



Dendritic nanodevices

Ferrocene-containing liquid-crystalline dendrimers

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Abstract

We describe the synthesis and liquid-crystalline properties of two ferrocene-containing liquid-crystalline dendrimers of second generation, which differentiate by the position of the ferrocene unit within the structure and by the nature of the mesomorphic promoters. Both dendrimers gave rise to smectic phases in agreement with their structures. The title compounds were prepared by applying a convergent synthesis. *To cite this article: T. Chuard et al., C. R. Chimie 6 (2003).*

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1. Introduction

Liquid-crystalline dendrimers have generated enthusiastic studies at the frontiers of chemistry, materials science and biology [1, 2]. The association of a well-defined macromolecular structure with the features of liquid crystals represents an ideal combination for the design of sophisticated supramolecular architectures that are capable to bring fundamental information to better our understanding of complex natural-occurring phenomena [3] and for the elaboration of novel materials for applications in nanotechnology.

A great variety of mesomorphic dendrimers have been reported, and all types of mesophases have been observed [4]. Of particular interest is the possible dependence of the nature of the mesophases with the dendrimer generation. Such a *structure–property* relationship offers the unique opportunity to tune the

liquid-crystalline behaviour with the size of the dendrimer.

With the view to develop new organometallic liquid crystals, we undertook the design, synthesis and study of ferrocene-containing thermotropic dendrimers. Owing to the presence of the ferrocene unit, such materials are of interest for the elaboration of dendritic switches, as reported for low molar-mass liquid crystals [5, 6] and side-chain liquid-crystalline polymers [7], and anisotropic molecular batteries [8].

The design of ferrocene-containing liquid-crystalline dendrimers with tailor-made properties is a difficult problem: (i) the properties associated with ferrocene should depend on its location within the dendrimer (in the core, at the branching points, at the periphery), and (ii) the type of the liquid-crystalline phases is connected to the dendrimer (generation), and to the mesogenic groups (structure, number, location). Obviously, the study of a large series of compounds is required to reach the point where the influence of all parameters can be controlled.

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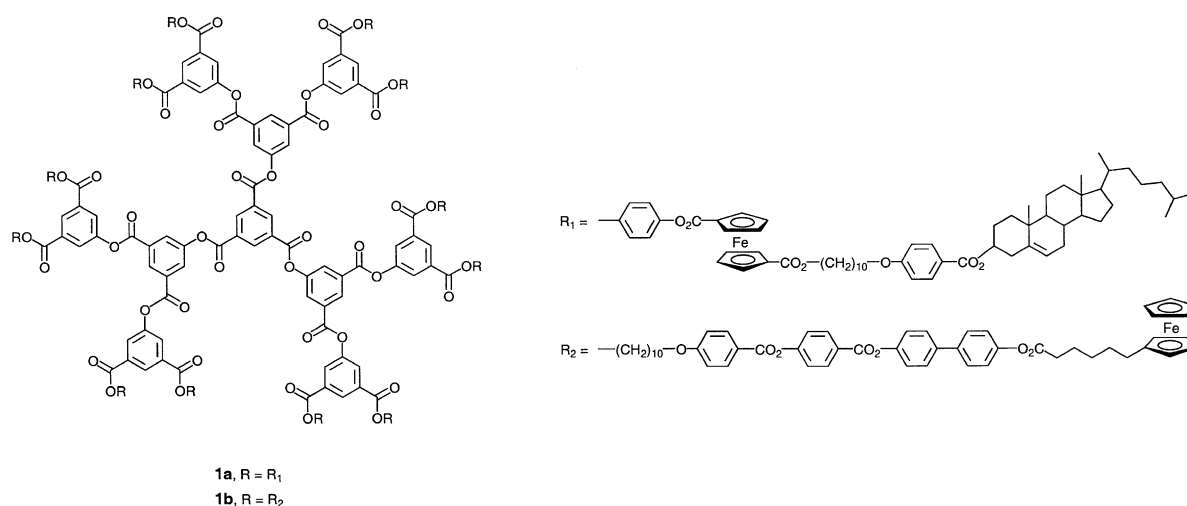


Fig. 1. Ferrocene-containing thermotropic liquid-crystalline dendrimers.

