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Ferrocene-containing liquid-crystalline dendrimers: a novel family of mesomorphic macromolecules

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The synthesis and liquid-crystalline properties of a first-generation dendritic core substituted with six mesomorphic ferrocene units are reported; the investigated compound exhibited a broad enantiotropic smectic A phase (polarized optical microscopy, DSC, and XRD studies) and good thermal stability (thermogravimetry).

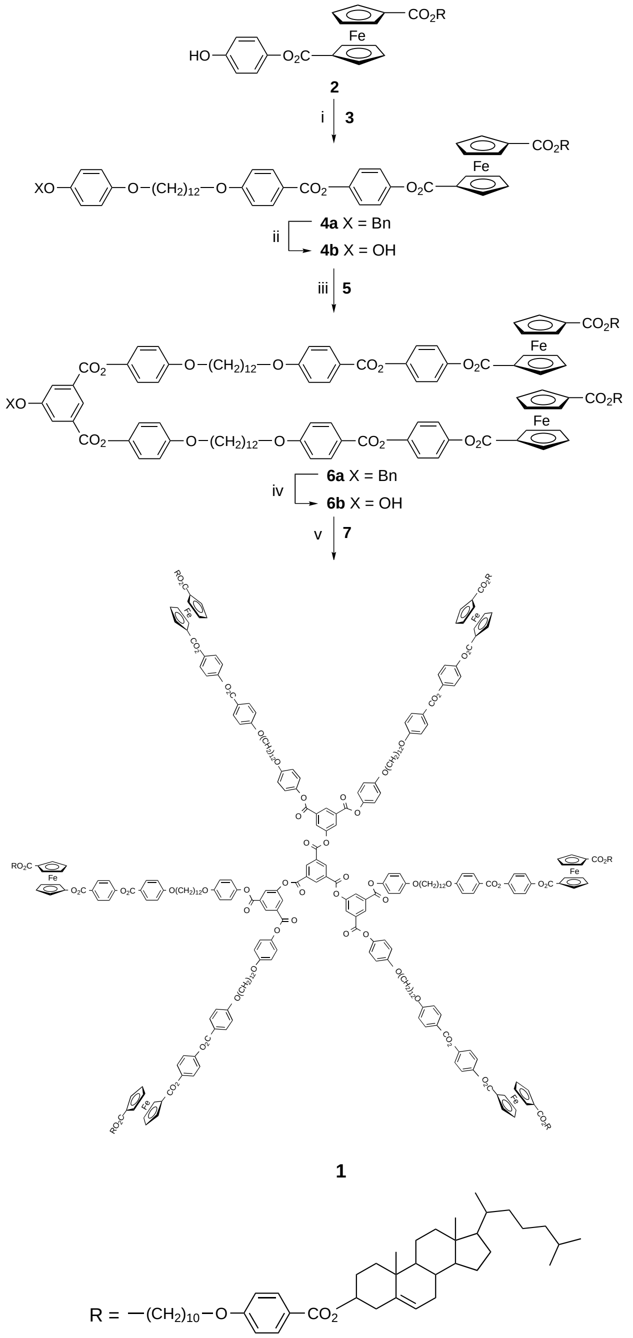
Increasing interest is currently accorded to the design and synthesis of dendrimers.[1] The possibility of creating new materials, characterized by a well defined and aesthetic macromolecular structure, displaying unique properties (such as catalysis,[2] encapsulation,[3] chiroptical activity[4] and redox activity[5]) strongly motivated these studies.

