Fullerodendrimers: A New Class of Compounds for Supramolecular Chemistry and Materials Science Applications

Jean-François Nierengarten*[a]

Abstract: Encapsulation of a fullerene sphere in the middle of a dendritic structure prevents unfavorable effects of the C_{60} unit, such as aggregation or steric hindering. Such fullerodendrimers appear to be promising compounds for materials science applications. On the other hand, fullerodendrons with peripheral C_{60} subunits or containing a C_{60} sphere at each branching unit appear to be versatile building blocks for the preparation of fullerene-rich macromolecules with intriguing properties.

Keywords: dendrimers · fullerenes · materials science · supramolecular chemistry

Introduction

In light of their multifunctionality and specific shape, dendrimers have attracted increasing attention in the past decade, and the design of functional dendrimers is an area with unlimited possibilities for fundamental new discoveries and practical applications.[1] Of the various electro- and photoactive chromophores utilized for dendrimer chemistry, C_{60} appears to be a versatile building block, and at present a growing interest is developing in fullerene-functionalized dendrimers, that is, *fullerodendrimers*. C_{60} itself is a convenient core for dendrimers, since its almost spherical shape leads to globular systems even with low-generation dendrons.[2] Furthermore, variable degrees of addition within the fullerene core, especially from mono- up to hexaadducts, are possible.[2, 3] Finally, the unusual chemical and physical properties of fullerene derivatives[4] make fullerodendrimers attractive candidates for a variety of interesting features in supramolecular chemistry and materials science.

[a] Dr. J.-F. Nierengarten
Groupe des Matériaux Organiques
Institut de Physique et Chimie des Matériaux de Strasbourg
Université Louis Pasteur and CNRS, 23 rue du Loess
67037 Strasbourg (France)
Fax: (+33)3-8810-7246
E-mail: niereng@ipcms.u-strasbg.fr

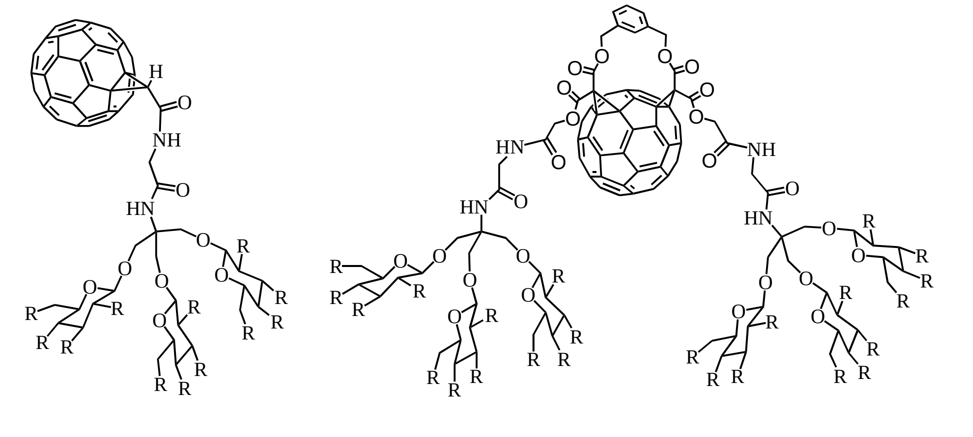
Discussion

Since the first reported preparation of dendrimers with a C_{60} core by Fréchet and co-workers,[5] several other examples have been described.[2, 3, 6] The functionalization of C_{60} with a controlled number of dendrons dramatically improves the solubility of the fullerenes and provides a compact insulating layer around the carbon sphere. This last peculiarity has been beautifully exploited in a collaborative work between the groups of Diederich, Stoddart, Echegoyen, and Leblanc.[7] Dendrimers with a fullerene core and peripheral acylated glucose units have been prepared and incorporated in Langmuir films.

The fullerene amphiphiles **1** and **2** (Figure 1) with their glycodendron headgroups are able to form stable ordered monomolecular layers at the air–water interface and show reversible behavior in successive compression/expansion cycles. The dendritic portion of **1** and **2** is effective in preventing the irreversible aggregation usually observed for amphiphilic fullerene derivatives.[8] Although the incorporation of fullerenes in thin, ordered films has been extensively studied during the past few years, liquid crystal ordering of such materials has been probed to a much lesser degree. In fact, the fullerene sphere does not behave as a mesogenic unit, and the preparation of fullerene-containing liquid crystals appears to be difficult. Deschenaux and co-workers have shown that the functionalization of C_{60} with a malonic ester bearing two mesogenic cholesterol subunits resulted in a fullerene derivative with liquid crystalline properties.[9] However, the mesomorphic behavior of this fullerene derivative is limited in comparison with that of the corresponding malonic ester precursor owing to the presence of the C_{60} core, which acts as a bulky spacer between the two mesogenic units. Recently, the same group has shown that a dendritic addend exhibits similar mesogenic properties as those of the corresponding fullerene-functionalized dendrimer **3** (Figure 2).[10, 11] As in the cases of **1** and **2**, the C_{60} core of **3** is buried in the middle of the dendritic structure and thus prevents unfavorable effects of the C_{60} unit, such as aggregation or steric hinderance. Therefore, incorporation of fullerenes into well-ordered structures can be easily achieved and such fullerodendrimers appear as promising compounds for materials science applications.

