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Cholesteric liquid crystal displays as optical sensors of barbiturate binding

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The influence on the optical properties of cholesteric liquid crystal displays (LCDs) was examined for neutral molecule binding by mesogen/receptors in the mesomorphic phase. The motivation was to prepare neutral molecule sensors that use a colour change to signal analyte binding. A receptor that binds barbiturate analytes was modified with two or one cholesteryl groups to yield compounds **2** and **3**, respectively. LCDs were prepared by incorporating one of the receptor/mesogen compounds into a cholesteric LC blend along with a potential H-bonding guest. The optical properties of the LCDs were then determined by measuring the absorbance of the displays. For various LCDs, the colour of the display depended upon several factors: the amount of guest molecule used, the number of cholesteryl side chains on the receptor and the mole concentration of receptor/mesogen in the blend. In particular, complementary host/guest binding of H-bonding analytes by the bis(cholesteryl) receptor **2** in a cholesteric LCD caused a change of up to +70 nm, which was observed by the naked eye as a blue-to-orange colour change. Control experiments confirm that the colour of an LCD is a consequence of molecular recognition in the mesomorphic phase.

1. Introduction

Liquid crystals have received attention as media for studying molecular recognition events [1–6]. These efforts have been based on the observation that the optical and electronic properties of some mesomorphic systems change upon analyte binding by a host. Consequently, liquid crystals are potentially a new class of chemical sensors that give a visible change when analyte recognition occurs.

A few reported examples of chemical sensors based on liquid crystals use cholesteric liquid crystals (CLCs) [5, 6]. CLCs have a chiral nematic structure and consequently possess a supramolecular helical pitch [7]. The helical pitch of a CLC interacts with incident light in such a way that one circular component is absorbed, whereas the other component experiences a Bragg-type reflection [7, 8]. CLC systems are usually coloured, since the reflected light typically appears as a band in the visible region. In addition, the wavelength of the reflected light depends on the magnitude of the helical pitch. Therefore, variations in the supramolecular CLC helical pitch lead to easily observed colour changes in the liquid crystal. Non-specific and non-selective host–guest binding events in CLCs have been detected by monitoring the optical changes of these mesomorphic systems [5, 6]. Presumably, guest binding causes a conformational change in the host that affects the supramolecular helical pitch of the CLC system.

We are interested in preparing selective and specific neutral molecule sensors that use a visible response as the signalling event. A series of hosts designed by Hamilton and co-workers [9, 10] contain two 2,6-diaminopyridine receptors that bind barbiturates through six hydrogen bonds [9–13]. The receptor **1** shown in figure 1 undergoes a large conformational change upon guest binding [9]. In preliminary experiments, we found that the unsubstituted host **1** was not cleanly incorporated into a CLC medium. Consequently, our strategy for preparing a liquid crystal sensor system that recognizes a barbiturate analyte was to covalently attach cholesteryl mesogen units via amide bonds to the receptor **1**. The cholesteryl groups appended to **2** [13] and **3**, as shown in figure 1, should facilitate formation of a homogeneous mesomorphic system and should also enhance transmission of conformational information about the receptor to the overall supramolecular architecture. Receptor **2** is substituted with two cholesteryl units, whereas **3** contains only one cholesteryl moiety. Consequently, **2** and **3** should also allow us to evaluate the importance of