In this report, we present two second-generation dendrimers (Fig. 1) that differentiate by the position of the ferrocene unit and by the liquid-crystalline promoter: in **1a**, the ferrocene is located near the branching point and cholesterol acts as liquid-crystalline promoter, whereas in **1b**, ferrocene is located at the periphery and the liquid-crystalline segment is a rod containing four aromatic rings.

2. Synthesis

The synthetic strategy applied to prepare **1a,b** is based on the convergent methodology [9, 10] illustrated in Fig. 2. The ferrocene unit was introduced at an early stage to obtain first-generation dendrons **2a,b**. Removal of the benzyl protected group under hydrogenation conditions gave **3a,b**. Condensation of **3a,b** with **4** (used to synthesize **2a,b**) furnished second-generation dendrons **5a,b**. Deprotection of **5a,b** under hydrogenation conditions yielded **6a,b**. Finally, esterification of **6a,b** with 1,3,5-benzenetricarbonyltrichloride (**7**) led to the targeted dendrimers **1a,b** [11, 12].

3. Liquid-crystalline properties

The liquid-crystalline properties of **1a,b** were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Both dendrimers are thermally stable (no decomposition was detected by POM or DSC). The

phase transition temperatures are reported in Table 1. Dendrimers **1a,b** displayed clear liquid-crystalline behaviour. They both gave rise to enantiotropic smectic phases. For **1a**, the mesophase could be identified by POM as a smectic A phase from the formation of focal-conic and homeotropic textures. In case of **1b**, no typical texture could be obtained by POM. The smectic nature of the mesophase (smectic A or smectic C) was established by XRD. Note that **1b** shows a much higher isotropization temperature than **1a**. The structure of the mesophases can be explained by the formation of layers containing the dendrimer cores with interdigitation of the mesogenic units from layer to layer. Both compounds gave similar *d* layer spacings (for **1a**: $d = 44.1 \text{ \AA}$ at $105 \text{ }^\circ\text{C}$ and for **1b**: $d = 47 \text{ \AA}$ at $140 \text{ }^\circ\text{C}$). The mesomorphic behaviour of **1a,b** is consistent with their structures.

Despite the fact that **1a,b** have the same dendrimer generation (i.e. same number of ferrocene and mesogenic units), direct comparison of their properties is not straightforward because of their structural differences (substitution and location of the ferrocene units; nature and location of the liquid-crystalline promoters). Further compounds are required to establish a *structure–property* relationship. However, the examples reported herein indicate that ferrocene-containing liquid-crystalline dendrimers can be designed with no limitation regarding the location of the ferrocene units. This is of interest for specific applications of ferrocene-based materials.