Following the preparation and study of dendrimers with a C_{60} core, we have recently succeeded in the preparation of

  0947-6539/00/0620-3667 $ 17.50+.50/0



1 R = OAc **2** R = OAc

Figure 1. Amphiphilic fullerodendrimers **1** and **2** with one and two glycodendron headgroups, respectively.[7]

dendrons with peripheral C_{60} subunits[12] or with a C_{60} sphere at each branching unit, compounds **4** and **5**, respectively (Figure 3).[13] These fullerodendrons are not only interesting building blocks for the preparation of monodisperse fullerene-rich macromolecules, they are also amphiphilic compounds capable of forming stable Langmuir films at the air–water interface.[14] A Brewster angle microscopy image of a Langmuir film of **4** is depicted at the bottom of Figure 3 and shows the high quality of the film in spite of a molecular mass of 7704.6 g mol^{-1}.[15] Furthermore, the molecular monolayers of **4** can be readily transferred onto solid substrates to yield Langmuir–Blodgett films.[14]

We have also shown that the fullerodendrons are useful building blocks for the preparation of monodisperse dendrimers of high molecular weight, and up to 16 fullerene π chromophores have been assembled around a bis(phenanthroline) copper(I) core (Figure 4).[16]

The central core in **6** appears inaccessible to external contacts as shown by molecular modeling and confirmed by electrochemical investigations.[17] Effectively, Gross and co-workers have shown that the bulky fullerodendrons around the Cu center prevent its approach on the electrode surface and its oxidation could no longer be observed.[17] Furthermore, due to the high number of fullerene subunits in **6**, a strong shielding effect is observed and only a small part of the incident light is available to the central core relative to the periphery. Photophysical studies carried out by Armaroli and co-workers revealed that the small portion of light energy able to reach the central Cu^{I} complex is returned to the external fullerenes by energy transfer.[17] Therefore, one can conclude that the central core is buried in a dendritic black box.

Conclusion

In conclusion, it appears that fullerodendrons are versatile building blocks for the preparation of fullerene-rich macromolecules with intriguing properties. By attachment of several of those dendrons to a functional group like a chromophore, ionophore, receptor, or electron donor, the fullerene-rich microenvironment should modulate the physical properties at the central core. Furthermore, due to the high number of C_{60} subunits, such dendrons could be useful as antennas for light

