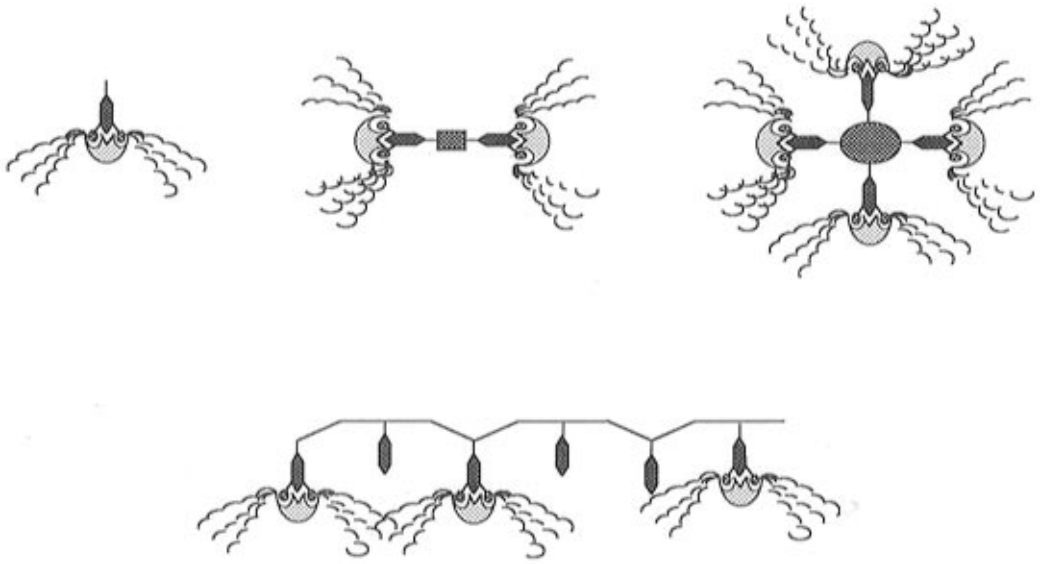

Figure 3. Schematic representation of the liquid crystalline complexes that can be obtained from clip molecules **1** and different types of guest molecules.

followed.[11] 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 CCl_4 (0.52 mL, 5.4 mmol), Et_3N (0.69 mL, 5.0 mmol), and PPh_3 (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 $CHCl_3$. The organic layer was extracted with aqueous 1 N HCl (2×), aqueous 1 N NaOH (2×), and water (1×) and dried ($MgSO_4$). After evaporation of the solvent, 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.

^{1}H NMR ($CDCl_3$, ppm) δ 7.36 (d, 4H, $(AllylO)_2ArH$, J = 2 Hz), 7.27 (s, 4H, Ar*H*), 6.78 (t, 2H, $(AllylO)_2ArH$, J = 2 Hz), 6.22−5.89 (m, 4H, C*H*═CH_2), 5.52−5.27 (m, 8H, CH═CH_2), 4.60 (d, 8H, OCH_2, 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*): 542 $(M)^+$, 217 $(COAr(OAllyl)_2)^+$, and 41 $(allyl)^+$. Anal. ($C_{32}H_{30}O_8$) C, H: calcd 70.84, 5.57; found 70.58, 5.53.

1,4-Bis[3,5-dihydroxybenzoyloxy]benzene (6). To a suspension of compound **5** (0.53 g, 0.97 mmol) in acetonitrile/water (4:1, v/v, 50 mL) were added triethylammonium formate (0.45 g, 3.0 mmol), PPh_3 (52 mg, 0.19 mmol), and $Pd(OAc)_2$ (8.0 mg, 3.6×10^{-2} mmol),[12] and the mixture was refluxed for 2.5 h. Workup was accomplished by evaporation of the solvent under reduced pressure. The residue was dissolved in ethyl acetate and washed with water. The organic layer was dried ($MgSO_4$) and evaporated *in vacuo*. After purification by flash column chromatography (eluent ethyl acetate−hexane 2:1 v/v) and precipitation of an acetone solution of **6** in water, the product was obtained in 90% yield. Mp >290 °C dec.

^{1}H NMR (acetone-d_6, ppm) δ 7.23 (s, 4H, Ar*H*), 7.04 (d, 4H, $(HO)_2$-Ar*H*, J = 2 Hz), 6.55 (t, 2H, $(HO)_2ArH$, J = 2 Hz). IR (KBr, cm^{-1}) ν 3440 (OH), 1720 (C═O), 1620 (arom C═C). FAB-MS (*m*-nitrobenzyl alcohol, *m*/*z*): 383 $(M + 1)^+$, and 137 $(COAr(OH)_2)^+$. Anal. ($C_{20}H_{14}O_8$) C, H: calcd 62.83, 3.69; found 62.58, 3.89.

L-(+)-Dioctyl Tartrate. A solution of L-(+)-tartaric acid (7.69 g, 50.6 mmol) and concentrated aqueous HCl (1.5 mL) in octanol (100 mL) was heated at 80 °C overnight. The excess of octanol was distilled off under high vacuum and the crude product was purified by column chromatography (eluent: ethyl acetate−hexane 1:3 v/v), which yielded 83% of L-(+)-dioctyl tartrate as white needles. Mp 41 °C.