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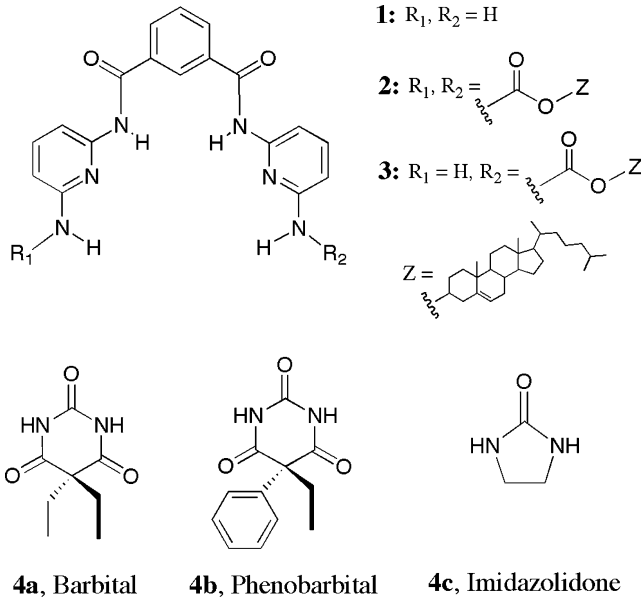

Figure 1. Molecular structures of the mesogen/hosts and potential guests.

cholesteryl substitution on the optical properties of the liquid crystal systems.

Three neutral guest species are also shown in figure 1. The barbiturate guests, **4a** and **4b**, bind strongly with **1** (reported K_a values for 1:1 binding are ca. 10^5 for **4a**) [9]. We expected that the surrogate guest **4c**, imidazoladone, would be bound much less strongly by the host **1** as the complex **1:4c** uses only three hydrogen bonds. A six-membered cyclic urea (5,5-bisethylhexahydro-2-pyrimidinone) that is a structural analogue of imidazoladone, **4c**, has a reported K_a value ca. 10^2 for 1:1 binding [9].

In this study we prepared a number of LCDs containing either **2** or **3** and a neutral molecule analyte. We then analysed the colour characteristics of the LCDs by measuring the wavelength of maximum reflectance, λ_R [14]. We found that the colour of an LCD prepared with either **2** or **3** and a H-bonding analyte depended upon the following factors: the number of guest equivalents in the LCD system; the number of cholesteryl substituents on the receptor/mesogen compound; and the amount of host compound in the mesomorphic blend. We also found that LCDs prepared with a 2.0 mol. % of molecule **2** serve as a selective molecular sensor for **4a** and **4b**. In some cases we observed maximum shifts in reflected light up to 70 nm that accompany guest binding by **2** in the CLC medium.

2. Results and discussion

Sandwich-type LCDs were prepared with a blend of cholesteryl chloride, cholesteryl pelargonate and either **2** or **3** [5, 6]. The LCDs discussed below are summarized in table 1. The cholesteryl blends contained 2.0–5.4 mol. % of a receptor/mesogen. Small amounts of a guest species were added to the mesogen blend in $CHCl_3$, and a 200 µl aliquot of this solution was placed on a glass cover slip. After the $CHCl_3$ evaporated, the sticky mesogen residue was sandwiched with a second cover slip. Uniform LCD thickness was maintained by placing 10 µm glass beads on the glass slide along with the liquid crystal blend solution. LCDs prepared using this protocol were stable for several hours. The optical properties of the LCDs described below were always evaluated immediately after preparation.

The optical properties of the LCDs were analysed by measuring the wavelength of maximum reflectance, λ_R, which was deduced from the absorbance of the sandwich cell [14]. The spectra in figure 2 illustrate the absorption measurements for a series of LCDs prepared with host/mesogen **2** and guest **4a**. The LCDs prepared with no guest molecules and 5.4 mol. % mesogen/host had initial average λ_R values (λ_{Ri}) of 492 nm and 576 nm for compounds **2** and **3**, respectively.

In all LCDs that contained one of the hydrogen-bonding guests (**4a**, **4b** or **4c**) and **2**, the λ_R value moved to a wavelength longer than λ_{Ri}. The observed optical changes for individual LCDs prepared with **2** and varying amounts of **4a** are shown in figure 2. The spectral changes for LCDs prepared with **2** and either of the other hydrogen bonding guests, **4b** or **4c**, were similar

Table 1. Summary of LCD blends. All LCDs were prepared as blends of cholesteryl chloride (C), cholesteryl pelargonate (P), either **2** or **3**, and small amounts of a potential guest.

