Liquid-crystalline fullerodendrimers†

Robert Deschenaux,*[a] Bertrand Donnio[b] and Daniel Guillon*[b]

Received (in Montpellier, France) 3rd December 2006, Accepted 2nd February 2007
First published as an Advance Article on the web 9th March 2007
DOI: 10.1039/b617671m

Addition of liquid-crystalline dendrimers onto [60]fullerene led to thermotropic liquid crystals which displayed various types of mesophases, including chiral nematic, smectic B, smectic A and columnar phases. This approach represents an interesting way for the design of self-organized structures based on [60]fullerene, and opens the way to optoelectronic applications for this carbon allotrope, such as for the development of photovoltaic devices and molecular switches.

Introduction

Two different approaches are usually considered in the elaboration of nanomaterials.[1] The first one is the "top-down" approach which has been developed during the last decades, and which consists in pushing the limit of the lithography techniques down to the nanometer scale. However, there are intrinsic limitations to go beyond 10 nm with such techniques. The second approach is the "bottom-up" one which consists in building up nanostructures and assembling them from individual atoms, molecules or macromolecules.[2] With this in view, dendrimers have been considered, during the last decade, as promising materials for the elaboration and assembly of nanostructures, *i.e.* Langmuir and Langmuir–Blodgett films,[3] micelles,[4] and membranes.[5] More specifically, dendrimers functionalized with mesogenic groups are of interest to generate self-organized nanostructures *à la carte*.[6]

Since their discovery in the late 1970s,[7] and the adjustment of perfectly controlled iterative synthetic processes, the chemistry of dendrimers has led to the most impressive developments and rapidly expanding areas of current science. Dendrons and dendrimers represent a unique class of aesthetic, practically monodisperse macromolecules possessing a regular and controlled branched architecture.[8] Moreover, they are potential candidates for various applications since dendrimers are able to concentrate an important number of functional groups in a small volume.[9] Interests may range from biology, as drug or gene delivery devices due to their resemblance and dimensions with some living components,[10] to molecular functional materials with dedicated physical properties.[11] As such, dendrimers represent an interesting alternative towards the development of materials in which information at

Robert Deschenaux was born in Switzerland in 1957. He obtained his PhD from the University of Neuchâtel under the supervision of Prof. K. Bernauer. After three postdoctoral fellowships (Colorado State University, Fort Collins, USA, with Prof. J. K. Stille; ETH-Zurich, Switzerland, with Prof. P. Pino; the University Louis Pasteur, Strasbourg, France, with Prof. J.-M. Lehn), he joined the Department of Materials at Ciba-Geigy, Marly, Switzerland. In 1989, he joined the Department of Chemistry at the University of Neuchâtel as an assistant professor. He was promoted full professor in 1991. His current research interests are in the area of supramolecular chemistry, including the design and synthesis of functional dendritic and polymeric materials based on fullerene and ferrocene, and the study of complex organization in the mesoscopic state.

Bertrand Donnio graduated in chemistry in 1991 from the University of Rennes (Bretagne, France) and obtained his PhD in 1996 from Sheffield University (UK) under the supervision of Professor D. W. Bruce. He then moved to Neuchâtel at the Institut de Chimie (Switzerland) in the group of Professor R. Deschenaux, and then joined the group of Professor H. Finkelmann at the Institut für Makromolekulare Chemie (Freiburg, Germany) for two consecutive postdoctoral fellowships where he worked on lyotropic ferrocene derivatives and liquid crystalline elastomers, respectively. Since 1999, he is Chargé de Recherche (CNRS) at the IPCMS-GMO. His research interests are focused on liquid crystals having original molecular architectures (design and synthesis of dendrimers, metallomesogens, elastomers, bent mesogens, dendronized hybrid systems) and in the way these molecules self-organise within liquid crystalline mesophases using small- and wide-angle X-ray diffraction and dilatometry.

---

[a] *Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, Case Postale 158, 2009 Neuchâtel, Switzerland. E-mail: robert.deschenaux@unine.ch; Fax: +41 32 718 2511; Tel: +41 32 718 2427*
[b] *Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, 23 rue du Loess, 67034 Strasbourg Cedex2, France. E-mail: daniel.guillon@ipcms.u-strasbg.fr; Fax: +33 388 107 246; Tel: +33 388 107 159*

† This paper was published as part of the special issue on Dendrimers and Dendritic Polymers: Design, Properties and Applications.

the molecular level is transferred from an initiator core to the periphery (or *vice versa*) at the nanometer scale, with the expectation of complementary and synergic phenomena, *i.e.* induction of new properties, and/or cooperative effects, *i.e.* amplification of the existing properties.

It was thus logical and of interest to functionalize such supermolecules with mesogenic elements in order to obtain a new class of liquid-crystalline materials.[6,12] Indeed, one issue is to obtain well-defined giant-like liquid-crystalline materials to discover new types of mesophases with uncommon morphologies. Molecular engineering of liquid crystals is also an important issue for controlling the self-organizing process and the ultimate mesomorphic properties. Since dendrimers are in principle monodisperse, the measurements of their physical properties are thus reproducible. Finally, an attractive approach in the field of materials science would be to use the ability of such polyfunctional and discrete dendritic structures to self-assemble into mesophases and their subsequent processing into multicomponent nanosize objects in which each constitutive element could be tailored independently.

The first liquid-crystalline dendrimers (LCDs) were obtained by incorporating mesogenic groups within a hyperbranched dendritic scaffold either by random self-polymerization of an appropriate difunctionalized mesogenic monomer[13] or by grafting of monofunctionalized mesogenic units at the terminal branches of a pre-formed tree-like polymer. The most important class of liquid-crystalline dendrimers is represented by the ''side-chain'' liquid-crystalline dendrimers, where induction of liquid-crystalline properties is achieved by grafting mesogenic promoters on the periphery of a dendrimer. Mesomorphism results essentially from both the enthalpic gain provided by anisotropic interactions, and the strong tendency for microphase separation due to chemical incompatibility between the flexible dendritic core and the terminal groups. The control of the ultimate molecular architecture (size and shape) can be modulated by the generation growth, the multiplicity of the branches and the connectivity of the focal core.[14] Other families of LCDs include supramolecular dendromesogens,[15] shape-persistent LCDs,[16] polypede LCDs,[12] metal-[17] and [60]fullerene-containing LCDs.[18]

[60]Fullerene-containing thermotropic liquid crystals represent an interesting class of materials. Indeed, the incorporation of [60]fullerene (C_{60}) into liquid-crystalline structures may open the way to novel molecular devices and molecular switches showing outstanding performances by combining the electrochemical and photophysical properties of C_{60}[19] with the self-assembling features of liquid crystals; for example, a hexapyrrolidine C_{60} adduct has been used to elaborate a single layer organic light emitting diode.[20]

In this review, we will consider only the case of liquid-crystalline fullerodendrimers for which dendritic moieties are covalently linked to C_{60}. Two main strategies have been developed for the preparation of this type of materials. The first one is to functionalize C_{60} with dendritic malonate derivatives *via* use of the Bingel reaction[21] leading to mesomorphic methanofullerenes; in the second one, derivatization of C_{60} is achieved using the 1,3-dipolar cycloaddition reaction[22] with liquid-crystalline aldehyde derivatives giving rise to mesomorphic fulleropyrrolidines.

