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Design, mesomorphic properties, and supramolecular organization of [60]fullerene-containing thermotropic liquid crystals

Thierry Chuard and Robert Deschenaux*

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, Case postale 2, 2007 Neuchâtel, Switzerland. Fax: +41 32 718 25 11; E-mail: robert.deschenaux@unine.ch

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Two concepts have been developed for the design of [60]fullerene-containing thermotropic liquid crystals, namely, the covalent and non-covalent concepts. In the covalent approach, C_{60} was functionalized with liquid-crystalline addends (malonate and aldehyde derivatives) by applying either the Bingel reaction or the 1,3-dipolar cycloaddition reaction. In the non-covalent approach, a liquid-crystalline inclusion complex was obtained from mesomorphic cyclotriveratrylene (CTV) derivatives and C_{60}. All of the covalent C_{60} derivatives showed smectic A phases. In one case, an additional nematic phase was detected. The $[C_{60}\subset(CTV)_2]$ complex gave rise to nematic-like and cubic phases. The covalent and non-covalent approaches demonstrate the various possibilities for C_{60} to give rise to mesomorphic materials.

1. Introduction

The design and study of organized molecular assemblies from fullerene-containing molecular units represent a field of growing interest in supramolecular fullerene (C_{60}) chemistry.[1] The elaboration of new anisotropic materials based on the properties of C_{60} strongly motivated such studies. Furthermore, adequate functionalization of the sphere-like structure of C_{60} to obtain molecular organization from C_{60} derivatives is a stimulating challenge in synthetic chemistry. Sustained efforts arising from synthetic chemistry, macromolecular chemistry, physical chemistry, supramolecular chemistry and materials science led to the successful formation of Langmuir and Langmuir–Blodgett films,[2] self-assembled monolayers,[3] membranes,[4,5] vesicles,[5,6] nanorods[6] and thermotropic liquid crystals.[7–14] Fascinating investigations were conducted with those systems.

Liquid crystals play a key role in everyday life (watches, calculators, mobile telephones, notebook computers) and are essential chemicals for the development of new technologies. The search for liquid crystals displaying novel and specific properties is an investment for the future. In this context, fullerene-containing liquid crystals are interesting materials for basic studies and applications purposes. Firstly, incorporation of C_{60} into liquid-crystalline structures will bring fundamental results in supramolecular chemistry: our understanding of the *structure* (of the liquid crystal)–*organization* relationship will be strengthened. Secondly, novel molecular devices and switches showing outstanding performances and characteristics could be developed; for example, a hexapyrrolidine C_{60} adduct was recently used to construct a single layer organic LED.[15]

The purpose of this feature article is to review the field of fullerene-containing thermotropic liquid crystals and emphasize the evolution of the structures that have been described within a relatively short period of time. The influence of C_{60} on the formation, stability and supramolecular organization of the liquid-crystalline phases will be discussed. This report will bring to the fore guidelines that could be followed to create mesomorphic fullerenes. A short account on liquid crystals based on C_{60} has been reported in the form of conference proceedings.[16]

2. Concepts and design

The design of fullerene-containing thermotropic liquid crystals is based on covalent[7–13] or non-covalent[14] concepts. In the former approach, two reactions have been applied, the Bingel reaction[17] (*i.e.* addition of a malonate derivative to C_{60} in the presence of a base) which yields methanofullerenes, and the 1,3-dipolar cycloaddition reaction[18] (*i.e.* addition of an aldehyde derivative and sarcosine to C_{60}) which leads to fulleropyrrolidines. Both reactions produce stable compounds with well-defined structures. To obtain mesomorphic fullerenes, liquid-crystalline malonate and aldehyde derivatives were used. In the non-covalent concept, C_{60} was complexed by mesomorphic cyclotriveratrylene (CTV) derivatives.

The covalent strategy led to a great variety of fullerenes: mono- and poly-adducts of C_{60} were synthesized, and the structure of the addends and the nature of the liquid-crystalline promoters were varied. A flexible chain was used to decouple the mesomorphic frameworks from the bulky C_{60}: this allows the liquid-crystalline units to position such as to interact favorably with their neighbors. As for the non-covalent approach, only one example has been described so far. Further investigations should yield important information for this class of liquid crystals.

In the following sections, the liquid-crystalline properties of the covalent fullerenes as a function of the degree of functionalization and structure of the addends are presented. Comparison of the mesomorphism of the addends with that of their fullerene analogues will bring to the fore the influence of C_{60} on the liquid-crystalline behavior of the studied materials. The non-covalent ensemble will then be described. In the last section, the supramolecular organization of the C_{60} derivatives within the liquid-crystalline phases will be illustrated.

