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Novel cholesteric glassy liquid crystals of monosubstituted ferrocenes: synthesis and selective reflection properties of a dimesogen, and crystal structure of a monomesogen

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Several monomesogens of ferrocene derivatives bearing the *N*-benzoyl-*N*′-arylthiourea (BATU) bidentate ligand have been synthesized. A non-symmetric dimesogen in which two structurally different mesogenic groups, namely the BATU and cholesteryl moieties, interlinked by a flexible spacer has also been synthesized. The achiral monomesogens exhibit enantiotropic smectic C and nematic phases, while the chiral monomesogens show exclusively a cholesteric phase with selective reflection in the infrared region. The dimesogen, on the other hand, exhibits an enantiotropic cholesteric phase with selective reflection in the visible region with iridescent colours. This represents the first ferrocene based organometallic liquid crystalline compound exhibiting this unique property. The cholesteric phases formed transform to glassy liquid crystals which can be fixed on sudden cooling to 0°C. The Grandjean texture observed in the cholesteric temperature range was retained in the glassy state depicting helical orientation in the glassy solid. Furthermore, X-ray crystal structure determination of one of the compounds (Fc-BATU-12) provided evidence implying the involvement of structure-determining intra- and inter-molecular interactions in all the liquid crystalline compounds involving BATU units. The crystallographic data confirms that these systems fulfil the two prerequisites for calamitic (rod-like) mesomorphism, namely critical length/depth ratio (>5) and an extended linear shape.

1. Introduction

The most important feature of the helical structure of the cholesteric phase is the selective reflection of circularly polarized light and the angular dependence of the reflected wavelength. The range of the reflected wavelength can vary from a few nm to the entire UV-Vis-IR spectral region. Recently there has been much development in the utilization of this property of cholesteric liquid crystals (CLCs) in the field of information technology, mainly in reflective displays, reflective polarizers, diffuse reflectors, optical filters, etc. [1]. In particular, a flat panel display in reflection mode using CLCs has the advantage of saving electric power, a memory property without electricity and good visibility under high illumination. The number of low molecular mass liquid crystals suitable for the fixation of the cholesteric molecular ordering by sudden cooling is limited compared with polymeric systems. Tamaoki *et al.* showed that cholesteric LCs can be used to develop full colour rewritable recording devices that can operate in the thermal and photon modes [2].

Recently there has been an upsurge of interest in unsymmetric dimesogens which contain two non-identical mesogenic cores, namely a cholesteryl ester unit attached to different moieties [3, 4]. This group of compounds belongs to a new class of LCs because in such systems two incommensurate smectic modulations can exist. One corresponds to the length of the cholesteryl part, the other is connected with the overall dimesogen length. From the applications point of view, the synthesis of non-symmetric ferroceno-dimesogens in which two structurally different mesogenic groups are interlinked by a flexible spacer, and exhibiting fixed cholesteric colours with glass transition (T_g), would be of great interest in the development of rewritable memory or recoding media. This is because ferrocene-based metallomesogens form one of the most widely studied classes of metal-containing liquid crystals, due to their high thermal stability and low oxidation–reduction potential. Ferrocene, due to its aromatic character, facilitates several possibilities for functionalizing

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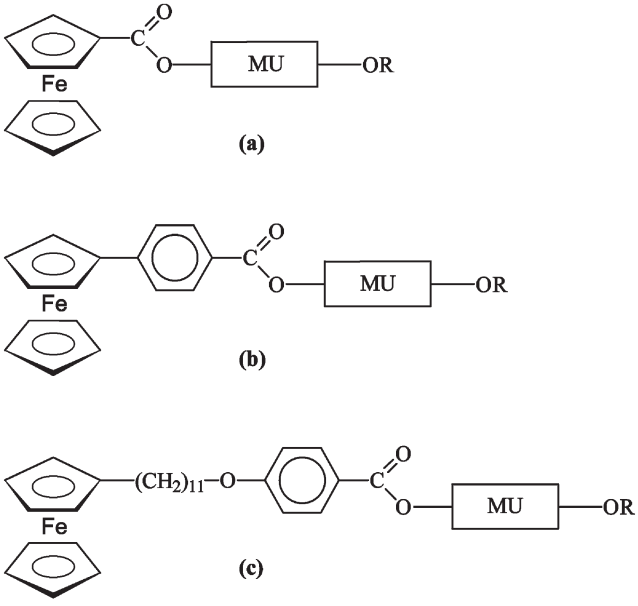
mesogenic units to manipulate their mesomorphic properties, for example through mono- or 1,1-, 1,3-disubstitution or 1,1,3-trisubstitution [5–9].

In monosubstituted ferrocenomesogens, the ferrocenyl unit is located at the terminus of the molecule as shown in figure 1. The mesogenic properties as well as chemical and thermal stability can be tuned by varying the nature of groups attached immediately adjacent to the ferrocenyl moiety. The series (a) gives compounds which possibly are susceptible to hydrolysis, whereas series (b) exhibit exclusively nematic phases [7 *a*], [10 *a*]. Nakamura *et al.* [7 *b*] synthesized several monosubstituted ferrocene derivatives containing a cholesteryl group which exhibited only monotropic smectic C phases.

We previously found that rich mesomorphic properties including TGBA and Blue phases can be obtained when a flexible alkyloxy chain $-(CH_2)_{11}-O-$ is placed between the ferrocenyl moiety and the phenyl group followed by a suitable mesogenic unit and flexible alkyl chain as a terminal group, series (c) in figure 1 [11]. Based on this we prepared compounds **1** and **2** [12] (see scheme 2) with a spacer which exhibited exclusively cholesteric (N*) phases with the unique property of selective reflection. The cholesteric phases formed transform to glassy liquid crystals (LCs) which could be fixed on sudden cooling to 0°C.



L-Shape: 1-Substitution
where MU: Mesogenic unit; R = Terminal alkylchain

Figure 1. Different ways of attaching a mesogenic unit to the ferrocenyl moiety.

Low molecular mass chiral ferrocenomesogens suitable for fixation of the cholesteric molecular ordering by sudden cooling have not been reported before. Compounds **1** and **2** are the first ferrocene-based non-steroid systems exhibiting this optical property. Recently Das and co-workers reported on azopyridine-containing silver complexes exhibiting similar behaviour [13]. However, compounds **1** and **2** exhibit only a very narrow range of light reflection in the visible region. Therefore, we have extended our investigations on glassy LCs in combination with a flexible alkyloxy chain placed between the ferrocenyl moiety and the phenyl group by incorporating a steroid unit like cholesterol in the mesogenic system, to attain a wide range of light reflection and to develop rewritable recording media using these and other systems; see series (c) in figure 1.

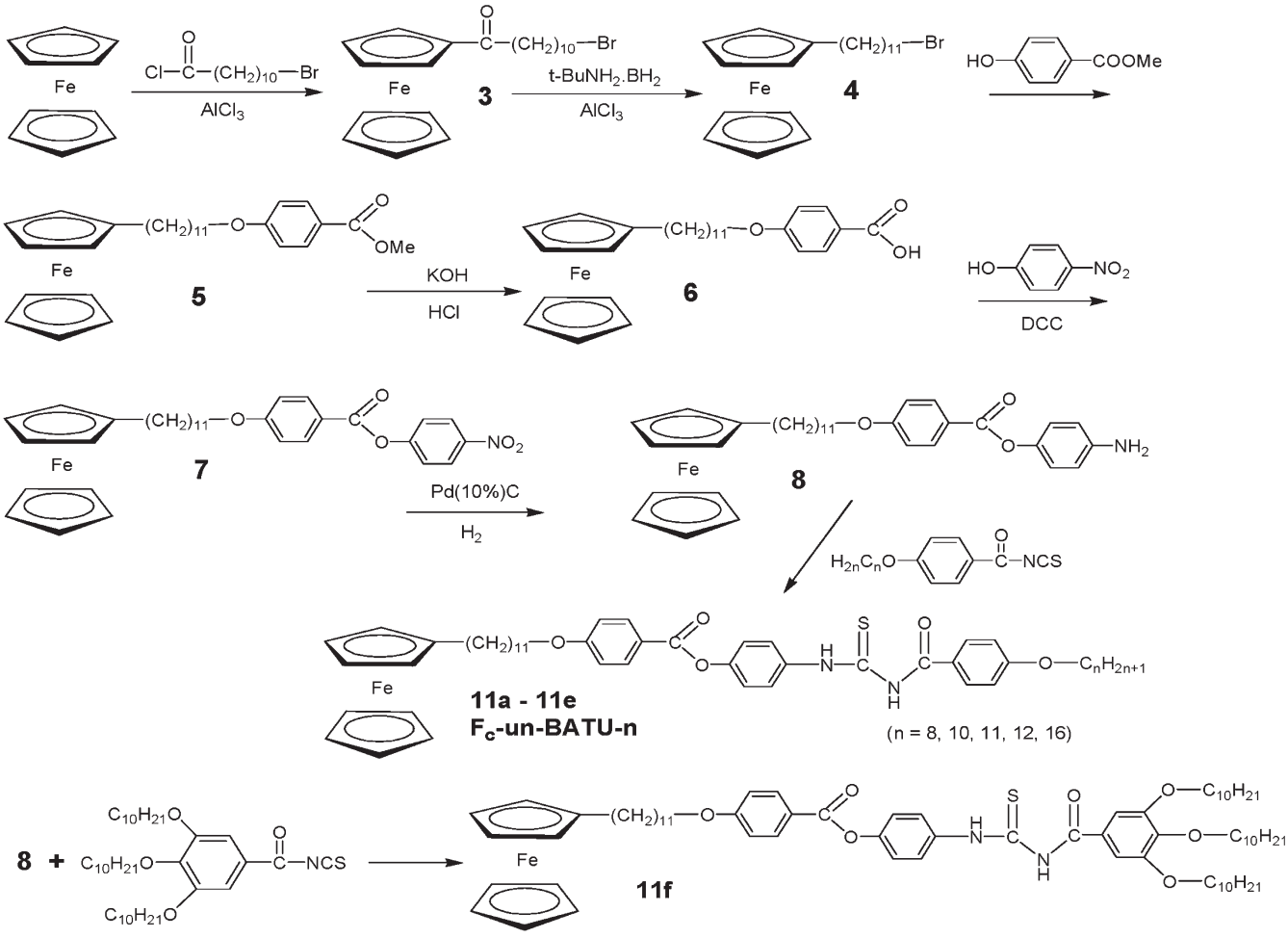
In continuation of our ongoing studies on the ferrocene compounds [7 *a*], [11] we report herein on the synthesis and characterization of a dimesogen containing a versatile bidentate ligand, namely *N*-benzoyl-*N*′-arylthiourea (BATU) [14] and cholesterol. For comparative purposes, we also prepared several monomesogens without cholesterol. We have chosen BATU in the system for two reasons. (i) It readily forms inter- and intra-molecular hydrogen bonding, a useful property which presumably inhibits the formation and growth of the nucleus of the crystal; this helps in the formation of glassy CLCs in combination with the cholesterol unit. (ii) It could serve as a building block for preparing heterometallic liquid crystal systems with novel magnetic, electrical and optical properties.