^{1}H NMR ($CDCl_3$, ppm) δ 4.54 (d, 2H, C*H*OH, J = 7 Hz), 4.26 (t, 4H, OCH_2CH_2), 3.21 (d, 2H, CHO*H*, J = 7 Hz), 1.90−1.10 (m, 24H, $OCH_2(CH_2)_6$), 0.88 (t, 6H, CH_2CH_3). IR (KBr, cm^{-1}) ν 3300 (OH), 3020−2800 (aliph C−H), 1750 and 1720 (C═O). MS (CI, *m*/*z*): 375 $(M + 1)^+$, 263 $(M + 1 - C_8H_{16})^+$, 151 $(M + 1 - 2*C_8H_{16})^+$. Anal. ($C_{20}H_{38}O_6$) C, H: calcd 64.14, 10.23; found 64.33, 10.10. $[\alpha]_D^{20}$ = +8.3° (*c* 0.5, EtOH).

Dioctyl (2*R*,3*R*)-*O*-Bis[3,5-bis(benzyloxy)benzoyl]tartrate (7). This compound was synthesized according to a literature procedure.[13] A solution of **4b** (110 mg, 0.3 mmol) and *N*,*N*-carbonyldiimidazole (67 mg, 0.5 mmol) in dry toluene was stirred overnight at room temperature. Subsequently dioctyl tartrate (60 mg, 0.16 mmol) was added to this solution. After 6 days the solvent was evaporated and the residue was dissolved in CH_2Cl_2. The organic layer was washed with water (2×), dried ($MgSO_4$), 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.

^{1}H NMR ($CDCl_3$, ppm) δ 7.3 (s, 20H, Ar*H*), 7.1 (s, 4H, Ar(C═O)-*H*), 6.7 (s, 2H, $Ar(OBz)_2H$), 5.9 (s, 2H, C*H*(OCOAr)), 5.0 (s, 8H, CH_2-Ph), 4.1 (m, 4H, OCH_2CH_2), 1.8−1.0 (m, 24H, C_6H_{12}), 0.8 (t, 6H, OCH_2CH_3). FAB-MS (*m*-nitrobenzyl alcohol, *m*/*z*): 1006 $(M + H)^+$, 915 $(M - CH_2Ph)^+$. $[\alpha]_D^{20}$ −26.6° (*c* 0.6, $CHCl_3$).

Dioctyl (2*R*,3*R*)-*O*-Bis(3,5-dihydroxybenzoyl)tartrate (8). Compound **7** (33 mg, 3.3×10^{-5} mol) was suspended in ethanol (20 mL) and subjected overnight to hydrogenation using palladium on carbon as a catalyst. The catalyst was filtered off and the solvent was evaporated under reduced pressure. The residue was extracted with ethyl acetate, and the organic layer was washed with water, dried ($MgSO_4$), and concentrated to afford **8** as a light yellow oil in 86% yield.

^{1}H NMR (acetone-d_6, ppm) δ 6.94 (s, 4H, Ar*H*), 6.51 (s, 2H, Ar*H*), 5.81 (s, 2H, C*H*$COOC_8H_{17}$), 3.6 (br s, 4H, O*H*), 4.23−3.75 (m, 4H, OCH_2CH_2), 1.6−0.8 (m, 24H, C_6H_{12}), 0.71 (t, 6H, CH_2CH_3). FAB-MS (*m*-nitrobenzyl alcohol, *m*/*z*): 647 $(M + H)^+$, 493 $(M - OCOAr(OH)_2)^+$. $[\alpha]_D^{20}$ −32.7° (*c* 0.7, $CHCl_3$).

5,10,15,20-Tetrakis(3,5-dimethoxyphenyl)porphyrin, H_2($T_{3,5}$diMeOPP) (9a). This compound was synthesized according to a literature procedure[14] from 3,5-dimethoxybenzaldehyde (2.48 g, 14.9 mmol) and pyrrole (1.0 mL, 14.4 mmol) in propionic acid (150 mL) as the solvent. The product was purified by column chromatography (eluent: ethyl acetate−hexane 1:1 v/v) and obtained in 53% yield. Mp >300 °C dec.

^{1}H NMR ($CDCl_3$, ppm) δ 9.0 (s, 8H, pyrrole-*H*), 7.4 (d, 8H, Ar*H*, J = 2 Hz), 6.9 (t, 4H, Ar*H*, J = 2 Hz), 4.0 (s, 24H, OCH_3), −2.8 (br

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s, 2H, N*H*). IR (KBr, cm^{-1}) ν 2950 (aliph C−H), 1600 (arom C═C), 1220 (C−O). FAB-MS (*m*-nitrobenzyl alcohol, *m*/*z*): 855 $(M + H)^+$, 824 $(M + 1 - OCH_3)^+$. UV−vis (CH_2Cl_2, λ/nm, log(ϵ/L·mol^{-1}·cm^{-1}): 419 (3.1), 514 (2.6), 549 (2.0), 588 (2.0), 645 (1.8).

5,10,15,20-Tetrakis(3,5-dihydroxyphenyl)porphyrin, H_2(T$_{3,5}$diHOPP) (9b). This compound was synthesized according to a literature procedure[14] from **9a** (0.85 g, 1.0 mmol) and BBr_3 (0.8 mL, 8.5 mmol) in CH_2Cl_2 (80 mL) as the solvent. Porphyrin **9b** was obtained in 94% yield. Mp >300 °C dec.

^{1}H NMR (acetone-d_6, ppm) δ 8.9 (s, 8H, pyrrole-*H*), 7.11 (d, 8H, Ar*H*, J = 2 Hz), 6.71 (t, 4H, Ar*H*, J = 2 Hz), −3.0 (br s, 2H, N*H*). IR (KBr, cm^{-1}) ν 3300 (OH), 1600 (arom C═C). FAB-MS (*m*-nitrobenzyl alcohol, *m*/*z*): 743 $(M + H)^+$. UV−vis (MeOH, λ/nm, log(ϵ/l·mol^{-1}·cm^{-1}): 417 (6.1), 512 (5.4), 547 (4.9), 587 (4.9), 644 (4.6).

