

Liquid-Crystalline Dendrimers Based on Ferrocene and Fullerene

Thierry Chuard and Robert Deschenaux*

Abstract: We present the synthesis and liquid-crystalline properties of a second generation ferrocene-containing liquid-crystalline dendrimer, and the liquid-crystalline behavior of a second generation mixed fullerene-ferrocene liquid-crystalline dendrimer. Both compounds gave rise to smectic A phases, which were identified by polarized optical microscopy and differential scanning calorimetry. The liquid-crystalline behavior is determined by the cholesterol units which have been selected as mesomorphic promoters. Therefore, both compounds display similar liquid-crystalline properties.

Keywords: Dendrimers · Ferrocene · Fullerene · Liquid crystals · Supramolecular chemistry

Introduction

The design and study of functionalized liquid-crystalline macromolecules (side-chain and main-chain polymers, dendrimers), which display specific properties (e.g. magnetic properties, optical properties, catalytic properties, mechanical properties) is a field of current interest both from fundamental and applied points of view. Furthermore, the pluridisciplinary character of such a research area, at the frontiers of chemistry, physics and materials science, is particularly promising for the discovery of new materials.

Appropriate functionalization of active sub-units with mesomorphic molecular units (= liquid-crystalline building-blocks) leads to liquid-crystalline materials, the properties of which depend on the selected sub-unit. If specific properties are to be studied and/or exploited, the choice of the sub-unit, and how it is related to the molecular unit are of prime importance. In this context, we have developed liquid-crystalline materials based on (η^6 -arene)tricarbonylchromium complexes [1], ruthenocene [2], ferrocene [3–6], and fullerene [7]. In the case of

ferrocene, we have recently reported on ferroelectric ferrocenyl liquid crystals with planar chirality [8], and switchable liquid crystals [9].

Dendrimers represent a class of materials which combine unique features (well-defined macromolecular structure, monodispersity, low viscosity) [10] with remarkable properties (encapsulation [11], catalysis [12], chiroptical properties). Functionalized dendrimers, *i.e.* dendrimers incorporating active or reactive functions, are considered as new materials with high potential applications, such as for the preparation of libraries [13].

With the view to combine the properties and features of dendrimers (see above) with the properties of ferrocene and/or fullerene, we oriented part of our research towards the design and study of ferrocene- [4] and fullerene- [7c] containing thermotropic liquid-crystalline dendrimers. The preparation of such compounds would also bring insights towards the development of new synthetic tools in the chemistry of dendrimers.

We present, herein, the synthesis and liquid-crystalline behavior of the ferrocene-containing liquid-crystalline dendrimer **1** [14] (Fig. 1) and the liquid-crystalline properties of the mixed ferrocene-fullerene liquid-crystalline dendrimer **2** [7c] (Fig. 2). These two compounds were specially designed in order to develop redox-active liquid-crystalline dendrimers. They are to be considered as prototypes (from which other structures can be de-

signed depending on their properties) rather than ideal compounds. In both examples, cholesterol was used as liquid-crystalline promoter. Dendrimers **1** and **2** are of second generation.

Results and Discussion

Synthesis

The synthesis of dendrimer **1** is illustrated in the Scheme. Condensation of the phenol derivative **3** [7c] with bis-acid-chloride **4** gave the protected bis-ferrocene intermediate **5**. Deprotection of **5** under hydrogenation conditions gave **6**, which was reacted with **4** to yield dendron **7**. Removal of the benzyl protecting group under hydrogenation conditions led to phenol derivative **8**. Finally, esterification of 1,3,5-benzenetricarbonyl trichloride (**9**) with **8** gave the targeted dendrimer **1**. The structures and purity of all of the compounds were confirmed by ^1H NMR spectroscopy and elemental analysis. The preparation of the mixed fullerene-ferrocene dendrimer **2** is reported in [7c].

Liquid-Crystalline Properties

The liquid-crystalline properties of **1** and **2** were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transition temperatures are reported in the Table.

Compounds **1** and **2** displayed clear liquid-crystalline behavior. They both

*Correspondence: Prof. R. Deschenaux
Institut de Chimie
Université de Neuchâtel
Avenue de Bellevaux 51
Case postale 2
CH-2007 Neuchâtel
Tel.: +41 32 718 24 27
Fax: +41 32 718 25 11
E-Mail: robert.deschenaux@unine.ch