				Mol. % in LCD	
Exp.	Guest	Host	Host	C	P
a	**4a**	**2**	5.4	37.2	57.4
b	**4b**	**2**	5.4	37.2	57.4
c	**4c**	**2**	5.4	37.2	57.4
d	**4a**	**3**	5.4	37.2	57.4
e	**4a**	**2**	2.0	39.0	59.0
f	**4c**	**2**	2.0	39.0	59.0

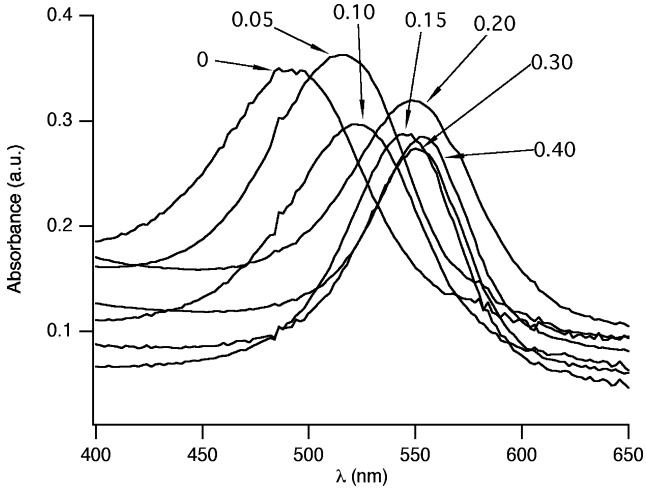

Figure 2. Absorbance spectra of individual LCDs prepared with **2** and varying equivalents of **4a**. In all cases, the LCDs were prepared as a blend with 5.4 mol. % **2**, 37.2% cholesteryl chloride and 57.4 mol. % cholesteryl pelargonate. The absorbance measurements were referenced to an air background.