3. Covalent fullerene-containing thermotropic liquid crystals

3.1. Linear-type mono-adducts of C_{60}

Compound **1** is the first fullerene-containing thermotropic liquid crystal which was reported.[7] A smectic A phase formed at 190 °C when the sample was cooled from the isotropic melt, revealing a monotropic character of the mesophase. Its malonate precursor **2** ($Cr\cdot112\cdot S_A\cdot214\cdot N^*\cdot224\cdot BP\cdot225\cdot I$) gave smectic A and chiral nematic phases and a blue phase. Therefore, grafting of C_{60} onto **2** led to a drastic change of the

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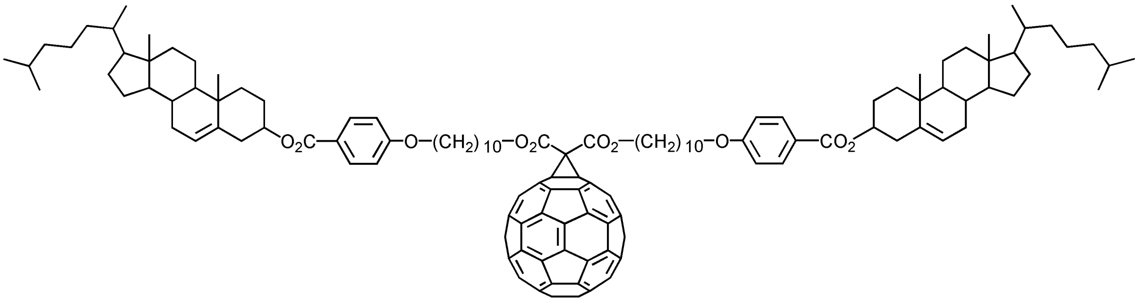
liquid-crystalline properties. This observation indicates that C_{60} disrupts the liquid-crystalline organization, as a consequence of its size and shape.†



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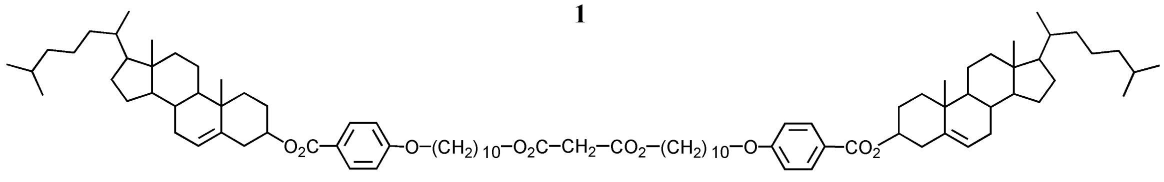

2

Fullerene–ferrocene derivative **3** was designed to elaborate multifunctional liquid-crystalline materials by associating an electron acceptor unit (C_{60}) and electron donor units (ferrocene).[8] Such materials are promising candidates for the elaboration of molecular switches: (1) electron transfer was shown to occur in solution with non-mesomorphic fullerene–ferrocene dyads,[19] and (2) chemical oxidation was applied to generate mesomorphic ferrocenium derivatives from non-mesomorphic ferrocenes,[20] and to control liquid-crystalline organization between mesomorphic ferrocene and ferrocenium species.[21] Therefore, photoinduced electron transfer in fullerene–ferrocene liquid crystals could be used as a switching mechanism because of the presence of either ferrocene (light off) or ferrocenium (light on). Both **3** ($Cr\cdot66\cdot S_A\cdot118\cdot I$) and its precursor **4** ($Cr\cdot73\cdot S_A\cdot134\cdot I$) gave rise to smectic A phases. The low enthalpy value (ΔH = 12.9 kJ mol^{-1}) associated with the melting process observed for **3** was an indication of the semicrystalline nature of the sample (**3** was purified by precipitation).

Cholesterol is a strong liquid-crystalline promoter. To explore the possible use of other mesogenic groups, C_{60} derivative **5**, bearing cyanobiphenyl derivatives, was synthesized.[9] A smectic A phase was obtained for **5** ($G\cdot29\cdot S_A\cdot142\cdot I$) which indicated that a wide range of mesomorphic promoters can, in principle, be used, providing they have the required anisotropy. Malonate **6** ($Cr\cdot97\cdot S_A\cdot153\cdot N\cdot162\cdot I$), precursor of **5**, led to smectic A and nematic phases.

The data presented in this section highlight two important features in case of linear-type mono-adducts : firstly, the fullerene derivatives showed exclusively smectic A phases. This result should be related, at least in part, to the disposition of the mesogenic moieties with respect to the C_{60} unit and to the intermolecular interactions such dispositions generate; this aspect will be discussed in Section 5. Secondly, C_{60} decreases the stability of the liquid-crystalline phases of their precursors. This is a consequence of the bulkiness of C_{60}.