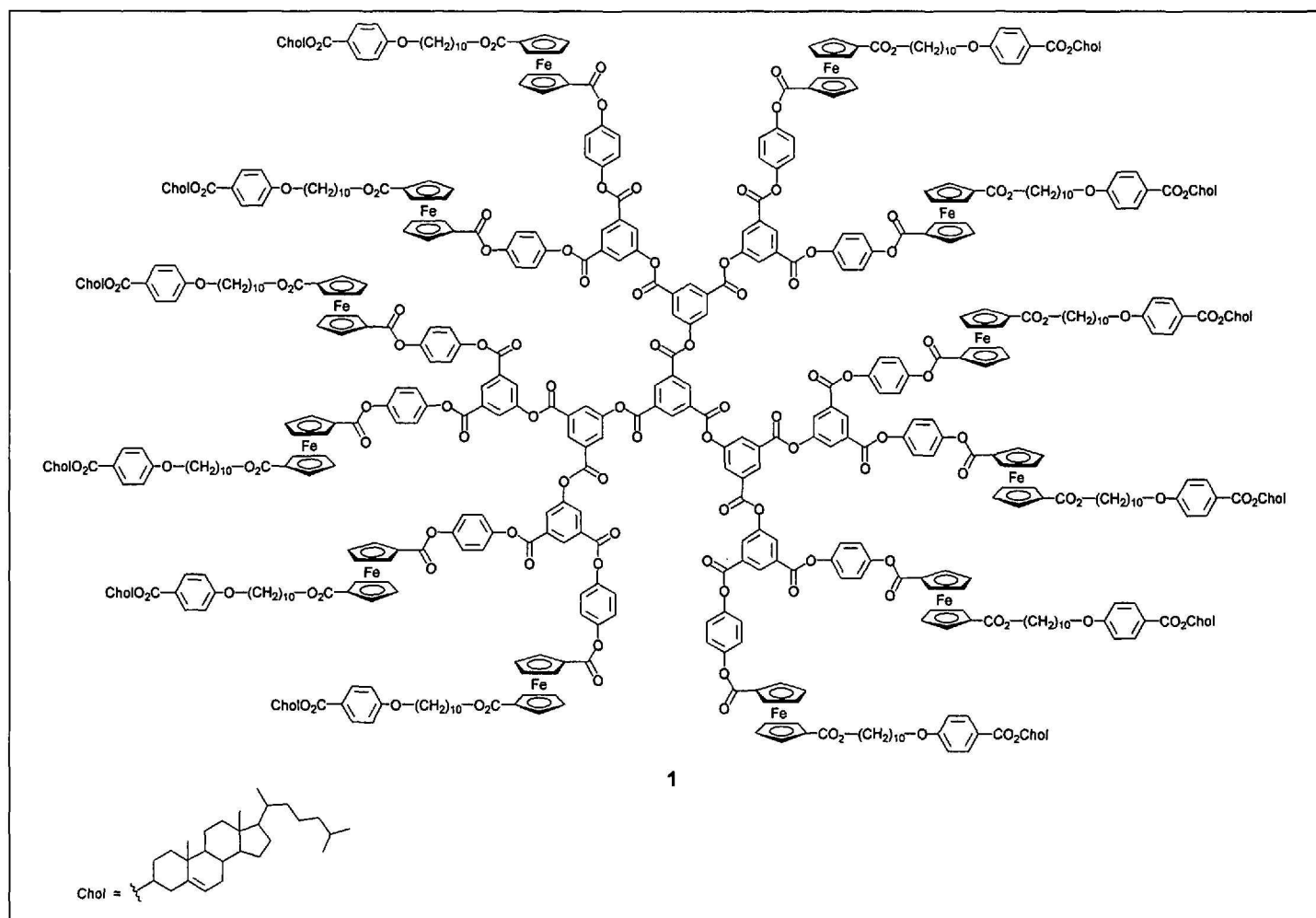


Fig. 1. Ferrocene-containing thermotropic liquid-crystalline dendrimer.

