Induction of liquid-crystallinity in molecular clips by binding of different guest molecules

Johanna L. M. van Nunen and Roeland J. M. Nolte*

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

The use of clip molecules based on diphenyl- and dimethyl-glycoluril as building blocks for liquid-crystalline materials is described. The synthesis is performed by an esterification of hydroxy-derived clip molecules with trialkoxybenzoyl chloride. ^{1}H NMR titrations show that these molecules, despite the steric crowding, are still able to bind guest molecules in the cleft. The clip molecules show no liquid-crystalline properties, except those based on dimethylglycoluril. However, clips with alkyl chains of at least ten carbon atoms display liquid-crystalline behaviour upon binding of guest molecules, which can be tuned by the substituent of the guest molecules.

Introduction

The development of molecular materials with tunable properties is a topic of great current interest and in this respect liquid-crystallinity is receiving much attention.[1] Recently, molecular recognition has been used as a tool to control the properties of liquid-crystalline materials. Different receptor molecules, *e.g.* macroheterocyclic ligands[2–4] and cone-shaped molecules,[5–8] have been synthesized and studied for this purpose. Percec *et al.*[2] investigated the engineering of the liquid-crystalline behaviour of crown-ether-containing polymers with the help of alkali metal ions, and Ringsdorf *et al.*[4a] demonstrated that liquid-crystallinity can be induced in aza-crown ether derivatives by complexation of metal ions. In cone-shaped mesogens, based on *e.g.* cycloveratrylenes[5] and calixarenes,[6,7] the bowl-like rigid central core can act as a receptor site. It has been shown that in the mesophase the bowl-like cores are stacked[5–7] and that this arrangement can be disturbed upon binding of a guest molecule in the receptor sites, leading to the loss of liquid-crystallinity.[7]

In previous work, we reported on molecular clips, which are able to bind neutral molecules, *e.g.* **1**[8] and **2**.[9] These clip molecules contain a concave framework, which is based on the molecule diphenylglycoluril. A cleft is formed when this framework is flanked by two aromatic walls. Compound **1** [Fig. 1(*a*)] has a rigid, well-defined binding site. It can bind dihydroxybenzenes, which are clamped in the cavity of the receptor by hydrogen bonding and π–π stacking interactions (association constant of the complex with resorcinol, $K_a = 2600 \pm 400$ dm^3 mol^{-1}). Hydrogen bonding takes place between the hydroxy functions of the guest molecule and the carbonyl groups of the glycoluril moiety of the host molecule. π–π Stacking occurs between the aromatic rings of host and guest. The molecules of compound **2** exist in three conformations [Fig. 1(*b*)]: *anti–anti* (*aa*), *syn–anti* (*sa*) and *syn–syn* (*ss*). The conformers differ in the way the walls are orientated relative to the phenyl groups of the diphenylglycoluril part. The molecules of **2** change from one conformation to another by the flipping of one naphthalene wall. Only the *aa* conformer has the right geometry to bind electron-poor aromatic guests in its cavity ($K_a = 115 \pm 20$ dm^3 mol^{-1} for 1,3-nitrobenzene in $CDCl_3$).[9]

We assumed that by using receptor molecules of types **1** and **2** as building blocks for liquid-crystalline materials, the properties of these materials might be influenced by the binding of guest molecules. To investigate this we have modified **1** and **2** with four 3,4,5-trialkoxybenzoyl groups in order to create a central rigid core surrounded by flexible chains.[10]

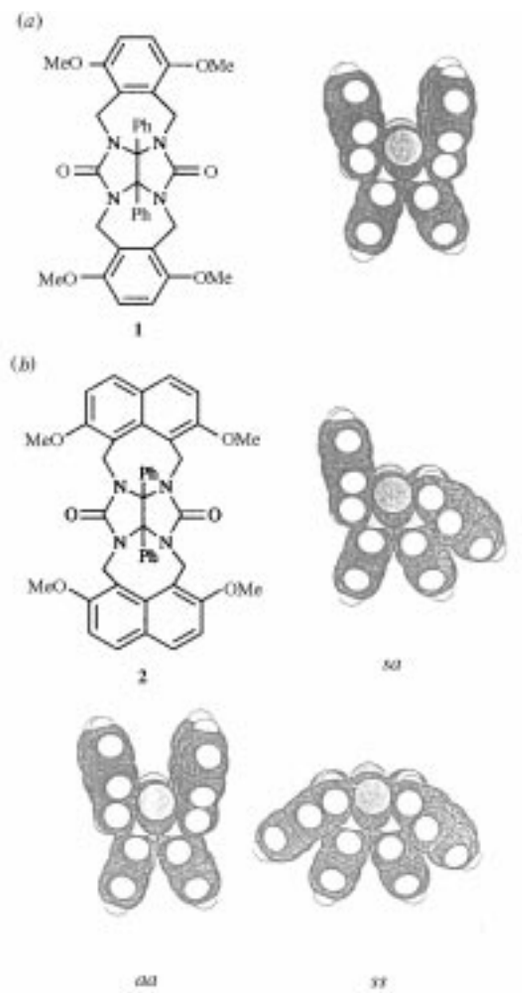


Fig. 1 Structures of receptor molecules **1** and **2**

The tendency of compounds to form liquid-crystalline phases is dependent on the lateral interactions between the molecules. If these interactions are too strong, no liquid-crystalline phase will form. If these are weakened, a layer type smectic phase may be generated, and if these are weakened even further, a nematic phase may appear. It occurred to us that the phenyl groups of the diphenylglycoluril moiety might be too bulky and as a result the interactions between the molecules

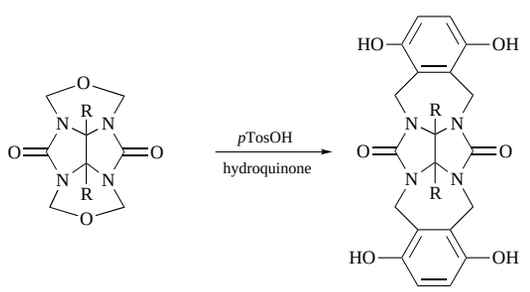
too weak. For this reason we also synthesized molecules derived from dimethylglycoluril.