3.2. Dendritic-type mono-adducts of C_{60}

Dendrimers are unique materials which combine fascinating characteristics (low viscosity, monodispersity) with a well-defined macromolecular structure.[22] Functionalization of dendrimers with various mesomorphic groups led to liquid-crystalline materials displaying rich mesomorphism.[23] Furthermore, modification of C_{60} with dendritic addends proved to be an elegant concept for the preparation of fullerene-based polymeric materials.[24] Interestingly, functionalization of C_{60} with hydrophilic dendrimers allowed the construction of stable and highly ordered Langmuir and Langmuir–Blodgett films.[2c,f,k] In such systems, C_{60} is buried in the dendrimer, the consequence of which is a decrease of the unfavourable C_{60}–C_{60} interactions (aggregation of C_{60} units is thus avoided) and a beneficial increase of the interactions between the polar groups and the water surface.[25]

The use of mesomorphic dendritic addends to functionalize C_{60} might open the way to fullerene-containing liquid crystals with tailor-made properties. The size of the dendrimers could counterbalance that of C_{60} and minimize its influence, as in the case of Langmuir and Langmuir–Blodgett films.[25]

As a first example, the second-generation dendrimer **7** (T_g: not detected, $S_A\cdot157\cdot I$) was synthesized.[10] The latter represents an extension of the work on mixed fullerene–ferrocene liquid crystals. A smectic A phase was detected. Its malonate precursor (structure not shown) also showed a smectic A phase (T_g: not detected, $S_A\cdot169\cdot I$).

To gain more information on the evolution of the mesomorphism as a function of the size of the addend, we prepared a series of materials in which the dendrimer generation was varied. First- (**8**), second- (**9**), third- (**10**), and fourth-generation (**11**) dendrimers were synthesized.[9] Dendrimers **8** ($G\cdot48\cdot S_A\cdot179\cdot I$), **10** ($T_g$: not detected, $S_A\cdot212\cdot I$) and **11** (T_g: not detected, $S_A\cdot252\cdot I$) gave rise to smectic A phases; dendrimer **9** (T_g: not detected, $S_A\cdot183\cdot N\cdot184\cdot I$) showed smectic A and nematic phases. Comparison of their clearing points indicates that the stability of the liquid-crystalline phase increases with the dendrimer generation, *i.e.* with the number of mesogenic units. The fullerene derivatives **9**, **10** and **11** and their malonate precursors (structures not shown) displayed the same mesophases [(a) precursor of **9**: $G\cdot46\cdot S_A\cdot196\cdot N\cdot202\cdot I$; (b) precursor of **10**: T_g: not detected, $S_A\cdot232\cdot I$; (c) precursor of **11**: T_g: not detected, $S_A\cdot259\cdot I$]. A difference was observed for **8**, the precursor of which (structure not shown) gave rise to a nematic phase (T_g: not detected, $N\cdot201$ I). In this case, introduction of C_{60} changed the nature of the liquid-crystalline phase (from nematic for the addend to smectic A for its fullerene analogue).

Second-generation dendrimer **12** represents the first liquid-crystalline fulleropyrrolidine.[11] Compound **12** was specially designed considering the electrochemical stability of fulleropyrrolidines. Indeed, while the Bingel adducts undergo retro-addition upon chemical[26] or electrochemical[27] reduction,

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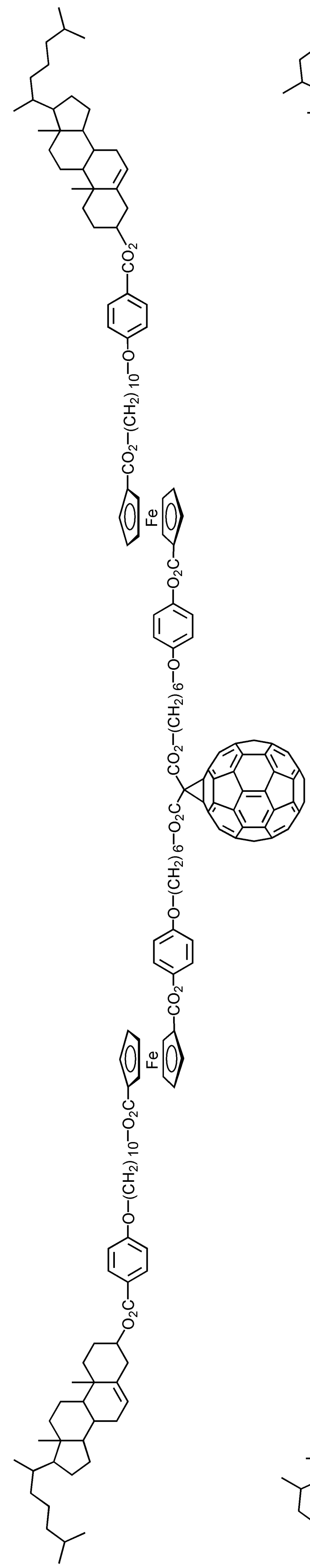
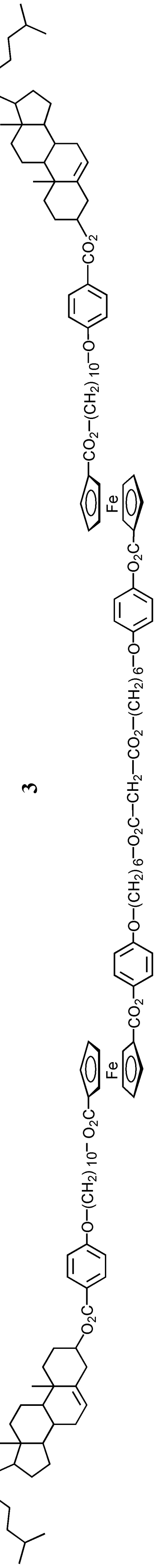
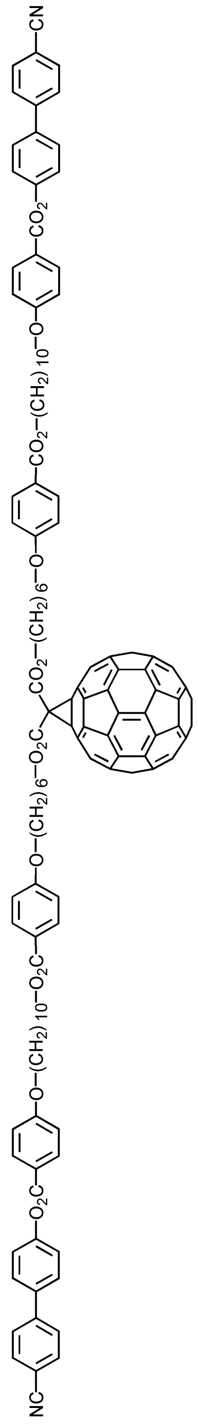
†The following abbreviations are used throughout the text: G: glass, T_g: glass transition temperature, Cr: crystal, S_A: smectic A phase, N*: chiral nematic phase, N: nematic phase, BP: blue phase, I: isotropic liquid. The temperatures are given in °C.