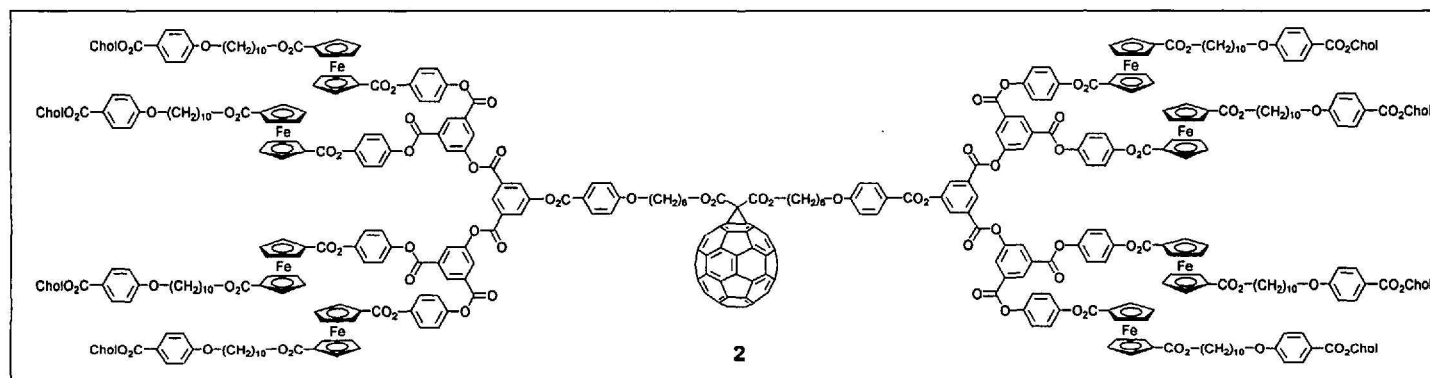


Fig. 2. Mixed fullerene-ferrocene liquid-crystalline dendrimer. Chol, see Fig. 1.

formed enantiotropic smectic A phases, which were identified by POM from the formation of focal-conic and homeotropic textures. Because of the viscosity of the samples, the focal conics formed only when the samples were cooled very slowly from the isotropic fluid. Dendrimers **1** and **2** showed good thermal stability: no decomposition was detected either by POM or by DSC within the mesomorphic domain.

The data reported in the Table indicate similar behavior for **1** and **2**: they both exhibited a glass transition temperature, they both gave rise to a smectic A

phase, and their clearing point (isotropization temperature) are not too different. The similarities displayed by **1** and **2** are the consequence of their dendritic structure functionalized by cholesterol moieties. The cholesterol fragments favor the formation of smectic A phases. The slightly higher clearing point observed for **1** is due to the fact that there are twelve cholesterol moieties in **1** and eight in **2**: the higher the number of mesomorphic moieties, the higher the stability of the liquid-crystalline phase. The properties observed for **1** and **2** are therefore in agreement with their structure.

Table. Phase transition temperatures of **1** and **2**

Compound	T _g [°C]	S _A →I [°C]
1	52	169
2	^a	157

T_g = glass transition, S_A = smectic A phase, I = isotropic liquid

^a Not detected. A baseline change was noticed in the 50–60 °C temperature range; however, the baseline deflection was too small to certify that this event corresponded to the T_g.

Electrochemical properties

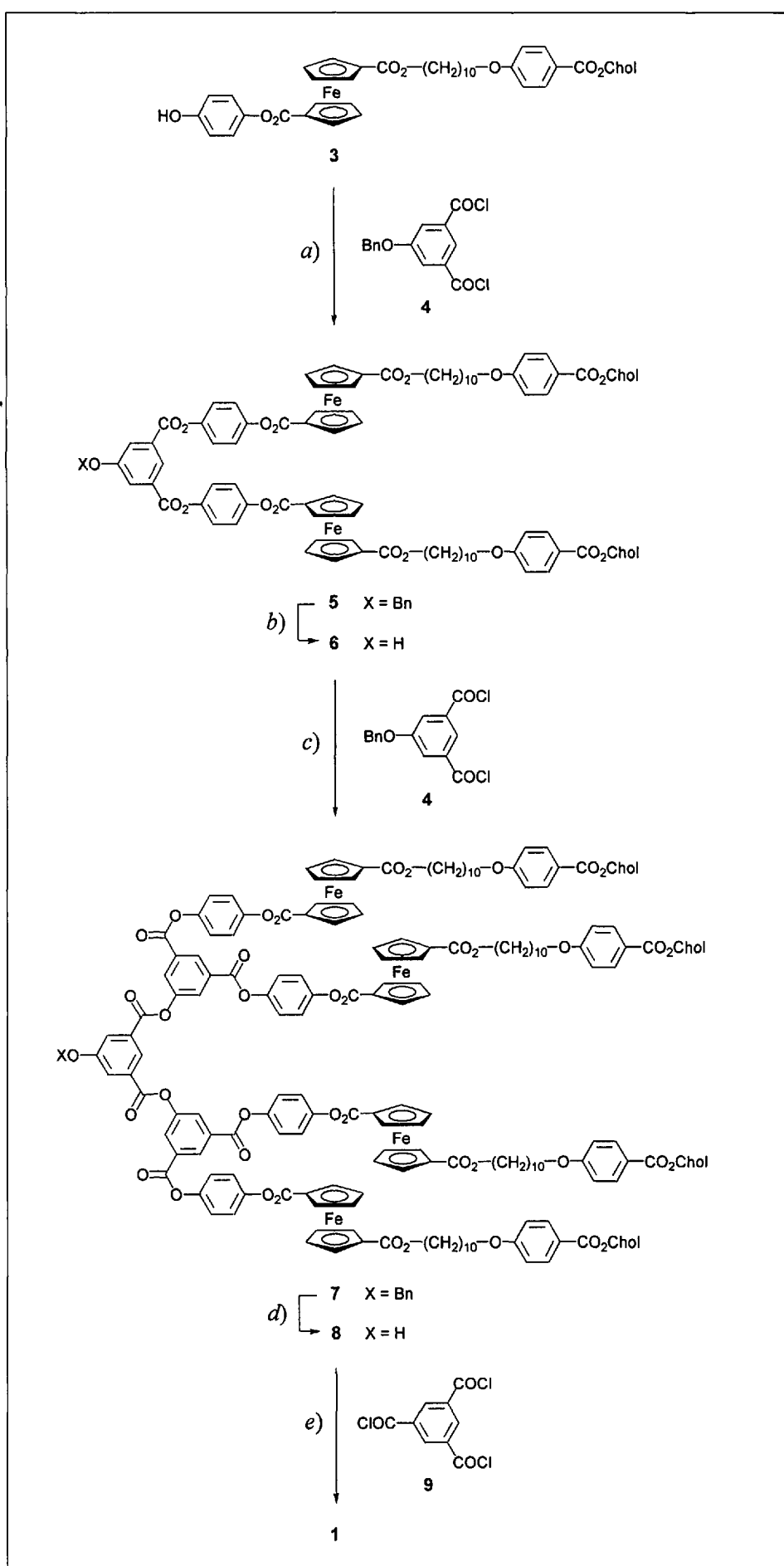
Dendrimer **1** was subjected to cyclic voltametry analysis [15], which revealed a reversible oxidation process with twelve electrons being transferred. A value of 0.93 V was obtained for the redox potential. In **1** and **2**, the ferrocene units are in similar chemical environments (*i.e.* number and type of functions located on the ferrocene). Therefore, **2** should show an electrochemical behavior close to that shown by **1**: reversible electron transfer with a redox potential near 0.93 V. Obviously, the differences between **1** and **2** would be the presence of the reduction waves due to the fullerene unit, and, at the ferrocene level, the oxidation potential would correspond to the transfer of eight electrons instead of twelve as in **1**.