[3,5-Bis(benzyloxy)phenyl]methanol (10). Under an argon atmosphere a solution of **3b** (2.8 g, 8.0 mmol) in diethyl ether (20 mL) was carefully added to a suspension of $LiAlH_4$ (780 mg) in diethyl ether (100 mL). The reaction mixture was refluxed for 24 h and afterwards cooled down to −78 °C. After the addition of water (20 mL) the mixture was allowed to warm up and was acidified with concentrated aqueous HCl. The organic layer was washed with aqueous 1 N HCl (2×) an aqueous saturated $NaHCO_3$ solution (1×), dried ($MgSO_4$), and concentrated until the crystallization started. In this way white needles were obtained in 81% yield. Mp 77 °C.

^{1}H NMR ($CDCl_3$, ppm) δ 7.4 (s, 10H, Ar*H*), 6.8−6.5 (m, 3H, Ar*H*), 5.0 (s, 4H, CH_2Ph), 4.6 (s, 2H, CH_2OH), 1.9 (br s, 1H, O*H*). IR (KBr, cm^{-1}) ν 3300 (OH), 3100−2980 (arom C−H), 2960−2800 (aliph C−H), 1590 (arom C═C). MS (EI, *m*/*z*): 320 $(M)^+$, 181, and 91 $(CH_2Ph)^+$. Anal. ($C_{21}H_{20}O_3$) C, H: calcd 78.73, 6.29; found 78.47, 6.27.

3,5-Bis(benzyloxy)benzaldehyde (11). This compound was prepared according to a literature procedure.[15] To a cooled solution (−78 °C) of oxalyl chloride (715 mg, 5.7 mmol) in dry CH_2Cl_2 (14 mL) was added, under an argon atmosphere and over a period of 5 min, a solution of dry DMSO (940 mg, 15.7 mmol) in CH_2Cl_2 (3 mL). After 10 min a solution of **10** (1.7 g, 5.2 mmol) in CH_2Cl_2 (5 mL) was added dropwise over a period of 5 min, and after 15 min Et_3N (3.7 mL) was added, also over a period of 5 min. The reaction mixture was allowed to warm up to room temperature and water (16 mL) was added. The organic layer was washed with water (2×), dried ($MgSO_4$), and evaporated to dryness *in vacuo*. Crystallization from hexane yielded 74% of the benzaldehyde **11**. Mp 79 °C.

^{1}H NMR ($CDCl_3$, ppm) δ 9.8 (s, 1H, C*H*O), 7.5−7.0 (m, 13H, Ar*H*), 5.1 (s, 4H, CH_2Ph). IR (KBr, cm^{-1}) ν 3150−3050 (arom C−H), 1690 (CH═O), 1600 (arom C═C). MS (EI, *m*/*z*): 318 $(M)^+$, 181, and 91 $(CH_2Ph)^+$. Anal. ($C_{21}H_{18}O_3$) C, H: calcd 79.23, 5.70; found 79.10, 5.65.

1,3-Bis(benzyloxy)-5-vinylbenzene (12). Under an argon atmosphere at −10 °C a solution of buthyllithium in hexane (0.5 mL of a 1.6 M solution, 0.8 mmol) was added to a solution of methyltriphenylphosphonium bromide (289 mg, 0.78 mmol) in dry THF (5 mL). After the mixture was stirred for 15 min a solution of 3,5-bis(benzyloxy)benzaldehyde (196 mg, 0.63 mmol) in THF (2 mL) was added. After another 2 h at room temperature water (3 mL) was added. The solvent was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2. The organic layer was washed with water (2×), dried ($MgSO_4$), and evaporated under reduced pressure. The product was purified by column chromatography (eluent: ethyl acetate−hexane 1:5 v/v) and obtained in 87% yield. Mp 46 °C.

^{1}H NMR ($CDCl_3$, ppm) δ 7.5−7.2 (m, 10H, Ar*H*), 6.9−6.6 (m, 3H, Ar*H*), 6.6−6.5 (m, 1H, C*H*═CH_2), 5.8−5.1 (m, 2H, CH═CH_2), 5.0 (s, 4H, CH_2Ph). IR (KBr, cm^{-1}) ν 3020 (arom C−H), 2940 (aliph C−H), 1600 (conj C═C), 1590 (arom C═C). MS (EI, *m*/*z*): 316 $(M)^+$, 225 $(M - CH_2Ph)^+$, 181, and 91 $(CH_2Ph)^+$. Anal. ($C_{22}H_{20}O_2$) C, H: calcd 83.52, 6.37; found 83.42, 6.37.

4-Benzyloxybenzaldehyde (13). This compound was synthesized as described for **3b**, using 4-hydroxybenzaldehyde (1.11 g, 9.1 mmol), benzyl bromide (1.98 g, 11.6 mmol), and K_2CO_3 (1.52 g, 11.0 mmol) in acetone (100 mL) as the solvent. Purification by column chromatography (eluent: ethyl acetate−hexane 1:10 v/v) and subsequent crystallization from methanol yielded 78% of the protected benzaldehyde. Mp 72 °C (lit.[16] mp 72 °C).

