# Liquid-Crystalline Fullerodendrimers which Display Columnar Phases

**Julie Lenoble, Bertrand Donnio, Daniel Guillon, Robert Deschenaux***

Université de Neuchâtel, Institut de Chimie, Rue Emile Argand 11, Case postale 158, 2009 Neuchâtel, Switzerland

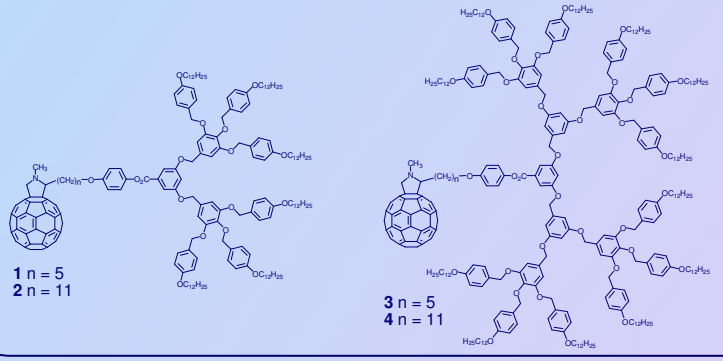
## Introduction

We have demonstrated that the use of liquid-crystalline dendrimers was an elegant and versatile way to obtain [60]fullerene-containing thermotropic liquid crystals,[1] which are promising chemical components for the development of nanotechnologies by the "bottom-up" approach. In particular, $C_{60}$-containing liquid crystals which display columnar phases are of interest for electronic and optoelectronic applications (e.g., one-dimensional electron transportation).

To synthesize fullerodendrimers which display columnar phases, we used the poly(benzylether) dendrons described by Percec and *al.*, which display columnar and/or cubic phases.[2]

Four fulleropyrrolidines have been synthesized, two of second generation (G2)[3] and two of third generation (G3).

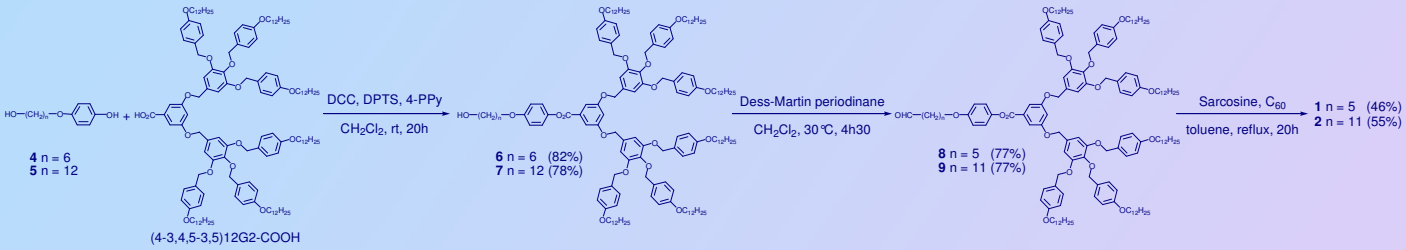
## Structures of Fullerodendrimers G2 and G3



**1** n = 5
**2** n = 11

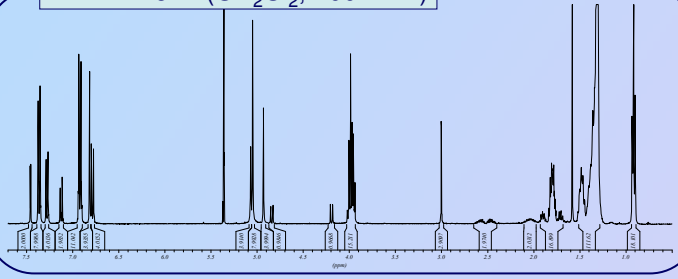
**3** n = 5
**4** n = 11

## Synthesis of Fulleropyrrolidines **1-4**




Fulleropyrrolidines **3** and **4** were synthesized following the same synthetic procedure, starting from the acid of third generation : (4-3,4,5-(3,5)$^2$)12G3-COOH

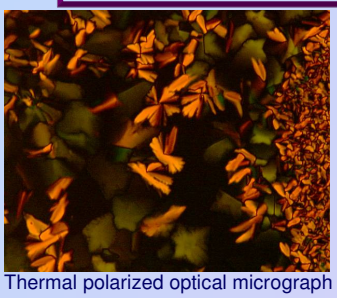
## $^1$H-NMR of **1** ($CD_2Cl_2$, 400 MHz)