O$_2$C
O–(CH$_2$)$_{10}$–O$_2$C
Fe
CO$_2$
O–(CH$_2$)$_6$–O$_2$C
CO$_2$–(CH$_2$)$_6$–O
O$_2$C
Fe
CO$_2$–(CH$_2$)$_{10}$–O
CO$_2$

3


O$_2$C
O–(CH$_2$)$_{10}$–O$_2$C
Fe
CO$_2$
O–(CH$_2$)$_6$–O$_2$C–CH$_2$–CO$_2$–(CH$_2$)$_6$–O
O$_2$C
Fe
CO$_2$–(CH$_2$)$_{10}$–O
CO$_2$

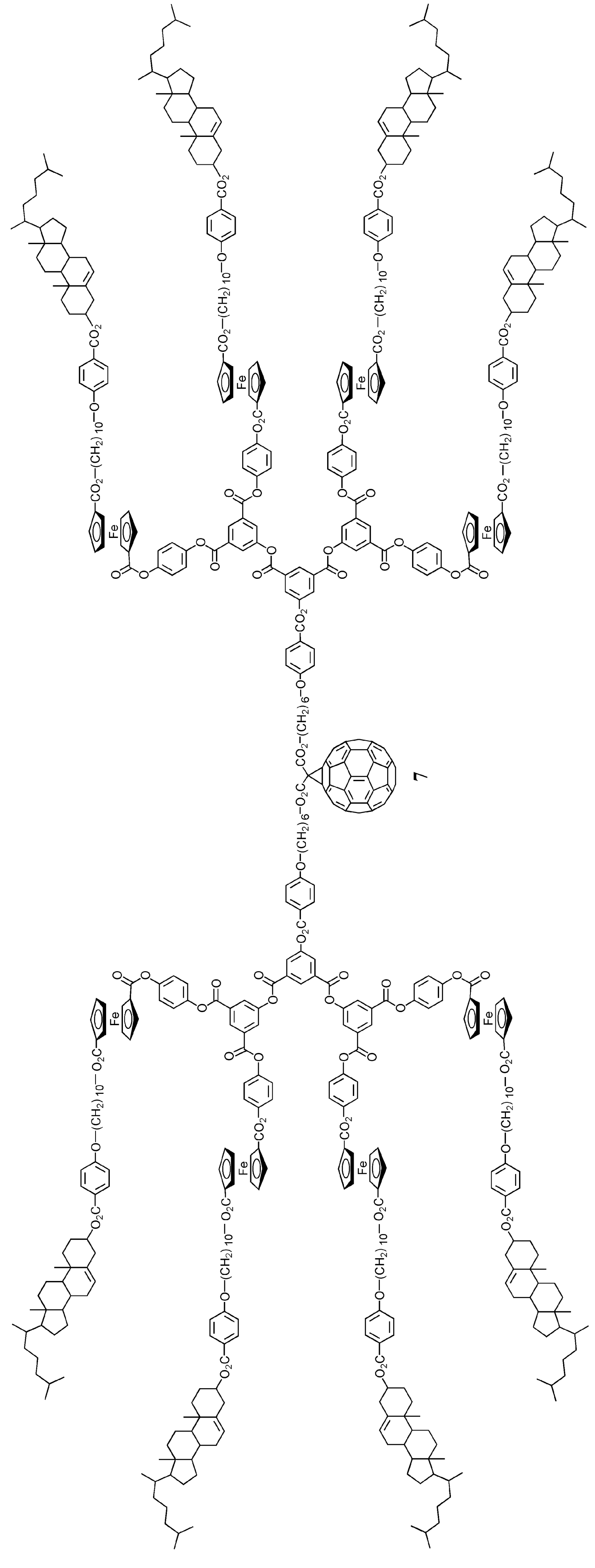
4


NC
O$_2$C
O–(CH$_2$)$_{10}$–O$_2$C
O–(CH$_2$)$_6$–O$_2$C