The synthetic route for the preparation of the monomesogens is shown in schemes 1 and 2, the route for the dimesogen is given in scheme 3. Further X-ray crystal structure determination of one of the related compound **11g** [7 *a*] (Fc-BATU-12) is presented. The crystallographic data confirm that these systems fulfil the two prerequisites to exhibit calamitic (rod-like) mesomorphism, namely critical length/depth ratio (>5) and an extended linear shape coupled with intra- and intermolecular interactions

2. Experimental

2.1. *General methods*

The solvents acetone and dichloromethane were distilled over P_2O_5 before use; benzene was distilled over sodium. All the reactions were carried out under argon. For column chromatography (CC) we used silica gel 60 (70–230 mesh), and thick layer chromatography (TPC) silica gel plates were prepared in our laboratory. Transition temperatures (endo- or exo-thermic onset



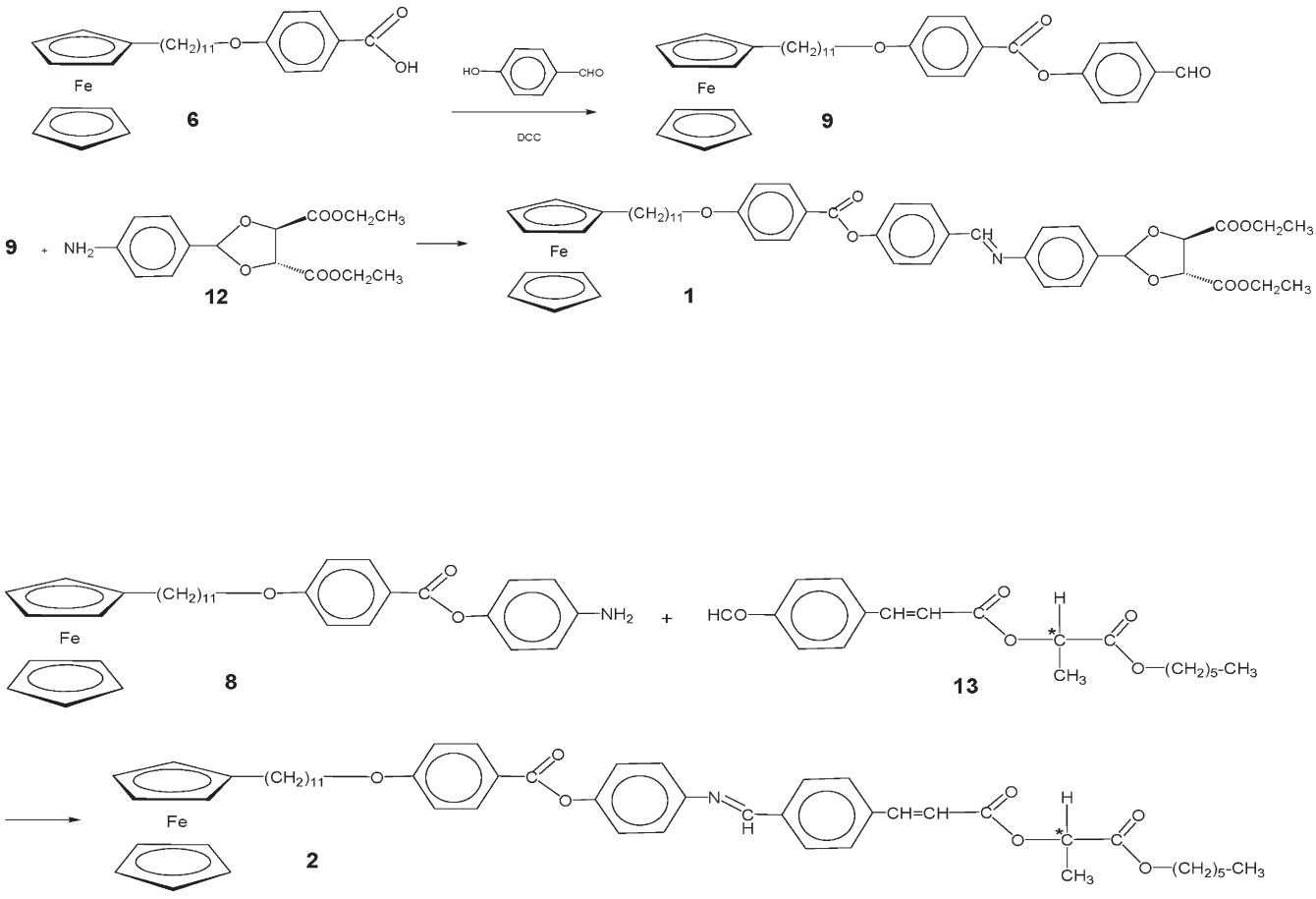
Scheme 1. Synthesis of monomesogens Fc-un-BATU-*n*.

point) and enthalpies were determined with a differential scanning calorimeter (Mettler DSC-30) connected to a Mettler TA 4000 processor, rate 10°C min^{-1} under nitrogen; data treatment used Mettler TA 72.2/.5 Graphware. Optical studies were conducted using a Zeiss-Acioscop polarizing microscope equipped with a Linkam-THMS-600 variable temperature stage under nitrogen. ^{1}H NMR spectra were recorded on a Bruker AMX 300 spectrometer and IR spectra on a Nicolet P 510 FTIR spectrometer. A Perkin-Elmer Microanalyses PE 240 system was used for elemental analysis.

Selective reflection wavelengths were determined as a function of temperature by measuring the reflection spectra of the cholesteric phase of Fc-un-BATU-chol. The samples were prepared between two parallel glass slides, and uniform Grandjean texture was achieved by shearing. The reflection spectra were measured using a microscope (Leitz Ortholux) equipped with a hot stage and a diode array spectrophotometer (Photo Research, Model PR 650). The transmittance spectrum of the Fc-BATU-MeBu cholesteric glassy phase was measured with a Perkin-Elmer Lambda 19 DM spectrophotometer.

For the X-ray structure analysis of Fc-BATU-12 (11g), crystals were obtained by slow diffusion of *n*-heptane into the CH_2Cl_2 solution. Data were collected on a Bruker SMART-CCD diffractometer with graphite monochromated Mo-K_α radiation. Pertinent crystallographic data are given in table 2. The structure solution was obtained with direct and conventional Fourier methods, with full-matrix least-squares refinement based on F^2; all non-H atoms were refined anisotropically, H-atoms derived from ΔF maps were placed at idealized positions and refined with a 'riding' model.

Fully completed cif-file is deposited with the CCDC and the returned deposition number is CCDC269508.



Scheme 2. Synthesis of compounds **1** and **2**.

