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Liquid-crystalline mixed [60]fullerene–ferrocene materials

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[60]Fullerene was functionalized with a mesomorphic malonate derivative containing two ferrocene units; the targeted compound showed thermotropic liquid-crystalline properties.

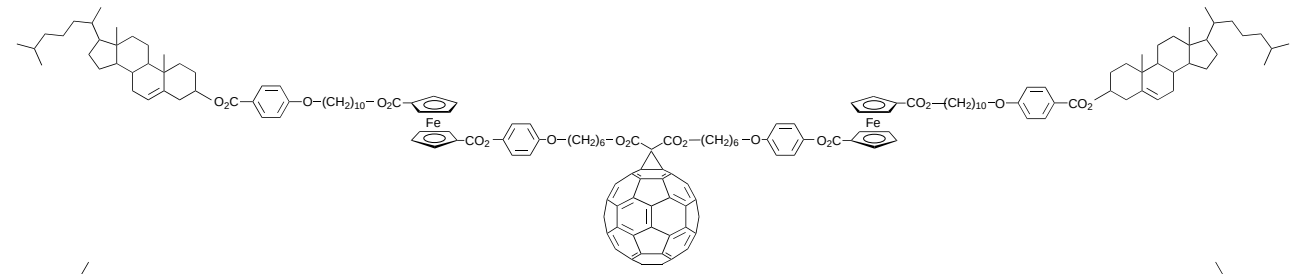
Recently, we reported the first [60]fullerene-containing thermotropic liquid crystal.[1] The C_{60} core was functionalized with a twin cholesterol malonate derivative following well established literature procedures.[2] The targeted fullerene derivative showed a monotropic smectic A phase.[1] This finding is of interest regarding the increasing activity which is currently devoted to the design of fullerene-based new materials.[3] On the other hand, photoinduced electron transfer reactions in fullerene–ferrocene dyads have been investigated[4] (intramolecular quenching of C_{60} singlet excited state by the ferrocene framework was observed). Such studies are interesting with a view to elaborating new optical and electronic molecular devices.[3,4] The design of fullerene–ferrocene compounds showing liquid-crystalline behavior is attractive as such structures would lead to new multicomponent mesomorphic materials.

This communication describes the synthesis and liquid-crystalline properties of the mixed fullerene–ferrocene thermotropic liquid crystal **1** which represents the first member of this new family of mesomorphic materials. Malonate derivative **2** was selected to functionalize the C_{60} core owing to the high mesomorphic character of the twin cholesterol liquid crystals.[1]

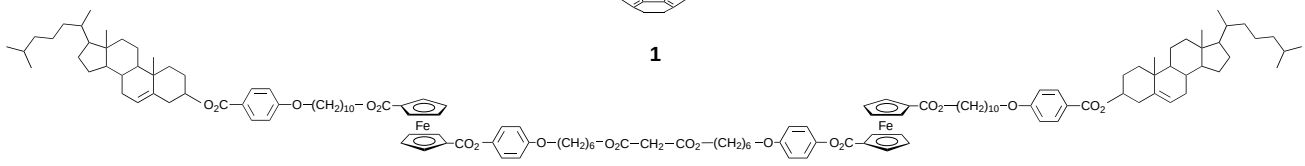
The synthesis of **1** is presented in Scheme 1. 1-Carboxybenzyloxy-1′-chlorocarboxyferrocene[5] (**3**) was reacted with cholest-5-en-3β-yl-4-(10-hydroxydecyloxy)benzoate[1] to give protected ferrocene **4**. Deprotection of the latter species gave acid **5**, the esterification of which with hydroquinone monobenzyl ether led to benzyl derivative **6**. Removal of the benzyl protecting group furnished phenol intermediate **7**, which was subsequently *O*-alkylated with 6-bromohexanol to give **8**. Condensation of **8** with malonyl chloride led to **2**. Finally, treatment of **2** with [60]fullerene adapting a literature procedure[6] gave the targeted structure **1**, as a dark solid. The latter species was purified by column chromatography (silica gel, eluent: toluene–AcOEt 20 : 1 v/v) and precipitation (dissolution in CH_2Cl_2 and precipitation in MeOH). Its structure and purity were confirmed by NMR spectroscopy, UV–VIS spectroscopy and elemental analysis.† As expected, the [6,6]-closed methanofullerene derivative was obtained.[1,2]