CO$_2$–(CH$_2$)$_6$–O
CO$_2$–(CH$_2$)$_{10}$–O
CO$_2$
CN

5


NC
O$_2$C
O–(CH$_2$)$_{10}$–O$_2$C
O–(CH$_2$)$_6$–O$_2$C–CH$_2$–CO$_2$–(CH$_2$)$_6$–O
CO$_2$–(CH$_2$)$_{10}$–O
CO$_2$
CN

6



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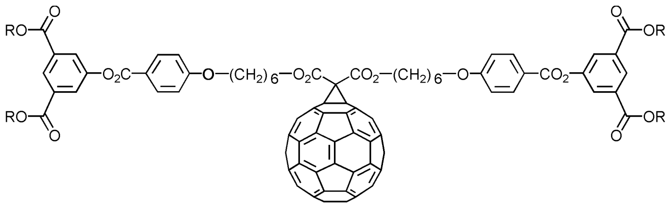
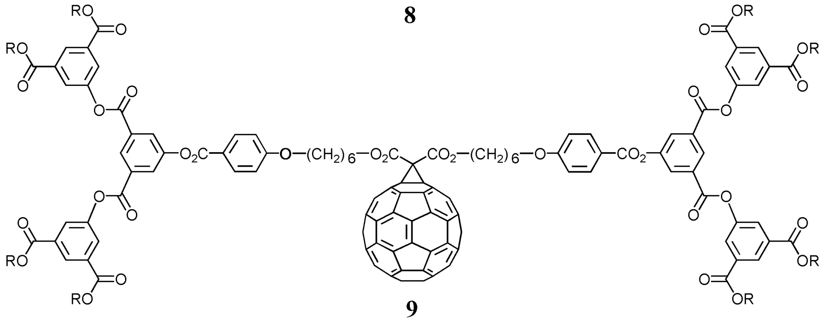
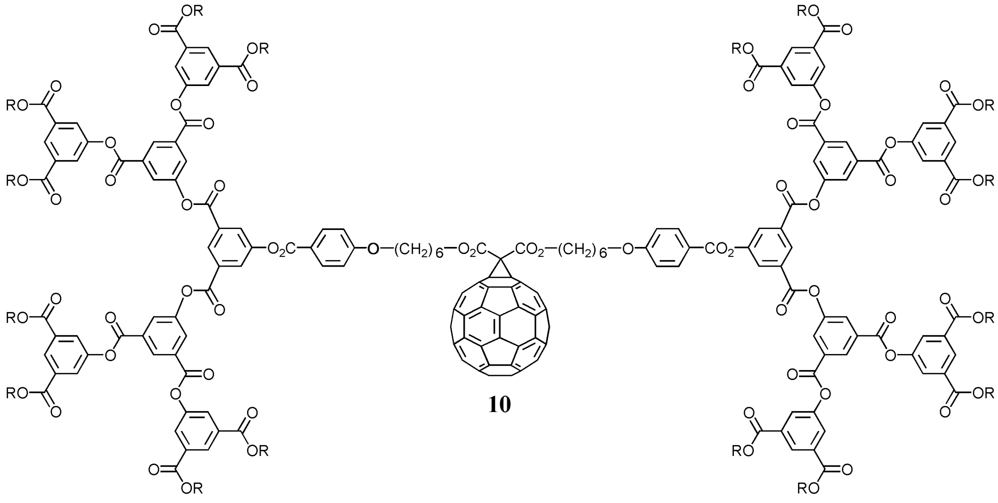