^{1}H NMR ($CDCl_3$, ppm) δ 9.9 (s, 1H, C*H*O), 7.6 and 7.0 (2*d, 4H, Ar(CHO)*H*, J = 9 Hz), 7.3 (s, 5H, Ar*H*), 5.1 (s, 2H, OCH_2). IR (KBr, cm^{-1}) ν 3120−3000 (arom C−H), 2960−2730 (aliph C−H), 1690 (CH═O), 1595 (arom C═C). MS (EI, *m*/*z*): 212 $(M)^+$, 91 $(CH_2Ph)^+$. Anal. ($C_{14}H_{12}O_2$) C, H: calcd 79.23, 5.70; found 79.17, 5.72.

1-Benzyloxy-4-vinylbenzene (14). This compound was synthesized as described for compound **12**, using methyl triphenylphosphonium bromide (2.84 g, 7.8 mmol), a solution of butyllithium in hexane (4.9 mL of a 1.6 M solution, 7.8 mmol), and 4-benzyloxybenzaldehyde (1.43 g, 7.1 mmol) in THF (40 mL) as the solvent. Purification by column chromatography (eluent: ethyl acetate−hexane 1:19 v/v) yielded 88% of compound **14**. Mp 67 °C (lit.[17] mp 68 °C).

^{1}H NMR ($CDCl_3$, ppm) δ 7.4−7.1 (m, 7H, Ar*H*), 7.0−6.8 (m, 2H, Ar*H*), 6.8−6.5 (m, 1H, C*H*═CH_2), 5.7−5.0 (m, 2H, CH═CH_2), 5.0 (s, 2H, OCH_2). IR (KBr, cm^{-1}) ν 3100−3000 (arom C−H), 2950−2780 (aliph C−H), 1625 (conj C═C), 1600 (arom C═C). MS (EI, *m*/*z*): 210 $(M)^+$, 91 $(CH_2Ph)^+$. Anal. ($C_{15}H_{14}O$) C, H: calcd 85.68, 6.71; found 85.34, 6.69.

Copolymer 15. 1,3-Bis(benzyloxy)-5-vinylbenzene (0.63 g, 2.0 mmol), styrene (0.18 g, 1.73 mmol), and AIBN (2.4 mg, 1.46×10^{-5} mol) were suspended in butanone (3 mL). The reaction mixture was degassed and heated overnight in an argon atmosphere at 80 °C. The solvent was evaporated and the residue was dissolved in $CHCl_3$ and precipitated in methanol. This afforded copolymer **15** as a white powder in 85% yield.

^{1}H NMR ($CDCl_3$, ppm) δ 7.2−5.8 (br s, Ar*H*), 4.6 (br s, OCH_2Ph), 2.1−0.8 (br s, C*H*Ph−CH_2). IR (KBr, cm^{-1}) ν 3020 (arom C−H), 2910 (aliph C−H), 1590 (arom C═C), 1150 (C−O ether). GPC (THF): M_w 35500, M_w/M_n = 2.26. Calculation of the composition of the polymer was performed by elemental analysis, *i.e.* from the oxygen content, which was assumed to be O = 100 − C − H − N. Elemental analysis C, H, N: found 84.83, 6.73, 0.64. From these data the ratio of 3,5-bis(benzyloxy)-5-vinylbenzene and styrene units was calculated to be 1.2.

Copolymer 16. Copolymer **15** (0.53 g) was stirred overnight at room temperature in a solution of hydrobromic acid in acetic acid (3 mL). The reaction mixture was concentrated and extracted with ethyl acetate, aqueous 1 N NaOH (2×), saturated aqueous $NaHCO_3$ (1×), and water (2×). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in methanol and precipitated in water. After filtration copolymer **16** was obtained as a beige solid in 93% yield.

^{1}H NMR (acetone-d_6, ppm) δ 7.4−5.9 (br s, Ar*H*), 2.1−1.0 (br s, C*H*Ph−CH_2). IR (KBr, cm^{-1}) ν 3400 (OH), 3030 (arom C−H), 2920 (aliph C−H), 1600 (arom C═C).

Copolymer 17. For the synthesis of this copolymer the same procedure was followed as described for copolymer **15** using 1-benzyloxy-4-vinylbenzene (0.55 g, 2.6 mmol), styrene (0.20 g, 1.9 mmol), and AIBN (4.4 mg, 2.68×10^{-5} mol) in butanone (3 mL) as the solvent. Precipitation yielded 90% of copolymer **17** as a white powder.

^{1}H NMR ($CDCl_3$, ppm) δ 7.4−6.3 (br s, Ar*H*), 4.9 (br s, OCH_2Ph), 2.0−1.0 (br s, C*H*Ph−CH_2). IR (KBr, cm^{-1}) ν 3040 (arom C−H), 2920 (aliph C−H), 1610 (arom C═C), 1250 (C−O ether). GPC (THF): M_w = 22 000, M_w/M_n = 2.46. Elemental analysis C, H, N: found 86.67, 6.94, <0.1. From these data the ratio of 1-benzyloxy-4-vinylbenzene and styrene units was calculated to be 2.6.

Copolymer 18. Copolymer **17** (0.30 g) was deprotected with a solution of hydrobromic acid in acetic acid (3 mL) as described for copolymer **15**. Precipitation afforded copolymer **18** as a beige powder in 100% yield.

^{1}H NMR (acetone-d_6, ppm) δ 7.5−6.3 (br s, Ar*H*), 2.0−1.0 (br s, C*H*Ph−CH_2). IR (KBr, cm^{-1}) ν 3440 (OH), 3020 (arom C−H), 2920 (aliph C−H), 1600 (arom C═C).