The thermal and liquid-crystalline properties of **1**, **2**, **7** and **8** were investigated by a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction studies.‡ Compounds **2** (Cr 73 S_A 134 I)§ and **7** (Cr 112 S_A 151 I)§ gave an enantiotropic smectic A phase and **8** (Cr 63 S_A 125 N* 127 I)§ showed enantiotropic smectic A and chiral nematic phases. The liquid-crystalline phases were identified by POM from the observation of typical textures (smectic A phase: focal conic texture and homeotropic areas; chiral nematic phase: plane texture). The POM observations were confirmed by X-ray diffraction analysis.

During the first heating, DSC analysis of **1** gave two endotherms at 66 (onset, ΔH = 12.9 kJ mol^{-1}) and 118 °C (onset, ΔH = 11.7 kJ mol^{-1}), which were indicative of the formation of a liquid-crystalline phase. On cooling an exotherm was obtained at 113 °C (onset, ΔH = 10.5 kJ mol^{-1}) as well as a T_g at 61 °C (onset). Reversibility of the cooling transitions was observed during the second heating run. POM observations supported the DSC data: a viscous liquid-crystalline phase formed between the two endotherms (fluidity increased from *ca*. 80 °C). The transition at 118 °C corresponded to the clearing point, whereas the transition at 66 °C reflected softening of the sample. The low enthalpy value which is associated to this latter transition could be the consequence of a semicrystalline character of the sample, which was precipitated during the purification process (see above). Neither slow cooling of the sample from the isotropic liquid nor annealing of the sample near the clearing point led to the formation of a typical texture. This is often the case for viscous materials. Careful examinations of small droplets revealed the presence of a focal-conic texture and homeotropic zones.



1



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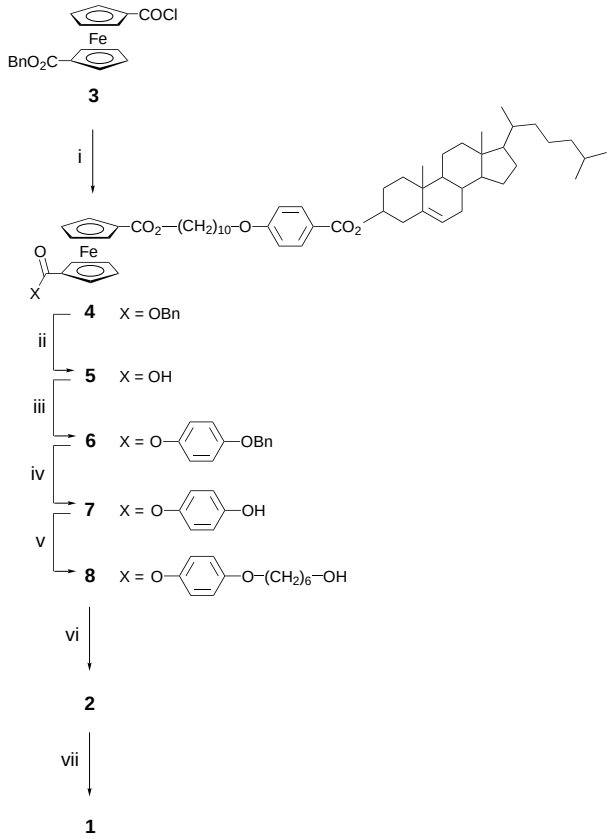

Scheme 1 *Reagents and conditions*: i, cholest-5-en-3β-yl-4-(10-hydroxydecyloxy)benzoate,[1] triethylamine (Et_3N), CH_2Cl_2, room temp. (16 h) and then reflux (overnight), 61%; ii, H_2, Pd/C, CH_2Cl_2–EtOH, room temp., 4 bar, overnight, 85%; iii, hydroquinone monobenzyl ether, *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine, CH_2Cl_2, room temp., 3 h, 76%; iv, H_2, Pd/C, CH_2Cl_2–EtOH, room temp., 4 bar, overnight, 93%; v, 6-bromohexanol, K_2CO_3, acetone–THF, 60 °C, 24 h, 36%; vi, malonyl chloride, Et_3N, CH_2Cl_2, room temp., 2 h, 76%; vii, [60]fullerene, I_2, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene, room temp., 3 h, under N_2, 35%

