JOURNAL OF
Materials
CHEMISTRY

Thermotropic properties of monosubstituted ferrocene derivatives bearing bidentate *N*-benzoyl-*N*′-arylthiourea ligands—novel building blocks for heterometallic liquid crystal systems†

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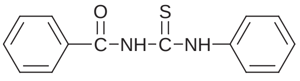
Ferrocene-based derivatives such as 4-{3-[4-(octyloxy)benzoyl]thioureido}phenyl 4-ferrocenylbenzoate and other higher homologues ($n=12$,16 and 18; $n=$length of alkoxy chain) were prepared by reacting 4-alkoxybenzoyl isothiocyanates with the corresponding amines containing the ferrocenyl moiety. Their mesomorphic properties were investigated by means of polarized optical microscopy and differential scanning calorimetry. All the compounds exhibit enantiotropic nematic phases and the nematic range increases with increasing terminal alkyl chain length. On cooling, the nematic phase persists below 0 °C in the first three compounds and in the case of $n=18$, a phase transformation, possibly to the S_C phase, around 72 °C during cooling was observed. In all cases, a glass transition was observed around $T_g=18$–35 °C, which is remarkable for low molecular mass calamitic metallomesogen systems.

Studies focussed on the synthesis and mesomorphic properties of ferrocene-based metallomesogens have gained increasing importance in recent years because of their novel thermal, optical and magnetic properties and they are well documented.[1,2] Ferrocene, because of its aromatic character, facilitates several substitution reactions whereby a range of low molecular mass calamitic (rod-like) systems can be prepared by monosubstitution, or 1,1-, 1,2-, 1,3-disubstitution or 1,1,3-trisubstitution of the ferrocene nucleus.[3,4] Little work has been reported on the monosubstituted-ferrocene derivatives in recent years. This is attributed partly to their unfavourable molecular shape (L-shaped geometry) and also to the repulsive steric effects of the ferrocene unit reducing the ability of the molecules to be placed in layers thus mostly favouring the formation of nematic and smectic A phases. Fig. 1 shows some of the monosubstituted ferrocene derivatives reported in recent years.

However, ferrocene derivatives with additional chelating groups used to attain homo- and hetero-metallic complexes have not been reported, except in the work of Galyametdinov[5] (see Fig. 1); such systems would allow investigations of the metal–metal interactions in the vicinity and through the π ligand system to be made. The ferrocene subunit in such systems might function as a redox switch by further complexation with suitable metal ions. We have selected *N*-benzoyl-*N*′-arylthiourea (BATU) ligands for this purpose.



N-benzoyl-N′-arylthiourea

These ligands possess strong donor groups, namely the amide and the thiourea group. The BATU ligands react with transition metal ions mostly in monoanionic and bidentate form by deprotonation, resulting in neutral complexes with *S*,*O*-coordination. The complex forming properties of these ligand systems have been intensively investigated.[6] We have synthesized several 4-alkloxy-substituted BATU ligands with increasing alkyl chain length and their mesomorphic properties have been investigated and found to exhibit enantiotropic S_C and S_A phases. A few of them are monotropic. The results on these will be communicated separately.

We report in this paper the synthesis and liquid crystalline properties of monosubstituted ferrocene derivatives bearing BATU ligands which form the building blocks for heterometallic liquid crystal systems.

Initially, we prepared ferrocene derivatives similar to BATU with two benzene rings in the mesogenic core. The fact that they did not exhibit any liquid crystalline properties clearly indicates the negative influence of the bulky metallocene in the system. Hence, we planned addition of a third ring into the core. In this connection we evaluated the different methods (see Fig. 2) of attaching mesogenic units to the ferrocene moiety. Imrie[7] observed that the nature of groups immediately adjacent to the ferrocenyl moiety is important, especially the electron withdrawing ability of the carbonyloxy group in (a), which may weaken greatly the chemical and thermal stability of the resulting compounds.

To circumvent this problem, we have synthesized only the last two series (b) and (c) of monosubstituted ferrrocene derivatives bearing BATU chelating groups. We report in this paper only the series (b) shown in Fig. 2, where the phenyl group is placed between the ferrocenyl moiety and the carbonyloxy link of the mesogenic core. The synthetic route to prepare these compounds is shown in Scheme 1. The preparation of the final compounds is very simple; they are abbreviated hereafter as Fc-BATU-*n*, where *n* is the number of carbon atoms in the flexible alkyl chain.