Daniel Guillon received his PhD degree in Chemical Physics in 1976 from the Louis Pasteur University of Strasbourg (France). He is director of research in CNRS, presently deputy director of the Institute of Physics and Chemistry of Materials of Strasbourg (IPCMS) since 2002 and head of the organic materials group of the institute since 1989. His main interests include the description at the molecular level of the mesomorphic structures exhibited by low molecular weight and polymer materials, the study of self-organisation processes in supramolecular chemistry, the bottom-up approach of organic and hybrid nanomaterials, and the structure of thin organic films. He is also Vice-President of the International Liquid Crystal Society since 2004.

Self-organization of fullerodendrimers

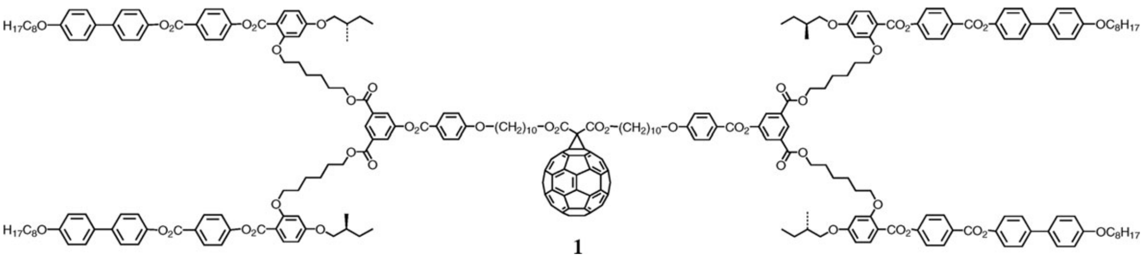
Chiral nematic phase

Liquid-crystalline chiral systems are generally designed for their ferroelectric and/or pyroelectric properties. Thus, chirality has been introduced into C_{60} systems by the Bingel reaction between the fullerene and dendritic malonates of several generations carrying chiral nematic mesogens attached in a side-on fashion.[12,23] Fullerodendrimer **1** shows an enantiotropic chiral nematic phase (N*) with the following phase sequence: Tg 26 N* 69 °C I.[23] The value of the pitch of the helix for **1** is 5 ± 0.5 μm and does not depend on the temperature. This value indicates that C_{60} fits within the helical structure formed by the mesogens themselves without causing any significant perturbation of the pitch itself. It is interesting to note that the dendritic moiety exhibits also a chiral nematic phase with an helical pitch of 2.5 ± 0.5 μm. This clearly indicates that C_{60} and the dendritic unit act as diluents to the self-organizing system provided by the unsubstituted mesogenic addends. Although C_{60} (diameter: 10 Å) may strongly disturb the mesogenic interactions (4–5 Å intermolecular distance), it can nevertheless be encapsulated within the self-organizing chiral nematic medium.

For **2** (g 24.3 N* 80.6 °C I), where the number of the mesogenic groups has been increased, thereby reducing the weight fraction of C_{60} in the dendritic supermolecule, the chiral nematic phase is more stable, indicating that C_{60} is hidden within the liquid-crystalline matrix.[12]

Smectic phases

A systematic study on the elaboration of fullerene-containing thermotropic dendrimers and on the understanding of how such a sphere-like structure could be inserted within liquid crystals, in order to ultimately control the properties *via* the dendrimer generation, has been undertaken. The use of mesomorphic dendritic addends to functionalize C_{60} was thought to



1

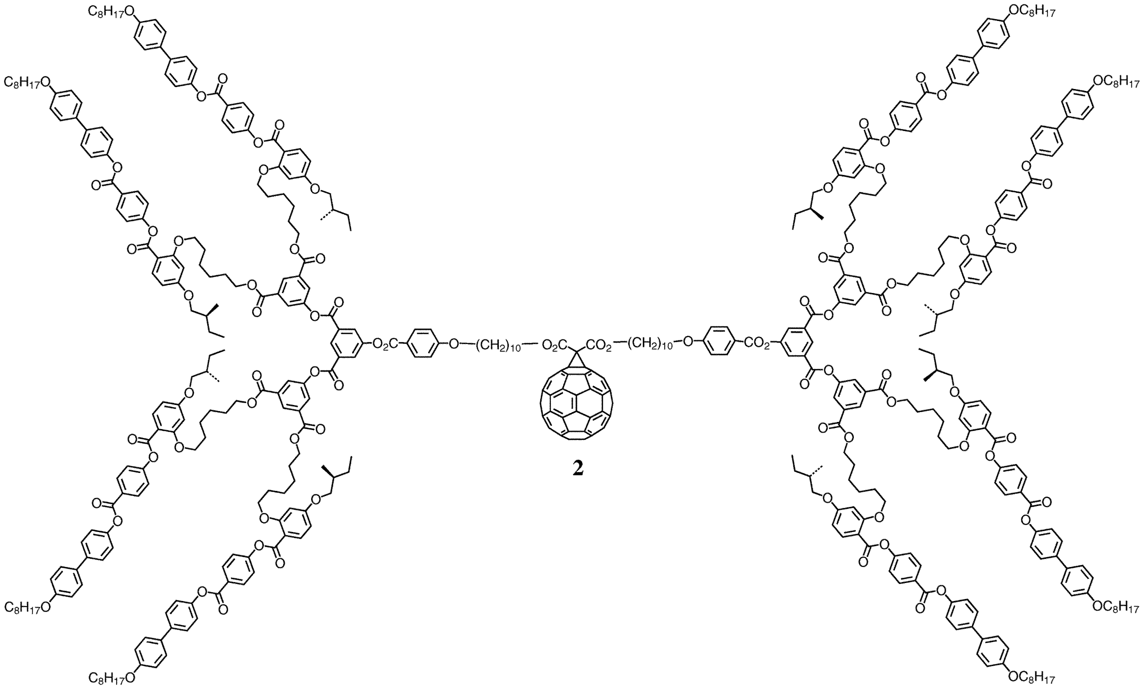
be a suitable solution to avoid aggregation of the C_{60} units, and thus to favor the formation of mesophases.

Addition reaction of malonate-based dendritic addends onto C_{60} led to methanofullerodendrimers **3** to **6**.[24] In **4–6** (corresponding to the second, third and fourth generation, *i.e.*, G2, G3 and G4), C_{60} is buried within the dendritic branches, and as a consequence, the supramolecular organization of these fullerodendrimers is independent to the change of the generation number of the dendrimer and is practically similar to that of the corresponding malonate precursors. The mesophase stability was however slightly enhanced with generation for both systems (Fig. 1). The only drastic change concerned **3** (corresponding to the first generation G1) where the nematic phase was suppressed and replaced by the smectic A (SmA) phase upon addition of C_{60}.

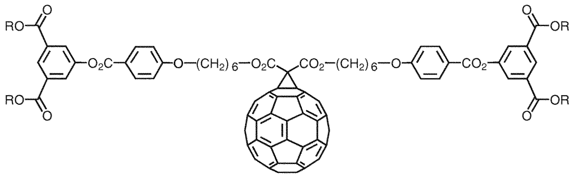
The supramolecular organization of these dendrimers was deduced from X-ray diffraction analysis and molecular simulation. In the case of **3**, the molecules adopt a V-shape (constituted by pairs of mesogenic groups), and arrange in a head-to-tail fashion favoured by the antiparallel packing of the polar end-groups. In the case of **4**, the branching part begins to have significant lateral extension with respect to the layer normal, and the two branches extend on both sides of C_{60}. Then, for **5** and **6** (Fig. 2), the structure is solely governed by the polar cyano groups. The central part of the layer is constituted by the fullerene moiety embedded by the dendritic segments, and the layer interface is formed by partially interdigitated mesogenic groups. In all cases, the mesophases are stabilized by dipolar interactions (antiparallel arrangement of the cyanobiphenyl units).