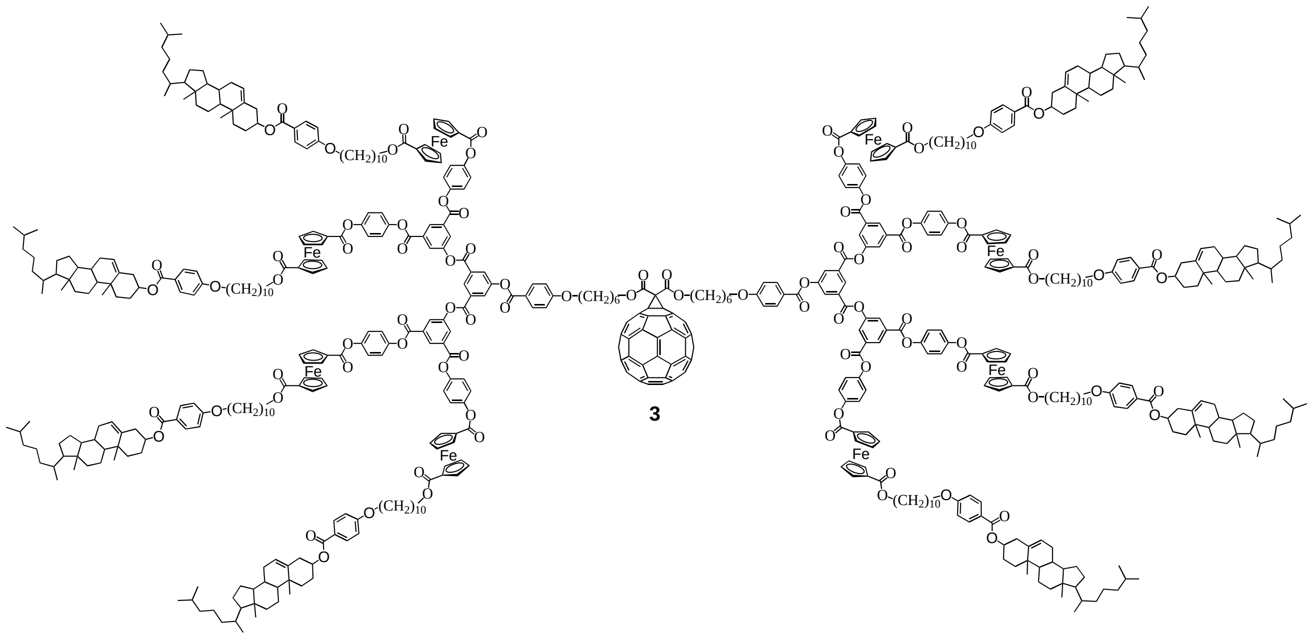


Figure 2. Liquid crystalline fullerodendrimer **3**.[10]