Experimental

General

The solvents acetone and dichloromethane were distilled over $CaCl_2$ and P_2O_5 prior to use. Benzene was distilled over sodium. All the reactions were carried out under argon. We used for column chromatography (CC) silica gel 60 (70–230 mesh) and thick-layer chromatography (TPC), silica gel plates prepared in our laboratory. Transition temperatures (onset point of endotherm or exotherm) 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; treatment of data used Mettler TA 72.2/.5

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† Presented at the International Symposium on metallomesogens, 3–6 June 1997, University of Neuchatel, Neuchatel, Switzerland.

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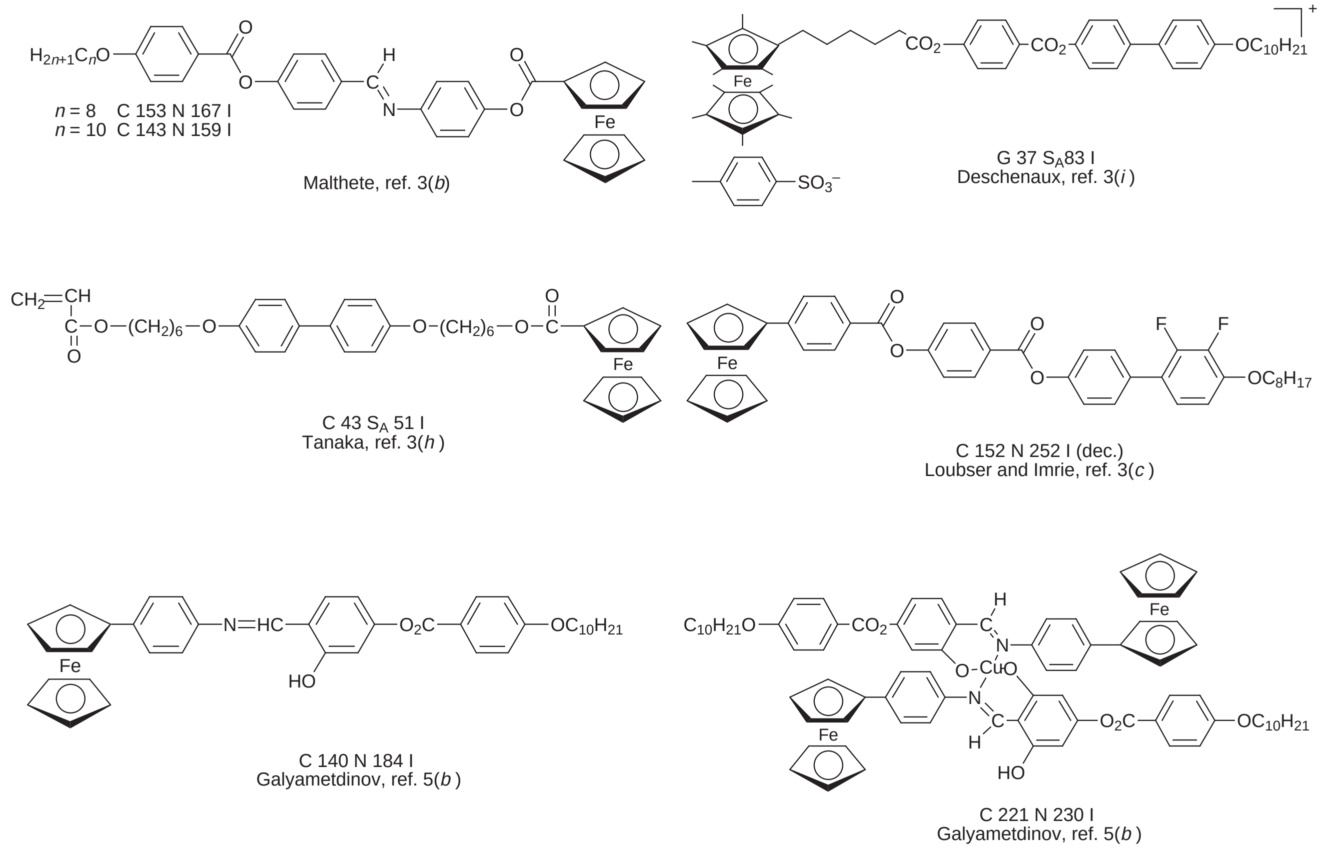


Fig. 1

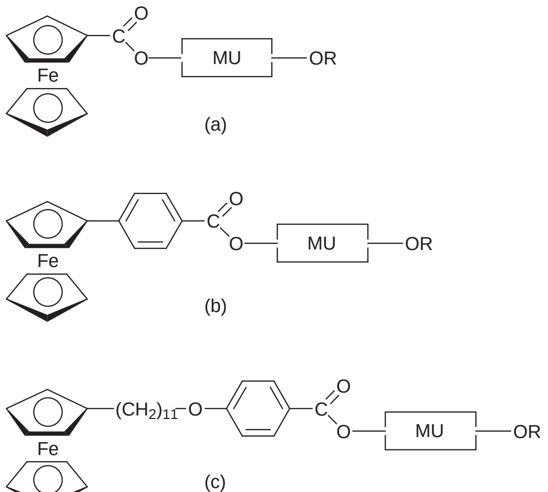


Fig. 2 Different ways of attaching mesogenic units to a ferrocenyl moeity. L-shape: 1-substitution where MU = mesogenic unit; R = terminal alkylchain.