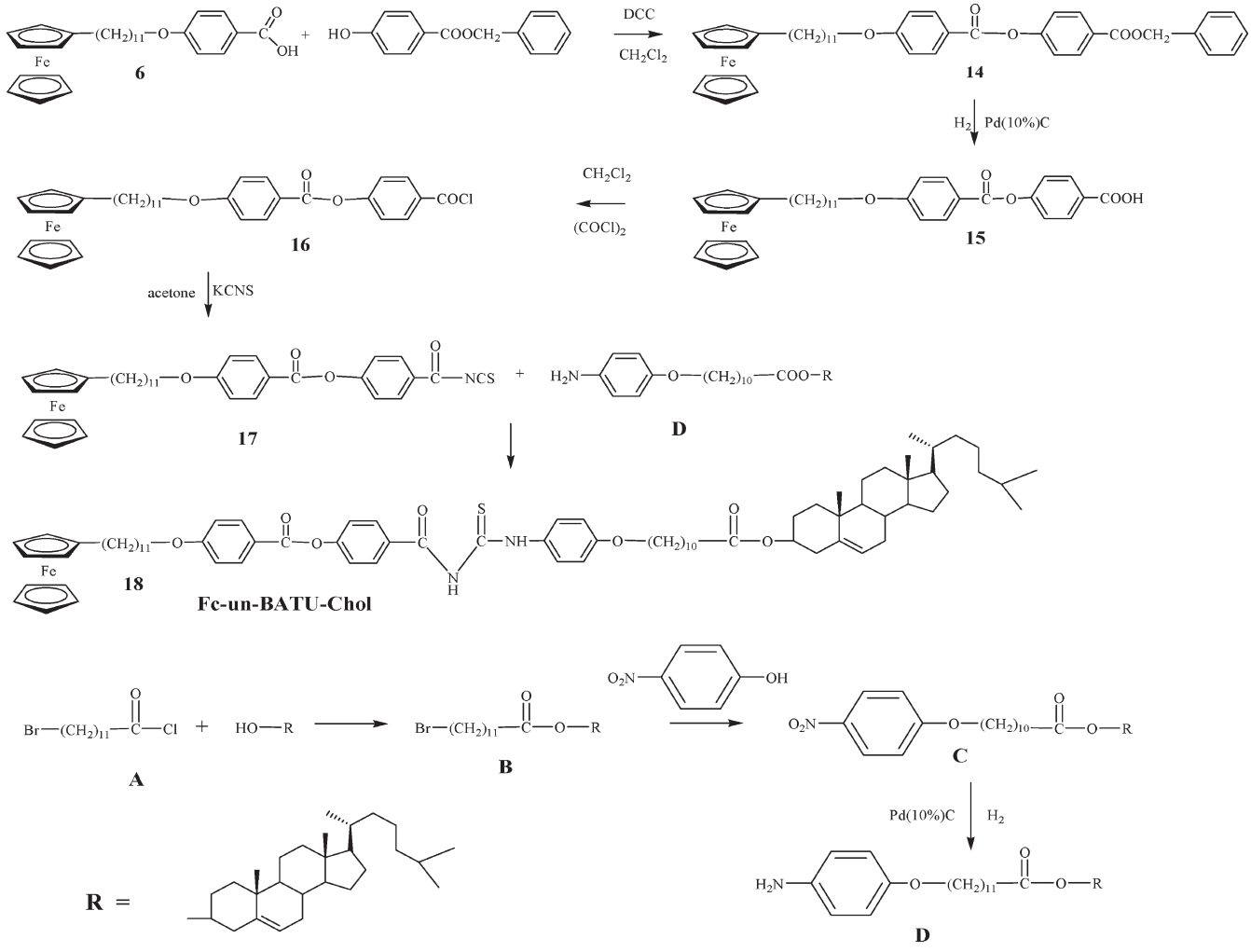
2.2. *Synthesis*

The synthetic routes for the preparation of monomesogens is shown in schemes 1 and 2, and that for a dimesogen is given in scheme 3.

2.2.1. 11-Bromoundecyloylferrocene, 3. A solution of 11-bromoundecyloyl chloride (10.77 g, 38 mmol) in 50 ml CH_2Cl_2 (DCM) was added dropwise to a mixture of ferrocene (6.7 g, 38 mmol) and $AlCl_3$ (5.06 g, 38 mmol) in 100 ml DCM. After stirring for 3 h at room temperature, the reaction mixture was quenched with brine (50 ml) and 100 ml of 10% HCl. The organic layer was separated, washed with dilute aqueous $NaHCO_3$ solution and dried over $MgSO_4$. The residue obtained after removing the solvent was subjected to flash chromatography (silica gel, petroleum ether/ether 99/1); yield 74.6%. ^{1}H NMR ($CDCl_3$): δ 1.30, 1.71 (m, 14 H), 1.85 (q, 2H, CH_2), 2.69 (t, 2H, CH_2), 3.40 (t, 2H, CH_2), 4.19 (s, 5H, C_5H_5), 4.49 (s, 2H, C_5H_4) 4.77 (s, 2H, C_5H_4).

2.2.2. 11-Bromoundecylferrocene, 4. To a suspension of $AlCl_3$ (9 g, 21.53 mol) in 40 ml DCM at 0°C, *t*-$BuNH_2BH_3$ (11.83 g, 136.6 mmol) was added with stirring over 10 min. To this mixture, a solution of **3** (9 g, 21.53 mmol) in 80 ml DCM was added dropwise and stirring continued for 2h at 0°C. The reaction mixture was treated with ethyl acetate, and the organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue chromatographed (silica gel; petroleum ether/ether 99/1). Compound **4** was obtained as an oil which solidified slowly on standing at room temperature; yield 94%. δ_H ($CDCl_3$) 1.30–1.71 (m, 16H, 8 × CH_2), 1.85 (q, 2H, CH_2), 2.34 (t, 2H, CH_2), 3.43 (t, 2H, CH_2), 4.06–4.10 (m, 4H, C_5H_4), 4.12 (s, 5H, C_5H_5).

2.2.3. Methyl 4-(11-ferrocenylundecyloxy)lbenzoate, 5. A mixture of 11-bromoundecylferrocene (7.19 g, 17.17 mmol), 2.61 g (17.17 mmol) of methyl 4-hydroxylbenzoate (2.61 g, 17.17 mmol), K_2CO_3 (4.5 g)



Scheme 3. Synthesis of dimesogen Fc-un-BATU-chol.

and a catalytic amount of KI in 200 ml acetone was stirred under reflux for 48 h and the solvent was removed *in vacuo*. To the residue, 200 ml water was added and the mixture was extracted with DCM. The organic phase was washed with water and dried over $MgSO_4$. The ester obtained after removing the solvent was found to be sufficiently pure; yield 81%. δ_H ($CDCl_3$) 1.19–1.61 (m, 16H, $8 \times CH_2$), 1.76–1.85 (m, 2H, CH_2), 2.17–2.34 (m, 2H, CH_2), 3.89 (s, 3H, OCH_3), 3.98–4.05 (m, 6H, C_5H_4+OCH_2), 4.10 (s, 5H, C_5H_5), 6.89–6.92 (d, 2H, Ar), 7.97–8.00(d, 2H, Ar).

2.2.4. 4-(11-Ferrocenylundecyloxy)benzoic acid, 6. To 7.4 g (15 mmol) of **5** in 40 ml of dioxane, 2 g (30 mmol) KOH in 2 ml of water was added and the mixture heated at 80°C for 8 h. The solvent was removed and the residue dissolved in 100 ml water and extracted with DCM. The organic phase was dried over $MgSO_4$ and the residue left after evaporation of the solvent was recrystallized from ethanol; yield 80%. δ_H ($CDCl_3$) 1.21–1.65(m, 16H, $8 \times CH_2$), 1.79–1.86(m, 2H, CH_2), 2.29–2.34 (m, 2H, CH_2), 3.89–4.09 (m, 6H, C_5H_4+OCH_2), 4.10 (s, 5H, C_5H_5), 6.92–6.95(d, 2H, Ar), 8.05–8.08 (d, 2H, Ar).

2.2.5. 4-Nitrophenyl 4-(11-ferrocenylundecyloxy)benzoate, 7. A mixture of the acid **6**, (3.45 g, 7.25 mmol), 4-nitrophenol (1.0 g, 7.25 mmol), DCC (1.45 g, 7.25 mmol) and 11 mg 4-pyrrolidinopyridine in 50 ml DCM was stirred at room temperature for 72 h and filtered. The residue left after removal of the solvent was recrystallized from ethanol; yield 85%. δ_H ($CDCl_3$) 1.21–1.50 (m, 16H, $8 \times CH_2$), 1.66–1.88 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 3.96–4.07 (m, 6H, C_5H_4+OCH_2), 4.09 (s, 5H, C_5H_5), 6.99 (d, 2H, Ar), 7.39 (2H, Ar), 8.13 (d, 2H, Ar), 8.31 (2H, Ar).

2.2.6. 4-Aminophenyl 4-(11-ferrocenylundecyloxy)benzoate, 8. The nitro derivative 7 (2.5 g) was dissolved in 40 ml THF and 500 mg Pd/C was added and stirred under H_2 for 2 days and filtered through celite to remove the catalyst. The residue left after removal of the solvent was recrystallized from ethanol. Yield: 90%. Anal. cald. for $C_{34}H_{41}NO_3Fe$(567.55): C, 71.95; H, 7.28; N, 2.47; found: C, 71.94; H, 7,28; N, 2.29. FT-IR (cm^{-1}) 3427 (as (NH_2)), 3361_{sy} NH_2), 1722 (C=O). δ_H ($CDCl_3$) 1.3–1.65 (m, 16H, $8\times CH_2$), 1.85 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 3.65 (s, 2H, NH_2), 4.04–4.06 (m, 6H, C_5H_4+$CHOCH_2$), 4.09 (s, 5H, C_5H_4), 6.73 (d, 2H, Ar), 6.90–7.0 (m, 4H, Ar), 8.27 (d, 2H, Ar).

2.2.7. 4-Formylphenyl 4-(11-ferrocenylundecyloxy)benzoate, 9. A mixture of the acid **6** (3.45 g, 7.25 mmol), 4-hydroxybenzaldehyde (0.89 g, 7.25 mmol), DCC (1.45 g, 7.25 mmol) and 11 mg 4-(1-pyrrolidino)pyridine in 50 ml DCM was stirred at room temperature for 72 h and filtered. The residue left after removal of the solvent was recrystallized from ethanol; yield 85%. Anal: cald for $C_{35}H_{40}O_4Fe$ (580.83), C 72.41, H 6.94; found, C 72.55, H 7,10%. δ_H ($CDCl_3$) 1.25–1.56 (m, 16H, $8\times CH_2$), 1.79–1.88 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 4.04–4.08 (m, 6H, C_5H_4+OCH_2), 4.10 (s, 5H, C_5H_5), 6.98 (d, 2H, Ar), 7.40 (2H, Ar), 7.99 (d, 2H, Ar), 8.15(d, 2H, Ar), 10.03 (s, 1H, –CHO).

