Novel ferrocene-based chiral Schiff's base derivative with a twist-grain boundary phase (TGBA) and a blue phase

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Synthesis of a monosubstituted ferrocene-based chiral Schiff's base derivative with unusual mesomorphic behavior is reported namely the first metallomesogen which exhibits TGBA and blue phases apart from S_C*, S_A and N* phase transformations.

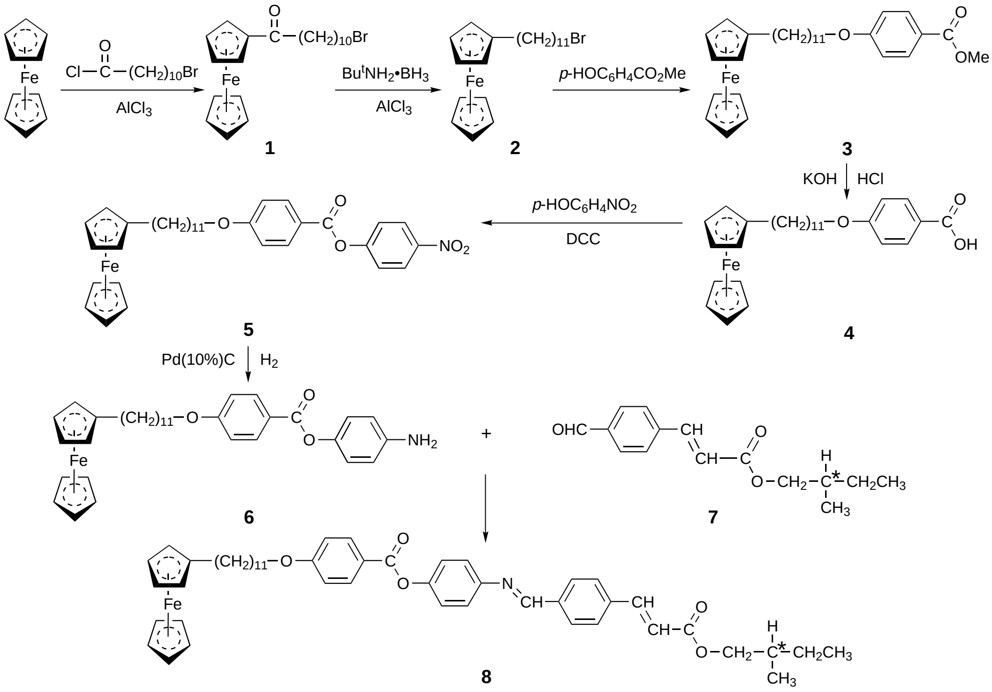
Chirality in ordered fluids has become one of the most fascinating and innovative fields of current research in liquid crystals. The quest to develop new chiral mesomorphic compounds led to the serendipitous discovery of new types of physical behavior namely the twist grain boundary (TGB)[1] and the blue phases[2] apart from the ferri- and antiferro-electric[2,3] liquid crystalline phases. The TGBA phase first discovered by Goodby *et al.*,[4] in 1989 was initially predicted by Gennes[5] in 1972. The appearance of the TGB phase[6] has induced enormous interest due to the formal analogy of its Landau free energy to that of the Shubnikov phase occurring in the type II superconductors.[5,7] Renn and Lubensky[7] in 1988 described this phase as a frustrated intermediate between N* and S_A phases. Since then, several new organic compounds showing such a phase were synthesized by different workers and their phase sequences were identified.[6]

Both the TGB and the blue phases are two kinds of frustrated phases which are found exclusively in chiral organic compounds. None of the chiral metallomesogens reported until now exhibited such phase formation, although several of their Pd, Cu and V complexes bearing one or more stereocenters were synthesized.[8] Nevertheless, incorporation of metals into the structures of low molar mass chiral liquid crystals to attain such phases must be a very challenging and attractive subject for study from both the academic and the applications point of view. Especially, introduction of ferrocene units as components of chiral liquid-crystalline materials may bring about high thermal stability and other additional properties among which its ability to undergo reversible one-electron transfer processes is one of the most important.[9]