In this paper we present the synthesis, characterization and binding properties of clip molecules substituted with long aliphatic chains. The influence of complexation of guest molecules on the liquid-crystalline behaviour of these molecules will be described.[11]

Results and discussion

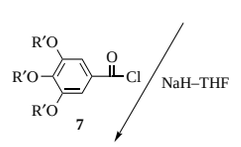
Synthesis

Receptor molecule **5** was synthesized in 75% yield by refluxing compound **3** with an excess of hydroquinone in 1,2-dichloroethane in the presence of toluene-*p*-sulfonic acid (TsOH) as a catalyst.[12] The same procedure starting from **4** could be used for the synthesis of compound **6**, giving almost the same yield. Before trying to synthesize the target molecules **8** and **9**, some test reactions were performed with benzoic acid and receptor molecule **5**. First, the esterification reaction of **5** with dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) in different solvents was attempted, but only the benzoylurea byproduct was obtained.[13] In an alternative procedure a suspension of the host molecule with sodium hydride in tetrahydrofuran (THF) was refluxed and after one hour benzoyl chloride was slowly added.[14] This procedure enabled us to synthesize all the target molecules **8** and **9** in yields ranging from 40–80% (Scheme 1). The syntheses of the target molecules **11**, which are derived from the receptor molecule with 2,7-dihydroxynaphthalene walls are presented in Scheme 2.

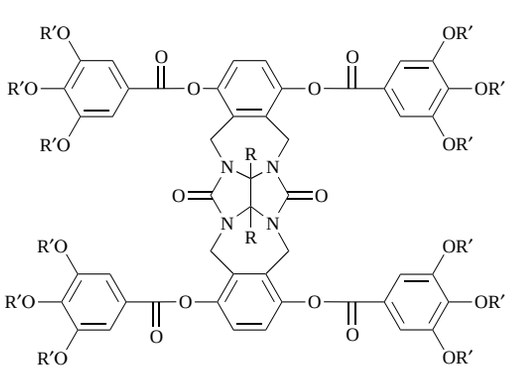


3 R = Ph
4 R = Me

5 R = Ph
6 R = Me

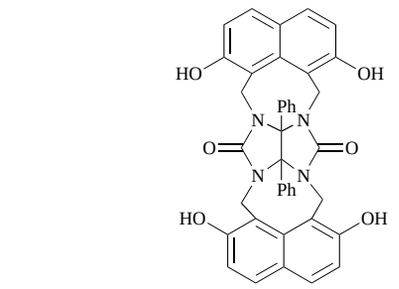


7

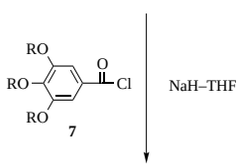


	R	R′
8a	Ph	C_6H_{13}
8b	Ph	C_8H_{17}
8c	Ph	$C_{10}H_{21}$
8d	Ph	$C_{12}H_{25}$
9a	Me	$C_{10}H_{21}$
9b	Me	$C_{12}H_{25}$

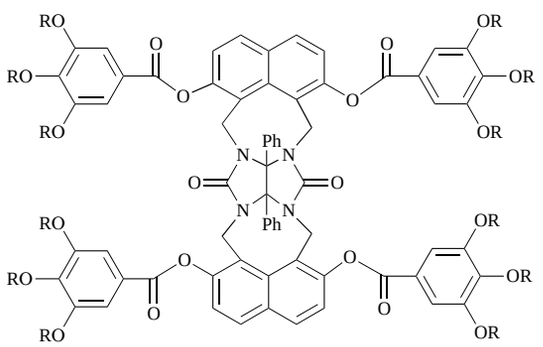
Scheme 1



10



7



	R	*aa*	*sa*	*ss*
11a	C_8H_{17}	29%	64%	7%
11b	$C_{10}H_{21}$	31%	63%	6%
11c	$C_{12}H_{25}$	33%	61%	6%

Scheme 2

Properties of the molecular clips derived from hydroquinone

^{1}H NMR titrations[8] were performed to determine the binding properties of the substituted molecular clips. The association constant for the complex of resorcinol (DHB) with compound **8a** was calculated to be $K_a = 1000 \pm 150$ dm^3 mol^{-1}. Substitution of a methoxy group (compound **1**) by a modified benzoyl group (compound **8a**) reduces the binding constant by a factor of approximately two. In order to study the influence of the length of the alkyl chains of the molecular clips on the binding properties, the association constants of the complexes between 1,3-dihydroxy-5-pentylbenzene (pentylresorcinol) and both **8a** and **8d** were determined. Pentylresorcinol was used instead of resorcinol because of the higher solubility of this guest. The association constants were calculated to be $K_a = 605 \pm 100$ dm^3 mol^{-1} for compound **8a** and $K_a = 645 \pm 100$ dm^3 mol^{-1} for compound **8d**. Apparently, the length of the alkyl substituent does not significantly influence the binding properties of these receptor molecules.