GRAPHWARE. Optical studies were conducted using a Zeiss-Acioscop polarizing microscope equipped with a Linkam-THMS-600 variable temperature stage under nitrogen. ^1H NMR spectra were recorded on a Bruker AMX 300 spectrometer and IR spectra on a Nicolet P 510 FTIR spectrometer. A Perkin Elmer Microanalyser PE 2400 was used for the elemental analyses.

Synthesis

4-Nitrophenyl 4-ferrocenylbenzoate 3

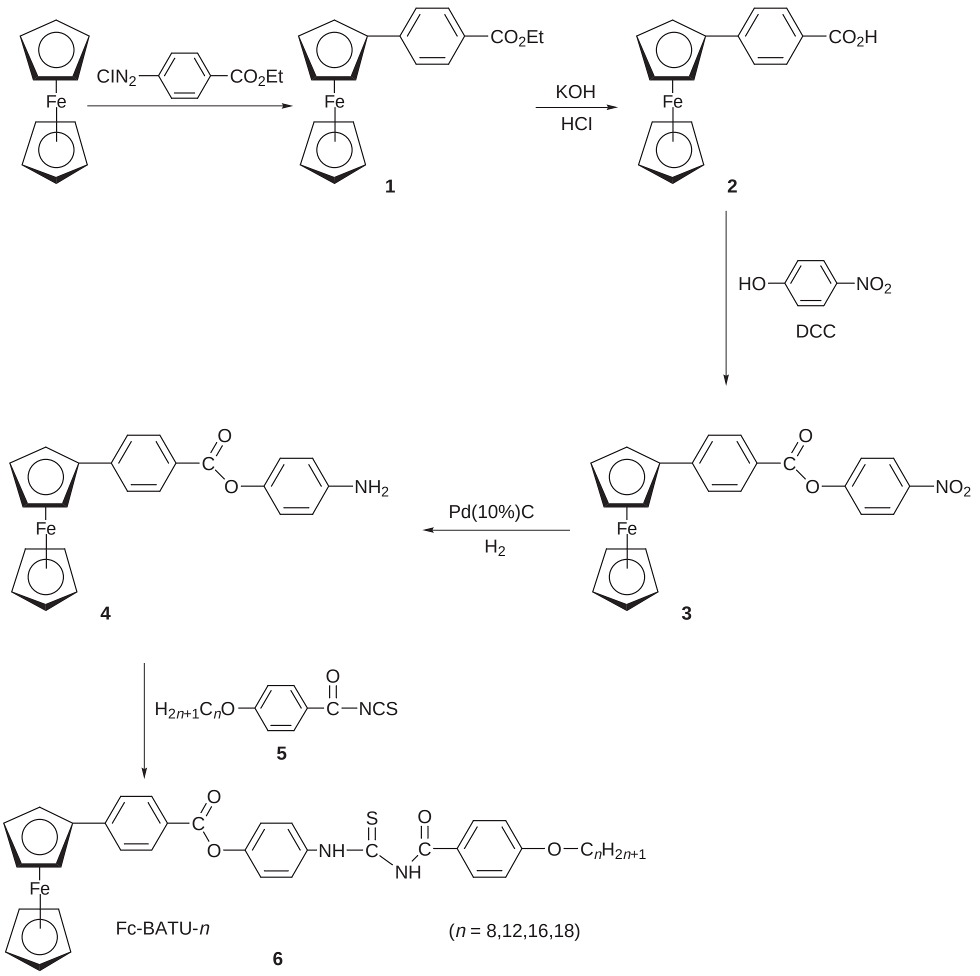
The starting compound, 4-ferrocenylbenzoic acid,[8] was prepared from ethyl *p*-aminobenzoate by diazotization, coupling with ferrocene and subsequent hydrolysis. A mixture of the acid (2.85 g, 9.31 mmol), 4-nitrophenol (1.29 g, 9.31 mmol), *N*,*N*′-dicyclohexylcarbodiimide (1.96 g, 9.31 mmol), and 4-pyrrolidinopyridine (0.1 g) in 100 ml of dry dichloromethane was stirred at room temperature for 48 h. The reaction mixture was filtered off and the solvent was removed *in vacuo*; the solid obtained was recrystallized from ethanol. Yield: 3.54 g (89%). δ_H ($CDCl_3$) 8.35 (d, 2H, Ar), 8.12 (d, 2H, Ar), 7.65 (d, 2H, Ar), 7.40 (d, 2H, Ar), 4.78 (t, 2H, C_5H_4), 4.46 (t, 2H, C_5H_4), 4.07 (s, C_5H_5). ν/cm^{-1} (FTIR: 1720 (C=O).