The corresponding hemi-dendrimers of first and second generations were also prepared for comparison purposes. Similar trends were observed, *i.e.* the SmA phase was preferred to the nematic one, which was suppressed upon addition of C_{60}. The same type of supramolecular organization is suggested. Interestingly, the mesomorphic temperature range was strongly reduced in the hemi-dendrimers compared to that of the corresponding dendrimers. It was also shown by electro-optical Kerr effect and hydrodynamics methods that the hemi-dendrimers are more sensitive than dendrimers to the presence of C_{60} in their structure (viscosity, shape changes).[25]

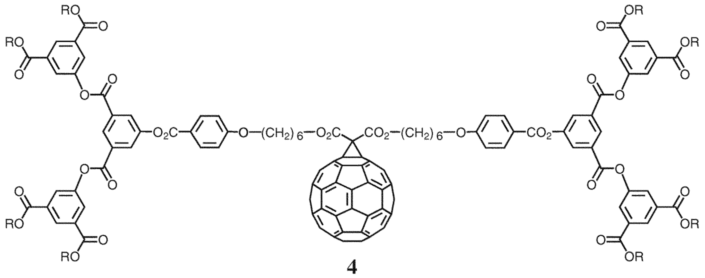
Fulleropyrrolidines constitute an important family of C_{60} derivatives which have the advantage over the methanofullerenes to lead to stable reduced species. To promote mesomorphism in fulleropyrrolidines, C_{60} was modified with dendritic addends bearing cyanobiphenyl groups leading to four generations of fulleropyrrolidines (**7–10**).[26] This appeared to be the right strategy since, with the exception of the first generation **7**, which was found to be non-mesomorphic (Cr 178 I), all the other fullerene-based dendrimers gave rise to a



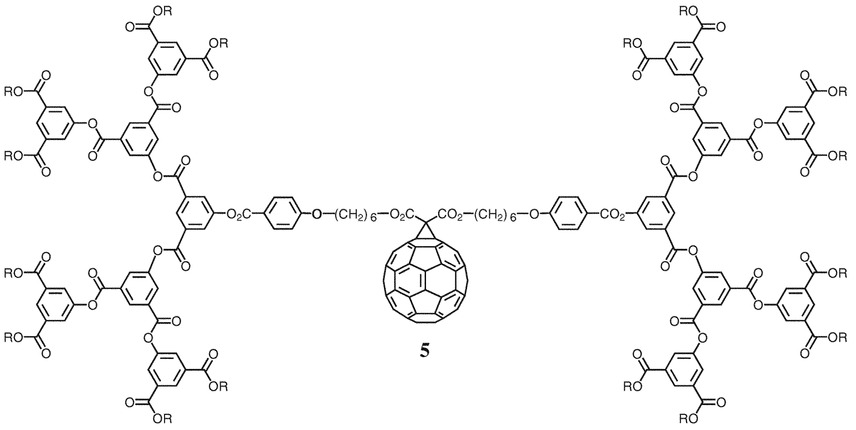
2


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

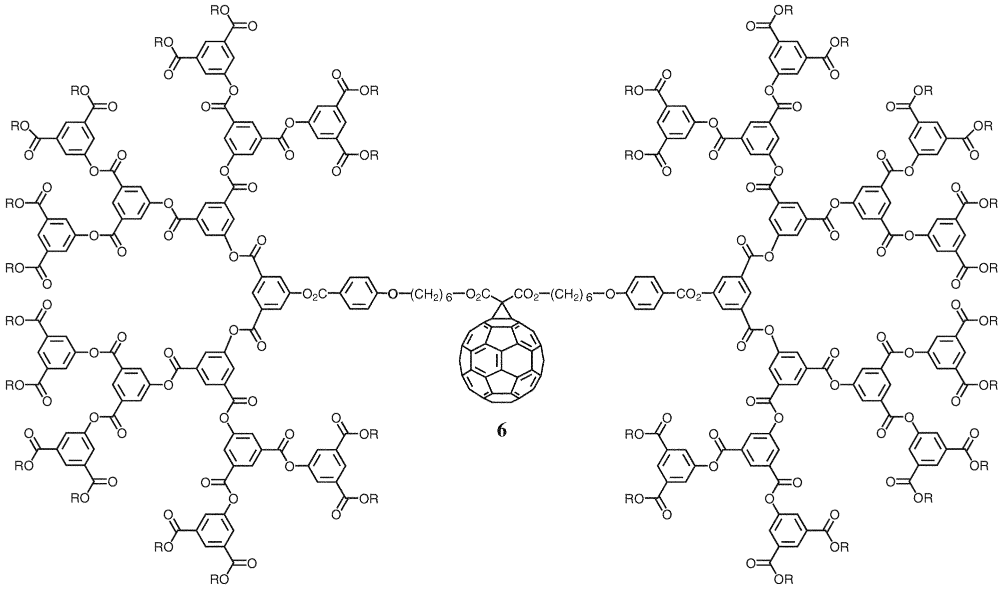
3


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

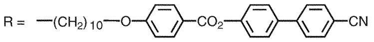
4


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

5


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

6


R =
—(CH₂)₁₀—O
CO₂
CN

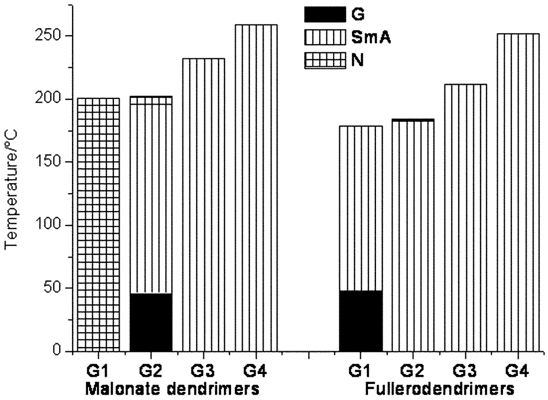


Fig. 1 Mesomorphic properties of the malonates and corresponding methanofullerodendrimers **3–6** (G1, G2, G3 and G4 represent the dendrimer generations).

SmA phase (**8**: Tg 44 SmA 168 I; **9**: Tg 51 SmA 196 I; **10**: Tg 36 SmA 231 I), the stability of which increased with the generation number. The aldehyde and alcohol precursors showed essentially a broad SmA phase, except those of the first generation which showed a nematic phase. As for the molecular organization within the SmA phase (Fig. 3), the second generation molecules **8** are oriented in a head-to-tail fashion within the layers, and for each molecule the mesogenic groups point in the same direction interdigitating with mesogenic groups of adjacent layers. For the higher generations, *i.e.* **9** and **10**, the mesogenic units are positioned above and below the dendritic core, and interdigitation occurs between layers; C_{60} is hidden in the dendritic core and has no influence in the supramolecular organization as this was the case for the methanofullerodendrimers discussed above.