Molecular clips **8a–d** were designed to be liquid-crystalline materials. Remarkably, compounds **8a** and **8b** were found to be crystalline compounds with melting points of 175 and 159 °C, respectively. Compound **8c** could only be crystallized by annealing for 2 h at 81 °C. The crystals melted at 93–96 °C. Compound **8d** did not crystallize even after annealing. In the case of **8a** and **8b** the rigid diphenylglycoluril framework clearly dominates the structure so crystalline materials are obtained. Due to their

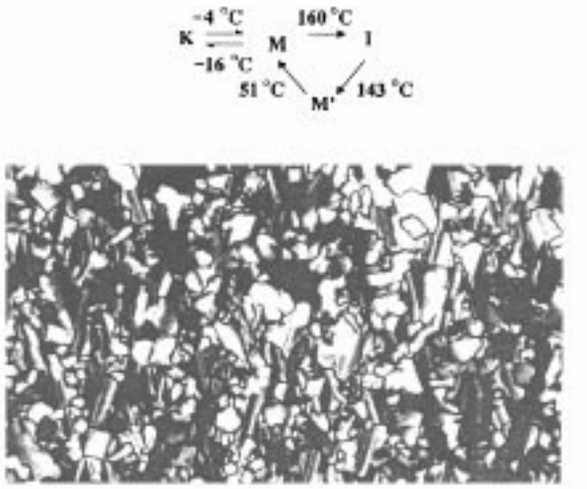


Fig. 2 Liquid-crystalline behaviour of molecular clip **9b** (top). Texture of the mesophase at 40 °C, as viewed under a polarizing microscope (bottom).

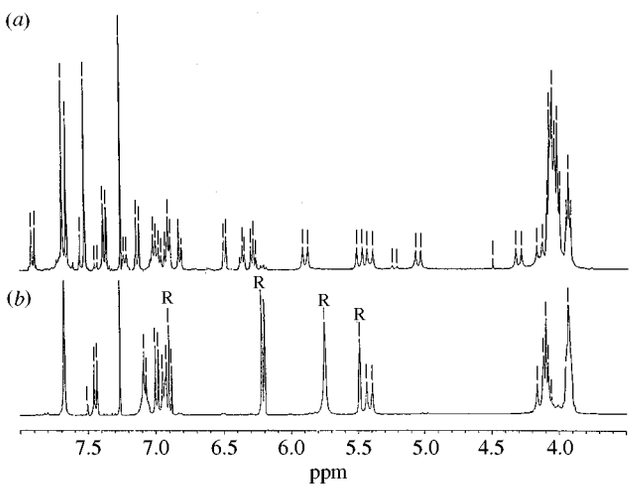


Fig. 3 ^{1}H NMR spectra of (*a*) molecular clip **11c** and (*b*) **11c** with 4 equiv. of resorcinol (R)

longer flexible alkyl chains, compounds **8c** and **8d** were expected to be liquid-crystalline, but for some unknown reason this was not the case. On the other hand, molecular clips **9a** and **9b**, derived from dimethylglycoluril, displayed liquid-crystalline behaviour. The nature of the optical textures, which were observed by polarizing microscopy, and the magnitudes of the enthalpy changes, which were measured by differential scanning calorimetry (DSC), indicated that a smectic phase was formed between 1 and 225 °C for compound **9a**, and between −4 and 160 °C for compound **9b**. Upon cooling an additional highly ordered smectic phase was visible for the latter compound (Fig. 2). Substitution of the phenyl groups on the convex side of the molecular clip with methyl groups leads, apparently, to liquid-crystalline properties. This is probably due to a decrease in steric bulk, allowing better stacking of the central cores of the molecules.

Properties of the molecular clips derived from 2,7-dihydroxynaphthalene

Interpretation of the ^{1}H NMR spectra of clips **11a–c** is complicated by the fact that these molecules have three conformations [*aa*, *sa* and *ss*, Fig. 1(*b*)], which interconvert slowly on the NMR timescale. Earlier work performed in our laboratory showed that the binding of a suitable guest molecule in receptor molecule **2** increases the relative amount of the *aa* conformer, which is the dominant binding conformer.[9] We found that upon addition of an excess of resorcinol to a solution of one of the receptor molecules **11**, the equilibrium of the conformers was almost completely shifted to the *aa* conformer (Fig. 3). 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, (*iii*) the methylene protons of the *sa* conformer must give rise to two AX systems with equal intensity.[9] The assignments of the most important signals of compound **11c** are given in Table 1. The positions of the ^{1}H NMR signals were found to be dependent on the concentration of receptor molecules **11a–c**, but the signals were independent of the chain length of the substituents. At the same concentration (5 mM), the ratio of the three conformers was almost identical for the different clip molecules. The association constants for complexation of resorcinol, determined by ^{1}H NMR titration experiments, did not differ significantly for receptor molecules **11a** and **11c**. These are calculated to be $K_a = 408 \pm 80$ and 450 ± 80 dm^3 mol^{-1}, respectively.

Table 1 Assignments of ^{1}H NMR resonances to conformations of **11c**[a]

Conformer	NC*H*HAr	NCH*H*Ar	Naph-*H*(3,6)	Naph-*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	*ca*. 7.0	6.23	*ca*. 7.0	7.56
aa	6.91	7.03	6.92	7.66

[a] In $CDCl_3$ with [**11c**] = 5 mM. Chemical shifts are in ppm relative to tetramethylsilane. The designations (*s*) and (*a*) are used for *syn* and *anti*, see text. [b] Due to the low abundance of the conformer or complexity of the signals, no assignments could be made.