RO
O
O₂C
O—(CH₂)₆—O₂C
CO₂—(CH₂)₆—O
CO₂
OR

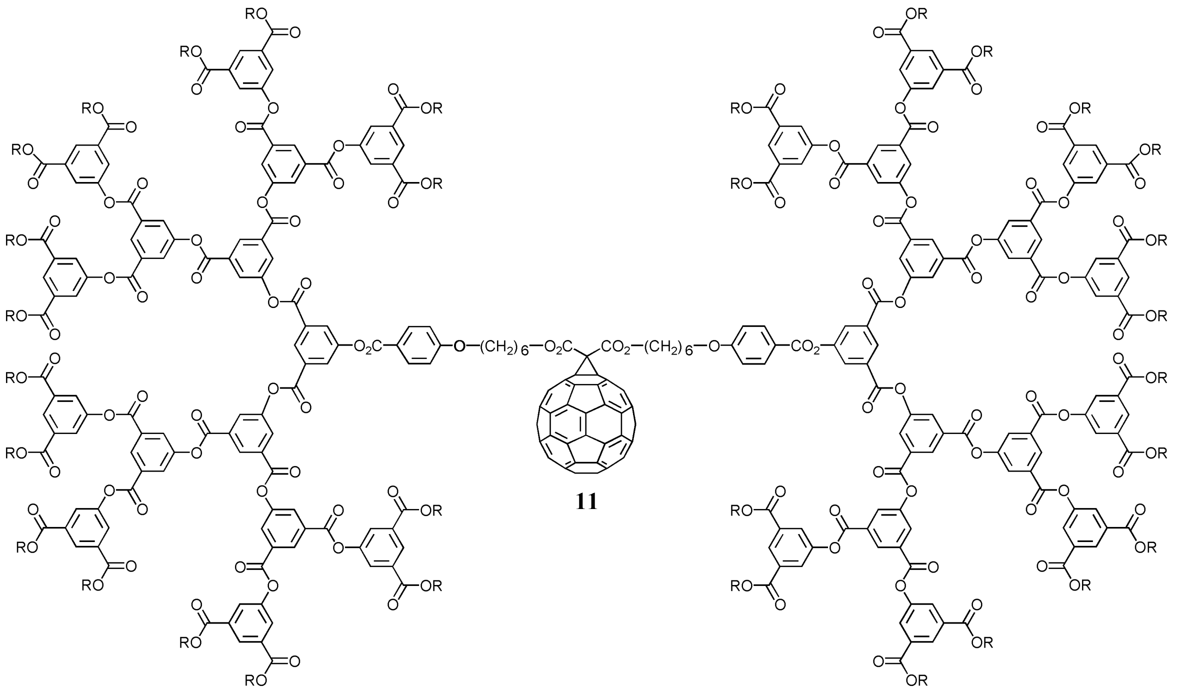
8


RO
O
O₂C
O—(CH₂)₆—O₂C
CO₂—(CH₂)₆—O
CO₂
OR

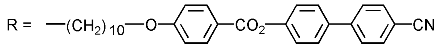
9


RO
O
O₂C
O—(CH₂)₆—O₂C
CO₂—(CH₂)₆—O
CO₂
OR

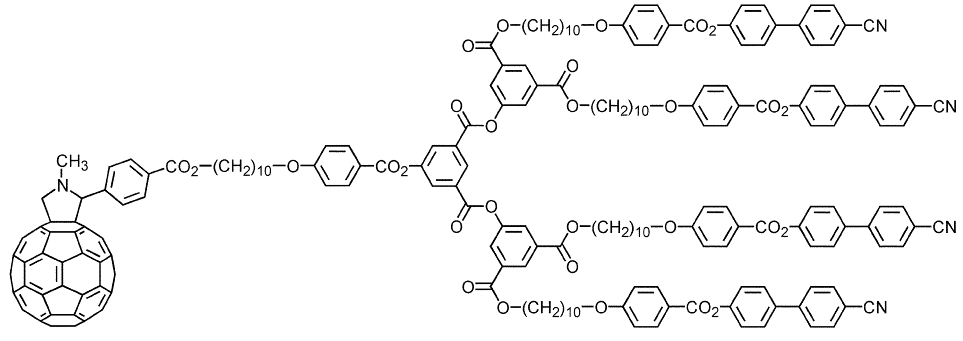
10


RO
O
O₂C
O—(CH₂)₆—O₂C
CO₂—(CH₂)₆—O
CO₂
OR

11


R =
—(CH₂)₁₀—O
CO₂
CN

fulleropyrrolidines lead to stable reduced species.[28] This is of interest to elaborate redox-active liquid-crystalline fullerenes. A smectic A phase was observed both for **12** (G·44·S_A·168·I) and for its aldehyde precursor (structure not shown) as well (G·35·S_A·185·I).



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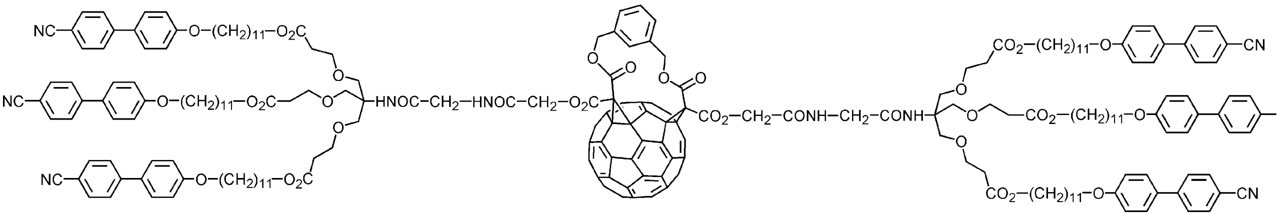
As in the case of the linear-type mono-adducts, the fullerene-based dendrimers gave lower clearing points than their corresponding precursors. This result further confirmed that the influence of C_{60} on the thermal and liquid-crystalline properties is not easy to manage.

3.3 Dendritic-type bis-adducts of C_{60}

Compound **13** was prepared by esterification of a bis(methanofullerene) carrying two carboxylic acid functions with an amine-based dendritic wedge. A mesophase was observed between ~40 and 70 °C but could not be identified.[12] The precursor of **13** (structure not shown) displayed a nematic phase between 48 and 63 °C.