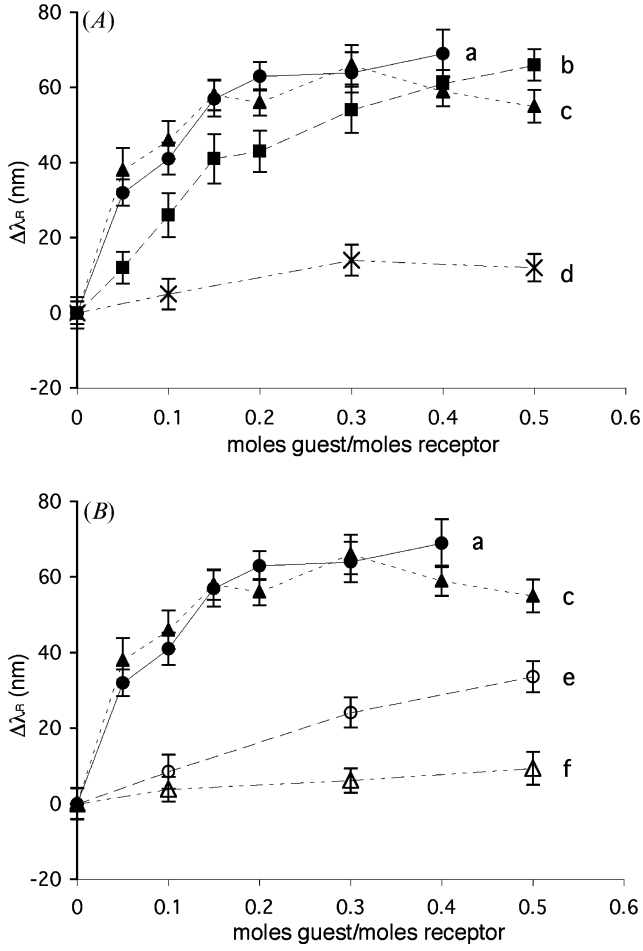

Figure 3. Plot of wavelength of maximum reflection, λ_R, vs. equivalents of guest for various sandwhich LCDs. All LCDs were prepared as blends of cholesteryl chloride (C), cholesteryl pelargonate (P), either **2** or **3**, and small amounts of a potential guest. The vertical error bars represent the 95% confidence intervals for all data points. (*A*): ● (a) **4a**, 5.4 mol. % **2**; ■(b) **4b**, 5.4 mol. % **2**; ▲ (c) **4c**, 5.4 mol. % **2**; × (d) **4a**, 5.4 mol. % **3**. (*B*): ● (a) **4a**, 5.4 mol. % **2**; ▲ (c) **4c**, 5.4 mol. % **2**; ○ (e) **4a**, 2.0 mol. % **2**; Δ(f) **4c**, 2.0 mol. % **2**.

to those depicted in figure 2. The optical changes may be caused by similar changes in the liquid crystal matrix for all LCDs prepared in this study, namely, an increase in the supramolecular helical pitch [8]. In a related system involving chiral ammonium cation binding by cholesteryl-modified crown ethers, Shinkai and co-workers observed that the direction of λ_R shifts depended upon the specific stereochemistry of the analyte [6]. None of the guests used here are chiral, so the positive changes observed in our study cannot result from preferential binding of a specific stereoisomer.

Changes in λ_R ($\Delta\lambda_R$) were calculated via

$$\Delta\lambda_R = \lambda_{Rf} - \lambda_{Ri}, \quad (1)$$

where λ_{Rf} is the wavelength of maximum absorbance for an LCD with some number of guest equivalents in the blend.

We found that for various LCDs, $\Delta\lambda_R$ depended upon several factors: the amount of guest molecule used, the number of cholesteryl side chains on the receptor and the mole concentration of receptor/mesogen in the blend. As seen in figures 2 and 3, $\Delta\lambda_R$ depends on the number of equivalents of guest molecules per moles of receptor species for displays prepared with either **2** or **3**. The error bars in figure 3 represent the 95% confidence interval for a series of identically prepared LCDs.

As shown in figure 3(*A*) (experiments a–c), the $\Delta\lambda_R$, and consequently the colour, of the LCDs changes as a function of the concentration of H-bonding guests **4a**, **4b**, and **4c** for LCDs with a set blend composition of 5.4 mol. % receptor **2**. Displays prepared with compounds **2** and **4a** show a maximum change of nearly +70 nm for $\Delta\lambda_R$. To the naked eye, this maximum optical response corresponds to a blue-to-orange colour change for the display. The change in $\Delta\lambda_R$ for LCDs prepared with 5.4 mol. % of **2** is nearly linear for systems that contain up to ca. 0.20 equivalents of the H-bonded guest molecules (figure 3(*A*), experiments a–c). Thereafter, the optical changes are essentially saturated for all LCDs. The optical saturation with LCDs with 5.4 mol. % receptor **2** suggests that a small amount of guest binding may lead to large changes in the supramolecular helical pitch, and consequently, the colour of the LCD.

In control experiments with benzene as a potential guest the change in $\Delta\lambda_R$ was <5 nm after 0.5 equivalents (data not shown). This strongly suggests that host–guest binding is responsible for the observed changes. In other control experiments, no changes in $\Delta\lambda_R$ were observed when either of the barbiturate guests or benzene was added to LCD blends that lacked either **2** or **3** (data not shown). This result indicates that the observed colour change is not a dopant effect caused by the guest. Clearly, both the receptor and a potential guest are required for a colour change to occur.