Conclusions

The structures presented herein give a flavor of our research activities. They demonstrate how synthetic chemistry can be used to synthesize macromolecular materials which show liquid-crystalline behavior, which is associated with redox activities. These properties are due to the combination of different sub-units: cholesterol which induces the liquid-crystalline behavior and ferrocene which acts as the redox active center. Furthermore, the dendritic core gives the system a regular and controlled molecular architecture. The presence of both the fullerene and ferrocene units opens the doors towards further investigations, *e.g.* photoinduced electron transfer. Such studies are currently under way.

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Scheme. Synthesis of dendrimer **1**. a) Triethylamine (Et_3N), CH_2Cl_2 , reflux, 7 h, 61%; b) H_2 , Pd/C, CH_2Cl_2 , 8 h, 94%; c) Et_3N , CH_2Cl_2 , reflux, overnight, 63%; d) H_2 , Pd/C, CH_2Cl_2 , overnight, 89%; e) Et_3N , CH_2Cl_2 , reflux, overnight, 84%. Chol, see Fig. 1.

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Polymerizable Amphiphilic Block Copolymers: From Nanostructured Hydrogels to Nanoreactors and Ultrathin Films

Corinne Nardin and Wolfgang Meier*

Abstract: Self-assembly of reactive amphiphilic block copolymers is used to prepare nanostructured hydrogels with exceptional permeability properties, vesicular structures and planar, freestanding membranes in aqueous solution. Although the underlying block copolymer membranes are two to three times thicker than conventional lipid bilayers they can be regarded as a mimetic of biological membranes and can be used as a matrix for membrane spanning proteins. Surprisingly the proteins remain functional despite the extreme thickness of the membranes and even after polymerization of the reactive block copolymers. The unique combination of block copolymers with membrane proteins allows the preparation of mechanically stable, defect-free membranes and nanocapsules that have highly selective permeability and/or specific recognition sites. This is documented by some representative examples.

Keywords: Amphiphilic block copolymer · Hydrogel · Membrane · Membrane protein

1. Nanostructured Hydrogels

A current topic in material sciences is the creation of nanometer-sized well-defined structures. One key step is to develop preparative procedures to control precisely the formation and the morphology of these structures. Self-assembled superstructures of surfactants and, especially

those of amphiphilic block copolymers have proven to be valuable tools. Actually block copolymers consisting of hydrophilic and hydrophobic blocks behave in water like conventional surfactants: similar to the latter, they self-assemble in water into micelles of various shapes and at higher concentrations into lyotropic liquid crystalline phases. Their aggrega-

*Correspondence: PD Dr. W. Meier
University of Basel
Institut für Physikalische Chemie
Klingelbergstrasse 80
CH–4056 Basel
Tel.: +41 61 267 38 35
Fax: +41 61 267 38 55
E-Mail: wolfgang.meier@unibas.ch