(15) Mancuso, J.; Swern, D. *Synthesis* **1981**, 165.

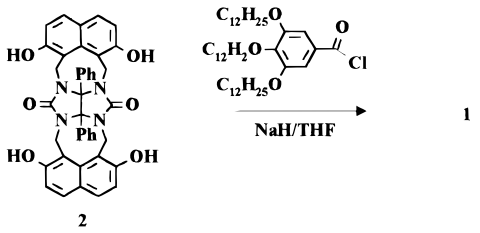
(16) Bergmann, E. D.; Sulzbacher, M. *J. Org. Chem.* **1951**, *16*, 84.

(17) Oda, U. *J. Soc. Chem. Ind. Jpn.* **1945**, *48*, 57. (C. A. **1952**, 8044).

(18) Bifunctional, tetrafunctional, etc. refers to the number of 1,3-dihydroxybenzene functions in the guest molecule that can be captured by clip molecule **1**.

(19) Nakahama, S.; Hirao, A. *Polym. Sci.* **1990**, *15*, 299.

Scheme 1



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), CCl_4 (0.16 mL, 1.7 mmol), triethylamine (0.05 mL, 0.36 mmol), and PPh_3 (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 $CHCl_3$ and precipitated in methanol. In this way 68% of the esterified copolymer was obtained.

^{1}H NMR ($CDCl_3$, ppm) δ 7.4−6.2 (br s, Ar*H*), 5.1 (br s, O*CH*$_2$Ph), 2.2−1.0 (br s, C*H*Ph−C*H*$_2$). 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): M_w = 24000, M_w/M_n = 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 acetone and precipitated in water. The copolymer was dried over P_2O_5 under high vacuum. In this way copolymer **20** was obtained as a beige powder in 96% yield.

^{1}H NMR (acetone-d_6, ppm) δ 7.8−6.5 (br s, Ar*H*), 2.5−1.3 (br s, C*H*Ph−C*H*$_2$). IR (KBr, cm^{-1}) υ 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^{-6} to 10×10^{-6} mol) and an equimolar amount (between 0.7 and 1.5 mg) of guest (5×10^{-6} to 10×10^{-6} mol) in 0.2 mL of $CHCl_3$. 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 μL). 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 ^{1}H-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.[3,4] 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.[3,4] 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 *as*, 33% in the *aa*, and 6% in the *ss* conformations. From a ^{1}H NMR titration the association constant for the complex with resorcinol was calculated to be K_a = 400 M^{-1} and for the complex with methyl 3,5-dihydroxybenzoate (MDB) K_a > 2500 M^{-1}.[8]

(20) A 1:1 complex of **1** and resorcinol, prepared using $CHCl_3$−methanol as the solvent mixture, showed a smectic phase with a clearing temperature of 110 °C. After repeated heating and cooling, phase separation took place, indicating that the complex was unstable when prepared from this solvent mixture. However, if this complex was prepared by evaporation of a $CHCl_3$−acetone solution a stable liquid-crystalline phase was observed. During the course of our study we found out that complex formation in general proceeds much better with the latter method than with the method we published previously (see ref 8).

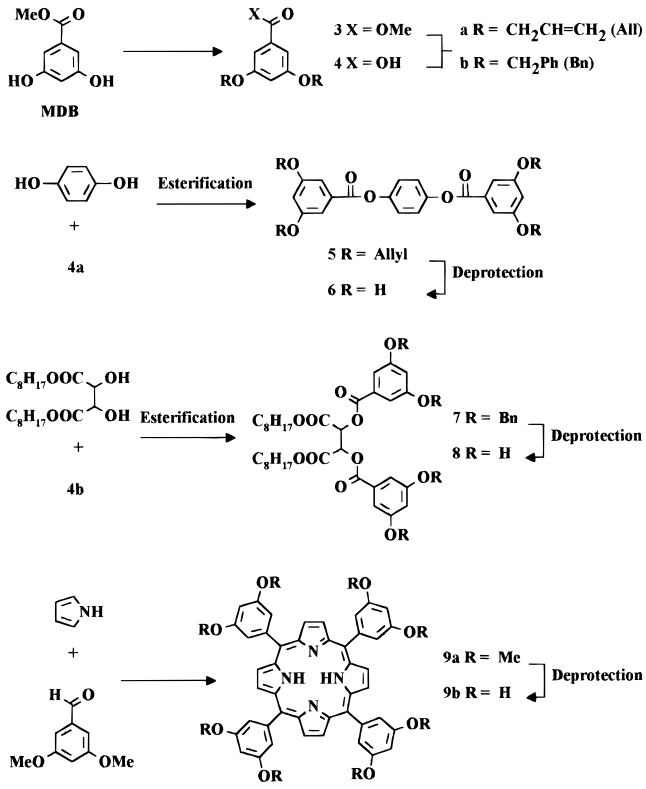
Table 1. Assignments of ^{1}H NMR Resonances to Conformations of **1**[a]

conformer	NC*H*HAr	NCH*H*Ar	napht-*H*(3,6)	napht-*H*(4,5)
sa	5.89 (*s*); 5.50 (*a*)	5.06 (*s*); 4.31 (*a*)	7.38 (*s*); 7.13 (*a*)	7.91 (*s*); 7.38 (*a*)
ss	5.89	5.23	7.44	*b*
aa	5.42	4.16	7.23	7.73

conformer	Ph-*H*(2,6)	Ph-*H*(3,5)	Ph-*H*(4)	$(RO)_3$Ar-*H*
sa	6.50 (*s*); 6.83 (*a*)	6.29 (*s*); 7.01 (*a*)	6.37 (*s*); 7.01 (*a*)	7.69; 7.53
ss	∼7.0	6.23	∼7.0	7.56
aa	6.91	7.03	6.92	7.66

[a] In $CDCl_3$ with [**1**] = 5 mM. Chemical shifts are in ppm relative to tetramethylsilane. The designation (*s*) and (*a*) are used for syn and anti, see text. [b] Due to the low abundance of the conformer and the complexity of the signals, no assignments could be made.