2.2.8. Preparation of Schiff's base compound 1. A mixture of the aldehyde **9** (0.58 g, 10 mmol) and 4-[4*R*,5*R*-bis(ethoxycarbonyl)-1,3-dioxalan-2-yl]aniline [4] **12** (0.31 g, 10 mmol) in 20 ml of benzene was heated under reflux in a Dean–Stark apparatus overnight. The residue left after removal of the solvent was recrystallized from ethanol to obtain a pale yellow solid; yield 45%. Anal: cald for $C_{50}H_{57}NO_9Fe$ (871.85), C 68.88, H 6.59, N 1.60; found, C 69.10, H 6,51, N 1.54%. δ_H ($CDCl_3$) 1.37–1.60 (m, 6H, $2\times CH_3$+16H, $8\times CH_2$), 1.84 (m, 2H, CH_2), 2.33 (m, 2H, CH_2), 4.04–4.06 (m, 6H, C_5H_4+OCH_2), 4.10 (s, 5H, C_5H_5), 4.33 (m, 4H, $2\times CH_2$), 4.85 (d, 1H, CH), 4.98 (d, 1H, CH), 6.19 (s, 1H, CH–Ar), 6.95 (d, 2H, Ar), 7.20 (d, 2H, Ar), 7.35 (d, 2H, Ar), 7.65 (d, 2H, Ar), 7.95(d, 2H, Ar), 8.15 (d, 2H, Ar), 8.45 (s, 1H, CH=N).

2.2.9. Preparation of the Schiff's base compound 2. The aldehyde **13** was prepared by following a method similar to that used for **7**. A mixture of 4-formylcinnamic acid (3.52 g, 20 mmol) and (*R*)-(-)-2-octanol (2.62 g, 20 mmol), DCC (4.13 g, 20 mmol) and 30 mg 4-(1-pyrrolidino)pyridine in 50 ml DCM was stirred at room temperature for 72 h and filtered. The residue left after removal of the solvent was subjected to flash chromatography (silica gel, DCM). The product obtained was found to be spectroscopically pure; yield 65%. δ_H ($CDCl_3$) 0.85 (t, 3H, CH_3), 1.20–1.85 (m, 13H), 5.02 (m, 1H, CH), 6.56 (d, 1H, =CH), 7.65 (m, 3H, –CH, and 2H, Ar), 7.87 (d, 2H, Ar), 10.01 (s, 1H, –CHO).

A mixture of the aldehyde **13** (0.144 g, 0.5 mmol) and amine **8** (0.283 g, 0.5 mmol) in 20 ml of absolute ethanol was heated under reflux until a clear solution was obtained. To this was added a few drops of acetic acid and refluxing continued for a further 2h. The product obtained after removing the solvent was dissolved in DCM and reprecipitated by the addition of heptane; yield 74%. Anal: cald for $C_{52}H_{63}NO_5Fe$ (837.92), C 74.54, H 7.58, N 1.67; found, C 74.70, H 7,57, N 1.57%. δ_H ($CDCl_3$) 0.90 (t, 3H, CH_3), 1,31–1.60 (m, 31H, $13\times CH_2$, $1\times CH_3$), 1.79–1.88 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 4.04–4.08 (m, 6H, C_5H_4+OCH_2), 4.10 (s, 5H, C_5H_5), 5.02 (m, 1H, CH), 6.56 (d, 1H, =CH), 6.98 (d, 2H, Ar), 7.23–7.32 (m, 4H, Ar), 7.65 (m, 3H, –CH, and 2H, Ar), 7.95 (d, 2H, Ar) 8.15 (d, 2H, Ar), 8.50 (s, 1H, CH=N).

2.3. *Preparation of 4-(S)-(+)-(2-methylbutoxy)-benzoylisothiocyanate, 10*

This compound was prepared by following the literature method [7 *a*] starting from 4-(*S*)-(+)-2-methyl-1-butoxy)benzoic acid [15]. FTIR (cm^{-1}): 1965 [ν(N=C=S)], 1693 [ν(C=O)]. This was further reacted with the corresponding amines to obtain compounds **22** and **23** (see figure 2). 4-octadecyloxybenzoylisothiocyanate and other 4-alkyloxybenzoylisothio-cyanates used here were prepared similarly starting from the corresponding acid chlorides [7 *a*].

2.4. *General procedure for preparation of 4-(11-ferrocenylundecyloxy)benzoate derivatives (Fc-un-BATU-n)*

To a DCM solution (5 ml) containing 256 mg (0.5 mmol) of 4-aminophenyl 4-(11-ferrocenylundecyloxybenzoate was added dropwise the corresponding 4-alkyloxybenzoylisothiocyanate (0.5 mmol) in 10 ml DCM and the reaction mixture was stirred at room temperature for 2 h. Addition of methanol facilitated the precipitation of the desired compound which was then filtered. The crude product was recrystallized from DCM and heptane mixture and dried over P_2O_5; yields 80–85%.

2.4.1. 4-{3-[4-(Octyloxy)benzoyl]thioureido}phenyl 4-(11-ferrocenylundecyloxy)benzoate (Fc-un-BATU-8),

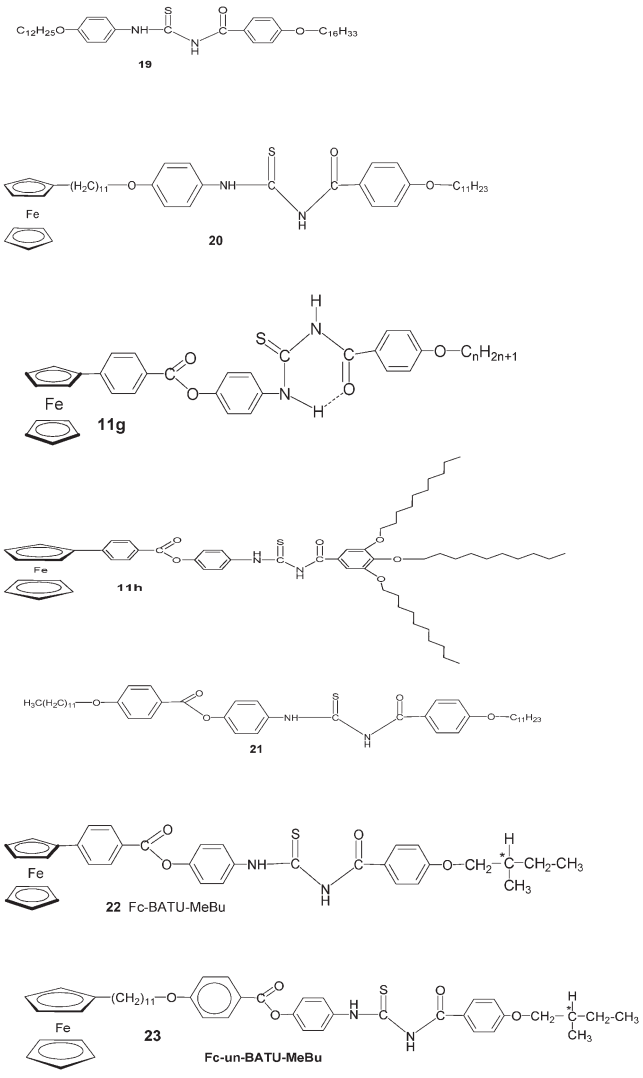


Figure 2. Other mesogens containing BATU.

11a. Anal: cald for $C_{50}H_{62}N_2O_5SFe$ (858.96), C 69.91, H 7.27, N 3.2; found, C 70.19, H 7,27, N 3.32%. FTIR (cm^{-1}): 3257 (NH), 1731 (C=O). δ_H ($CDCl_3$) 0.90 (t, 3H, CH_3), 1.30–1.60 (m, 28H, $14 \times CH_2$), 1.83 (m, 4H, $2 \times CH_2$), 4.03–4.08 (m, 8H, C_5H_4+$2 \times CH_2$), 4.09 (s, 5H, C_5H_5), 6.97–7.02 (t, 4H, Ar), 7.27 (d, 2H, Ar), 7.80–7.88 (dd, 4H, Ar), 8.13–8.16 (d, 2H, Ar), 9.04 (s, 1H, NH–C=O), 12.73 (s, 1H, NH–Aryl).

2.4.2. 4-{3-[3,4,5-Tris-decyloxy)benzoyl]thioureido}-phenyl 4-(11-ferrocenylundecyloxy)benzoate (Fc-un-BATU-tris-decyl), 11f. 3,4,5-Tris(*n*-decyloxy)benzoylisothiocyanate was prepared by following the method described before, starting from 3,4,5-tris(*n*-decyloxy)-benzoyl chloride [16] and was reacted with compound **8** to obtain **11f**.

2.4.3. 4-{3-[3,4,5-Tris-decyloxy)benzoyl]thioureido}-phenyl 4-ferrocenylbenzoate (Fc-BATU-tris-decyl), 11g. This was prepared similarly to **11f**, starting from the corresponding amine **7a**. δ_H ($CDCl_3$) 0.90 (t, m, 9H, $3 \times CH_3$), 1.20–1.60 (m, 42H, $21 \times CH_2$), 1.77–1.87 (m, 6H, $3 \times CH_2$), 3.81–3.95 (m, 2H, $-OCH_2$), 4.03–4.07 (m, 11H, $3 \times OCH_2$+C_5H_5), 4.44 (t, 2H, C_5H_4), 4.76 (t, 2H, C_5H_5), 7.07 (s, 2H, Ar), 7.29 (d, 2H, Ar), 7.61 (d, 2H, Ar), 7.79 (d, 2H, Ar), 8.12 (d, 2H, Ar), 9.05 (s, 1H, NH–C=O), 12.70 (s, 1H, –NH–Aryl).