Compounds **11a–c** are crystalline compounds with melting ranges of 203–205 for **11a**, 177–179 for **11b** and 159–164 °C for **11c**. Upon fast cooling from the liquid state, compound **11c** showed a thermodynamically unstable (monotropic) liquid-crystalline phase, *viz*. a nematic phase with a clearing point of 161 °C.[11]

Induction of liquid-crystallinity by complexation of guest molecules

In order to study the influence of host–guest complexation on the melting behaviour we prepared complexes of clip molecules **8** and **11** with dihydroxybenzene derivatives.[15] Two different guest molecules, *viz*. resorcinol and methyl 3,5-dihydroxybenzoate (MDB), were used. The complexes with molecular clips **8** are described in Table 2. From earlier studies it is known that MDB binds approximately six times as strongly as DHB in clip **1**.[16]

Complexation of guest molecules in clips **8a** and **8b** only slightly changes the melting points of the host molecules, as is described in Table 2. In clips **8c** and **8d**, however, complexation of DHB or MDB induces a liquid-crystalline phase. The complex of **8c** with DHB displayed a nematic phase directly after cooling, whereas the complex of **8c** with MDB and both complexes of **8d** exhibited smectic-like phases (Fig. 4). For some complexes the more highly ordered mesophase (described as **M** in Table 2), which is present in the DSC-thermogram, could not be assigned unequivocally as the transition temperature of the mesophase upon cooling fell outside the temperature range of the polarizing microscope. A comparison of the data of the complexes in Table 2 shows that the melting points of the complexes of **8a** and **8b** are almost the same as the melting points of the free clips. For the liquid-crystalline complexes of **8c** and **8d**

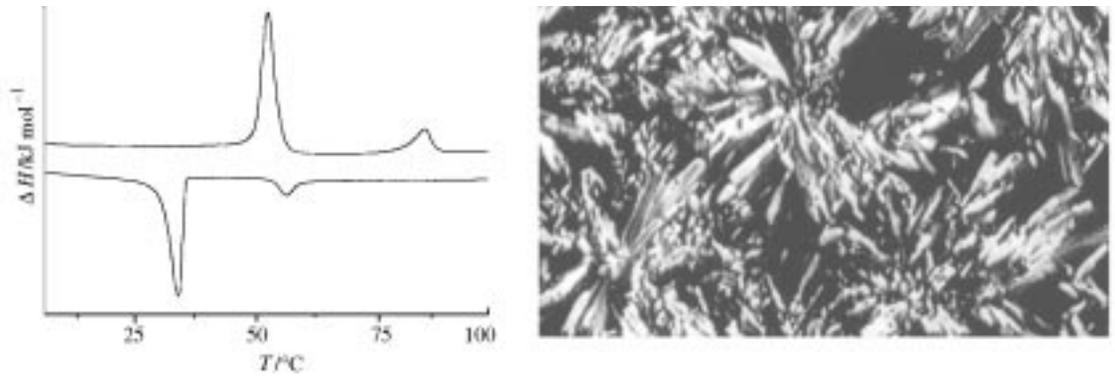


Fig. 4 Thermogram of the 1:1 complex of DHB with **8d** (left) and the texture of the mesophase at 51 °C, as viewed under a polarizing microscope (right)

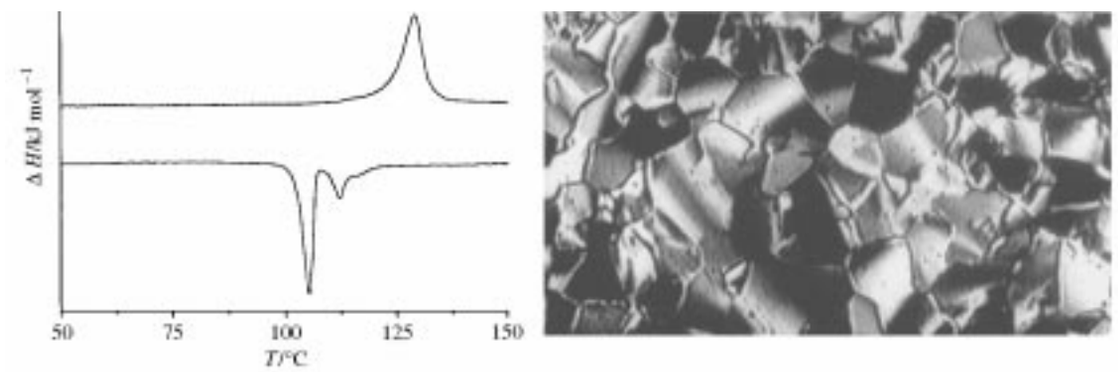


Fig. 5 Thermogram of the 1:1 complex of MDB with **11b** (left) and the texture of the mesophase at 109 °C as viewed under a polarizing microscope (right)

Table 2 Phase transition temperatures (°C) and (in parentheses) enthalpy changes (kJ mol^{-1}) of complexes of dihydroxybenzene derivatives with molecular clips **8a–d**[a]

Clip	Uncomplexed host	1:1 Complex with DHB	1:1 Complex with MDB
8a	**K**175**I**	**K**179(65.87)**I**	**K**181(57.72)**I**
8b	**K**159**I**	—	**K**149(28.20)**I**
8c	**K**93–96**I**	**K**47(50.75)**M**64(0.92) **N**81(3.91)**I**	**K**2(37.05)**M**37(0.57) **S**107(16.86)**I**
8d	—	**K**54(79.19)**S**88(15.01)**I**	**K**48(47.06)**M**59(1.27) **S**102(29.96)**I**

[a] DHB: 1,3-dihydroxybenzene, MDB: methyl 3,5-dihydroxybenzoate. Values were determined by DSC. **K**: crystalline phase, **S**: smectic phase, **N**: nematic phase, **D**: sicotic phase, **I**: isotropic phase.