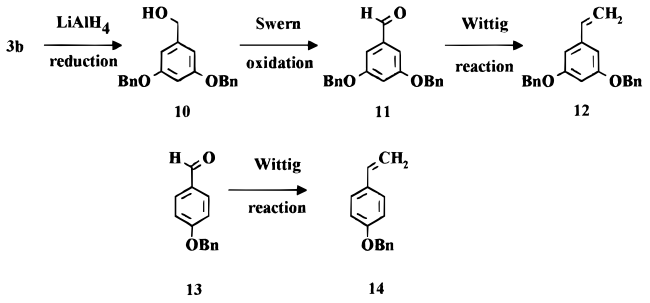
Scheme 2



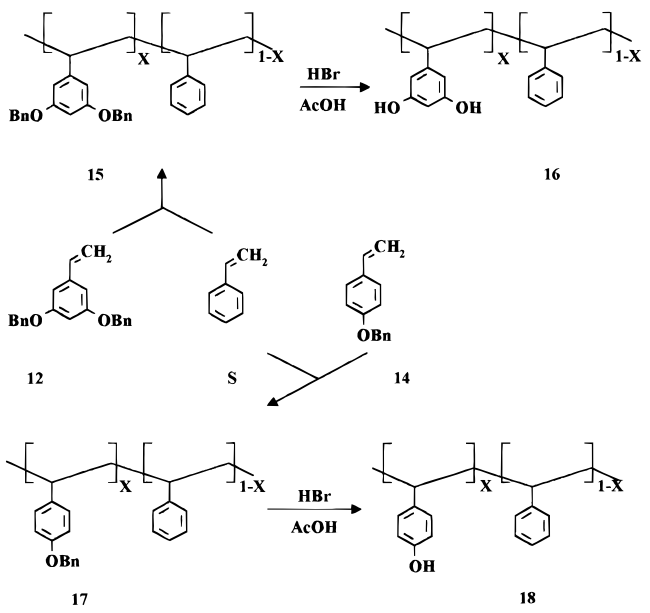
Bi- and Tetrafunctional Guest Molecules.[18] Hydroquinone was used as a spacer in the bifunctional molecule **6** (Scheme 2). This compound was synthesized from **4a** and hydroquinone by an esterification reaction using carbon tetrachloride, triphenylposphine, and triethylamine[11] in 61% yield. Removal 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



Scheme 4

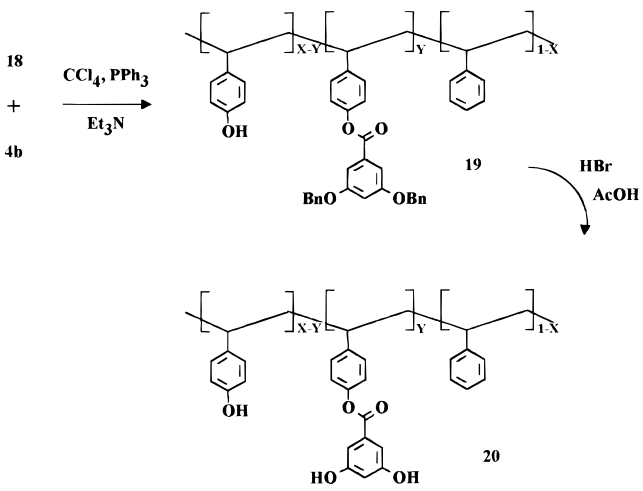


in 81% yield.[13] Deprotection of the benzyl groups was achieved by catalytic hydrogenolysis in ethanol to give **8** in 86% yield.

The synthesis of 2,6-disubstituted tetraphenylporphyrins 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_2Cl_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_2Cl_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).

Scheme 5



Copolymerization reactions were carried out using styrene (S) and the benzyloxystyrene 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(benzyloxy)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]

comonomer (BS)	comonomer ratio (BS:S)	polymer	polymer yield (%)	composition of polymer[b] (X:1 − X)	M_w[c]	M_w/M_n[c]
12	0.55:0.45	**15**	85	0.55:0.45	35500	2.26
14	0.58:0.42	**17**	90	0.72:0.28	22000	2.46
		19			24000	2.38

[a] S = styrene, BS = benzyl protected styrene derivative. [b] Determined by elemental analysis, X = BS. [c] Determined by GPC.

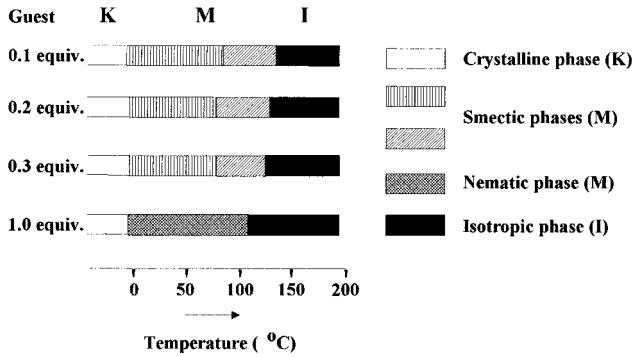


Figure 4. Liquid-crystalline behavior of clip **1** in the presence of different amounts of methyl 3,5-dihydroxybenzoate.