The magnitude of change in $\Delta\lambda_R$ also clearly depends upon the extent of cholesteryl substitution on the receptor/mesogen. A comparison of experiments a and d in figure 3(*A*) shows that for guest **4a**, systems prepared with the bis(cholesteryl) substituted receptor **2** display a more significant optical response than do equivalent LCDs made with the mono(cholesteryl) **3**. Indeed, the optical response for **3** with barbital is very similar to that observed with the non-complementary guest benzene. Note that we compared LCDs with the same mole percent of compound **2** or **3**. This result shows that the conformational changes that accompany host–guest binding are more effectively communicated by receptor **2** than by compound **3** to the liquid crystal supramolecular architecture. It is odd that essentially no colour change is observed with the mono(cholesteryl)-substituted receptor. In previous work, Shinkai and co-workers observed that analyte binding by various receptors modified with one steroidal moiety lead to observable colour changes in similar cholesteric LCD systems [5, 6]. The different responses of mono-substituted receptors reported here and by Shinkai may be related to differences in the amount of conformational change that accompanies host/guest binding in the two systems.

We were surprised by the results of LCDs prepared with **2** and the more weakly bound barbiturate surrogate **4c**. As seen in figure 3(*A*), the $\Delta\lambda_R$ for identically prepared LCDs containing **2:4c** (c) was essentially indistinguishable to the optical changes observed for binding of the barbiturate guests **4a** and **4b** (a and b). Because of the weaker binding of urea analytes [9], we expected that the optical changes would be less pronounced for **4c** relative to the barbiturate guests. We observed similar behaviour in LCDs prepared with another weakly binding analyte, glutarimide [12]. The $\Delta\lambda_R$ for LCDs prepared with **2** and glutarimide followed the same trend as that observed for **4a**, **4b** and **4c** (data not shown). The samples prepared with 5.4 mol. % loading of **2** are sensitive to guest binding, but the LCDs are not selective sensors of the target barbiturate analytes.

As our primary objective was to prepare selective neutral molecule sensors we investigated ways to reduce or eliminate the optical changes in LCDs that contain the weakly binding **4c** or glutarimide. We hypothesized that the similar optical results for LCDs prepared with **4a**, **4b** or **4c** and **2** might be related to the optical saturation noted earlier for LCDs that contain 5.4% mole fraction of mesogen/receptor. To investigate this point, we prepared a series of LCDs with a 2.0% mole fraction of receptor **2**. The LCDs prepared with no guest molecules and 2.0 mol. % **2** had an initial average λ_{Ri} value of 546 nm. The observed optical changes for individual LCDs prepared with 2.0 mol. % **2** and varying amounts of **4a** and **4c** are shown in figures 4(*A*) and 4(*B*) respectively.

Once again, figure 4(*A*) shows that a colour change was observed for LCDs prepared with 2.0 mol. % **2** as a