2.5. *Preparation of compounds 14–18 (scheme 3)*

Compound **6** from scheme 1 was used as starting material. It was converted into benzylester **14** by following the method used for preparing **7** in scheme 1. δ_H ($CDCl_3$) 1.40–1.65 (m, 16H, $8 \times CH_2$), 1.80–1.90 (m, 2H,CH_2), 2.35(m, 2H, CH_2), 4.05–4.20 (11H, C_5H_5+OCH_2+C_5H_5), 5.50 (s, 2H, CH_2Ar) 6.9 (d, 2H, Ar) 7.20–7.48 (m 7H, Ar), 8.16 (m, 4H, Ar).

The benzyl group was deprotected by means of Pd/C and the acid **15** obtained was converted into chloride **16** by using oxalyl chloride; further refluxing with KCNS in acetone resulted in compound **17**. δ_H ($CDCl_3$) 1.50–1.62 (m, 16H, $8 \times CH_2$), 1.80–1.90 (m, 2H, CH_2) 2.35 (m, 2H, CH_2), 4.04–4.11 (11H, C_5H_4+OCH_2+C_5H_5), 6.9 (d, 2H, Ar) 7.36 (d, 2H, Ar),8.15 (dd, 4H, Ar).

2.7. *Preparation of cholesteryl 11-(4-nitrophenoxy)-undecyloate, C*

This was prepared by reacting cholesteryl 11-bromoundecyloate with 4-nitrophenol by following the method described for compound **7** (scheme 1). It was recrystallized from CH_3OH/DCM mixture. Anal: cald for $C_{44}H_{69}NO_5$ (692.02), C 76.37, H 10.05, N 2.02%; found, C 75.72, H 10.18, N 2.17%. δ_H ($CDCl_3$) 0.68 (s, 3H, CH_3), 0.85 (d, 3H, CH_3), 0.88 (d, 3H, CH_3), 0.91 (d, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.05–2.10 (m, 42H, chol, (CH_2) 8), 2.29 (m, 4H, $2 \times C=CH_2$), 4.04 (t, 2H, OCH_2), 4.60–4.62 (brm, 1H, CHO), 5.37 (brd, 1H, C=CH), 6.94 (d, 2H, Ar), 8.18 (d, 2H, Ar).

2.8. *Preparation of cholesteryl 11-(4-aminophenoxy)-undecyloate, D*

The nitro-derivative **C** was converted into **D** by following the method adopted for compound **8** (scheme 1). The compound was purified by column chromatography over silica gel using DCM. Anal: cald for $C_{44}H_{71}NO_3$ (662.04), C 79.82, H 10.81, N 2.11; found, C 79.18, H 11.02, N 2.20%. δ_H ($CDCl_3$) 0.65 (s, 3H, CH_3), 0.86 (d, 3H, CH_3), 0.88 (d, 3H, CH_3), 0.91 (d, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.05–2.04 (m, 42H, chol, $(CH_2)_8$), 2.29 (m, 4H, $2 \times C=CH_2$), 3.41 (sbr, 2H,

NH_2), 3.90 (t, 2H, OCH_2), 4.60–4.67 (brm, 1H, CHO), 5.39 (brd, 1H, C=CH) 6,62 (d, 2H, Ar), 6.75 (d, 2H, Ar).

2.9. *Preparation of 4-{3-[4-(11-cholesteryloxycarbonyl)decyloxybenzoyl]thioureido}phenyl 4-(11-ferrocenylundecyloxy)benzoate (FC-un-BATU-chol), 18*

This was prepared by reacting **17** with compound **D**. Anal: cald for $C_{80}H_{110}N_2O_7SFe$ (1299.68), C 73.93, H 8.53, N 2.15; found, C 73.74, H 8,54, N 2.21%. δ_H ($CDCl_3$) 0.70 (s, 3H, CH_3), 0.88 (d, 3H, CH_3), 0.89 (d, 3H, CH_3), 0.94 (d, 3H, CH_3), 1.05–2.04 (m, 63H, chol, $18\times CH_2$), 2.28–2.39 (m, 6H, $2\times C{=}CH_2$, $1\times CH_2$), 3.99 (t, 2H, OCH_2), 4.07 (d, 2H, OCH_2), 4.08 (s, 4H, C_5H_4), 4,12 (s, 5H, C_5H_4), 4.60–4.67 (brm, 1H, CHO), 5.40 (brd, 1H, C=CH), 6,62 (d, 2H, Ar), 6.95 (d, 2H, Ar), 6,97 (d, 2H, Ar), 7.45 (d, 2H, Ar) 7,58 (d, 2H, Ar), 8.01 (d, 2H, Ar), 8.16 (d, 2H, Ar), 9.08 (s, 1H, NH–C=O), 12.40 (s, 1H, NH–Aryl).

2.10. *Preparation of 4-{3-[4-(S)-(+)-(2–methyl-1-butoxy)benzoyl]thioureido}phenyl 4-ferrocenylbenzoate (Fc-BATU-MeBu), 22*

Anal: cald for $C_{36}H_{34}N_2O_4SFe$ (647.55), C 66.77, H 5.29, N 4.32; found, C 66.90, H 5,44, N 4.24%. FTIR (cm^{-1}) 3257 (NH), 1731 (C=O). δ_H ($CDCl_3$) 0.96–1.07 (tm, 6H, $2\times CH_3$), 1.29–1.36 (m, 2H, CH_2), 1.90 (m, 1H, CH), 3.81–3.95 (m, 2H, $-OCH_2$), 4.07 (s, C_5H_5), 4.43 (t, 2H, C_5H_4), 4.76 (t, 2H, C_5H_5), 7.02 (d, 2H, Ar), 7.26 (d, 2H, Ar), 7.61(d, 2H, Ar), 7.79–7.88 (dd, 4H, Ar), 8.12 (d, 2H, Ar), 9.04 (s, 1H, NH–C=O), 12.74 (s, 1H, NH–Aryl).

2.11. *Preparation of 4-{3-[4-(S)-(+)-(2-methyl-1-butoxy)benzoyl]thioureido}phenyl 4-(11-ferrocenylundecyloxy)benzoate (Fc-un-BATU-MeBu), 23*

Anal: cald for $C_{47}H_{56}N_2O_5SFe$ (816.88), C 69.10, H 6.91, N 3.43; found, C 68.90, H 7,34, N 3.24%. FTIR (cm^{-1}) 3257(NH), 1731 (C=O). δ_H ($CDCl_3$) 0.95–1.04 (tm, 6H, $2\times CH_3$), 1.3–1.81 (m, 18H, $9CH_2$), 1.85 (m, 3H, CH, CH_2), 2.32 (m, 2H, CH_2), 3.84–3.91 (m, 2H, OCH_2); 4.05–4.07 (m, C_5H_4+CH_2), 4.10 (s, 5H, C_5H_5), 6.96–7.02 (t, 4H, Ar), 7.27 (d, 2H, Ar), 7.78–7.88 (dd, 4H, Ar), 8.13–8.16 (d, 2H, Ar), 9.05 (s, 1H, NH–C=O), 12.73 (s, 1H, NH–Aryl).

3. Results and discussion of structure-mesomorphic properties relationship

The complex-forming properties of simple BATU derivatives have been intensively investigated by Beyer *et al.* [14]. Recently, we have synthesized several organic compounds containing BATU groups with increasing alkyl chain length and their liquid crystalline properties have been evaluated. These compounds were found to exhibit enantiotropic SmC and SmA phases (see figure 2 compound **19**). Some of them are monotropic [17].

The monosubstituted ferrocenomesogens containing the BATU unit are prepared by reacting the 4-alkoxybenzoylisothiocyanates with the corresponding amine attached to a ferrocenyl moiety. Initially we synthesized ferrocene derivatives similar to **19** with two benzene rings in the mesogenic core and the resulting compound **20** was found to be non-mesogenic [17].

The introduction of a phenyl ester function in compound **11c** dramatically alters the thermotropic properties, whereby not only nematic but also smectic C phases are found. This shows that three rings are the minimum necessary to generate a mesophase. Changes in crystal packing, probably through intermolecular interactions between the ester groups with the hydrogens of the neighbouring aromatic unit, may be a crucial factor for the observed change in the liquid crystalline properties. Furthermore, insertion of the flexible spacer thwarts the repulsive steric and adverse effects of the bulky ferrocene unit, which possibly imparts packing conditions favourable to attain the ordered phases. The thiourea unit (–NH–CS–NH–CO–) acts as a flexible spacer and the anisotropy is extended by the formation of a strong intramolecular hydrogen bond; see crystal structure of **11g** [7*a*, page 12]. The almost six-membered ring formed in the central part of the molecule becomes conformationally locked and acts as a rigid spacer that links the terminal mesogenic groups together.

The compound with triply branched alkyl flexible chains, Fc-un-BATU-3,4,5-decyl (**11f**), and the compound without spacer, Fc-BATU-3,4,5-decyl (**11h**), were found to be non mesogenic. Compared with **11g**, in these compounds intermolecular hydrogen bond formation is not possible as the space between two adjacent molecules is completely disturbed.

A closer look at the thermal properties of compound **11c** and its counterpart compound **21** [17], where the ferrocene unit is replaced by a methyl group (see table 1) shows that the former has significantly reduced clearing temperatures, by about 33°C, in spite of the presence of the bulky ferrocenyl group, suggesting that the ferrocenyl group lengthens the core in the present system. This is attributed to a kinked structure with some rotational freedom introduced by the ferrocene unit. However, suppression of the range of the highly ordered smectic phase was observed in **11c**.