Table 3 Phase transition temperatures (°C) and (in parentheses) enthalpy changes (kJ mol^{-1}) of complexes of dihydroxybenzene derivatives with molecular clips **11**[a]

Clip	Uncomplexed host	1:1 Complex with DHB	1:1 Complex with MDB
11a	**K**203–205**I**	—	**K**173**I**[b]
11b	**K**177–179**I**	**K**114**S**130**I**[b]	**K**124**S**134**I**[b]
11c	**K**159–164**I**	**K**14(58.40)**S**78(1.12) **S′**141(9.18)**I**	**K**14(68.56)**N**131(3.53)**I**

[a] DHB: 1,3-dihydroxybenzene, MDB: methyl 3,5-dihydroxybenzoate. Values were determined by DSC. [b] Values were determined by polarizing microscopy. **K**: crystalline phase, **S**: smectic phase, **N**: nematic phase, **D**: sicotic phase, **I**: isotropic phase.

a broadening of the liquid crystalline range is observed when MDB, instead of DHB, is bound in the clip molecules. Remarkably, the MDB complex of **8c** showed a liquid-crystalline phase over a wider temperature range, *viz*. 105 °C, than the corresponding complex of **8d** (54 °C), whereas this difference is not that significant for the complexes of **8c** and **8d** with DHB. In general we may conclude that the rigid diphenylglycoluril framework is the determining factor for the melting behaviour of **8a** and **8b**, whereas in the case of **8c** and **8d** the bulk of the alkyl chains are dominant.

The influence of guest molecules on the melting behaviour of molecular clips **11** is presented in Table 3. When a dihydroxybenzene derivative is bound in clip **11a** only a decrease in the melting point was observed, whereas a corresponding complexation in clips **11b** and **11c** induced liquid-crystalline behaviour, *i.e.* the formation of smectic and nematic phases.

The smectic phases observed for the complexes of clip **11b** covered only a small range of 10–15 °C. For the complex with MDB a smectic phase was formed over such a small temperature range that peak separation was only obtained in the cooling curve of the thermogram (Fig. 5). An increase in the length of the alkyl chains as in the complexes with **11c**, however, broadened the liquid-crystalline range to more than 100 °C. The complex of **11c** with resorcinol exhibited two different smectic phases, whereas the complex with MDB displayed only one, nematic, phase. If the complexes of the three different clips are compared (Table 3), one can conclude that a decrease in the alkyl chain length is accompanied by a strong increase of the melting point together with a relatively small change in the clearing point. At a certain chain length the melting point will become higher than the clearing point, which may explain why no mesophase is observed for the complex of MDB with **11a**.

Conclusions

We have shown that clip molecules, derived from diphenyl- and dimethyl-glycoluril, modified with alkoxy-substituted benzoyl groups can be conveniently prepared by an esterification reaction. The introduction of bulky trialkoxybenzoyl substituents decreases the binding of resorcinol derivatives in these receptor molecules compared to the methoxy derivative. The length of the aliphatic chains (C_6H_{13} to $C_{12}H_{25}$ derivative) does not influence the binding strength.

Elongation of the alkyl substituent does not lead to liquid-crystallinity in molecular clips **8a–d**. The dimethylglycoluril derivatives **9a** and **9b**, however, do have a mesophase. Apparently, a smaller substituent on the convex side of these receptor molecules allows a better stacking of the central cores. In the case of the molecular clips with naphthalene walls, we were more successful in introducing liquid-crystalline properties by changing the length of the alkyl chains, *viz*. for compound **11c** a monotropic liquid-crystalline phase was observed.

Complexation of DHB or MDB induces liquid-crystallinity in the trialkoxybenzoyl substituted clips, when the alkoxy groups are at least ten carbon atoms long. The MDB complexes of **8c** and **8d** have more ordered liquid-crystalline phases over a wider temperature range than the complexes of DHB. This effect is less pronounced in the complexes with clips **11a** and **11b**. Apparently, enlargement of the rigid core from two 1,4-dihydroxybenzene to two 2,7-dihydroxynaphthalene walls masks, to some extent, the influence of the alkyl substituents and the complexation of guest molecules on the melting behaviour. In conclusion, the receptor molecules described are very promising building blocks for the construction of liquid-crystalline materials. As far as we know, this is the first example of induction of liquid-crystallinity in receptor molecules by the complexation of neutral guest molecules.

Experimental

General methods

CH_2Cl_2 was distilled from CaH_2 and THF from $LiAlH_4$. For flash column chromatography Merck silica gel 60H was used. Melting points were measured with a Jeneval polarizing microscope connected to a Linkam THMS 600 hot stage. Thermograms were recorded at a rate of 10 °C min^{-1} using a Perkin-Elmer DSC 7 instrument. Samples were prepared in stainless-steel large volume pans (75 μl).

8b,8c-Dihydro-8b,8c-dimethyl-1*H*,3*H*,4*H*,5*H*,7*H*,8*H*-2,6-dioxa-3a,4a,7a,8a-tetraazacyclopenta[*def*]fluorene-4,8-dione 4. This compound was synthesized as described in ref. 17.