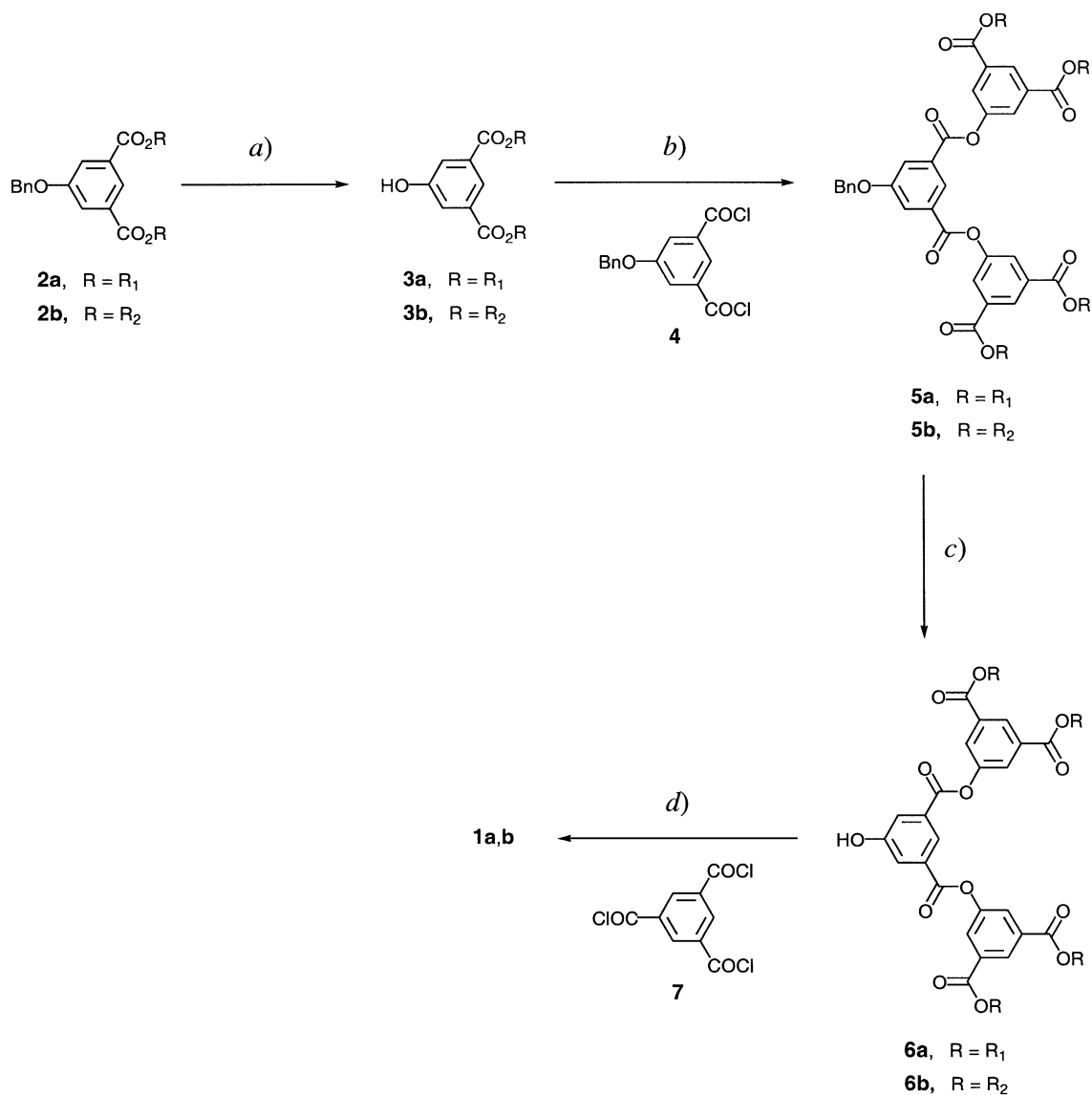


Fig. 2. Reagents and conditions. For **1a**: (a) H₂, Pd/C, CH₂Cl₂, 8 h, 94%; (b) triethylamine (Et₃N), CH₂Cl₂, reflux, overnight, 63%; (c) H₂, Pd/C, CH₂Cl₂, overnight, 89%; (d) Et₃N, CH₂Cl₂, reflux, overnight, 84%. For **1b**: (a) H₂, Pd/C, CH₂Cl₂/EtOH, 7 h, 91%; (b) Et₃N, CH₂Cl₂, reflux, overnight, 90%; (c) H₂, Pd/C, CH₂Cl₂/EtOH, room temperature, overnight, 73%; (d) Et₃N, CH₂Cl₂, reflux, 21 h, 88%. For R₁ and R₂, see Fig. 1.

3. Conclusion

We have developed synthetic tools for the preparation of liquid-crystalline metallodendrimers. Our strategy is not limited to ferrocene, but other organometallics can be used. Regarding the fascinating results reported for ferrocene-based dendrimers [13–16], the incorporation of ferrocene or other organometallic units within ordered structures capable to self-

Table 1
Phase-transition temperatures of **1a** and **1b**

Compound	Transition ^a	Temperature (°C)
1a	T _g	52
	S _A → I	169
1b	Cr → S _X	119
	S _X → I	256

^aT_g = glass transition temperature; S_A = smectic A phase; S_X = smectic A or smectic C phase; I = isotropic liquid.

assemble into mesomorphic organizations could lead to polyfunctional materials exhibiting novel properties and functions.

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