Second-generation fulleropyrrolidine **8** was chosen as a representative reference for a systematic variation of the R group located on the nitrogen atom, in order to evaluate the effects of the latter on the mesomorphic properties. When R = H (**11**),[26] the compound exhibited a SmA phase (SmA 162 I). Substitution of the R group by oligophenylenevinylene (OPV) conjugated moieties led to similar results (**12**: Tg 50 SmA 171 I; **13**: Tg 50 SmA 169 I) and indicated that the overall behavior is dominated by the dendritic framework.[27] Fulleropyrrolidine bearing a ferrocene unit **14** showed a SmA phase between 40 and 135 °C with a partial bilayered arrangement in which the cyanobiphenyl groups are interdigitated from layer to layer.[28] In such a supramolecular organization, already proposed for the liquid-crystalline methanofullerenes containing cyanobiphenyl groups, the ferrocene moieties are localized between the C_{60} units and the dendritic cores. Furthermore, the C_{60} moieties of adjacent layers are located side-by-side, giving rise

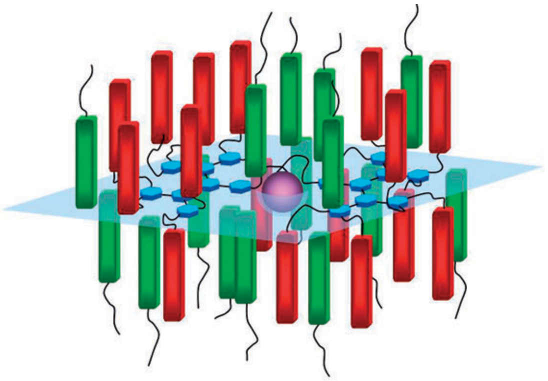
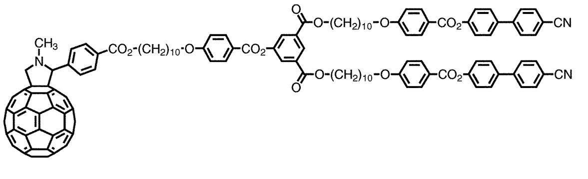
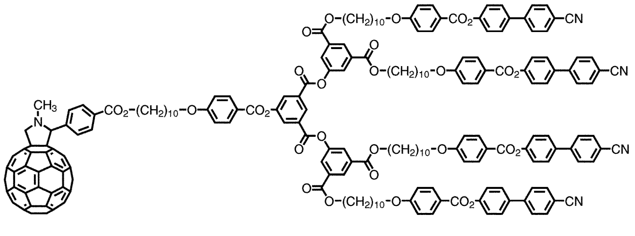


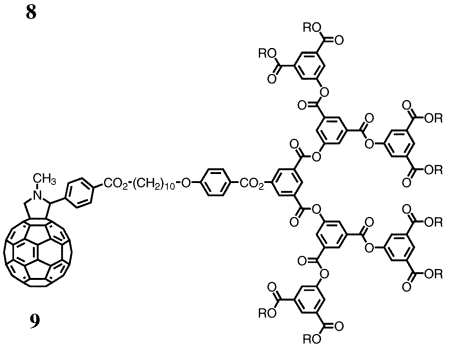
Fig. 2 Proposed supramolecular organization of **5** within the smectic A phase. The interdigitation is illustrated by the red and green cyanobiphenyl units: the red units belong to the dendrimer which is displayed on the drawing, and the green units belong to dendrimers of adjacent layers. Compounds **4** and **6** show a similar supramolecular organization.



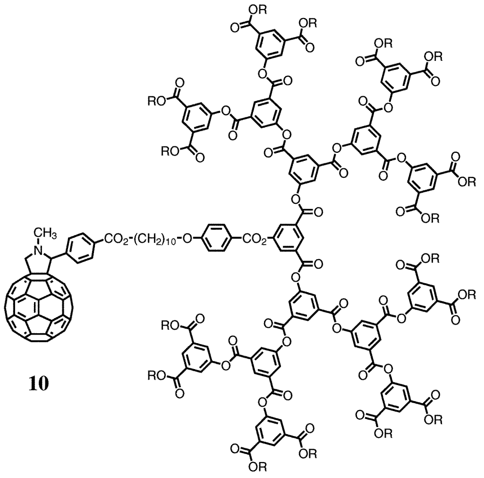
7



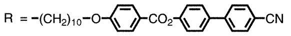
8

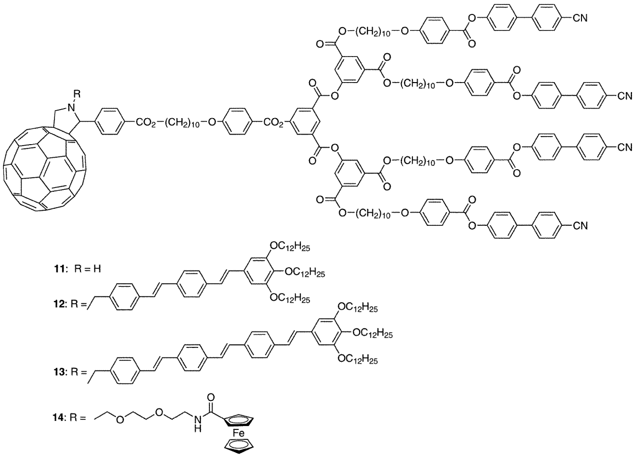


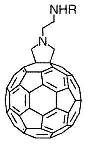
9



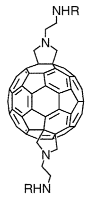
10



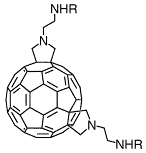




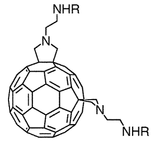
15



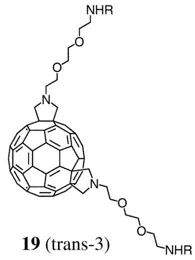
16 (trans-2)



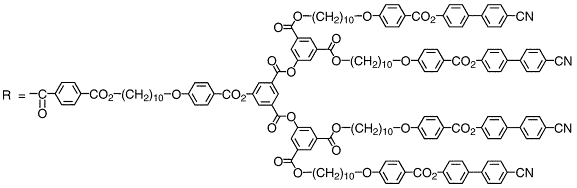
17 (trans-3)



18 (equatorial)



19 (trans-3)



to a superstructure with alternating sublayers containing either the mesogenic groups or the C_{60} units, respectively.

With the view to exploit C_{60} as a synthetic platform for the design of liquid-crystalline materials with unconventional shapes, the mesomorphic properties of fullerodendrimers based on the bis-addition pattern were investigated.[29] Indeed, such materials retain most of the properties of C_{60}, knowing that the major drawback of the poly-addition pattern is that the properties of C_{60} are considerably altered. The bis-addition onto C_{60} leads to a variety of interesting structures, including V-shaped structures with different angles. Thus, the same second generation cyanobiphenyl-based dendrimer was also used as a liquid-crystalline promoter for the synthesis of mesomorphic bisadducts of C_{60}. Liquid-crystalline *trans*-2, *trans*-3, and equatorial bisadducts were obtained by condensation of the liquid-crystalline promoter, which carries a carboxylic acid function, with the corresponding bisaminofullerene derivatives. A monoadduct of fullerene was also prepared for comparative purposes.[29]

For monoadduct **15** (Cr 44 SmA 153 I), the molecular organization within the smectic layers is mainly governed by steric factors, that is, the required adequacy between the cross-sectional areas of C_{60} (90–100 Å^2) and that of the mesogenic units (22–25 Å^2 per mesogenic unit). Thus, the cyanobiphenyl units of one molecule point in the same direction, and the molecules are organized in a head-to-tail fashion, forming a bilayered smectic A phase.