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrahydroxy-13b,13c-diphenyl-6*H*,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno-[2,1,8-*ija*]benz[*f*]azulene-6,13-dione 5. This compound was synthesized from **3** according to a procedure developed previously in our laboratory.[12]

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrahydroxy-13b,13c-dimethyl-6*H*,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno-[2,1,8-*ija*]benz[*f*]azulene-6,13-dione 6. This compound was synthesized according to a procedure developed in our laboratory[12] using compound **4** (1.0 g, 3.9 mol), TsOH (3.0 g, 16 mmol) in 1,2-dichloroethane (30 ml), and hydroquinone (1.7 g, 15 mmol). In order to remove traces of water a suspension of product **6** in triethyl orthoformate was heated under reflux for 1 h. The precipitate was filtered, washed with CH_2Cl_2, and dried *in vacuo*. Yield 71%. Mp >225 °C (decomp.); δ_H(100 MHz; [$^2H_6$]DMSO; *J* values in Hz throughout) 6.43 (4H, s, O*H*), 5.74 (4H, s, Ar*H*), 5.14 and 4.93 (4H, 2 d, *J* 16, CH_2N), 1.70 (3H, s, CH_3). FAB-MS (*m*-nitrobenzyl alcohol) *m*/*z* 439 $(M + H)^+$.

3,4,5-Trialkoxybenzoyl chloride 7. The corresponding 3,4,5-trialkoxybenzoic acid[10] was refluxed in pure $SOCl_2$. After 2 h the reaction mixture was evaporated to dryness *in vacuo* and the product was used without further purification.

17b,17c-Dihydro-1,6,10,15-tetrahydroxy-17b,17c-diphenyl-7*H*,8*H*,9*H*,16*H*,17*H*,18*H*-7a,8a,16a,17a-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 10. This compound was synthesized according to a procedure developed previously in our laboratory.[18]

General procedure for the synthesis of compounds 8, 9 and 11

Receptor molecule **5**, **6** or **10** (*n* mmol) and NaH (10*n* mmol) were refluxed for 1 h in THF (10*n* ml). The appropriate 3,4,5-trialkoxybenzoyl chloride **7** (4.4 equiv.), in a mixture of THF and 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 twice with aqueous 1 M HCl, then with H_2O, and dried ($MgSO_4$). The crude product was subjected to flash column chromatography (eluent ethyl acetate–hexane, 1:19–25 v/v).

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrakis[(3,4,5-trihexyloxy)benzyloxy]-13b,13c-diphenyl-6*H*,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno[2,1,8-*ija*]benz[*f*]azulene-6,13-dione 8a. Yield 50%. **K** 175 °C **I**. δ_H(100 MHz, $CDCl_3$) 7.57 [8H, s, Ar*H*(OR)$_3$], 7.15 (4H, s, Ar*H*), 7.03 (10H, br s, Ar*H*), 5.25 (4H, d, *J* 16, NC*H*HAr), 4.22–3.73 (28H, m, NCH*H*Ar and OCH_2), 2.00–1.10 [96H, m, OCH$_2$(CH_2)$_4$], 0.88 (36H, t, CH_3). FAB-MS (*m*-nitrobenzyl alcohol) *m*/*z* 2179 $(M + H)^+$ (Found: C, 72.48; H, 8.55; N, 2.61. Calcd. for $C_{132}H_{186}N_4O_{22}$: C, 72.70; H, 8.60; N, 2.57%).

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrakis[(3,4,5-trioctyloxy)benzyloxy]-13b,13c-diphenyl-6*H*,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno[2,1,8-*ija*]benz[*f*]azulene-6,13-dione 8b. Yield 78%. **K** 159 °C **I**. δ_H(100 MHz, $CDCl_3$) 7.56 [8H, s, Ar*H*(OR)$_3$], 7.13 (4H, s, Ar*H*), 7.00 (10H, br s, Ar*H*), 5.23 (4H, d, *J* 16, NC*H*HAr), 4.22–3.78 (28H, m, NCH*H*Ar and OCH_2), 2.00–1.10 [144H, m, OCH$_2$(CH_2)$_6$], 0.88 (36H, t, CH_3) (Found: C, 74.60; H, 9.58; N, 2.24. Calcd. for $C_{156}H_{234}N_4O_{22}$: C, 74.43; H, 9.37; N, 2.23%).

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrakis[(3,4,5-tridecyloxy)benzyloxy]-13b,13c-diphenyl-6*H*,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno[2,1,8-*ija*]benz[*f*]azulene-6,13-dione 8c. Yield 40%. **K** 93–96 °C **I**. δ_H(100 MHz, $CDCl_3$) 7.58 [8H, s, Ar*H*(OR)$_3$], 7.16 (4H, s, Ar*H*), 7.00 (10H, br s, Ar*H*), 5.22 (4H, d, *J* 16, NC*H*HAr), 4.39–3.79 (28H, m, NCH*H*Ar and OCH_2), 2.00–1.12 [192H, m, OCH$_2$(CH_2)$_8$], 0.87 (36H, t, CH_3) (Found: C, 75.18; H, 9.98; N, 1.92. Calcd. for $C_{180}H_{282}N_4O_{22}$: C, 75.75; H, 9.96; N, 1.96%).