4-Aminophenyl 4-ferrocenylbenzoate 4

A mixture of the nitro derivative obtained above (4.10 g, 10 mmol), 10% Pd/C (0.5 g) and dioxane (50 ml) was stirred under H_2 in an autoclave for several hours till no more H_2 was consumed and then filtered through Celite. Removal of the solvent resulted in a solid residue which was recrystallized from ethanol. Yield: 3.30 g (90%). ν/cm^{-1} (FTIR) 3405 (s), ν_{as} (NH_2), 3330 (sb), ν_{sy} (NH_{2}), 1726 [ν(C=O)]. δ_H ($CDCl_3$) 8.09 (d, 2HAr), 7.57 (d, 2H, Ar), 7.03 (d, 2H, Ar), 6.74 (d, 2H, Ar), 4.75 t, 2H, C_5H_4), 4.42 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 3.75 (br, 2H, NH_2).

Preparation of methyl 4-hexadecyloxybenzoate

A mixture of 1-bromohexadecane(0.11 mol), methyl 4-hydroxybenzoate (0.1 mol), potassium carbonate (0.2 mol) and a few mg of potassium iodide in 250 ml of acetone was heated under reflux for 72 h and allowed to cool to room temperature. The solvent was removed under reduced pressure and the residue was taken up in 200 ml of water, extracted with CH_2Cl_2 and dried over $MgSO_4$. The crude product obtained after removal of solvent was recrystallized from ethanol. Yield: 80%. δ_H (CDCl) 8.0 (d, 2H, Ar), 6.9 (d, 2H, Ar), 4.05 (t, 2H, OCH_2), 3.88 (s, 3H, OCH_3), 1.85 (m, 2H, CH_2), 1.30 (m, 28H), 0.9 (t, 3H, CH_3).



Scheme 1

4-Hexadecyloxybenzoic acid

The ester obtained above (5.6 g, 15 mmol) was dissolved in 60 ml of dioxane and KOH (1.7 g, 30 mmol) in 2 ml of water and the mixture was heated under reflux for 8 h. The solvent was removed under reduced pressure and the residue was taken up in water and acidified with 6 M HCl. The resulting precipitate was filtered off and washed with water and dried in air. Yield: 4.30 g (80%).

4-Hexadecyloxybenzoyl chloride

To 4-hexadecyloxybenzoic acid (3.6 g, 10 mmol) in 50 ml of CH_2Cl_2 was added $SOCl_2$ (2.38 g, 20 mmol) and a few drops of dimethylformamide. The reaction mixture was refluxed overnight and the excess thionyl chloride was removed under vacuum. δ_H ($CDCl_3$) 8.10 (d, 2H, Ar), 6.9 (d, 2H, Ar), 4.05 (t, 2H, OCH_2), 1.85 (m, 2H, CH_2), 1.20–1.60 (m, 30H), 0.9 (t, 3H, CH_3).

4-Hexadecyloxybenzoyl isothiocyanate 5

The crude acid chloride which is free from $SOCl_2$ obtained above was suspended in dry acetone (100 ml) and to it was added potassium thiocyanate (1.94 g, 20 mmol) and refluxed for 4 h. After cooling, the reaction mixture was filtered and the solvent was removed. The residue was treated with benzene and filtered again to remove the solid formed. The benzene solution was evaporated under vacuum and the oily residue was chromatographed (silica gel, CH_2Cl_2) to give a pure light-yellow compound. Yield: 1.75 g (40%). δ_H ($CDCl_3$) 8.05 (d, 2H, Ar), 6.95 (d, 2H, Ar), 4.05 (t, 2H, OCH_2), 1.85 (m, 2H, CH_2), 1.20–155 (m, 26H), 0.9 (t, 3H, CH_3). ν/cm^{-1} (FTIR) 1988, [ν(N=C=S)] 1685, [ν(C=O)].

The other 4-alkyloxybenzoyl isothiocyanates used here were prepared in 40–50% yields by following the same method mentioned above using the corresponding acid chlorides.