For bisadducts **16–19** (**16**: Tg 60 SmA 167 M 170 I, M: unidentified mesophase; **17**: Tg 61 SmA 169 I; **18**: Cr 42 SmA 166 I; **19**: Tg 52 SmA 161 I), two dendrons are located on the C_{60} unit. The dendrimers expand laterally with respect to C_{60} so that the latter is embedded within the layers formed by the dendrimers and has no influence on the supramolecular organization. The bisadduct derivatives are organized into a monolayered smectic A phase, similar to that obtained for fulleropyrrolidines and methanofullerenes functionalized by analogous liquid-crystalline dendrimers (see Figs. 2 and 3). For these bisadducts, the supramolecular organization is essentially governed by the nature and the structure of the mesogenic units and of the dendritic core.

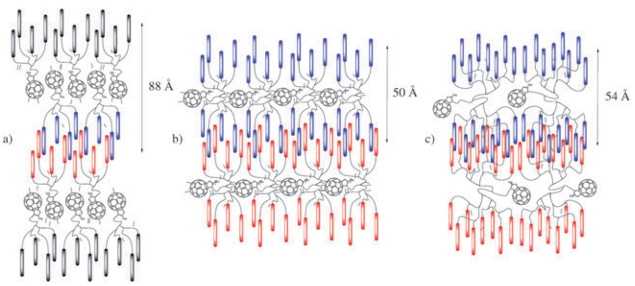


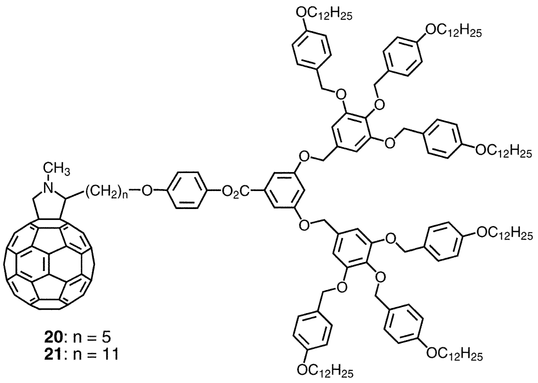
Fig. 3 Postulated supramolecular organization of fulleropyrrolidines **8** (a), **9** (b) and **10** (c) within the smectic A phase.

A comprehensive investigation of the photophysical properties of several of these fulleropyrrolidine dendrimers in solution reveals that in these materials, the basic fullerene features are largely preserved, and no spectroscopic evidence for strong π–π interactions between individual fullerenes could be detected.

Columnar phases

Fullerene-containing liquid crystals, which display columnar phases, are of interest for electronic and optoelectronic applications. Functionalization of C_{60} with liquid-crystalline dendrimers, which exhibit columnar mesomorphism, led to fullerenes which also showed columnar phases. To functionalize C_{60}, it was decided to use poly(benzyl ether) dendrimers since these compounds give rise to either spherical or cylindrical supramolecular dendrimers that subsequently self-organize into cubic or columnar lattices, respectively.[30]

For fullerodendrimers **20** (Tg not detected, Col_r 80 I) and **21** (Tg 46 Col_r 74 I), the XRD diffraction patterns registered within the temperature range of the mesophases displayed six sharp reflections, which were unambiguously indexed as the (11), (20), (02), (22), (40) and (13) reflections of a two-dimensional rectangular lattice of *c*2*mm* symmetry (for **20**, a = 128.6 Å and b = 86.0 Å; for **21**, a = 129.6 Å and b = 89.4 Å).[31]



Two broad reflections located at h_{ch} = 4.6 Å and $h_{full} \approx$ 8.7 Å are present in the wide-angle region. The first reflection is related to the molten aliphatic terminal chains of the dendrons, and the second one was attributed to interactions between C_{60} units.

The number of molecules included in a slice of 8.7 Å thickness was calculated. From the values of the lattice parameters and the estimated molecular volumes (4550 and 4700 $Å^3$ for **20** and **21**, respectively), this number turned out to be about 10 for each compound. Then the supramolecular organization results in bundles of 10 dendrons superposed one over the other to form an elliptic columnar core, the shape of which is in agreement with the *c*2*mm* symmetry. The dendritic moieties are arranged around this elliptic core in such a way that they fill the intercolumnar space. This result demonstrates that C_{60} can be organized along one single direction (here, the columnar axis) provided a suitable molecular design has been achieved. The supramolecular organization of **20** and **21** within the columns and the texture of the columnar phase displayed by **20** are shown in Figs. 4 and 5, respectively.

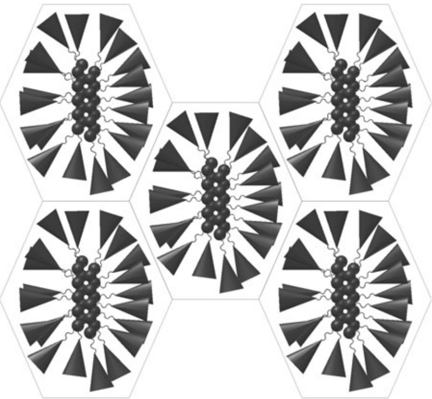


Fig. 4 Postulated supramolecular organization of **20** and **21** within the rectangular columnar phase.

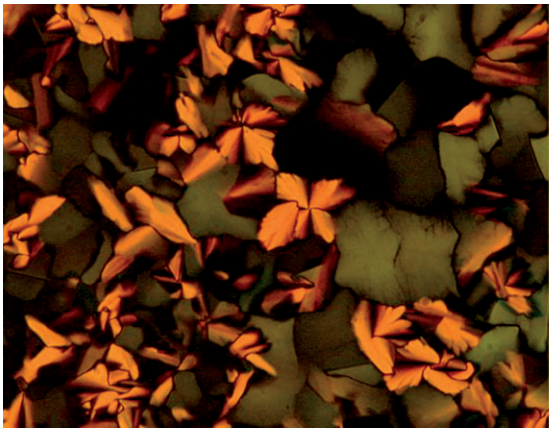


Fig. 5 Thermal polarized optical micrograph of the rectangular columnar texture displayed by **20** at 78 °C.

Towards applications

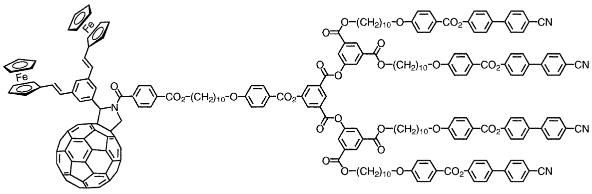
Photovoltaic properties

The synthesis and study of fullerene derivatives bearing π-conjugated oligomers have attracted considerable attention in recent years. In particular, exploitation of their electronic properties for solar energy conversion has become a field of intense investigations. For example, photovoltaic devices using thin films of C_{60}–OPV conjugates have shown promising results for large area photodetectors and solar cells.[32] This molecular approach is attractive for two reasons: (1) it allows a detailed structure/activity exploration which will better our understanding of the photovoltaic systems, and (2) it offers the possibility of controlling the morphology of the organic film in the devices. To further improve the quality of the organic films, the use of liquid-crystalline C_{60}–OPV conjugates could be a successful concept: such materials would spontaneously form ordered assemblies which could then be oriented and lead to high-performance thin films; thus, compounds **12** and **13** have been designed for this purpose.