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrakis[(3,4,5-tridodecyloxy)benzyloxy]-13b,13c-diphenyl-6*H*,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno[2,1,8-*ija*]benz[*f*]azulene-6,13-dione 8d. Yield 43%. δ_H(400 MHz, $CDCl_3$) 7.59 [8H, s, Ar*H*(OR)$_3$], 7.16 (4H, s, Ar*H*), 7.07–7.05 (6H, m, Ar*H*), 6.98–6.96 (4H, m, Ar*H*), 5.22 and 3.99 (4H, 2 × d, *J* 16, NC*H*HAr), 4.09–3.96 (24H, m, OCH_2), 1.82–1.26 [240H, m, OCH$_2$(CH_2)$_{10}$], 0.87 (36H, t, CH_3) (Found: C, 76.44; H, 10.57; N, 1.82. Calcd. for $C_{204}H_{330}N_4O_{22}$: C, 76.79; H, 10.42; N, 1.76%).

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrakis[(3,4,5-tridecyloxy)benzyloxy]-13b,13c-dimethyl-6*H*,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno[2,1,8-*ija*]benz[*f*]azulene-6,13-dione 9a. Yield 63%. **K** 1 °C **M** 225 °C **I**. δ_H(100 MHz, $CDCl_3$) 7.54 [8H, s, Ar*H*(OR)$_3$], 7.14 (4H, s, Ar*H*), 5.12 (4H, d, *J* 16, NC*H*-HAr), 4.28–3.77 (28H, m, NCH*H*Ar and OCH_2), 2.00–1.10 [198H, m, OCH$_2$(CH_2)$_8$ and CH_3], 0.88 (36H, t, CH_3) (Found: C, 74.55; H, 10.51; N, 2.08. Calcd. for $C_{170}H_{278}N_4O_{22}$: C, 74.79; H, 10.26; N, 2.05%).

5,7,12,13b,13c,14-Hexahydro-1,4,8,11-tetrakis[(3,4,5-tridodecyloxy)benzyloxy]-13b,13c-dimethyl-6*H*,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno[2,1,8-*ija*]benz[*f*]azulene-6,13-dione 9b. Yield 37%. **K** −4 °C **M** 160 °C **I**. δ_H(100 MHz, $CDCl_3$) 7.54 [8H, s, Ar*H*(OR)$_3$], 7.14 (4H, s, Ar*H*), 5.12 (4H, d, *J* 16, NC*H*-HAr), 4.24–3.73 (28H, m, NCH*H*Ar and OCH_2), 2.00–1.10 [246H, m, OCH$_2$(CH_2)$_{10}$ and CH_3], 0.88 (36H, t, CH_3) (Found: C, 75.89; H, 10.70; N, 1.87. Calcd. for $C_{194}H_{326}N_4O_{22}$: C, 75.98; H, 10.71; N, 1.83%).

17b,17c-Dihydro-1,6,10,15-tetrakis[(3,4,5-trioctyloxy)benzyloxy]-17b,17c-diphenyl-7*H*,8*H*,9*H*,16*H*,17*H*,18*H*-7a,8a,16a,17a-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 11a. Yield 63%. **K** 204 °C **I**. δ_H(400 MHz, $CDCl_3$); see Table 1 for uncomplexed host. Host–guest complex: host: 7.66 [8H, s, Ar*H*(OR)$_3$], 7.41 and 7.01 (8H, 2 × d, *J* 9, naph-*H*), 7.15–7.04 (6H, m, Ar*H*),

6.94 (4H, d, Ar*H*), 5.41 and 4.15 (8H, 2 × d, *J* 17, NC*H*HAr), 4.13–3.85 (24H, m, OCH_2), 1.89–1.09 [144H, m, OCH$_2$(CH_2)$_6$], 0.98–0.80 (36H, m, CH_3); guest (resorcinol) 6.83 (t), 6.12 (dd), 5.40 (s), 5.27 (br s) (Found: C, 74.96; H, 9.22; N, 2.19. Calcd. for $C_{164}H_{238}N_4O_{22}$: C, 75.25; H, 9.16; N, 2.14%).

17b,17c-Dihydro-1,6,10,15-tetrakis[(3,4,5-tridecyloxy)benzyloxy]-17b,17c-diphenyl-7*H*,8*H*,9*H*,16*H*,17*H*,18*H*-7a,8a,16a,17a-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 11b. Yield 40%. **K** 178 °C **I**. δ_H(400 MHz, $CDCl_3$) see Table 1 for uncomplexed host. Host–guest complex: host 7.68 [8H, s, Ar*H*(OR)$_3$], 7.45 and 7.00 (8H, 2 × d, *J* 9, naph-*H*), 7.13–7.04 (6H, m, Ar*H*), 6.94 (4H, d, Ar*H*), 5.42 and 4.15 (8H, 2 × d, *J* 17, NC*H*HAr), 4.13–3.78 (24 H m, OCH_2), 1.87–1.18 [192H, m, OCH$_2$(CH_2)$_8$], 0.95–0.81 (36H, m, CH_3), guest (resorcinol) 6.93 (t), 6.24 (dd), 5.60 (br s) (Found: C, 76.12; H, 9.48; N, 1.95. Calcd. for $C_{188}H_{286}N_4O_{22}$: C, 76.43; H, 9.76; N, 1.90%).