However, studies on the synthesis of chiral smectic C mesophases comprising monosubstituted ferrocenyl group are scanty except the one reported by Imrie and Loubser.[10] The limited studies in this direction are attributed to the fact that monosubstituted ferrocenes, because of their unfavourable molecular shape (L-shape) and also due to repulsive steric effects of the ferrocene unit which hinders the ability of the molecules to pack in layers thus favouring mostly the formation of nemetic phases.[11–13]

We therefore attempted to prepare several ferrocene based chiral mesophases and surprisingly synthesized a compound that exhibits enantiotropic S_C*, S_A, a twist grain boundary phase (TGBA), a cholesteric as well as a blue phase. This is the first chiral metallomesogen which exhibits a TGBA and a blue phase.

The synthesis of the chiral Schiff's base derivative **8** is described in Scheme 1. To start with, we used the readily available (*S*)-(−)-2-methylbutan-1-ol for this purpose. In **8** the chiral centre with a small terminal chain is located adjacent to the rigid molecular core in order to couple strongly with the



Scheme 1

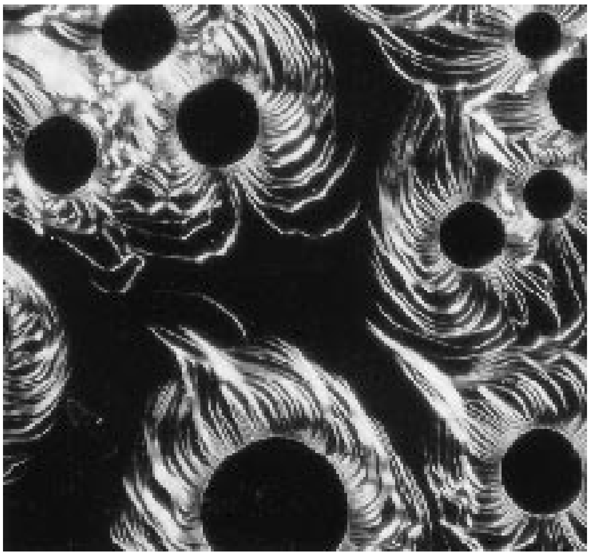


Fig. 1 Polarized optical micrograph of the TGBA phase on heating to 143.8 °C; magnification × 100

dipolar regions of the core. The phase assignments and transition temperatures (°C) of **8** shown below were determined by polarized optical microscopy using clean, untreated glass microscopic slides and cover slips as well as by differential scanning calorimetry (DSC) measurements.

C 116 S_C* 136 S_A 143.8 TGBA 144.9 N* 158 BP 159.2 I
I 157.2 BP 154.6 N* 143.1 TGBA 141.2 S_A 132.6 S_C* 77.9 C

At the S_A–S_C* transition, a dramatic textural change was observed whereby the dark homeotropic texture of the S_A phase gives rise to a *schlieren* texture characteristic of the S_C phase. The thermogram indicates that owing to the small enthalpy associated with these transitions, some of the peaks could not be detected. The calculated enthalpies (kJ mol^{-1}) are as follows. S_C*–S_A, 0.28; S_A–TGBA–N*, 0.55 and BP–I, 0.81.

When heating slowly (0.2° min^{-1}), the filament structure of the TGBA phase shown in Fig. 1, grows slowly in the homeotropic regions of the smectic A phase and ends up in a fire ball which coalesces into a cholesteric phase with a fan-shaped texture. Also oily streaks are seen upon subjecting the preparation to mechanical stress.

Both during heating and cooling cycles (0.2° min^{-1}), the formation of the blue phase is clearly seen as a platelet texture which is shown in Fig. 2.