Liquid-crystalline dendrimers have been recently reported. An AB_2 rod-like mesogenic monomer was used to synthesize dendrimers up to the fourth generation.[6] Nematic and smectic phases were observed for these materials. First-[7] and second-generation[8] polysiloxane dendrimers were functionalized by mesogenic moieties, and showed smectic A or smectic C phases. Metal complexes were prepared from various metal ions and first- or second-generation ethyleneimine dendrimers and a hexagonal columnar phase was identified for a Cu^{II} complex.[9] These novel structures form a most interesting class of anisotropic materials from a fundamental and practical viewpoint: the structural features of such compounds should lead to important basic information for a better understanding of the structure–mesomorphic properties relationship for liquid-crystalline macromolecules and, ultimately, could be exploited for elaborating new liquid-crystalline devices. To our knowledge, organometallic-type liquid-crystalline dendrimers have not been reported.

To further explore the capability of mesogenic ferrocene derivatives to act as mesomorphic building blocks for the construction of liquid-crystalline macromolecules,[10] we extended our interest to ferrocene-containing thermotropic dendrimers. This communication describes the synthesis and mesomorphic properties of the ferrocene-containing thermotropic dendrimer **1**, which represents the first organometallic-type liquid-crystalline dendrimer.

A first-generation dendrimer was selected to explore the thermal and liquid-crystalline behavior of such a new structure. A ferrocene-based cholesterol framework was used as a mesomorphic promoter owing to the high liquid-crystalline tendency of cholesterol derivatives: recently, we reported the first fullerene[60]-containing thermotropic liquid crystal obtained by derivatizing the C_{60} core with a twin-cholesterol derivative.[11]

The synthesis of **1** is outlined in Scheme 1. Condensation of ferrocene derivative **2**† with 4-(4′-benzyloxyphenoxy)-dodecyloxybenzoic acid chloride **3**† gave the protected ferrocene-containing unramified sub-unit **4a**. Deprotection of the latter species under standard conditions gave the phenol derivative **4b**, which was subsequently reacted with 5-benzyloxyisophthaloyl dichloride **5**† to furnish the protected ferrocene-containing ramified branch **6a**. Removal of the benzyl protecting group under standard conditions led to the phenol intermediate **6b**. Finally, treatment of **6b** with 1,3,5-ben-



Scheme 1 *Reagents and conditions*: i, 4-(4′-Benzyloxyphenoxy)-dodecyloxybenzoic acid chloride **3**, Et_3N, CH_2Cl_2, reflux, overnight, 96%; ii, H_2, Pd/C, CH_2Cl_2–EtOH, room temp., overnight, 96%; iii, 5-Benzyloxyisophthaloyl dichloride **5**, Et_3N, CH_2Cl_2, reflux, overnight, 73%; iv, H_2, Pd/C, CH_2Cl_2–EtOH, room temp., 2 d, 63%; v, 1,3,5-benzenetricarbonyl trichloride **7**, Et_3N, CH_2Cl_2, reflux, 24 h, 86%.

zenetricarbonyl trichloride **7** gave the targeted ferrocene-containing dendrimer **1** as an orange solid. The latter species was purified by column chromatography (silica gel, eluent: CH_2Cl_2–acetone–heptane 10 : 0.5 : 2 v/v/v) and crystallization (CH_2Cl_2–heptane). Its structure and purity were confirmed by ^1H NMR spectroscopy and elemental analysis.[‡]

The thermal and liquid-crystalline properties of **1** were investigated by a combination of differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction studies.[§]

A glass transition temperature (T_g) was detected by DSC (second heating run) at 47 °C (onset transition) followed by an endotherm at 150 °C (peak transition, ΔH = 69.6 kJ mol^{-1}).

POM examinations clearly revealed the formation of a liquid-crystalline phase between T_g and the endothermic peak. The latter corresponded to the clearing point. Slow cooling of the sample from the isotropic liquid into the mesophase gave rise to a focal conic texture and homeotropic areas. From these observations, the mesophase was identified as an enantiotropic smectic A phase.