17b,17c-Dihydro-1,6,10,15-tetrakis[(3,4,5-tridodecyloxy)-benzyloxy]-17b,17c-diphenyl-7*H*,8*H*,9*H*,16*H*,17*H*,18*H*-7a,8a,16a,17a-tetraazapentaleno[1″,6″:5,6,7;3″,4″:5′,6′,7′]dicyclo-octa[1,2,3-*de*:1′,2′,3′*d*′*e*′]dinaphthalene-8,17-dione 11c. Yield 57%. **K** 159–162 °C **I**. δ_H(400 MHz, $CDCl_3$) see Table 1 for uncomplexed host. Host–guest complex: host: 7.67 [8H, s, Ar*H*(OR)$_3$], 7.44 and 6.99 (8H, 2 × d, *J* 9, naph-*H*), 7.11–7.05 (6H, m, Ar*H*), 6.94 (4H, d, Ar*H*), 5.41 and 4.14 (8H, 2 × d, *J* 17, NC*H*HAr), 4.12–3.84 (24H, m, OCH_2), 1.84–1.08 [240H, m, OCH$_2$(CH_2)$_{10}$], 1.04–0.80 (36H, m, CH_3), guest (resorcinol) 6.90 (t), 6.21 (dd), 5.75 (br s), 5.49 (s) (Found: C, 77.13; H, 10.56; N, 1.67. Calcd. for $C_{212}H_{334}N_4O_{22}$: C, 77.37; H, 10.23; N, 1.70%).

Complex formation

The 1:1 complexes were prepared by mixing *ca*. 20 mg of clip molecule (5–10 × 10^{-6} mol) and an equimolar amount (between 0.7–1.5 mg) of guest (5–10 × 10^{-6} mol) in 0.2 ml of $CHCl_3$. If necessary 1–3 drops of acetone were added. 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 in a stainless-steel large volume pan (75 μl). Thermograms were recorded at 10 °C min^{-1} and repeated heating and cooling runs were recorded to study the stability of the complex and the reproducibility of the measurements. Polarizing microscopy was carried out using the same heating and cooling rates.

References

1 V. Percec and D. Tomazos, *Comprehensive Polymer Science*, 1992, **I**, 300.
2 (*a*) V. Percec, G. Johansson and R. Rodenhouse, *Macromolecules*, 1992, **25**, 2563; (*b*) V. Percec and G. Johansson, *J. Mater. Chem*., 1993, **3**, 83.
3 (*a*) J.-M. Lehn, J. Malthête and A. M. Levelut, *J. Chem. Soc*., *Chem. Commun*., 1985, 1794; (*b*) J. Malthête, A. M. Levelut and J.-M. Lehn, *J. Chem. Soc*., *Chem. Commun*., 1992, 1434.
4 (*a*) A. Liebmann, C. Mertesdorf, T. Plesnivy, H. Ringsdorf and J. H. Wendorff, *Angew. Chem*., 1991, **103**, 1358; (*b*) G. Lattermann, S. Schmidt and B. Gallot, *J. Chem. Soc*., *Chem. Commun*., 1992, 1091; (*c*) G. Lattermann, S. Schmidt, R. Kleppinger and J. H. Wendorff, *Adv. Mater*., 1992, **4**, 30.
5 J. Malthête and A. Collet, *J. Am. Chem. Soc*., 1987, **109**, 7544.
6 T. Komori and S. Shinkai, *Chem. Lett*., 1993, 1455.
7 B. Xu and T. M. Swager, *J. Am. Chem. Soc*., 1993, **115**, 1159.
8 (*a*) R. P. Sijbesma, A. P. M. Kentgens and R. J. M. Nolte, *J. Org. Chem*., 1991, **56**, 3199; (*b*) R. P. Sijbesma, A. P. M. Kentgens, E. T. G. Lutz, J. H. van der Maas and R. J. M. Nolte, *J. Am. Chem. Soc*., 1993, **115**, 8999.
9 (*a*) R. P. Sijbesma and R. J. M. Nolte, *J. Am. Chem. Soc*., 1991, **113**, 6695; (*b*) R. P. Sijbesma, S. S. Wijmenga and R. J. M. Nolte, *J. Am. Chem. Soc*., 1992, **114**, 9807.
10 V. Percec, M. Lee, J. Heck, H. E. Blackwell, G. Ungar and A. Alvarez-Castillo, *J. Mater. Chem*., 1992, **2**, 931.
11 For a related study see: J. L. M. van Nunen, B. J. B. Folmer and R. J. M. Nolte, *J. Am. Chem. Soc*., 1997, **119**, 283.
12 J. W. H. Smeets, R. P. Sijbesma, L. van Dalen, A. L. Spek, W. J. J. Smeets and R. J. M. Nolte, *J. Org. Chem*., 1989, **54**, 3710.
13 E. Vowinkel, *Chem. Ber*., 1967, **100**, 16.
14 The reaction product of **5** and benzoyl chloride was obtained in 61% yield. δ_H(400 MHz, $CDCl_3$) 8.38 (8H, d, *J* 16, Ar*H*), 7.71–7.67 (12H, m, Ar*H*), 7.18 (4H, s, Ar*H*), 7.10–7.00 (10H, m, Ar*H*), 5.27 and 3.94 (8H, 2 d, *J* 16, CH_2N).
15 During the course of our study we found out that complex formation proceeds much better with the method described in this paper than with the method published previously by us, *cf*. J. L. M. van Nunen, R. S. A. Stevens, S. J. Picken and R. J. M. Nolte, *J. Am. Chem. Soc*., 1994, **116**, 8825.
16 J. Reek, unpublished results. Binding constants of clip **1** with DHB and MDB amount to $K_a = 2600$ and $K_a = 15\,000$ dm^3 mol^{-1}, respectively.
17 F. G. M. Niele and R. J. M. Nolte, *J. Am. Chem. Soc*., 1988, **110**, 172.
18 R. P. Sijbesma and R. J. M. Nolte, *Recl. Trav. Chim. Pays-Bas*, 1993, **112**, 643.

Paper 7/00936D
Received 3*rd February* 1997
Accepted 21*st March* 1997