General procedure for preparing 4-ferrocenylbenzoate derivatives (Fc-BATU-*n*) 6

To a benzene solution (5 ml) containing 256 mg (0.5 mmol) of 4-aminophenyl 4-ferrocenylbenzoate was added dropwise the corresponding 4-alkyloxybenzoyl isothiocyanate(0.5 mmol) in 10 ml of benzene 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 off. The residue was recrystallized from CH_2Cl_2–heptane and dried over P_2O_5. Yields: 80–85%.

4-{3-[4-(Octyloxy)benzoyl]thioureido}phenyl 4-ferrocenylbenzoate (Fc-BATU-8). Elemental analysis: Calc. for $C_{39}H_{40}N_2O_4SFe$: C, 68.02; H, 5.85 and N, 4.07%; Found: C, 67.92; H, 5.80 and N, 4.12%. δ_H ($CDCl_3$) 0.89 (t, 3H, CH_3), 1.30–1.60 (m, 26H), 1.83 (m, 2H, CH_2), 4.05 (t, 2H, OCH_2), 4.07 (s, 5H, C_5H_5), 4.44 (s, 2H, C_5H_4), 4.76 (s, 2H, C_5H_4), 7.10 (d, 2H, Ar), 7.27 (d, 2H, Ar), 7.58 (d, 2H, Ar), 7.79–7.88 (dd, 4H, Ar), 8.13 (d, 2H, Ar), 9.04 (s, 1H, —NH—C=O), 12.74 (s, 1H, NH-aryl).

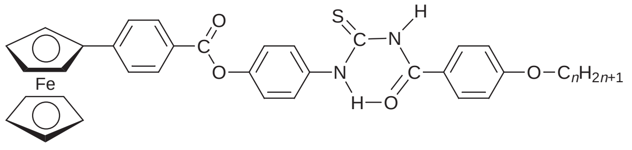
4-{3-[4-(Dodecyloxy)benzoyl]thioureido}phenyl 4-ferrocenylbenzoate (Fc-BATU-12). Elemental analysis: Calc. for $C_{43}H_{48}O_4N_2SFe$: C, 69.36; H, 6.50 and N, 3.76%; Found C, 69.73, H, 6.45 and N, 3.81%. δ_H (CDCl) 0.89 (t, CH_3), 1.28–1.63 (m, 18H), 1.85 (m, 2H, CH_2), 4.05 (t, 2H, OCH_2), 4.07 (s, 5H, C_5H_4), 4.43 (s, 2H, C_5H_4), 4.76 (s, 2H, C_5H_4), 7.0 (d, 2H, Ar), 7.32 (d, 2H, Ar), 7.61 (d, 2H, Ar), 7.82–7.88 (dd, 4H, Ar), 8.12 (d, 2H, Ar), 9.05 (s, 1H, —NH—C=O), 12.75 (s, 1H, —NH—aryl).

4-{3-[4-(Hexadecyloxy)benzoyl]thioureido}phenyl 4-ferrocenylbenzoate (Fc-BATU-16). Elemental analysis: Calc. for $C_{47}H_{56}N_2O_4SFe$: C, 70.47, H: 7.05 and N, 3.50%; Found C, 70.37; H, 7.04 and N, 3.58%. δ_H ($CDCl_3$) 0.91 (t, 3H, CH_3), 1.30–1.65 (m, 26H), 1.83 (m, 2H, CH_2), 4.03 (t, 2H, OCH_2), 4.07 (s, 5H, C_5H_5), 4.44 (s, 2H, C_5H_4), 4.76 (s, 2H,C_5H_4), 7.02 (d, 2H, Ar), 7.27 (d, 2H, Ar), 7.61 (d, 2H, Ar), 7.79–7.88 (dd, 4H, Ar), 8.13 (d, 2H, Ar), 9.07 (s, 1H, —NH—C=O), 12.75 (s, 1H, NH—aryl).

4-{3-[4-(Octadecyloxy)benzoyl]thioureido}phenyl 4-ferrocenylbenzoate (Fc-BATU-18). Elemental analysis: Calc. for $C_{49}H_{60}N_2O_4SFe$: C, 71; H, 7.29 and N, 3.38%; Found: C, 71.05; H, 7.30; N, 3.38%. δ_H (CDCl3) 0.89 (t, 3H, CH_3), 1.27–1.61 (m, 30H), 1.83 (m, 2H, CH_2), 4.03 (t, 2H, OCH_2), 4.07 (s, 5H, C_5H_5), 4.44 (s, 2H, C_5H_4), 4.76 (s, 2H, C_5H_4), 7.02 (d, 2H, Ar), 7.29 (d, 2H, Ar), 7.59 (d, 2H, Ar), 7.83–7.88 (dd, 4H, Ar), 8.12 (d, 2H, Ar), 9.05 (s, —NH—C=O), 12.74 (s, 1H, —NH—aryl).