Table 1. Phase transition temperatures and enthalpy changes of ferrocene derivatives obtained from DSC data. Cr=crystal, N=nematic, N*=cholesteric, I=isotropic, T_g=glass transition,

Ferrocene	Transition	T/°C	ΔH/kJ mol^{-1}
Compound **2**	Cr–N*	88.	39.9
	N–I	99	1.7
	I–N*	94	1.9
	N*–Cr	32	23.5
F_C-un-BATU-8 (**11a**)	Cr–N	104	34.0
	N–I	147	1.6
	I–N	146	1.5
	N–Cr	93	31.7
F_C-un-BATU-10 (**11b**)	Cr–SmC[b]	110	—
	SmC–N	112	35.0
	N–I	145	1.3
	I–N	142	1.1
	N–SmC	107	—[a]
	SmC–Cr	102	32.8[a]
F_C-un-BATU-11 (**11c**)	Cr–SmC[b]	117	—
	SmC–N	119	44.8
	N–I	145	1.9
	I–N	144	1.7
	N–SmC	114	1.8
	SmC–Cr	107	38.5
F_C-un-BATU-12 (**11d**)	Cr–SmC[b]	112	—
	SmC–N	117	39.6
	N–I	144	1.9
	I–N	143	1.6
	N–SmC	119	2.4
	SmC–Cr	109	34.0
F_C-un–BATU-16 (**11e**)	Cr–SmC	113	36.0
	SmC–N	129	—[a]
	N–I	138	8.1[a]
	I–N	138	1.8
	N–SmC_B	129	3.6
	SmC–Cr	105	35.5
F_C-un-BATU-MeBu (**23**)	Cr–N*	120	—[a]
	N*–I	122	39.1[a]
	I–N*	121.5	1.1
	N*–I	73.5	41.0
F_C-un-BATU-chol (**18**)	Cr–Cr_1	86	1.4
	Cr_1–Cr_2	94	2.0
	Cr_2–Cr_3	102	2.5
	Cr_3–N*	119	36.6
	N*–I	171	1.3
	I–N*	165	—
	N*–T_g	30	
F_C-BATU-MeBu (**23**)	Cr–N*	161.5	34.8
	N*–I	168.0	3.2
	I–N*	151.0	1.7
	N*–T_g	47.7	—

lines followed by
a=ΔH cumulative, b=not detected by DSC.

Table 1. (*Continued*).

Ferrocene	Transition	T/°C	ΔH/kJ mol^{-1}
Compound **19**	Cr–SmC	108	30.40
	SmC–SmA[b]	119	0.43
	SmA–I	121	0.40
	I–SmA	119	0.50
	SmA–SmC	117	0.11
	SmC–Cr	91	30.90
Compound **20**	Cr–I	92	—
Compound **21**	Cr–SmC	130	40.1
	SmC–N	154	2.5
	N–I	177	2.4
	I–N	176	2,3
	N–SmC	145	2.1
	SmC–Cr	112	37.9
Compound **11f**	Cr–I	59	—
Compound **11h**	Cr–I	72	—
Compound **11g**	Cr–N	144	52.0
	N–I	157	1.6
	I–N	154	2.2
	N–T_g	18	—

3.1. *Mesomorphic properties*

The thermal and liquid crystal properties were investigated by a combination of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The DSC data and the type of mesophases observed by microscopy are collected in table 1. The achiral compounds, Fc-un-BATU-*n*, exhibit enantiotropic schlieren texture of the smectic C phase, as well as the formation of nematic schlieren texture and appearance of droplets immediately below the clearing point. The smectic C phase transition was not observed by DSC for compounds $n=10$ and $n=12$ during the heating process because of peak overlap, but was observed by means of POM. During cooling, the SmC phase was found in both POM and DSC. The smectic C range increases with an increase of terminal alkyl chain length and, correspondingly, a fall in the nematic range was observed.

3.2. *Thermotropic properties of chiral monomesogens bearing BATU bidentate carbonyl and thiocarbonyl functional groups*

The chiral monomesogens containing ferrocene were prepared with the introduction of chirality in the system located adjacent to the rigid mesogenic core. The chiral unit was based on the readily available compound (*S*)-(-)-methylbutan-1-ol. The resulting compounds, for example, compounds **22** (Fc-un-BATU-MeBu) and **23**

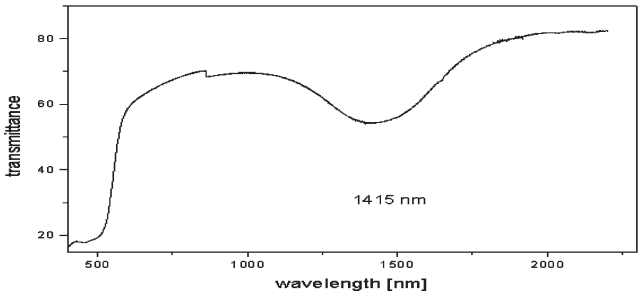


Figure 3. Transmission spectrum of the cholesteric glassy crystal of Fc-BATU-MeBu obtained on slow cooling to room temperature.

(Fc-BATU-MeBu) show only a cholesteric phase (N*) with oily streaks texture.

The DSC curve of **22** showed an endothermic peak at 161.5°C which corresponds to the melting point, followed by the appearance of a plane texture of cholesteric phase with discontinuities. The isotropic melt was found at 166.4°C. On cooling, the Grandjean textures of the cholesteric phase appeared at 163.4°C, persisting below 0°C with a baseline shift at 47.7°C, which resembles the typical shape of a glass transition curve and corresponds to a glass transition point T_g. In the second heating, the compound underwent a glass transition at 42.5°C followed by an isotropic melt at 153°C. Compound **22** shows selective reflection only in the infrared region (figure 3). The low transmittance below 500 nm is due to the absorption of the sample. The cholesteric glassy phase was retained even after slow cooling to room temperature (figure 4).

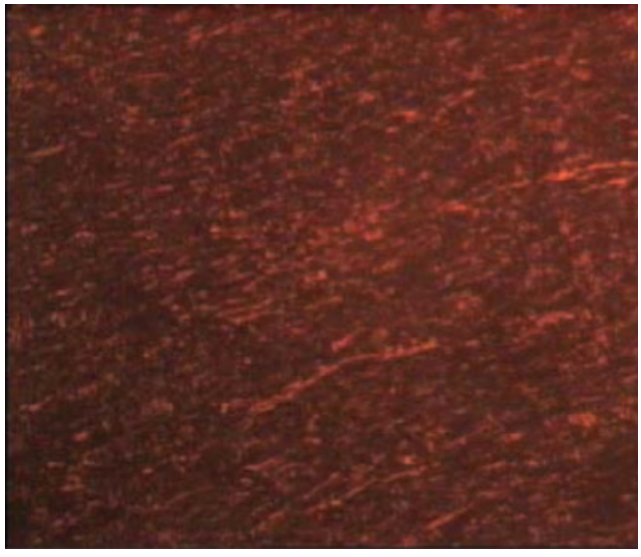


Figure 4. Polarizing optical micrographs of the cholesteric glassy liquid crystal of Fc-BATU-MeBu on slow cooling to room temperature.

Compound **23**, with a spacer, also exhibits a cholesteric phase but without any glass transition (T_g), and it crystallizes at 73.5°C during cooling. However, a significant reduction in clearing temperature of about 47°C compared with compound **22** is observed. This is ascribed to the presence of the spacer. The second heating curve superimposes the first, suggesting that the compound is thermally highly stable.

3.3. *Thermotropic properties of chiral dimesogen Fc-un-BATU-chol (18)*

This is the first case of a chiral ferroceno–unsymmetric dimesogen designed to contain two non-identical mesogenic cores, namely the BATU unit and cholesteryl ester.This compound does not exhibit a polymorphic sequence that includes an incommensurate smectic A (SmA_{ic}) phase. Compared with chiral monomesogens **22** and **23**, it displays only on enantiotropic cholesteric mesophase with selective reflection in the visible region with iridescent colours (blue and green, see figures 5, 6 and 7). This property is based on the reflected light generated by a molecular order which has a helical structure, and the wavelengths of the reflected colours depend on the helical pitch of the cholesteric liquid crystals.

When a sample of compound **18** between two glass plates, and showing iridescent colours, was quickly cooled to 0°C by dropping in ice-water, glassy materials retaining the cholesteric colours were obtained, see figures 7 (*a*) and 7 (*b*). The Grandjean texture observed at the cholesteric temperature range was retained in the glassy state, depicting helical orientation in the glassy solid. The stability of the glassy liquid crystal was found to be very high and no change was observed even after

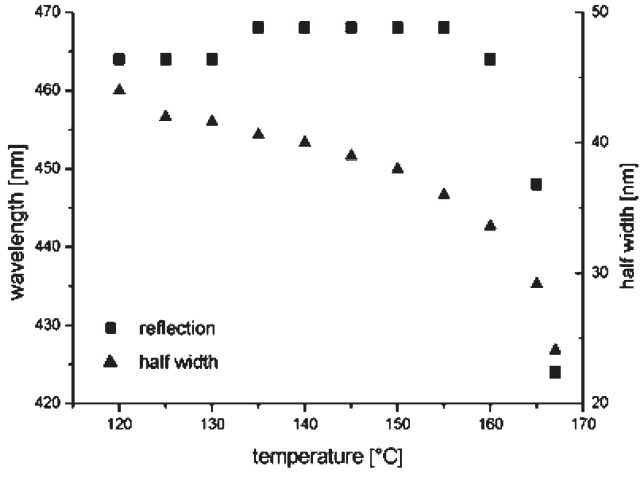


Figure 5. Selective reflection wave lengths λ_{sel}(nm)/half width (nm) of the cholesteric phase of Fc-un-BATU-chol plotted as a function of temperature.