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

guest	host−guest ratio	transition	temp (°C)	ΔH (kJ/mol)
MDB	10:1	K → S	0 [−8]	58.8
		S → S′	95 [86]	1.0
		S′ → I	144 [136]	5.9
MDB	10:2	K → S	−1 [−8]	50.6
		S → S′	84 [78]	1.5
		S′ → I	141 [133]	5.3
MDB	10:3	K → S	−3 [−13]	45.6
		S → S′	82 [74]	2.1
		S′ → I	131 [127]	3.8
MDB	1:1	K → N	−4 [−12]	29.5
		N → I	110 [94]	1.1
6	1:1	K → S	49	123.7
		S → S′	90	12.4
		S′ → I	157	24.8
8	2:1	K → S	18 [4]	135.5
		S → S′	111 [102]	3.9
		S′ → I	133 [121]	9.9
8	1:1	K → S′	12 [−2]	66.2
		S′ → I	114 [99]	6.8
16	1:2	K → D	21 [10]	73.7[c]
		D → D′	86 [75]	0.7[c]
		D′ → I	131 [118]	4.8[c]
20	1:1[b]	K → D′	30 [19]	75.3[c]
		D′ → I	141 [129]	7.0[c]

[a] 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. [b] Ratio **1**/modified and unmodified 4-HS = 1:1. [c] Per mole repeating unit (mru) of the polymer that contains one receptor molecule.

Induction of Liquid Crystallinity by Complexation of Guest Molecules. 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.[20] In the following we will describe the influence of the complexation of mono-, bi-, tetra-, and polyfunctional guest molecules on the mesogenic properties of receptor molecule **1**.

Monofunctional Guest Molecules. Variation of the host−guest ratio in complexes of clip **1** and MDB gave rise to the appearance of different mesophases covering a wide temperature range as shown in Figure 4 and Table 3. At low concentrations of guest two mesophases were present, which were interpreted, on the basis of the polarizing microscopy pictures, as being smectic phases. At higher concentrations of guest only a nematic phase was visible. Figure 4 shows that an increase in the amount of guest molecule is accompanied by a slight change of the melting point, whereas a large decrease of the clearing 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.

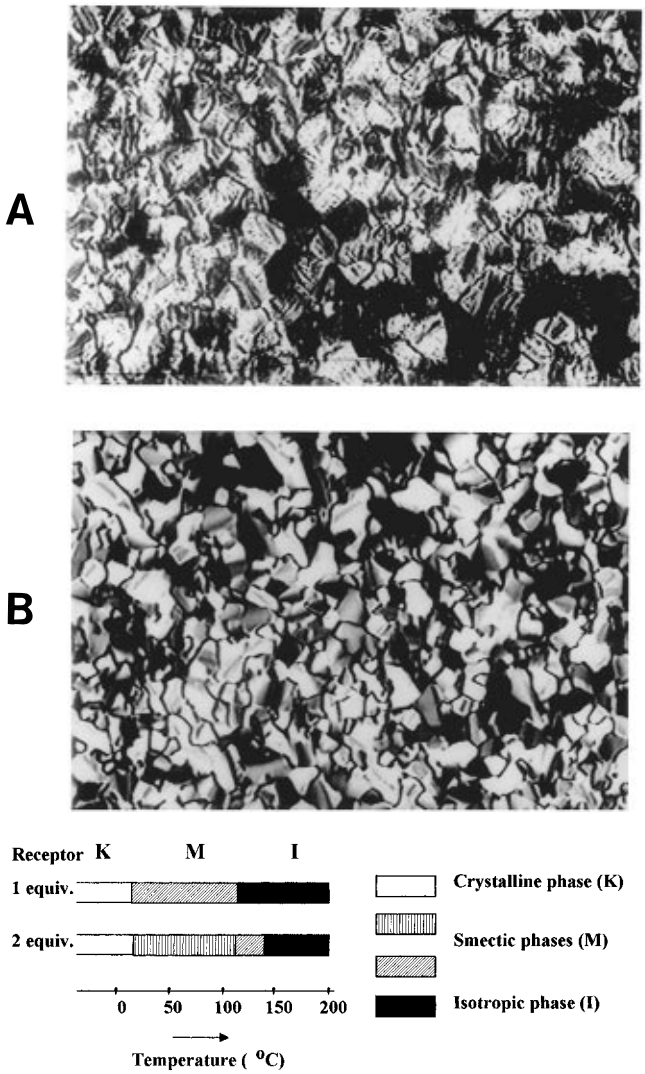


Figure 5. (A) Textures of the smectic mesophases of the 2:1 host−guest complex of **1** and **8** observed at 95 °C (top) and at 110 °C (bottom), as viewed under the polarizing microscopy during a cooling run from the isotropic phase. (B) Influence of the host−guest ratio on the liquid-crystalline behavior of the complex.