Results and Discussion

These compounds can be readily prepared by reacting the 4-alkoxybenzoyl isothiocyanates with the corresponding amine-containing ferrocenyl moiety. The completion of the reaction can be easily monitored by FTIR by the disappearance of stretching and deformation bands of the primary amine as well as the isothiocyanate band around 2000 cm^{-1}. Further, these derivatives are most likely to undergo intramolecular hydrogen bond formation between the H atom of the NH group in position 3 and the O atom of the carbonyl group as shown or the molecules are linked into dimers by N—H···S intermolecular hydrogen bonds in addition to intramolecular hydrogen bonding. The NH between 4′-aryl and thiocarbonyl groups is at δ *ca.* 12.70 (lower field) and the NH between the carbonyl and thiocarbonyl groups is at δ *ca.* 9.05 (higher field) which may be ascribed to the deshielding effect of the intramolecular hydrogen bond. Such hydrogen bond formation was observed in the case of 1-aroyl-3-arylthioureas as well as 1-(*p*-chlorobenzoyl)-3-phenylthiourea by Dago *et al.*[9]



All the compounds Fc-BATU-*n* where $n=8$, 12, 16 and 18 exhibit purely nematic phases on heating which are characterized by the formation of a nematic schlieren texture and the appearence of droplets immediately below the clearing point. The nematic range increases with an increase in the terminal alkyl chain length (see Fig. 3). On cooling, the nematic phase reappears and persists to below 0 °C in the first three derivatives (see Fig. 4) whereas in the case of Fc-BATU-18 there is a phase transition from nematic to (possibly) S_C at about 72 °C which remains unchanged below −20 °C.

Mesomorphic properties

The thermal and liquid crystal properties of Fc-BATU-*n* where $n=8$, 12, 16 and 18 were investigated by a combination of differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The data are collected in Table 1.

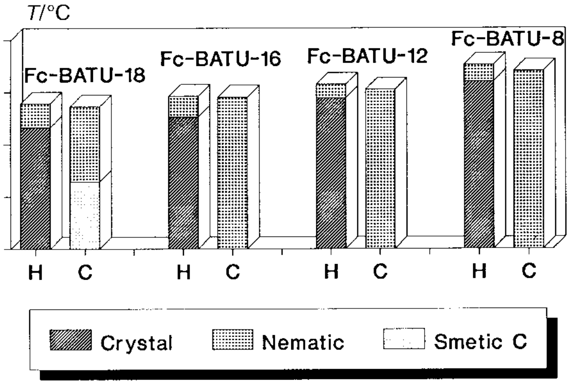


Fig. 3 Effect of increasing chain length, *n*

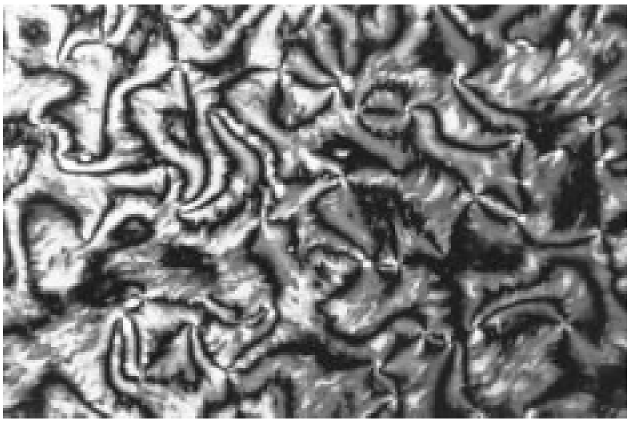


Fig. 4 Representative thermal polarized optical micrograph of the nematic schlieren texture displayed by Fc-BATU-12 on cooling from the isotropic liquid to 28 °C

Table 1 Phase-transition temperatures[a] and enthalpy changes of ferrocene derivatives

ferrocene	transition	T/°C	ΔH/kJ mol^{-1}
Fc-BATU-8	C–N	160	47.0
	N–I	176	2.0
	I–N	170	2.1
	T_g	21	—
Fc-BATU-12	C–N	144	52.0
	N–I	157	1.6
	I–N	154	2.2
	T_g	18	—
Fc-BATU-16	C_1–C_2	114	49.0
	C_2–N	126	13.8
	N–I	146	1.8
	I–N	144	2.2
	T_g	26	—
Fc-BATU-18	C–C_1	94	20.8
	C_1–C_2	102	18.5
	C_2–N	116	16.1
	N–I	139	2.1
	I–N	134	1.2
	T_g	31	—

[a] C: crystal, N: nematic; I: isotropic, T_g: glass transition.