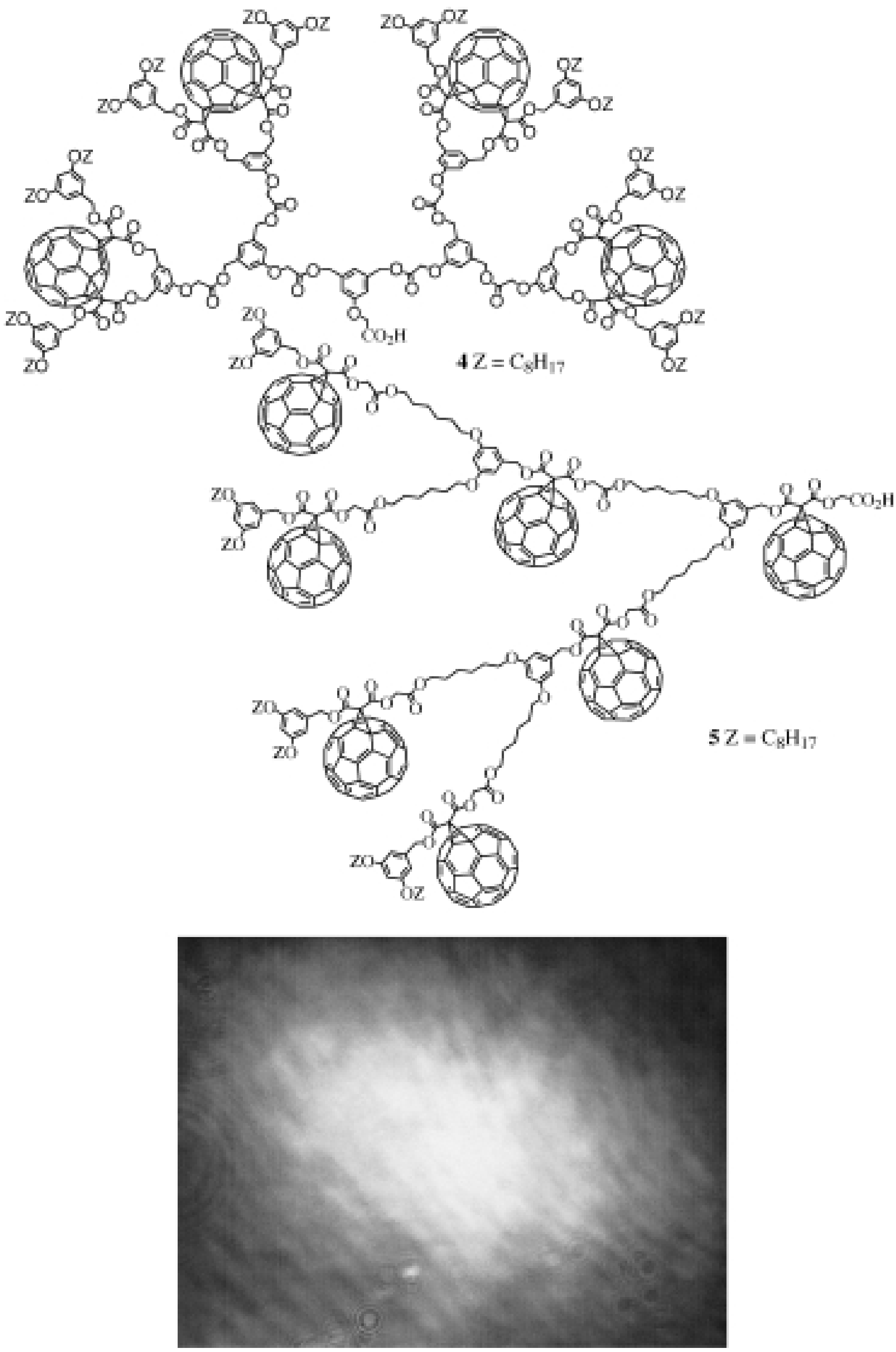


Figure 3. Top: fullerodendrons with peripheral C_{60} units (**4**)[12] and containing C_{60} spheres at each branching unit (**5**).[13] Bottom: Brewster angle microscopy image for **4** at $A = 480$ Å^2, the stripes that can be seen are interferences due to the laser light.

harvesting when attached to a suitable functional group able to act as a terminal receptor of the excitation energy. This could be achieved if the lowest excited state of the central core is lower in energy than that of the surrounding fullerene spheres.

Acknowledgement

I would like to warmly thank all my co-workers and collaborators for their outstanding contributions, and Prof. J.-F. Nicoud for his interest and his continuous support.

[1] G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic molecules: Concepts, Synthesis, Perspectives*, VCH, Weinheim, **1996**; F. Zeng,

  0947-6539/00/0620-3669 $ 17.50+.50/0

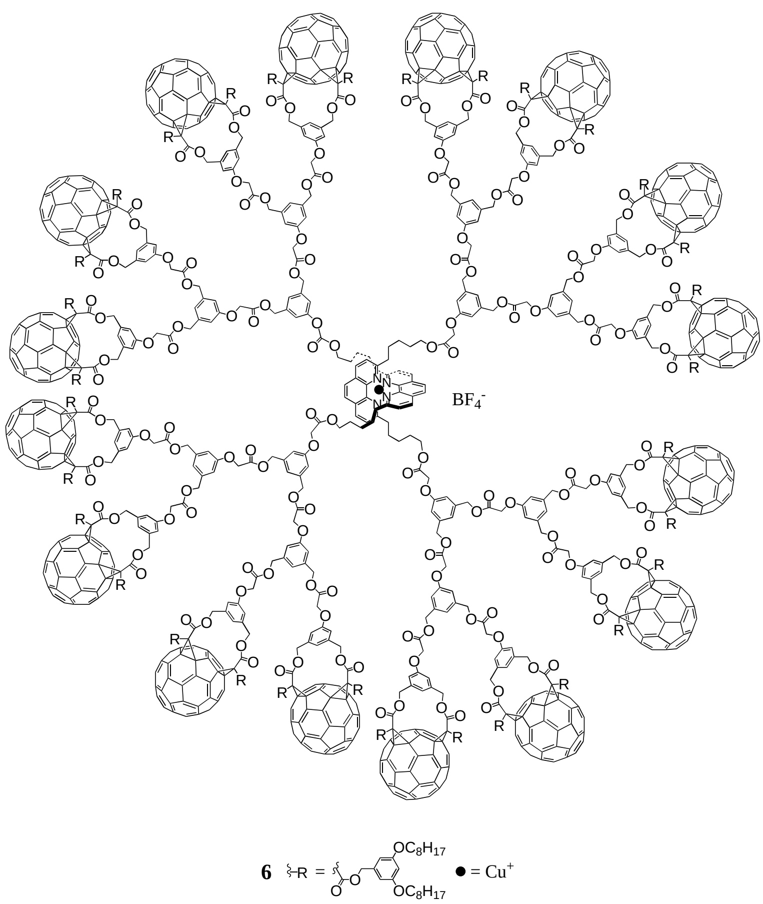


Figure 4. A fullerodendrimer with a bis(phenanthroline)Cu^I core and 16 peripheral C_{60} subunits.[16]

S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681 – 1712; D. K. Smith, F. Diederich, *Chem. Eur. J.* **1998**, *4*, 1353 – 1361; A. Archut, F. Vögtle, *Chem. Soc. Rev.* **1998**, *27*, 233 – 240; H. Frey, *Angew. Chem.* **1998**, *110*, 2313 – 2318; *Angew. Chem. Int. Ed.* **1998**, *37*, 2193 – 2197; C. Gorman, *Adv. Mater.* **1998**, *10*, 295 – 309; V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26 – 34; M. Fischer, F. Vögtle, *Angew. Chem.* **1999**, *111*, 934 – 955; *Angew. Chem. Int. Ed.* **1999**, *38*, 884 – 905; M. A. Hearshaw, J. R. Moss, *Chem. Commun.* **1999**, 1 – 8; G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689 – 1746; A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665 – 1688; A. J. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747 – 1785.