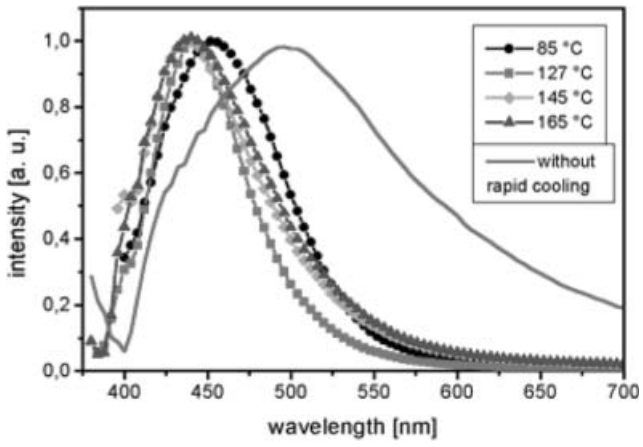


Figure 6. Relationship between the temperature at which rapid cooling started and the selective reflection wavelengths λ_{sel}(nm) of the cholesteric glassy liquid crystal (Fc-un-BATU-chol).

long exposure to daylight. Compounds showing slow orientation to the crystalline structure are found to be suitable for attaining such glassy liquid crystals. Furthermore compounds with high molecular mass, or compounds associated with strong intermolecular interaction (multiple hydrogen bonding) are supposed to inhibit formation and growth of crystal nuclei [18, 19]. Deschenaux and co-workers [20] reported a high molecular mass (around 9 000) ferrocene–containing liquid crystalline dendrimer based on a cholesterol framework which exhibited only a smectic A phase. Similarly, a monoferrocene derivative containing the cholesterol group reported by Nakamura *et al.* [10 *b*] shows only a monotropic smectic phase. In both of these compounds a glass transition was observed but no selective reflection. Furthermore, the thermal properties of two ferrocene derivatives, substituted by either one or two cholesteryloxycarbonyl units have also been reported [21]. Only the disubstituted derivative exhibited liquid crystalline properties (crystal B phase only on cooling). These results clearly demonstrate that the presence of the cholesterol unit in this system alone cannot bring the desired glassy CLCs, but only in combination with a suitable mesogenic core such as BATU. Although its molecular mass is not high Fc-un-BATU-chol still retains the glassy state on cooling, suggesting a strong dipolar nature of the BATU unit due to the *cis* and *trans* positions of donor groups, as well as due to the existence of multiple intermolecular interactions in its crystal packing. There is no observable change to the initial peak wavelength of the reflection bands when the temperature at which the rapid cooling starts is raised.

Figure 8 shows the DSC curve of compound **18**. On first heating the compound exhibited a series of endo- and exo-thermic peaks between 86.11 and 102.74°C, corresponding to melting and recrystallization processes, respectively. The metastable crystal formed at the latter temperature transforms to a stable crystal followed by melting. The temperature (119°C) was confirmed to be the melting point by polarizing microscopy observations followed by the formation of the plane texture of the cholesteric phase (with discontinuities). The isotropic melt was found at 169°C. On cooling the isotropic liquid, however, the enantiotropic cholesteric phase was formed at 165°C and persisted below 10°C, with a baseline shift at about 30°C which resembles a typical glass transition T_g curve. The small exothermic peak at 60.7°C may probably be due to a negligible amount of crystallization of the sample, although no texture change was observed under the polarizing microscope. The compound was found to be stable and no decomposition was noticed even after repeated heating and cooling cycles.

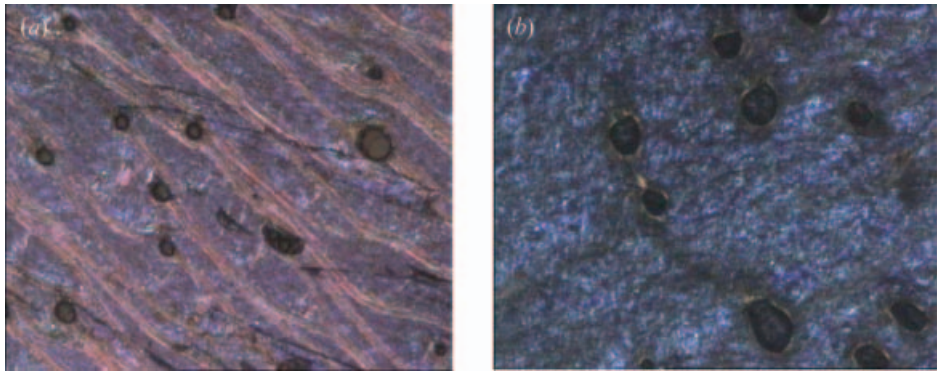


Figure 7. Polarizing optical micrographs of the cholesteric glassy liquid crystal of Fc-un-BATU-chol (*a*) upon rapid cooling from 152° to 0°C and (*b*) upon rapid cooling from 112°C to 0°C.

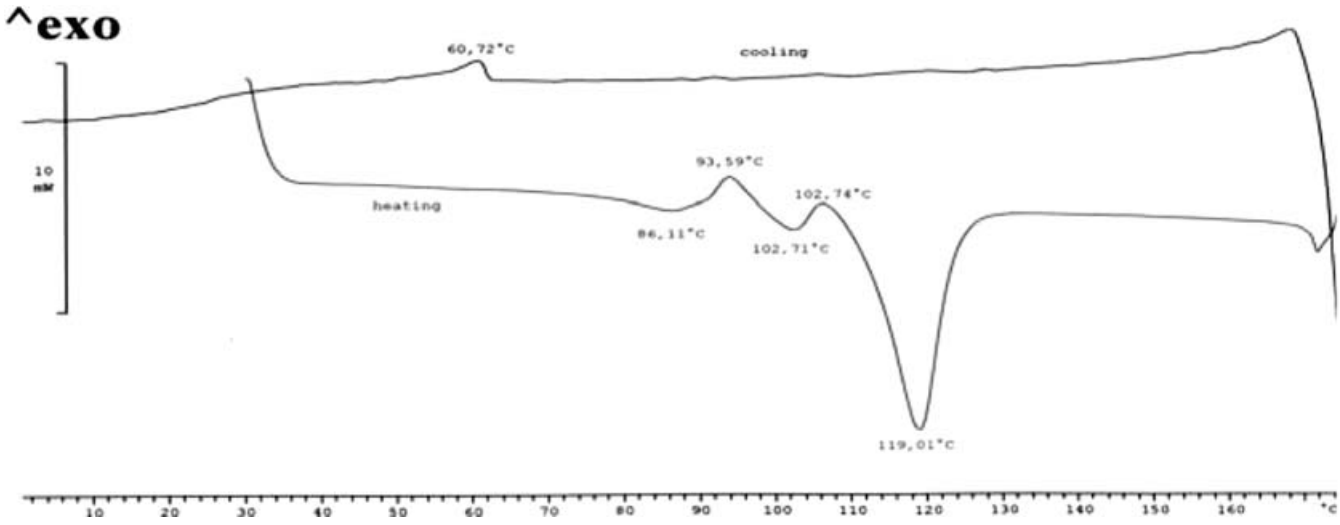


Figure 8. DSC curve of FC-un-BATU-Chol. Scanning rate: $10^{\circ}C\,min^{-1}$.

3.4. *Infrared and NMR spectral studies*

The addition reaction between the corresponding amine and isothiocyanate functions (see schemes 1 and 3) can be easily monitored by FTIR, following the disappearance of stretching and deformation bands of the primary amine as well as the isothiocyanate band around $1965\,cm^{-1}$. Furthermore, these derivatives are most likely to undergo intramolecular hydrogen bond formation between the H atom of the NH group at position 3 and the O atom of the carbonyl group, as in **11g**, or the molecules are linked into dimers by N–H–S intermolecular hydrogen bonds in addition to intramolecular hydrogen bonding. The NH between the 4'aryl and thiocarbonyl groups around 12.70 ppm at lower field, and the NH between the carbonyl and thiocarbonyl around 9.05 ppm at high field, may be attributed to the deshielding effect of the intramolecular hydrogen bond. Such hydrogen bond formation was observed in the case of simple 1-aroyl-3-arylthioureas [22, 23] as well as in compound **11g**, which clearly supports our assumption. We could get no single crystals for the compounds with spacer F_c-un-BATU-*n*, but orange-red prisms were obtained for **11g** whose crystal structure is discussed below.

3.5. *Crystal structure of 4-{3-[4-dodecyloxy)benzoyl]-thioureido}phenyl 4-ferrocenylbenzoate Fc-BATU-12 (11g)*

The crystal structure of compound **11g** [7 *a*] provides evidence in general for the involvement of structure-determining intra-and inter-molecular interactions in all the liquid crystalline compounds containing BATU units. The crystallographic data and details of structure determination are as follows. Empirical formula: $C_{43}H_{48}FeN_2O_4S$; fw: 744.74; temp: 153(2)K; wavelength: 0.71073 Å, crystal syst.: triclinic; spacegroup: *P*–1 (No 2); *Z*: 2; unit cell dimensions: $a=11.006(8)$ Å, $\alpha=71.523(1)^{\circ}$; $b=12.5117(9)$ Å; $\beta=85.578(1)^{\circ}$; $\gamma=84.856(2)^{\circ}$; volume: 1868.7(2) $Å^3$; density calculated: $1.324\,Mg\,m^{-3}$; abs coeff: $0.505\,mm^{-1}$; cryst shape: prism; cryst size: $0.20\times0.16\times0.14\,mm^3$; θ range for data collection: 1.53 to 28.30°; index ranges: *h*: −15/9, *k*: −16/11, *l*: −18/18: reflns collected:12 033; indepreflns: 8355[*R*(int)=0.0210]; max and min transmission: 0.822 and 0.790; refinement method: full-matrix-least-squares on F^2; data/parameters: 8355/460; GOF on F^2; 0.918; final *R* indices[$I>2$sigma(I)], $R1=0.049$, $R2=0.1045$; *R* indices (all data): $R1=0.0675$, $wR2=0.1119$: largest diff peak and hole: 0.877 and $-0.482\,e\,Å^{-3}$. The defined least-squares planes and dihedral angles are given in table 2.