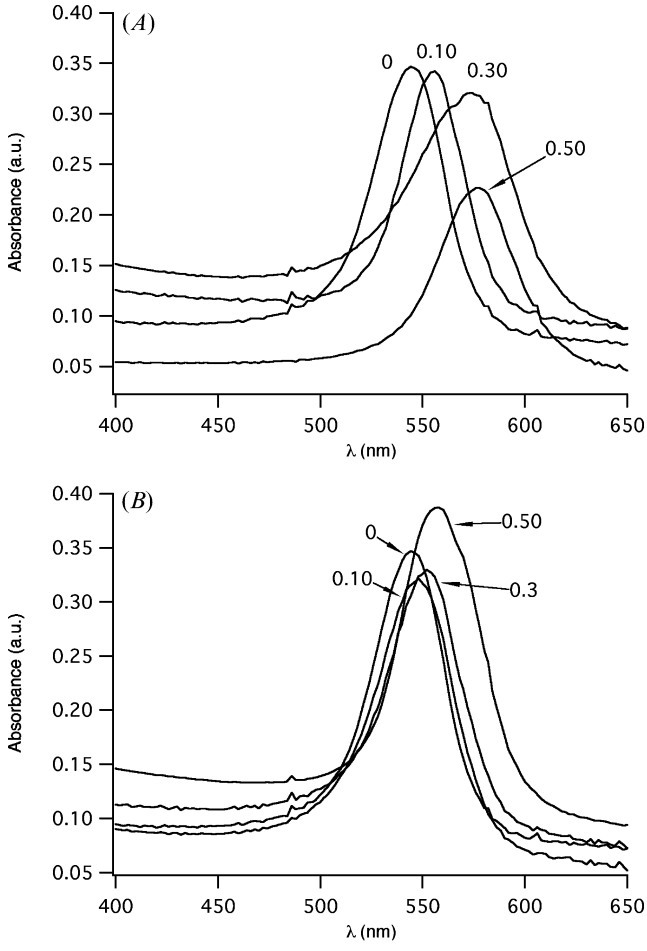

Figure 4. Absorbance spectra of individual LCDs prepared with **2** and varying equivalents of neutral guest molecules. In all cases, the LCDs were prepared as a blend with 2.0 mol. % **2**, 39.0% cholesteryl chloride and 59.0 mol. % cholesteryl pelargonate. The absorbance measurements were referenced to an air background. (*A*): guest **4a**; (*B*): guest **4c**.

function of the amount of barbiturate guest **4a**. The effect of host loading on $\Delta\lambda_R$ for several LCDs is illustrated in figure 3(*B*). Not surprisingly, we found that $\Delta\lambda_R$ depends upon the mole concentration of receptor/mesogen in the blend. The optical responses for the LCDs that contained 2.0 mol, % **2** were smaller than the changes observed when equivalent amounts of a barbiturate molecule were added to systems with a 5.4 mol. % loading of the bis(cholesteryl) receptor/mesogen (figure 3(*B*), (a and e)). However, the optical changes caused by binding of **4a** were nearly linear over the entire range of experiments with 2.0 mole % **2**. The optical changes for LCDs prepared with **4b** and 2.0 mol. % **2** were similar to those observed for guest **4a** (data not shown).

Likewise, as shown in figure 3(*B*), (c and f), we observed a large difference in the optical changes for LCDs prepared with **4c** and 2.0 % mole fraction of host **2** when compared with the $\Delta\lambda_R$ values for systems with 5.4 % of the bis(cholesteryl) mesogen/receptor. In fact, over the range of experiments investigated here, we observed very little change in the optical properties of LCDs prepared with 2.0 mol. % **2** and **4c** (figure 4(*B*)). Indeed, the $\Delta\lambda_R$ values for LCDs prepared with 2.0% mole fraction **2** and **4c** are similar to the optical responses observed in the control experiments with benzene guest. The $\Delta\lambda_R$ values for LCDs prepared with 2.0% mole fraction **2** and the weakly binding glutarimide parallel the behaviour observed for samples that contain **4c** (data not shown). It is clear that the colour of the LCDs depends on the amount of receptor/mesogen in the mesomorphic blend.

The results depicted in figures 3(*B*) and figure 4 show that the optical responses for binding of barbiturate **4a** and the more weakly bound **4c** could be distinguished in LCDs that contained 2.0 mol. % receptor **2** (e and f). These results indicate that the formulation of an LCD sensor is an important consideration for the discrimination of different analytes.

3. Conclusions

In summary, we have demonstrated that hydrogen bonding of neutral guest molecules can be detected by evaluating the optical changes of a cholesteric liquid crystal display. Host–guest molecular recognition of barbiturates and a surrogate urea induces a visible colour change in LCDs that contain the bis(cholesteryl)-substituted host **2**. The magnitude of the colour change depends upon the extent of cholesteryl substitution on the receptor, with more cholesteryl groups leading to a more substantial optical response. The colour of the LCDs also depends on the number of guest equivalents in the mesogen blend. In addition, the optical response is saturated under certain conditions and the binding of different analytes can not be distinguished. Therefore, the formulation of the LCD blend is an important consideration in the preparation of sensors based on this approach. In this study, LCDs prepared with lower amounts (2.0 mol. %) of the mesogen/receptor serve as selective sensors for barbiturates. In the system described here, LCDs that contain 5.4 mol. % mesogen/receptor are sensitive sensors in that significant visible changes are observed with small levels of guest amounts. However, the LCDs with 5.4 mol. % **2** are not able to discriminate between the target analytes and more weakly binding surrogates. The sensitivity of guest binding is sacrificed to improve the selectivity of analyte recognition. We are continuing to investigate this and other molecular recognition systems in cholesteric liquid crystals with the goal to prepare highly sensitive and selective sensors.