[2] X. Camps, A. Hirsch, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1595 – 1596; X. Camps, H. Schönberger, A. Hirsch, *Chem. Eur. J.* **1997**, *3*, 561 – 567; X. Camps, E. Dietel, A. Hirsch, S. Pyo, L. Echegoyen, S. Hackbarth, B. Röder, *Chem. Eur. J.* **1999**, *5*, 2362 – 2373; A. Herzog, A. Hirsch, O. Vostrowsky, *Eur. J. Org. Chem.* **2000**, 171 – 180.

[3] J.-F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J.-P. Gisselbrecht, C. Boudon, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 2238 – 2276.

[4] A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, **1994**; F. Diederich, C. Thilgen, *Science* **1996**, *271*, 317 – 323; Y. Rubin, *Chem. Eur. J.* **1997**, *3*, 1009 – 1016; M. Prato, *J. Mater. Chem.* **1997**, *7*, 1097 – 1109; L. Echegoyen, L. E. Echegoyen, *Acc. Chem. Res.* **1998**, *31*, 593 – 601; A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123 – 2165; T. Chuard, R. Deschenaux, *Chimia* **1998**, *52*, 547 – 550; F. Diederich, R. Kessinger, *Acc. Chem. Res.* **1999**, *32*, 537 – 545.

[5] K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, F. Wudl, G. Srdanov, S. Shi, C. Li, M. Kao, *J. Am. Chem. Soc.* **1993**, *115*, 9836 – 9837.

[6] C. J. Hawker, K. L. Wooley, J. M. J. Fréchet, *J. Chem. Soc. Chem. Commun.* **1994**, 925 – 926; V. J. Catalano, N. Parodi, *Inorg. Chem.* **1997**, *36*, 537 – 541; M. Brettreich, A. Hirsch, *Tetrahedron Lett.* **1998**, *39*, 2731 – 2734.

[7] F. Cardullo, F. Diederich, L. Echegoyen, T. Habicher, N. Jayaraman, R. M. Leblanc, J. F. Stoddart, S. Wang, *Langmuir* **1998**, *14*, 1955 – 1959.

[8] U. Jonas, F. Cardullo, P. Belik, F. Diederich, A. Gügel, E. Harth, A. Herrmann, L. Isaacs, K. Müllen, H. Ringsdorf, C. Thilgen, P. Uhlmann, A. Vasella, C. A. A. Waldraff, M. Walter, *Chem. Eur. J.* **1995**, *1*, 243 – 251, and references cited therein.

[9] T. Chuard, R. Deschenaux, *Helv. Chim. Acta* **1996**, *79*, 736 – 741.

[10] B. Dardel, R. Deschenaux, M. Even, E. Serrano, *Macromolecules* **1999**, *32*, 5193 – 5198.

[11] The thermotropic behavior of fullerodendrimers that display 4-cyano-4′-oxybiphenyl mesogens has been recently reported, see: N. Tirelli, F. Cardullo, T. Habicher, U. W. Suter, F. Diederich, *J. Chem. Soc. Perkin Trans. 2* **2000**, 193 – 198.

[12] J.-F. Nierengarten, D. Felder, J.-F. Nicoud, *Tetrahedron Lett.* **1999**, *40*, 269 – 272.

[13] J.-F. Nierengarten, D. Felder, J.-F. Nicoud, *Tetrahedron Lett.* **2000**, *41*, 41 – 44.

[14] D. Felder, J.-L. Gallani, D. Guillon, B. Heinrich, J.-F. Nicoud, J.-F. Nierengarten, *Angew. Chem.* **2000**, *112*, 207 – 210; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 201 – 204.

[15] In this case, the encapsulation of the fullerene sphere in a cyclic addend is able to prevent the aggregation encountered with amphiphilic fullerene derivatives, see: J.-F. Nierengarten, C. Schall, J.-F. Nicoud, B. Heinrich, D. Guillon, *Tetrahedron Lett.* **1998**, *39*, 5747 – 5750.

[16] J.-F. Nierengarten, D. Felder, J.-F. Nicoud, *Tetrahedron Lett.* **1999**, *40*, 273 – 276.

[17] N. Armaroli, C. Boudon, D. Felder, J.-P. Gisselbrecht, M. Gross, G. Marconi, J.-F. Nicoud, J.-F. Nierengarten, V. Vicinelli, *Angew. Chem.* **1999**, *111*, 3895 – 3899; *Angew. Chem. Int. Ed.* **1999**, *38*, 3730 – 3733.