The influence of orientation of ester linkages which directs the electron delocalization and the coplanarity of the two aromatic rings of benzylideneaniline (the angle between the two planes of these rings deduced from X-ray[14] and UV data[15] was found to be 66°) probably enhances the polarisability of the rigid core due to extended conjugation. This in turn enhances the preponderance of smectic phases and also creates favourable packing conditions. Furthermore, the presence of the flexible spacer between the phenyl ring and the ferrocenyl unit in **8** is primarily responsible for the formation of highly ordered phases, in the absence of which only a cholesteric phase was observed.

Compound **8** is very stable and no decomposition was seen during repeated heating and cooling cycles. Furthermore, a free-standing film can be prepared by heating the compound into its smectic state (130 °C) without any decomposition.

In conclusion, we report here a monosubstituted ferrocene-based metallomesogen with a chiral Schiff's base which shows for the first time a relatively long S_C* domain, a TGBA phase which mediates between S_A and N* and a blue phase just before the clearing point, in spite of a bulky pendant ferrocene unit on the one side and a relatively small terminal group appended to the chiral centre on the other side. This ferrocene derivative and derivatives thereof should be interesting candidates for preparing ferroelectric smectic C* materials useful in fast switching electro-optic devices.

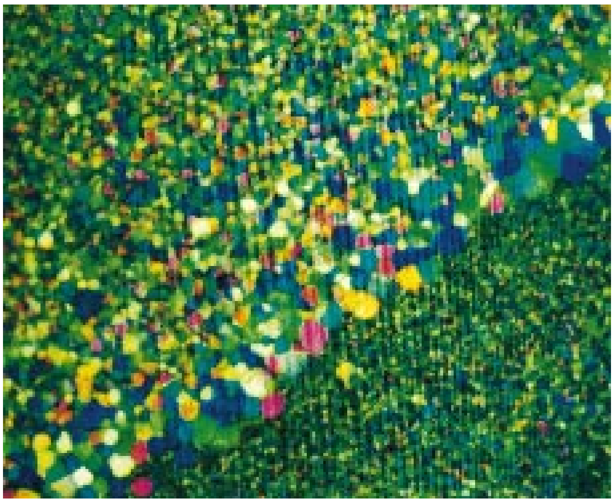


Fig. 2 Polarized optical micrograph of the blue phase platelet texture on cooling from the isotropic liquid to 156.1 °C; magnification × 100.

Notes and References

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‡ Detailed synthetic procedures for the intermediate ferrocenyl derivatives **1**–**6** will be reported separately. The final Schiff's base compound **8** is obtained by refluxing equimolar amounts of **6** and **7** in ethanol containing a few drops of acetic acid for 1 h and filtered hot through a sintered glass. The precipitate obtained after cooling was dissolved in dichloromethane and reprecipitated by the addition of heptane. Yield: 82%. Anal. Calc. for $C_{49}H_{57}FeNO_5$: C, 73.95; H, 7.22; N, 1.76. Found: C, 74.32; H, 7.27, N. 1.89%. FTIR (KBr) ν/cm^{-1}: 2919, 2848, 1714, 1606, 1513, 1311, 1253, 1188, 1162, 1068. ^{1}H NMR ($CDCl_3$), δ 0.90–0.99 (m, 6 H, CH_3), 1.20–1.70 (m, 18 H, 8 × CH_2, 1 CH_2), 1.85 (m, 3 H, 1 CH_2, 1 CH), 2.35 (m, 2 H, CH_2), 4.03–4.09 (m, 4 H, C_5H_4 + 4 H, 2 × OCH_2), 6.57 (d, 1 H, =CH), 7.75 (d, 2 H, Ar), 7.93–7.96 (d, 1 H, =CH), 7.14–7.17 (d, 2 H, Ar), 8.50 (s, 1 H, N=CH)

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Received in Cambridge, UK, 22nd December 1997; 7/09140K