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, $\mathbf{I}142\mathbf{M}_1103\mathbf{M}_2$) 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 L-(+)-dioctyl tartrate, between the resorcinol

Table 4. Phase Transition Temperatures and Enthalpy Changes of Different Host−Guest Complexes of **1** and Porphyrin **9b**[a]

host:guest ratio	run	T (°C)[b]	ΔH (kJ/mol)	T (°C)[c]	ΔH (kJ/mol)	T (°C)[d]	ΔH (kJ/mol)	T (°C)[e]	ΔH (kJ/mol)
4:1	1							157	74.2
	2	17 [5]	157.4	127 [115]	2.50	149 [132]	27.0		
	3	17 [5]	166.5	126 [114]	2.78	148 [131]	26.0		
3:1	1							206	155.9
	2	15 [3]	189.9	130 [118]	2.76	150 [132]	17.3		
	3	15 [3]	183.7	124 [112]	1.91	146 [131]	17.9		
1:1	1							202	55.3
	2	13 [2]	66.3			152 [121]	5.97	199 [138]	14.12
	3	13 [2]	73.9			150 [121]	5.81	197 [136]	8.51
	4	14	53.8	128	0.61	148	5.85	197	2.98

[a] Determined by DSC. The values in square brackets are obtained from cooling runs. [b] K → S transition. [c] S → S′ transition. [d] S′ → I transition. [e] K → I transition.

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 dioctyl 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 smectic 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.[14] 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

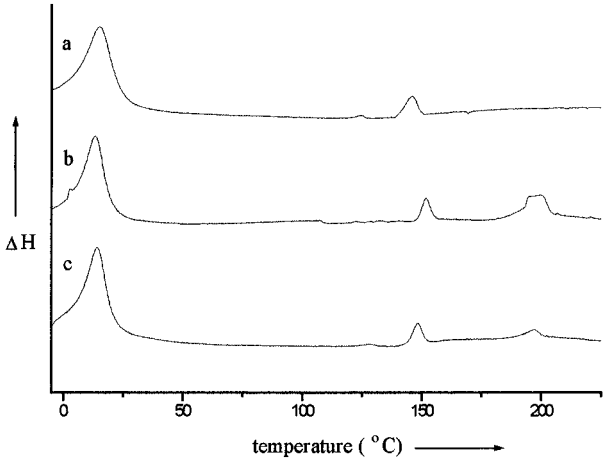


Figure 6. Thermograms of (a) the second heating run of the 4:1 complex and (b) the second and (c) the fourth heating runs of the 1:1 complex of **1** and **9b**.

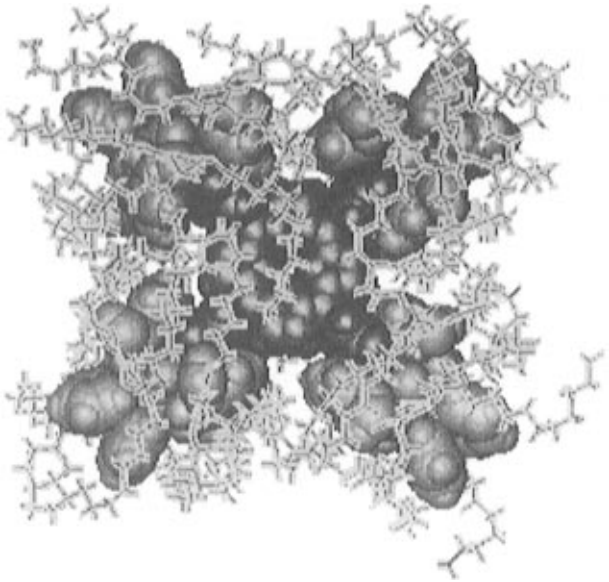


Figure 7. Computer generated structure of a 4:1 complex of molecular clip **1** and porphyrin **9b**.

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

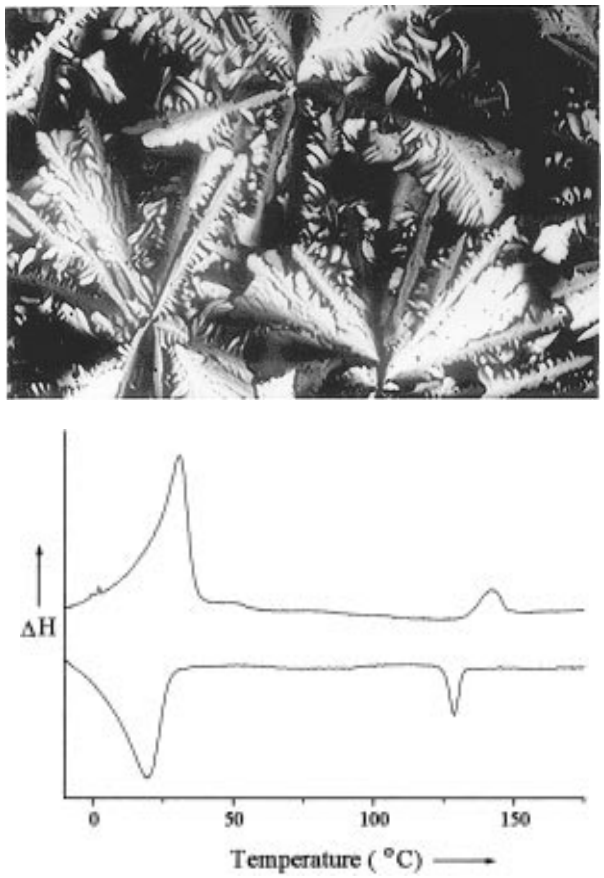


Figure 8. The discotic-like (fan-shaped) texture observed at 120 °C, viewed under the polarizing microscope during a cooling run from the isotropic liquid (top) and a thermogram of the complex of polymeric guest molecule **20** with clip **1** (bottom), showing the K → D′ and the D′ → I transitions in 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.[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, *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 goups.[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.

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