4. Experimental

4.1. *Materials*

Chloroform and tetrahydrofuran (THF) were distilled (from P_2O_5 and potassium, respectively) before use. All other solvents, starting materials and reagents were used as received. Receptors **1** [9] and **2** [13] were prepared as described in previous reports.

4.2. *Synthesis of compound 3*

Mesogen/receptor **1** (2.79 mmol), TEA (2.79 mmol) and DMAP (0.56 mmol) were dissolved in 200 ml THF. Cholesteryl chloroformate (2.79 mmol) in 75 ml THF was added dropwise to the reaction. After stirring for 48 h the solvent was removed *in vacuo*. The residue was dissolved in 100 ml CH_2Cl_2 and washed sequentially with 100 ml 5 % $NaHCO_3$ and $2\times$ 100 × ml water. The solvent was removed from the organic layer to yield a tan residue. The solid was purified on a silica column with 98/2 CH_2Cl_2/MeOH, then recrystallized from CH_2Cl_2/MeOH. TLC and elemental analysis results indicated the presence of a small amount of an impurity that could not be removed with repeated chromatography separations and crystallizations. TLC results also indicated that the impurity was not the bis-substituted receptor **2**. The impurity was not resolved in ^{1}H NMR experiments. We estimate that the impurity represented ca. 5% of the sample mixture. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.69 (s, 3 H), 0.78–2.50 (m, 40 H), 4.27 (br, 2 H), 4.55–4.74 (m, 1 H), 5.31–5.48 (m, 1 H), 6.32 (d, 1H), 7.53 (t, 1 H), 7.63 (t, 1 H), 7.69–7.80 (m, 3 H), 8.01 (d, 1 H), 8.09 (d, 2 H), 8.32–8.47 (m, 2 H), 8.51 (s, 1H), 8.60–8.80 (br, 1H). Melting point: 191–200°C.

4.3. *Preparation of LCDs*

Sandwich-type LCDs were prepared as a blend of cholesteryl chloride, cholesteryl pelargonate and either **2** or **3** [5, 6]. The cholesteryl blends were dissolved in 0.5 ml $CHCl_3$ and contained 2.0 or 5.4 mol. % of receptor/mesogen. A guest solution was prepared separately in 10.0 ml $CHCl_3$. A small amount of the guest solution was added by syringe to the mesogen blend and the final solution was diluted to 1.0 ml with $CHCl_3$. A 200 µl aliquot of the host/guest solution and 10 µm glass beads were placed on a glass cover slip. After the mixture dried for 30 min, the sticky mesogen residue was sandwiched with a second cover slip. Four identical LCDs were prepared from each host/guest solution. The entire procedure was repeated at least three more times for each host/guest combination so that a minimum of 16 identical LCDs were prepared. LCDs prepared using this protocol were stable for several hours. The optical properties of the LCDs described below were always evaluated immediately after preparation.

4.4. *Evaluation of optical properties of LCDs*

The transmittance of an LCD corresponds to the wavelength of maximum reflectance, λ_R for the system [14]. In control experiments we found that the absorption maximum was numerically equivalent to the transmittance minimum. Moreover, the absorption spectra were easier to obtain and yielded better signal-to-noise than the transmittance measurements. Consequently, the optical properties of the LCDs were analysed by measuring the absorbance of the sandwich cell with an air background.

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