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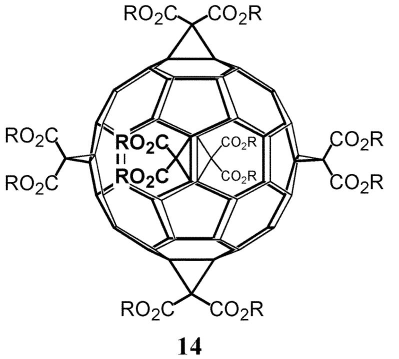
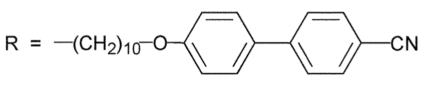
3.4. Poly-adducts of C_{60}

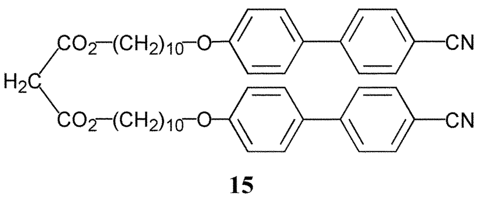
[60]Fullerene offers multiple possibilities for the design of functionalized derivatives. To further explore the capability of C_{60} to give rise to mesomorphic structures, we focussed on hexa-adducts, and synthesized **14**.[13] The latter gave remarkable liquid-crystalline properties. Indeed, though its precursor **15** (I·87·N·57·Cr) showed a monotropic nematic phase, an enantiotropic smectic A phase was observed for **14** (G· ~80·S_A·133·I).

The liquid-crystalline behavior of **14** emphasizes the role played by C_{60} in the case of hexa-addition : assembling twelve cyanobiphenyl units around a focal point generates the required structural anisotropy and intermolecular interactions for mesomorphism to occur. It is noteworthy that poly-addition can be used for the preparation of fullerene-containing liquid crystals from addends with low liquid-crystalline tendency, and, most likely, from non-mesomorphic addends.



14





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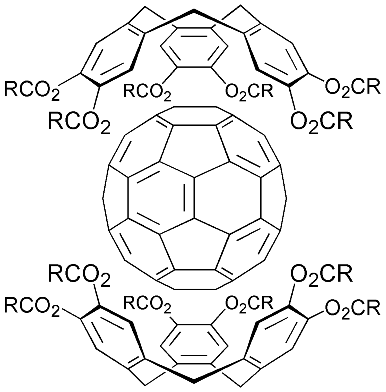
4. Non covalent fullerene-containing thermotropic liquid crystals

Complex **16** was prepared by slow evaporation of a benzene solution containing the appropriate liquid-crystalline cyclotriveratrylene (CTV) derivative and C_{60}.[14] From room temperature to 70 °C, compound **16** displayed a nematic phase characterized by cybotactic groups with local lamello-columnar order. Above 70 °C, a cubic phase of $I4_132$ symmetry formed. The clearing point could not be determined. The liquid-crystalline CTV derivative showed a nematic phase (from room temperature to 75 °C) similar to that of **16**. The nature of the nematic-like and cubic phases was established on the basis of X-ray diffraction data.

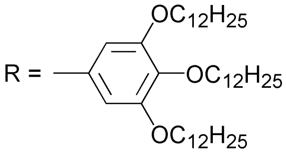
The non-covalent approach is interesting since it does not require the development of specific reactions to render C_{60} mesomorphic. A disadvantage of such inclusion compounds, compared to covalent C_{60} derivatives, is their limited thermal stability at elevated temperature where C_{60} is expelled from the complex. Interestingly, **16** showed mesomorphic properties at room temperature.

5. Supramolecular organization

To illustrate the role played by C_{60} on the supramolecular organization of the fullerene-based molecular units within the



16



liquid-crystalline phases, we selected compounds **5**, **10** and **14** as representative examples. The latter show three different situations: C_{60} functionalized by a small addend (*i.e.* **5**), by a large addend (*i.e.* **10**), and by small but numerous addends *(i.e.* **14**). The supramolecular organization of **5** and **10** (as well as that of **3**, **4**, **8**, **9** and **11**) is based on X-ray diffraction experiments and molecular modelling.

For convenience, we consider first **14**. The formation of a smectic A phase indicates that the cyanobiphenyl units are not oriented radially around C_{60} but form a cylinder-like structure with the mesogenic fragments oriented upward and downward (Fig. 1). Such a structure favors the formation of layers as reported for liquid-crystalline dendrimers[29] and siloxysilanes[30] which are analogous to **14**, *i.e.* a central core is functionalized by a large number of mesogenic groups.

For **5**, the molecules organize in a head-to-tail fashion with the two mesogenic groups on each molecule pointing to the same direction (Fig. 2). The cross-sectional area of four mesogenic segments ($4\ x \sim 22$–25 Å^2) is in agreement with that of C_{60} ($\sim$90–100 Å^2). The supramolecular organization is, in this case, governed by steric considerations.