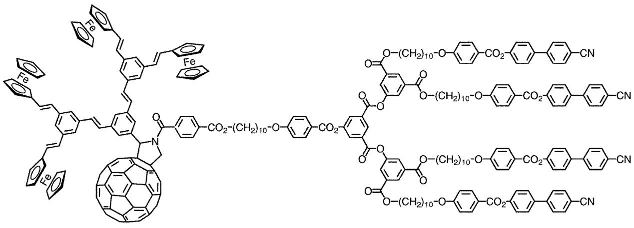
Luminescence measurements of **12** and **13** in solution revealed a strong quenching of the OPV fluorescence by C_{60}, indicating that these donor–acceptor systems are suitable candidates for good mobility of the charge carriers. Thus, functionalization of C_{60}–OPV conjugates with a mesomorphic dendrimer allows the liquid-cristalline ordering of such donor–acceptor conjugates, which present all the characteristic features required for photovoltaic applications.[27]

Redox switching properties

Ferrocene is a good electron donor moiety to be used in building up molecular switching devices. On this basis, compound **14**, where fullerene, ferrocene and a second generation liquid-crystalline cyanobiphenyl-based dendrimer have been assembled, was designed.[28] In this material, the ferrocene located at the end of a flexible chain was expected to act independently of the mesomorphic fragment, so that long lifetimes of the charge separated state could be obtained. Such a structure is of interest as the redox potential of ferrocene can be controlled with the degree of substitution, and the mesomorphic properties can be tuned from the choice of the liquid-crystalline groups since ferrocene does not interfere with the mesomorphic moiety. Oxidation and reduction processes were investigated by electrochemical techniques. Photoinduced electron transfer from ferrocene to fullerene was identified with lifetimes for the charge-separated state of 560 ns (THF) and 490 ns (benzonitrile), indicating that such liquid-



22



23

crystalline dyads are valuable candidates for the development of molecular switches.

To further explore the properties of liquid-crystalline ferrocene-fullerene dyads, dendritic-like ferrocene architectures, containing either two or four ferrocene units, have been used as a source of electrons. Compounds **22** (Tg 47 SmA 171 I) and **23** (Tg 34 SmA 168 I) exhibit a smectic A phase in agreement with the nature of the cyano-based dendrimers (see above).[33] The supramolecular organization is driven by steric constraints resulting from the difference of the cross-sectional area of C_{60} (90–100 Å^2), ferrocene (45 Å^2) and the four mesogenic groups (22–25 Å^2 per mesogenic unit). The overall lamellar structure consists of sublayers of different chemical nature, *i.e.* ferrocene and fullerene sublayers separated from the cyanobiphenyl interdigitated sublayers (Fig. 6).

The electrochemical behavior is in agreement with the redox-activity of the building blocks. Steady-state emission spectra showed that the fluorescence is totally quenched, suggesting the existence of an efficient electron transfer process from the ferrocene dendrimer to C_{60}. It should be noted that another possibility to assemble fullerene, ferrocene and a liquid-crystalline dendrimer has been achieved by using a dendritic moiety containing both the ferrocene and the mesogenic units (**24**) (Tg not detected, SmA 157 I).[34] For this compound, no physical properties have been determined.

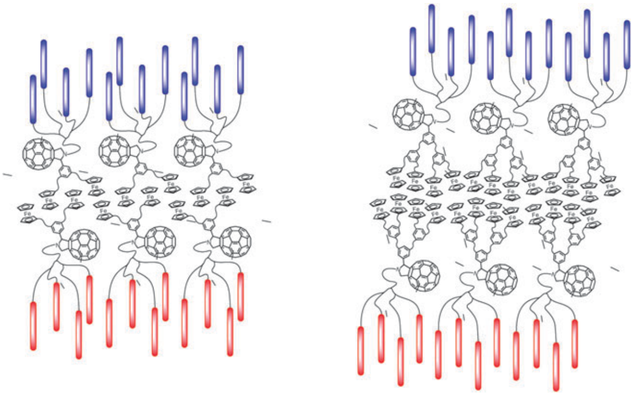
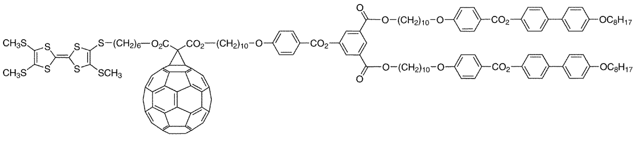


Fig. 6 Postulated supramolecular organization of **22** (left) and **23** (right) within the smectic A phase.

One major drawback of those chemicals is, however, the short life-times (in solution) of the charge separated state. Improvement of this parameter is not straightforward because of the number of structural features related to it (*i.e.*, distance between the donor and acceptor units, orientation of the donor and acceptor moieties with respect to each other, various conformations of the linkers, redox potential of the donor groups). To establish a structure–property relationship, and put to the fore the influence of each structural parameter on the photophysical characteristics of the dyads, further candidates were considered. Tetrathiafulvalene (TTF) and π-extended TTF derivatives, which transform into aromatic structures upon oxidation, have been used in the preparation of C_{60}-based dyads[35] and triads.[36] Upon photoexcitation, long-lived charge separated states were detected.[37] On this basis, liquid-crystalline C_{60}–TTF dyads appeared as candidates of choice.

Compound **25** (Tg 64 SmB 129 SmA 156 I) represents the first member of this family of liquid-crystalline C_{60}–TTF dyads.[38] The supramolecular organization of **25** is based on a head-to-tail arrangement into a bilayer structure as shown in Fig. 7. With such a disposition, strong donor–acceptor interactions are optimized between C_{60} and TTF, stabilizing even more the packing. This leads to an overall smectic layer structure in which the active moieties, *i.e.* C_{60} and TTF, are confined within sub-layers separated from each other by organic outer layers. This strategy is thus a perfect illustration of the use of liquid crystals to confine active layers.



25

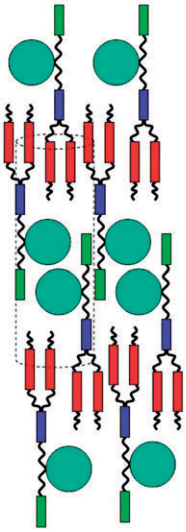
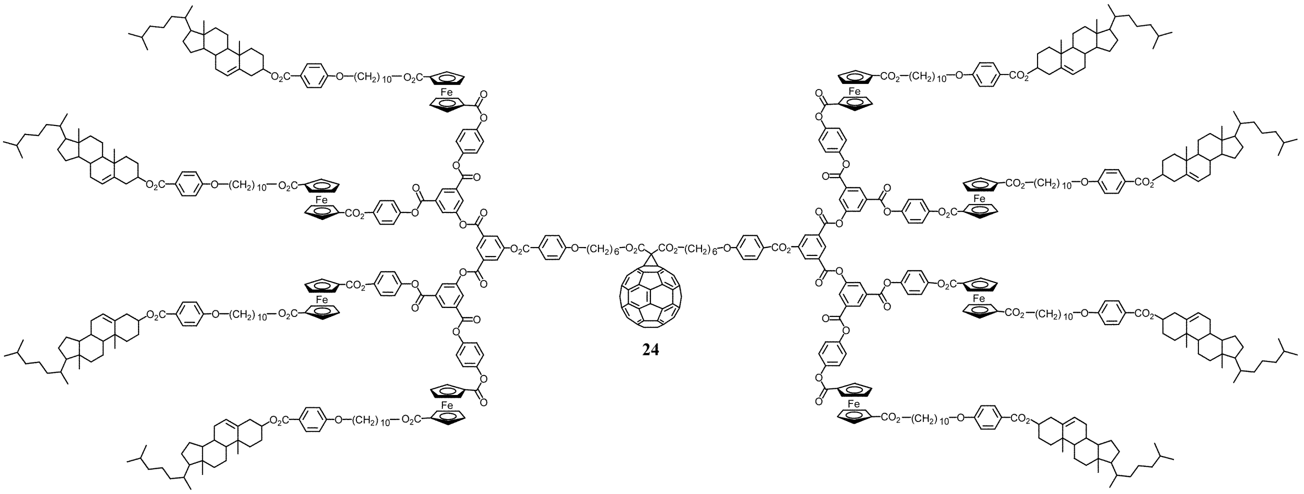


Fig. 7 Proposed supramolecular organization of **25** within the smectic phases.