To further investigate the nature of the liquid-crystalline phase displayed by **1**, X-ray diffraction studies were performed from 120 to 30 °C (the sample was heated into the isotropic fluid and then cooled to the desired temperature). Diffraction patterns typical of disordered smectic phases (*i.e.* smectic A or C) were recorded. They consisted, in the low-angle region, of two sharp diffraction peaks, the corresponding spacings of which are in a 1 : 2 ratio, and in the wide-angle region, of a diffuse signal. A representative diffractogram is shown in Fig. 1. The *d*-layer spacing was found to be independent of the temperature (a *d*-value of 74.5 Å was measured at 110 °C; from CPK molecular models, an approximate molecular length of 120 Å was measured for **2** in its fully extended conformation). The layered structure was retained at room temperature. The X-ray diffraction data and POM observations suggest that the liquid-crystalline phase could be smectic A in nature.

Finally, thermogravimetry (10 °C min^{-1}, under N_2) revealed good thermal stability for **1**: mass losses of 1, 5 and 10% were detected at 270, 295 and 309 °C, respectively.

The possibility to exploit the properties of the fullerene[3] and ferrocene[7] units within the same liquid-crystalline molecular framework represents an important step towards the development of multifunctional new materials.

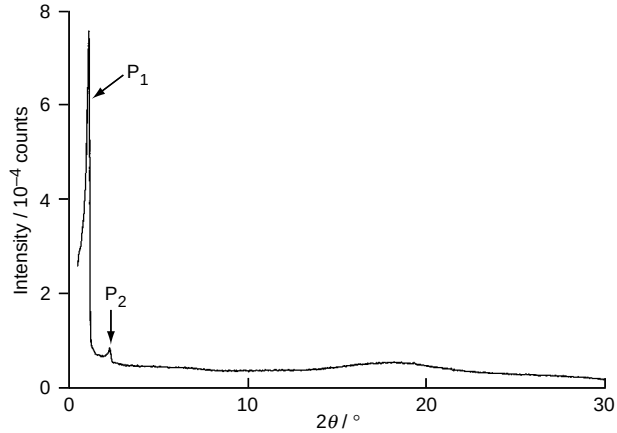

Fig. 1 X-Ray diffraction pattern of **1** recorded at 110 °C. P_1 and P_2 refer to the first and second order signals corresponding to the layer periodicity. The diffuse signal at large angles corresponds to the liquid-like arrangement of the molecules within the smectic layers.

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Notes and References

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† *Selected data* for **1**: VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 426 (3080), 476 (1990), 686 (246). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, 4 H, arom.), 7.11 (d, 4 H, arom.), 6.92–6.87 (2 × d, 8 H, arom.), 5.41 (d, 2 H, CH=C, cholesteryl), 4.94 (t, 4 H, Cp), 4.89 (t, 4 H, Cp), 4.83–4.81 (m, 2 H, CHO, cholesteryl), 4.52 (t, 4 H, $C_{60}CCO_2CH_2$), 4.49–4.47 (m, 8 H, Cp), 4.19 (t, 4 H, $CpCO_2CH_2$), 4.00–3.93 [2 × t, 8 H, $(CH_2)_8CH_2O$ and $(CH_2)_4CH_2O$], 2.45 (d, 4 H, cholesteryl), 2.03–0.65 (series of m, 130 H, 82 cholesteryl protons and 48 aliphatic protons). Anal. Calc. for $C_{199}H_{186}Fe_2O_{20}$ (3009.34): C, 79.43; H, 6.23. Found: C, 79.37; H, 6.21%.

‡ For instrumentation, see: R. Deschenaux, F. Turpin and D. Guillon, *Macromolecules*, 1997, **30**, 3759.

§ Cr = Crystal state, S_A = smectic A phase, N* = chiral nematic (cholesteric) phase, I = isotropic liquid. The transition temperatures (onset point, rate 10 °C min^{-1} under N_2) reported (in °C) are taken from the first DSC heating run. Upon cooling from the isotropic liquid, none of compounds **2**, **7** and **8** crystallized. In each case, a T_g was detected by DSC.

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