The nature of the liquid-crystalline phase was clearly and unambiguously established from X-ray data. Firstly, diffraction patterns typical of disordered smectic phases, characterized by a sharp diffraction peak at the low-angle region (a second-order diffraction peak was observed in some cases) and a diffuse peak at the wide-angle region, were obtained. The layered structure was retained below T_g. The *d*-layer spacing was found to be 40.7 Å at room temperature and 41.3 Å at 86 °C (the sample was heated to the isotropic liquid, cooled to room temperature, and re-heated to the desired temperature). Secondly, a sample was oriented by mechanical shearing on mica close to the clearing point, and was analysed at room temperature. A diffraction pattern typical of a smectic phase, consisting of aligned equidistant sharp spots at small angles and of two diffuse arcs at wide angles, was obtained. The sharp spots are aligned along the shearing direction (meridian) and the points of highest intensity in the diffuse arcs are located in the equatorial plane. Therefore the director is parallel to the shearing direction and perpendicular to the layer planes. The mesophase is actually smectic A.

Finally, compound **1** showed good thermal stability as confirmed by thermogravimetry (10 °C min^{-1}, under N_2), which indicated that no decomposition occurred up to *ca.* 250 °C. Mass losses of 1, 5 and 10% were detected at 258, 281 and 322 °C, respectively.

The above results demonstrate that ferrocene-containing liquid-crystalline dendrimers represent a valuable family of mesomorphic macromolecules, showing a pronounced liquid-crystalline tendency and good thermal stability. Furthermore, ferrocenyl functionalized dendrimers have emerged as an interesting class of electro-active macromolecules.[5a,b] The presence of the ferrocene unit in mesomorphic dendrimers is particularly attractive with potential for elaborating dendrimer-based switchable molecular units: we have recently shown that electron transfer can be used to generate mesomorphism in the ferrocene–ferrocenium redox system.[13]

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Footnotes and References

[†] The syntheses of **2** [from ferrocene-1,1′-dicarboxylic acid chloride,[12] cholest-5-en-3β-yl-4-(10-hydroxydecyloxy)benzoate[11] and hydroquinone monobenzyl ether], **3** (from 12-bromododecanol, 4-hydroxymethyl benzoate, and hydroquinone monobenzyl ether), and **5** (from dimethyl 5-hydroxyisophthalate and hydroquinone monobenzyl ether) and thermal and liquid-crystalline properties (smectic A and/or chiral nematic phases) of all ferrocene intermediates will be described in a full report.

[‡] *Selected data* for **1**: ^1H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 3 H, arom.), 8.96 (s, 3 H, arom.), 8.37 (s, 6 H, arom.), 8.14 (d, 12 H, arom.), 7.97 (d, 12 H, arom.), 7.28 (s, 24 H, arom.), 7.15 (d, 12 H, arom.), 6.96–6.86 (m, 36 H, arom.), 5.42 (d, 6 H, C=CH, cholesteryl), 4.97 (t, 12 H, Cp), 4.91 (t, 12 H, Cp), 4.90–4.70 (sh, 6 H, CHO, cholesteryl), 4.51 (m, 24 H, Cp), 4.20 [t, 12 H, $CO_2C\mathit{H}_2(CH_2)_9$], 4.11–3.97 [3×t, 36 H, $(CH_2)_9C\mathit{H}_2O$ and $OC\mathit{H}_2(CH_2)_{10}C\mathit{H}_2O$], 2.45 (d, 12 H, cholesteryl), 2.04–0.65 (series of m, 462 H, 246 cholesteryl protons and 216 aliphatic protons). Anal. Calc. for $C_{555}H_{687}Fe_6O_{84}$ (9037.56): C, 73.76; H, 7.66. Found: C, 73.48; H, 7.69%.

[§] For instrumentation, see: R. Deschenaux, I. Kosztics and B. Nicolet, *J. Mater. Chem.*, 1995, **5**, 2291; M. Veber, P. Sotta, P. Davidson, A.-M. Levelut, C. Jallabert and H. Strzelecka, *J. Phys. Fr.*, 1990, **51**, 1283.

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