Fig. 5 shows the DSC curve of Fc-BATU-8. On the first heating, the compound exhibited an endothermic peak at 159.9 °C which corresponds to the melting point followed by the formation of a nematic schlieren texture and the appearence of droplets below the clearing point reached at 177.7 °C. On first cooling from the isotropic liquid, however, the enantiotropic nematic phase persisted below −20 °C with a baseline shift at 21 °C. The cooling curve A (5 mW) is a magnified

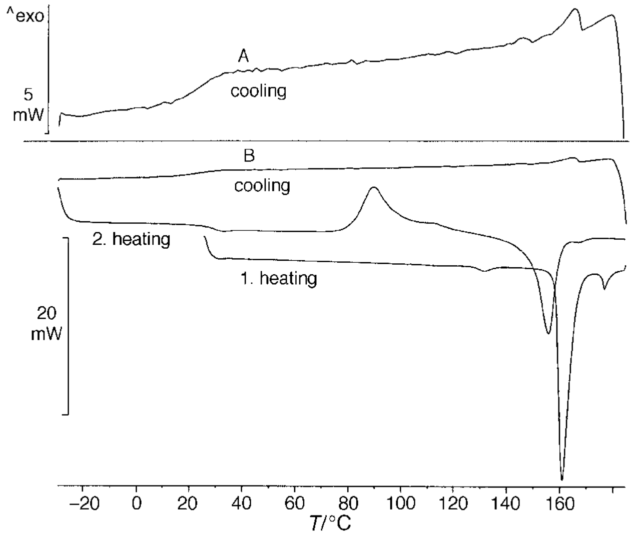


Fig. 5 DSC curves of Fc-BATU-8. Scanning rate: 10 °C min^{-1}.

version of curve B (20 mW) and resembles a typical glass transition T_g curve. On second heating from the glassy state, two exothermic peaks at 94.9° and 119 °C and a sharp endothermic peak at 157 °C were observed; the former peaks are due to cold crystallization and the latter corresponds to a crystal–nematic transition followed by an isotropic melt at 170.6 °C.

On first heating compound Fc-BATU-12 (see Fig. 6), two exothermic peaks were observed at 113 and 144 °C which correspond to a crystal–crystal transition (C_1–C_2) and a crystal–nematic transition. The isotropic melt was found at 157 °C. On cooling, the nematic phase reappears and persists below 0 °C with a baseline shift at 18 °C which resembles the typical shape of a glass transition curve and correponds to a glass transition point T_g. On a second heating from the glassy state, a metastable crystal (C_1) at onset peak temperature 73.2 °C is found which melted at 82.3 °C followed by crystallization. A sharp endothermic peak was seen at 131 °C which corresponds to a crystal–nematic transition (C_2–N) followed by an isotropic melt at 155 °C. This phenomenon is typical of double melting behaviour as was observed by Nakamura *et al.*[3a] for their ferrocene compounds as well as by Ohta *et al.*[10] The second cooling proceeds in a similar manner to the first.

The first heating of compound Fc-BATU-16 (see Fig. 7), shows a sharp endothermic peak at 113.6 °C, which is the melting point, followed by an exothermic peak at 120 °C corresponding to crystallization of the metastable crystal C_1 which melts immediately at 128.4 °C. At this temperature, formation of the mesophase was observed, which was identified by the appearence of droplets and the formation of a typical nematic schlieren texture. The first cooling of this compound shows a small exothermic peak at 142 °C corresponding to an isotropic–nematic transition. The nematic texture remains unchanged below −20 °C and a baseline shift is observed at 31 °C. Again, the shape of the curve clearly resembles that of the typical glass transition point T_g of a DSC curve.

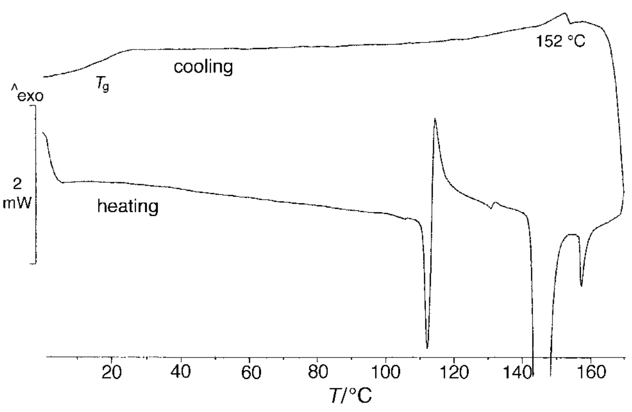


Fig. 6 DSC curves of Fc-BATU-12. Scanning rate: 10 °C min^{-1}.