Table 2. The defined least - square planes and dihedral angles for compound **11g**.

Plane No	Least-square planes	Planes	Dihedral Angles/°
1	substituted Cp-ring	1–2	3.17(2)
2	unsubstituted Cp-ring	1–3	0.91(1)
3	phenyl ring (C11–C16)	3–4	59.60(8)
4	phenyl ring (C18–C22)	3–6	6.54(5)
5	phenyl ring (C26–C31)	3–5	77.20(8)
6	phenyl ring (C17–O1–O2)	4–7	35.6(3)
7	N1-C24-S1	4–6	53.8
8	N2-C25–O3	7–8	6.7(6)
9	C26-C31–O4	6–9	85.1(3)

The two CP rings in the ferrocenyl moiety run in parallel conformation to each other with a dihedral

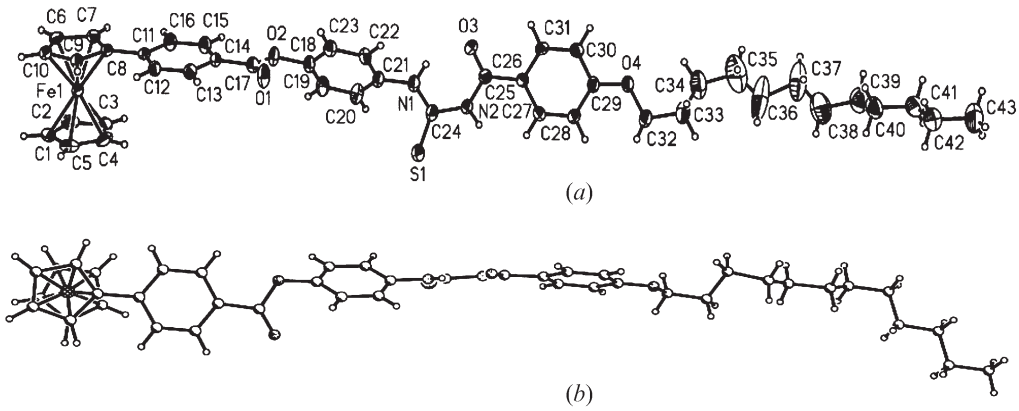


Figure 9. ORTEP view of the molecular structure of compound **11g**, thermal ellipsoids are drawn at 50% probability level: (*a*) showing the crystallographic numbering scheme, (*b*) overview into cyclopentadienyl rings

angle of 3.17(2)°. Eclipsed confirmations are mostly found in monosubstituted ferrocene [10 *c*], [24] and staggered in 1,1- and 1,3-disubstituted ferrocenomesogens [25]. Perfect staggering of the two rings requires a rotational offset of 36° but the conformation adopted by the present compound is 20.7° of axial twist, placing the rings roughly halfway between an eclipsed and staggered conformation, see figure 9 (*b*). Other geometric parameters of the $FeCp_2$ group have expected values [26].

The Cp ring (plane 1) and the adjacent phenyl ring (C11–C16, plane 3) are coplanar, planes 3 and 4 set up a dihedral angle of 59.60(8)°. The torsion angle (1.9°) for C28–C29–O4–C32 and almost *trans* confirmation of the alkyl chain also indicate that the molecule is arranged in the most extended fashion. A strong intramolecular hydrogen bond N1–H1B–O3, with H–O 1.876(2) Å, N–H–O 140.9(1)°, completes a nearly planar six-member ring with the C24–N2–C25 atoms. In order to restore liquid crystalline properties in the elongated ferrocenes, intensification of intermolecular attractions is necessary. This can be achieved by increasing the *l*/*d* ratio (*l*=length of the rigid core, *d*=the distance between the two Cp rings) to greater than 5–7 [25 *c*].

The length of the rigid core in the present system is found to be 18.98 Å and the depth of the ferrocene is 3.3 Å [27]; the resulting *l*/*d* ratio of 5.75 suggests the liquid crystalline nature of the compound. Deschenaux and co-workers [25 *c*] and Loubser *et al*. [24 *b*] observed similar behaviour with 1,3-disubstituted as well as monosubstituted ferrocenomesogens, respectively. The placement of the phenyl ring between the ferrocenyl moiety and carbonyloxy link of the mesogenic core is very important; in its absence the *l*/*d* ratio will fall short below 5, i.e. 3.3 Å, as the length of the core without phenyl ring was found to be 11.2 Å.

The six-member ring attained from the intramolecular hydrogen bond in the N-bezoylthiourea unit mentioned above further enhances the rigidity of the mesogenic unit. This would assist the molecule to exhibit calamitic mesomorphism, maintaining a long linear shape.

The carbonyl (C25–O3) and the thiocarbonyl (C24–S1) moieties point in approximately opposite directions. In spite of that no N–H–S interactions are observed, as is found generally in simple benzoylthiourea compounds. Such interactions normally facilitate the formation of dimers. However, molecules are arranged in a head-to-tail manner through weak intermolecular C–H–O interactions C13–H13A–O3($-x$–2, $-y$+1, $-z$–2) with H–O 2.619(2) Å, C–H–O 153.8(2)°, and C22–H22A–O1($-x$–2, $-y$+1, $-z$–2) with 2.497(2) Å and 154.2(2)°, respectively. Figures 10 and 11 show pairs of molecules arranged in an anti parallel fashion.

4. Conclusion

A new series of novel monosubstituted ferrocenomesogens in combination with a flexible spacer inserted between the ferrocenyl moiety and the phenyl group have been synthesized. From the data, it is clear that the fixing of cholesteric colour in solid films with dimesogen F_C-un-BATU-Chol was possible, but the fixing of several colours in one film or fixing images was not possible, because the spectral range in which the colours can be fixed was too narrow. Selective reflection bands covering the whole visible region could possibly be achieved to a considerable extent by increasing the molecular mass of this dimesogenic system, maintaining the same molecular architecture through 1,1-, 1,3-disubstitution or 1,1,3-trisubstitution on the ferrocene nucleus. Preliminary studies on 1,1′-disubstituted ferrocene derivatives showed promising results. Rewritable full-colour recording may

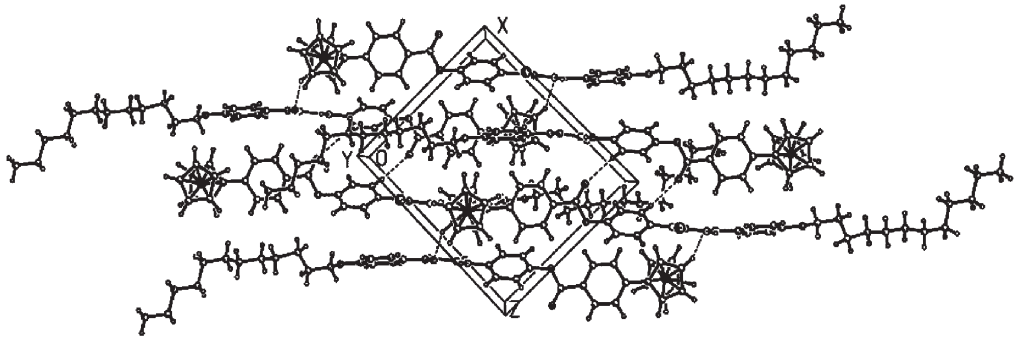


Figure 10. Crystal packing of Fc-BATU-12 viewed along [0 1 0].

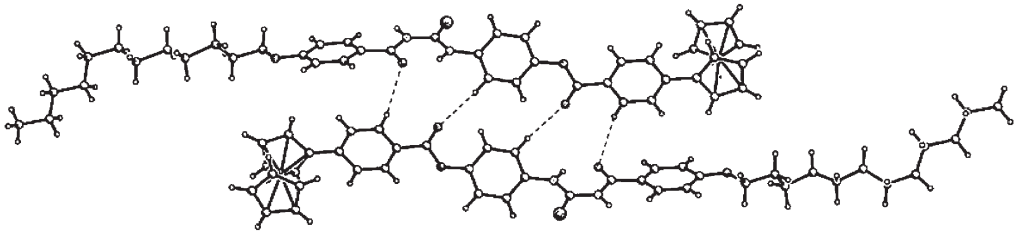


Figure 11. Close view of the relative positions of the molecule pairs with intermolecular H-bonds represented by dashed lines (Fc-BATU-12).

be possible using the latter type of compound. Chiral nematic fullerenes with selective reflection properties can also be prepared by functionalizing fullerene (C_{60}) with these dimesogenic systems.

The X-ray crystal structure of one of the compounds reveals that these systems fulfil the two prerequisites for calamitic mesomorphism, namely critical length/depth ratio (>5) and an extended linear shape coupled with intra- and inter-molecular interactions.

Critical evaluation of F_c-un-BATU-Chol systems led us to the basic information important for attaining a better understanding of the structure–mesomorphic properties relationship for low molecular mass LCs, especially cholesteric glassy LCs which show the property of selective reflection. This could be exploited to construct devices for full colour recording media on the thermal mode. Further work is now focused on exploring this area.

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