24

The electrochemical properties of **25** were studied by cyclic voltammetry at room temperature in dichloromethane. Two quasi-reversible one-electron reduction waves which correspond to the reduction of the fullerene core were observed. As expected, these reduction potentials are shifted to more negative values relative to C_{60}.[39] This shift arises from the saturation of a double bond in C_{60} which raises the lowest unoccupied molecular orbital (LUMO) energy of the resulting modified fullerene. On the anodic side, two reversible oxidation waves are observed and assigned to the formation of the radical cation and dication species of the TTF fragment, respectively. These cyclic voltammetry measurements confirmed that both the donor and acceptor units preserve their individual electroactive identity.

Conclusions and perspectives

In this review, we have shown that incorporation of C_{60} into dendritic architectures leads to self-organizing supermolecular systems which display various mesophases, including chiral nematic, smectic A, smectic B and columnar phases. Fullerene was selected, on one hand, due to its fascinating physical properties and, on the other hand, in order to see if such a non-mesogenic unit would affect significantly the mesomorphic properties of the addends. This approach represents an interesting way in the design of self-organized structures containing bulky functional units, and could be used for other functional groups which are not a priori adapted to be organized in nanoscale structures. The limitations of our concept, with respect to other approaches that have been reported,[40–42] lie in the efforts that need to be invested for the synthesis, purification and characterization of the liquid-crystalline dendrons and dendrimers used for the functionalization of C_{60}. However, considering the enormous possibilities that dendritic compounds offer for tailoring the properties of the materials, such efforts are worthwhile. Future developments will be devoted to the design of new structures, such as liquid-crystalline bis-fullerene derivatives, and to the study of physicochemical properties within the liquid-crystalline phases.

Acknowledgements

R. D. acknowledges the Swiss National Science Foundation for financial support. B. D. and D. G. thank ULP and CNRS for their support.

References

1 G. Cao, *Nanostructures and Nanomaterials*, Imperial College Press, London, 2004.
2 P. Yong, *The Chemistry of Nanostructured Materials*, World Scientific, Singapore, 2003.
3 (*a*) F. Cardullo, F. Diederich, L. Echegoyen, T. Habicher, N. Jayaraman, R. M. Leblanc, J. F. Stoddart and S. Wang, *Langmuir*, 1998, **14**, 1955; (*b*) J.-F. Nierengarten, J.-F. Eckert, Y. Rio, M. del Pilar Carreon, J.-L. Gallani and D. Guillon, *J. Am. Chem. Soc.*, 2001, **123**, 9743.
4 S. Burghardt, A. Hirsch, B. Schade, K. Ludwig and C. Böttcher, *Angew. Chem., Int. Ed.*, 2005, **44**, 2976.
5 M. Brettreich, S. Burghardt, C. Böttcher, T. Bayerl, S. Bayerl and A. Hirsch, *Angew. Chem., Int. Ed.*, 2000, **39**, 1845.
6 (*a*) S. A. Ponomarenko, N. I. Boiko and V. P. Shibaev, *Polym. Sci., Ser. C*, 2001, **43**, 1; (*b*) D. Guillon and R. Deschenaux, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 515; (*c*) B. Donnio and D. Guillon, *Adv. Polym. Sci.*, 2006, **201**, 45.
7 D. A. Tomalia and J. M. Fréchet, *J. Polym. Sci. A, Polym. Chem.*, 2002, **40**, 2719.
8 (*a*) D. A. Tomalia and H. Dupont Durst, *Top. Curr. Chem.*, 1993, **165**, 193; (*b*) N. Ardouin and D. Astruc, *Bull. Soc. Chim. Fr.*, 1995, **132**, 875; (*c*) G. R. Newkome, C. N. Moorefield and F. Vögtle, in *Dendrimers and Dendrons: Concepts, Synthesis and Applications*, WILEY-VCH, Weinheim, 2001; (*d*) J. M. J. Fréchet and D. A. Tomalia, *Dendrimers and other Dendritic Polymers*, Wiley Series in Polymer Sciences, Wiley, Weinheim, 2001.
9 (*a*) J. Issberner, R. Moors and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2413; (*b*) G. M. Dykes, *J. Chem. Technol. Biotechnol.*, 2001, **76**, 903.
10 (*a*) D. Astruc, *C. R. Acad. Sci. Paris, Ser. II*, 1996, **322**, 757; (*b*) D. K. Smith and F. Diederich, *Chem. Eur. J.*, 1998, **4**, 1353; (*c*) S. Hecht and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2001, **40**, 74; (*d*) U. Boas and P. M. Heegaard, *Chem. Soc. Rev.*, 2004, **33**, 43.
11 (*a*) H. F. Chow, T. K. K. Mong, M. F. Nongrum and C. W. Wan, *Tetrahedron*, 1998, **54**, 8543; (*b*) M. Fischer and F. Vögtle, *Angew. Chem., Int. Ed.*, 1999, **38**, 884; (*c*) K. Inoue, *Prog. Polym. Sci.*, 2000, **25**, 453; (*d*) D. K. Smith, A. R. Hirst, C. S. Love, J. G. Hardy, S. V. Brignell and B. Huang, *Prog. Polym. Sci.*, 2005, **30**, 220.
12 I. M. Saez and J. W. Goodby, *J. Mater. Chem.*, 2005, **15**, 26.
13 (*a*) V. Percec and M. Kawasumi, *Macromolecules*, 1992, **25**, 3843; (*b*) S. Bauer, H. Ringsdorf and H. Fischer, *Angew. Chem., Int. Ed.*

Engl., 1993, **32**, 1589; (*c*) V. Percec, P. Chu and M. Kawasumi, *Macromolecules*, 1994, **27**, 4441; (*d*) S. W. Hanh, Y. K. Yun, J.-I. Jin and O. H. Han, *Macromolecules*, 1998, **31**, 6417; (*e*) S.-H. Choi, N.-H. Lee, S. W. Cha and J.-I. Jin, *Macromolecules*, 2001, **34**, 2138.

14 J. Barberá, B. Donnio, L. Gehringer, D. Guillon, M. Marcos, A. Omenat and J. L. Serrano, *J. Mater. Chem.*, 2005, **15**, 4093.

15 (*a*) V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, *J. Am. Chem. Soc.*, 1997, **119**, 1539; (*b*) S. D. Hudson, H. T. Jung, V. Percec, W. D. Cho, G. Johansson, G. Ungar and V. S. K. Balagurusamy, *Science*, 1997, **278**, 449; (*c*) V. Percec, W. D. Cho and G. Ungar, *J. Am. Chem. Soc.*, 2000, **122**, 10273.

16 H. Meier, M. Lehmann and U. Kolb, *Chem. Eur. J.*, 2000, **6**, 2462.

17 (*a*) U. Stebani, G. Lattermann, M. Wittenberg and J. H. Wendorff, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1858; (*b*) J. Barberá, M. Marcos, A. Omenat, J. L. Serrano, J. I. Martínez and P. J. Alonso, *Liq. Cryst.*, 2000, **27**, 255; (*c*) R. Deschenaux, E. Serrano and A.-M. Levelut, *Chem. Commun.*, 1997, 1577.