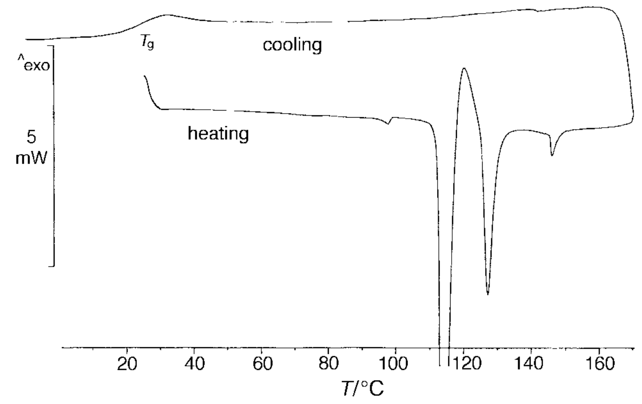


Fig. 7 DSC curves of Fc-BATU-16. Scanning rate: 10 °C min^{-1}.

In the second heating, Fc-BATU-16 underwent a glass transition at 37 °C followed by a complex melting and crystallization process. A broad exothermic peak was seen at 111 °C corresponding to a crystal–nematic transition again followed by an isotropic melt at 146 °C.

The second cooling cycle gave the same results as the first cooling. The thermal behaviour is reversible which suggests that the liquid crystal structures are frozen unchanged even below the glass transtion temperatures.

The first heating of compound Fc-BATU-18 (see Fig. 8) shows two sharp endothermic peaks at 94 and 102 °C due to a crystal–crystal (C–C_1) transition followed by an exothermic peak at 107 °C corresponding to the the crystallization of the metastable crystal C_1, which melts immediately at 116 °C. At this temperature, formation of the nematic phase was observed followed by an isotropic melt at 139 °C. On first cooling, the nematic phase reappears and a change of texture was observed

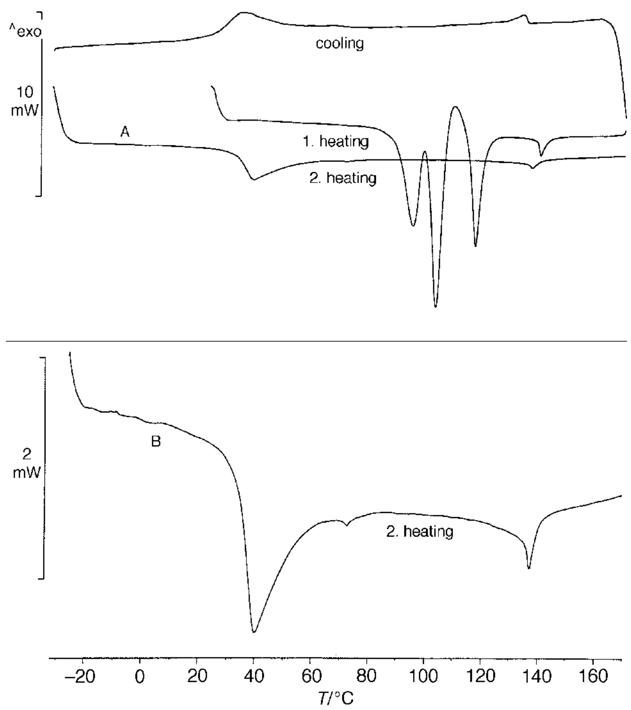


Fig. 8 DSC curves of Fc-BATU-18. Scanning rate: 10 °C min^{-1}.

at 72 °C under the polarizing optical microscope to a texture resembling the schlieren texture of the S_C phase. This is also evidenced from the DSC curves of both the heating and cooling cycles of this compound. Curve B is a magnified version (2 mW) of curve A (10 mW). One can clearly see in this curve a peak at 72 °C indicating a change of phase. This S_C phase continues to persist below −20 °C with a baseline shift at 31 °C which corresponds to a glass transition T_g.

The absence of first order peaks during the second heating from the glassy state is presumably due to delayed crystallization of the alkyl chains.

Conclusion

The ferrocene derivatives bearing BATU ligands reported here represent the first steps to achieving the desired heterometallic complexes. Work is in progress on their preparation, as well as studying their mesomorphic properties.

The persistence of the nematic phase below the glass transition (T_g) temperatures in Fc-BATU-*n* compounds (remarkable for low molecular mass calamitic sytems) suggests possible applications in display devices. The synthetic route reported here provides several opportunities for structural variations and we are exploring these and investigating their mesogenic properties in detail. Work is also in progress on the synthesis of selenium analogues such as *N*-benzoyl-*N*′-arylselenourea derivatives containing ferrocene.

We thank Professor R. Deschenaux for helpful discussions and Dr B. Donnio for his help in DSC as well as OPM studies in the initial stages of this work.

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Paper 7/08738Ad; *Received* 4*th December*, 1997