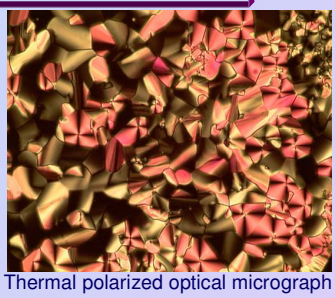
## Liquid-Crystalline Properties

The liquid-crystalline properties of fulleropyrrolidines **1-4** were studied by POM, DSC, and XRD. Compounds **1**, **2**, and **4** display columnar phases identified from their typical textures. Compound **3** does n0t display any typical texture.

| | | | | | |
|---|---|---|---|---|---|
| **1** : $Col_r$ | ⟶ I | 80 °C | **3** : Cr | ⟶ $Col_h$ | 54 °C |
| | | | $Col_h$ | ⟶ I | 84 °C |
| **2** : $Col_r$ | ⟶ I | 74 °C | **4** : $Col_h$ | ⟶ I | 84 °C |



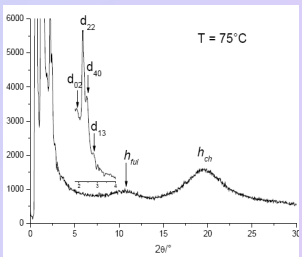
Thermal polarized optical micrograph of the texture displayed by **1** at 78 °C in the rectangular columnar phase



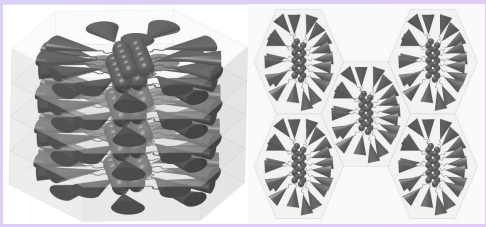
Thermal polarized optical micrograph of the texture displayed by **4** at 83 °C in the hexagonal columnar phase

## XRD Studies and Supramolecular Organizations

For fullerodendrimers **1** and **2**, the XRD diffraction patterns registered within the temperature range of the mesophases displayed six sharp reflections, which were indexed as the (11), (20), (02), (22), (40), and (13) reflections of a two-dimensional rectangular lattice of *c2mm* symmetry (for **1**, $a$ = 128.6 Å and $b$ = 86.0 Å; for **2**, $a$ = 129.6 Å and $b$ = 89.4 Å). Two broad reflections located at $h_{ch}$ = 4.6 Å and $h_{ful}$ 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 the $C_{60}$ units arranged according to a hexagonal close compact packing ($h_{ful}$ = √3/2 x ϕ, ϕ being the diameter of $C_{60}$, i.e., 10 Å). To understand the molecular organization of **1** and **2** in the columnar phases, 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 **1** and **2**, respectively), this number turned out to be about 10 for each compound.




XRD diffractogramm of **1**



Postulated supramolecular organizations of **1** and **2** within the rectangular columnar phases

For fullerodendrimers **3** and **4**, the XRD diffraction patterns displayed only one sharp reflection, which was indexed as the (10) reflection of a two-dimensional hexagonal lattice of *p6mm* symmetry ($a$ = 45.3 Å for **3** and **4**) according to POM observation for **4**. Only the broad reflection located at $h_{ch}$ = 4.5 Å is present in the wide angle region. The number of molecules included in a slice of 10 Å thickness was calculated. From the values of the lattice parameters and the estimated molecular volumes (8050 and 8200 Å$^3$ for **3** and **4**, respectively), this number turned out to be about 2 for each compound.

## Conclusion

Four new fullerodendrimers have been synthesized using poly(benzylether) dendrons of second or third generations. G2 compounds display rectangular columnar phases of *c2mm* symmetry, while G3 compounds display hexagonal columnar phases of *p6mm* symmetry.
XRD studies allowed postulating supramolecular organization within the columnar phases.

## Bibliography

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2. Percec V., Cho W.-D., Ungar G., Yeardley D. J. P. *J. Am. Chem. Soc.* **2001**, *123*, 1302.
3. Lenoble J., Maringa M., Campidelli S., Donnio B., Guillon D., Deschenaux R. *Org. Lett.* **2006**, *8*, 1851.

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