18 T. Chuard and R. Deschenaux, *J. Mater. Chem.*, 2002, **12**, 1944.

19 D. M. Guldi, *Chem. Commun.*, 2000, 321.

20 K. Hutchison, J. Gao, G. Schick, Y. Rubin and F. Wudl, *J. Am. Chem. Soc.*, 1999, **121**, 5611.

21 (*a*) C. Bingel, *Chem. Ber.*, 1993, **126**, 1957; (*b*) J.-P. Bourgeois, F. Diederich, L. Echegoyen and J.-F. Nierengarten, *Helv. Chim. Acta*, 1998, **81**, 1835.

22 (*a*) M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519; (*b*) N. Tagmatarchis and M. Prato, *Synlett*, 2003, **6**, 768.

23 S. Campidelli, C. Eng, I. M. Saez, J. W. Goodby and R. Deschenaux, *Chem. Commun.*, 2003, 1520.

24 B. Dardel, D. Guillon, B. Heinrich and R. Deschenaux, *J. Mater. Chem.*, 2001, **11**, 2814.

25 (*a*) N. P. Yevlampieva, B. Dardel, P. Lavrenko and R. Deschenaux, *Chem. Phys. Lett.*, 2003, **382**, 32; (*b*) P. Lavrenko, N. Yevlampieva, B. Dardel and R. Deschenaux, *Prog. Colloid Polym. Sci.*, 2004, **127**, 61.

26 S. Campidelli, J. Lenoble, J. Barberá, F. Paolucci, M. Marcaccio, D. Paolucci and R. Deschenaux, *Macromolecules*, 2005, **38**, 7915.

27 S. Campidelli, R. Deschenaux, J.-F. Eckert, D. Guillon and J.-F. Nierengarten, *Chem. Commun.*, 2002, 656.

28 S. Campidelli, E. Vázquez, D. Milic, M. Prato, J. Barberá, D. M. Guldi, M. Marcaccio, D. Paolucci, F. Paolucci and R. Deschenaux, *J. Mater. Chem.*, 2004, **14**, 1266.

29 S. Campidelli, E. Vázquez, D. Milic, J. Lenoble, C. Atienza Castellanos, G. Sarova, D. M. Guldi, R. Deschenaux and M. Prato, *J. Org. Chem.*, 2006, **71**, 7603.

30 (*a*) V. Percec, C. H. Ahn, W. D. Cho, A. M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S. A. Prokhorova, S. S. Sheiko, S. Z. Cheng, A. Zhang, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 1998, **120**, 8619; (*b*) V. Percec, W. D. Cho, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 2001, **123**, 1302; (*c*) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H. W. Spiess, S. D. Hudson and H. Duan, *Nature*, 2002, **419**, 384; (*d*) G. Ungar, Y. Liu, X. Zeng, V. Percec and W. D. Cho, *Science*, 2003, **299**, 1208; (*e*) V. Percec, M. R. Imam, T. K. Bera, V. S. K. Balagurusamy, M. Peterca and P. A. Heiney, *Angew. Chem., Int. Ed.*, 2005, **44**, 4739; (*f*) V. Percec, A. Dulcey, M. Peterca, M. Ilies, M. J. Sienkowska and P. A. Heiney, *J. Am. Chem. Soc.*, 2005, **127**, 17902.

31 J. Lenoble, N. Maringa, S. Campidelli, B. Donnio, D. Guillon and R. Deschenaux, *Org. Lett.*, 2006, **8**, 1851.

32 (*a*) J.-F. Nierengarten, J.-F. Eckert, J.-F. Nicoud, L. Ouali, V. Krasnikov and G. Hadziioannou, *Chem. Commun.*, 1999, 617; (*b*) J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S.-G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov and G. Hadziioannou, *J. Am. Chem. Soc.*, 2000, **122**, 7467; (*c*) E. Peeters, P. A. van Hal, J. Knol, C. J. Brabec, N. S. Sariciftci, J. C. Hummelen and R. A. J. Janssen, *J. Phys. Chem. B*, 2000, **104**, 10174.

33 S. Campidelli, L. Pérez, J. Rodríguez-López, J. Barberá, F. Langa and R. Deschenaux, *Tetrahedron*, 2006, **62**, 2115.

34 B. Dardel, R. Deschenaux, M. Even and E. Serrano, *Macromolecules*, 1999, **32**, 5193.

35 (*a*) M. Prato, M. Maggini, C. Giacometti, G. Scorrano, G. Sandona and G. Farina, *Tetrahedron*, 1996, **52**, 5221; (*b*) N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín and J. Ordúna, *Tetrahedron Lett.*, 1996, **37**, 5979; (*c*) D. Kreher, M. Cariou, S. G. Liu, E. Levillain, J. Veciana, C. Rovira, A. Gorgues and P. Hudhomme, *J. Mater. Chem.*, 2002, **12**, 2137; (*d*) N. Martín, L. Sánchez and D. M. Guldi, *Chem. Commun.*, 2000, 113; (*e*) S. González, N. Martín, A. Swartz and D. M. Guldi, *Org. Lett.*, 2003, **5**, 557.

36 (*a*) J. L. Segura, E. Priego and N. Martín, *Tetrahedron Lett.*, 2000, **41**, 7737; (*b*) J. L. Segura, E. M. Priego, N. Martín, C. Luo and D. M. Guldi, *Org. Lett.*, 2000, **2**, 4021; (*c*) S. González, N. Martín and D. M. Guldi, *J. Org. Chem.*, 2003, **68**, 779.

37 (*a*) E. Allard, J. Cousseau, J. Ordúna, J. Garín, H. Luo, Y. Araki and O. Ito, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5944; (*b*) L. Sánchez, I. Pérez, N. Martín and D. M. Guldi, *Chem.-Eur. J.*, 2003, **9**, 2457; (*c*) M. C. Díaz, M. A. Herranz, B. M. Illescas, N. Martín, N. Godbert, M. R. Bryce, C. Luo, A. Swartz, G. Anderson and D. M. Guldi, *J. Org. Chem.*, 2003, **68**, 7711.

38 E. Allard, F. Oswald, B. Donnio, D. Guillon, J. L. Delgado, F. Langa and R. Deschenaux, *Org. Lett.*, 2005, **7**, 383.

39 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.

40 Non-covalent liquid crystals: (*a*) D. Felder, B. Heinrich, D. Guillon, J.-F. Nicoud and J.-F. Nierengarten, *Chem.-Eur. J.*, 2000, **6**, 3501; (*b*) M. Kimura, Y. Saito, K. Ohta, K. Hanabusa, H. Shirai and N. Kobayashi, *J. Am. Chem. Soc.*, 2002, **124**, 5274.

41 (*a*) M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato and E. Nakamura, *Nature*, 2002, **419**, 702; (*b*) Y. Matsuo, A. Muramatsu, R. Hamasaki, N. Mizoshita, T. Kato and E. Nakamura, *J. Am. Chem. Soc.*, 2004, **126**, 432; (*c*) Y. Matsuo, A. Muramatsu, Y. Kamikawa, T. Kato and E. Nakamura, *J. Am. Chem. Soc.*, 2006, **128**, 9586.

42 R. J. Bushby, I. W. Hamley, Q. Liu, O. R. Lozman and J. E. Lydon, *J. Mater. Chem.*, 2005, **15**, 4429.