The supramolecular organization of **10** can be explained as follows: C_{60} is embedded in the dendritic core which is oriented parallel to the layer plane, and the mesogenic units orient above and below the dendritic core (Fig. 3). Interdigitation occurs from one layer to the adjacent one. In this case, C_{60} has little (if any) influence on the supramolecular organization; the nature and structure of the mesophase is essentially governed by the mesogenic units. This behavior is in agreement with literature data.[31]

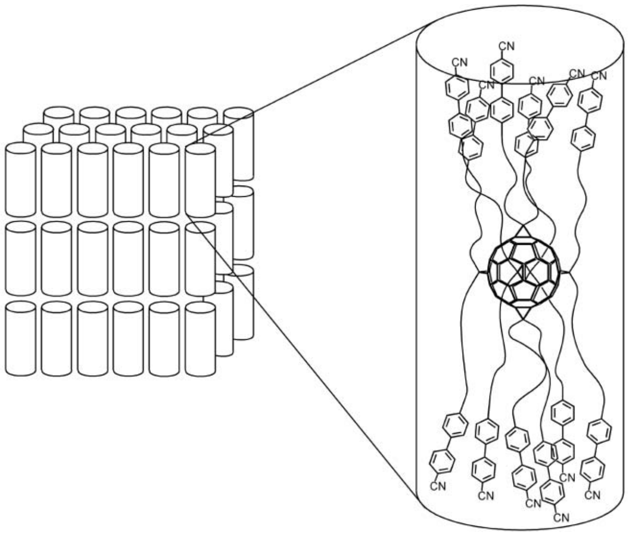


Fig. 1 Proposed supramolecular organization of **14** within the smectic A phase. For details, see ref. 13.

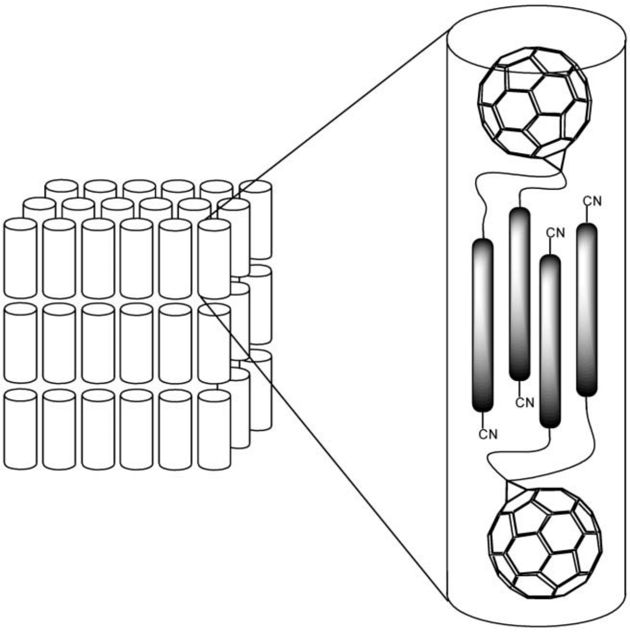


Fig. 2 Proposed supramolecular organization of **5** within the smectic A phase. For details, see ref. 9.

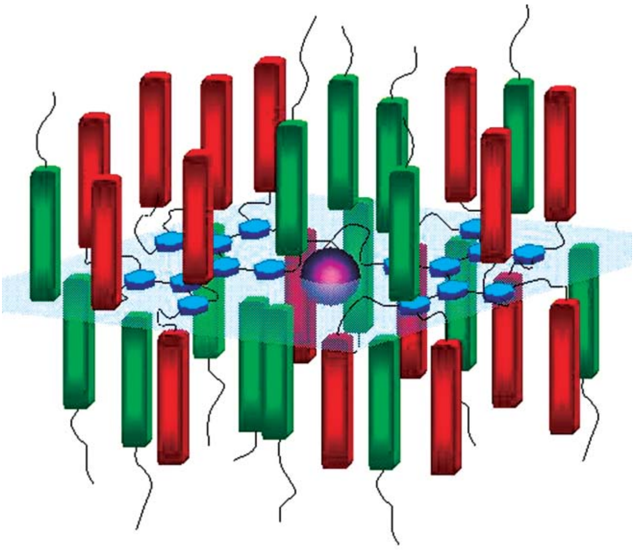


Fig. 3 Proposed supramolecular organization of **10** within the smectic A phase. The interdigitation is illustrated by the red and green cyanobiphenyl units : the red units belong to the dendrimer which is displayed on the drawing, and the green units belong to dendrimers of adjacent layers. For details, see ref. 9.

Conclusions

The research on fullerene-containing thermotropic liquid crystals has enriched the family of C_{60} derivatives as new structures with specific properties had to be designed and synthesized. The covalent and non-covalent concepts clearly demonstrate the various possibilities of C_{60} to give rise to mesomorphism if placed in the adequate environment. We believe that both approaches complement each other and are not in competition. In supramolecular chemistry, as in other areas, C_{60} has not yet revealed all its secrets. Many fascinating and unexpected results are to be discovered. This guarantees a bright and exciting future!

Acknowledgement

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