Liquid-Crystalline Dendrimers : Versatile Synthetic Plateforms for the Design of Supramolecular Functional Materials

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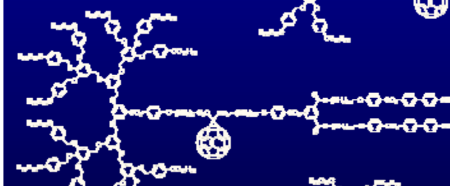
Convergent-type dendrimers are interesting macromolecules which possess a well-defined structure. Furthermore, their size, shape and functionality can be modulated by synthesis. We have shown that grafting liquid-crystalline dendrimers onto C_{60} by cycloaddition reactions (Bingel reaction → methanofullerenes; 1,3-dipolar cycloaddition reaction → fulleropyrrolidines) is an effective and elegant way to control the unfavorable effect (on the mesomorphic behavior) of the isotropic C_{60} unit. We demonstrate here the precise role played by dendrimers for the design of fullerene-containing liquid crystals with tailor-made properties.

Methanofullerenes

1

2



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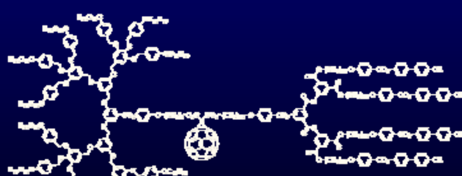

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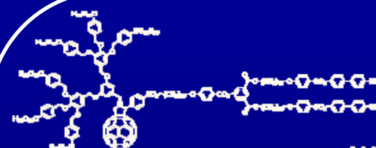
Fulleropyrrolidines



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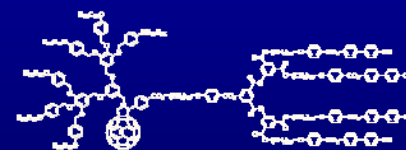

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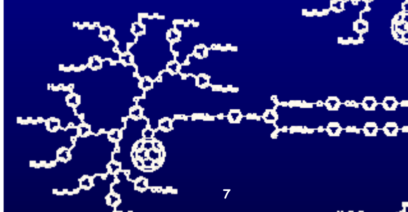

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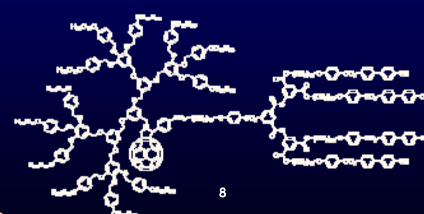

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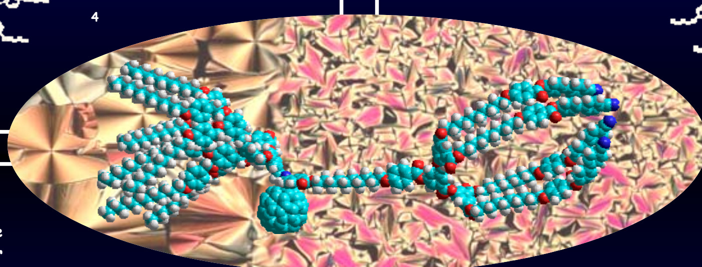


Mesomorphic properties

When the generation of the poly(benzyl ether) dendron is higher than the generation of the poly(aryl ester) dendron (compounds 1, 3, 4, 5, 7 and 8), the nature of the liquid-crystalline phase is dictated by the poly(benzyl ether) dendrimer and the fullerodendrimers display columnar phases.

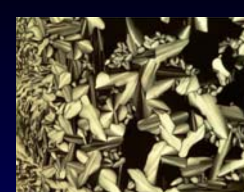
When the dendrons have the same generation (compounds 2 and 6), the fullerodendrimers display smectic phases. In this case, the liquid-crystalline properties are governed by the poly(aryl ester) dendrimer.

Composé	Tg (°C)	Transition	T (°C)	ΔH (kJ/mol)
1	-	$G \rightarrow Col_r$	75	0.4
		$Col_r \rightarrow I$	97	17.7
2	45	$SmA \rightarrow I$	147	22.2
3		$G \rightarrow Col_r$	83	1.4
		$Col_r \rightarrow I$	110	18.7
4	a	$Col_r \rightarrow Col_{r'}$	99	3.5
		$Col_{r'} \rightarrow Col_h$	150	6.2
		$Col_h \rightarrow I$	157	10.3
5	31	$Col_r \rightarrow I'$	105[b]	
		$I' \rightarrow I$	108[b]	13.9[c]
6	a	$SmC \rightarrow SmA$	116[d]	
		$SmA \rightarrow I$	155	21.7
7	a	$Col_r \rightarrow I$	109	16.4
8	a	$Col_r \rightarrow I$	152	23.7

[a]Not detected. [b]Rate: 5°·min^{-1}. [c]Sum of enthalpies. [d]Determined by polarized optical microscopy.

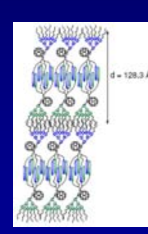
Liquid-crystalline phases

Smectic A phase displayed by compound **2** at 146°C.



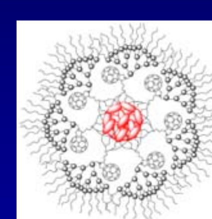
Rectangular columnar phase displayed by compound **8** at 145°C.

Typical textures of the mesophases were observed by POM.



Postulated supramolecular organization of **2** within the smectic A phase.

XRD investigations and molecular modeling revealed that the supramolecular organization of the title compounds is governed by (1) the "aliphatic therminal chains/mesogenic groups" ratio, (2) the effective lateral interactions between the cyanobiphenyl mesogenic groups, (3) the effective microsegregation of the dendrons, and (4) the deformation of the dendritic core.



Postulated supramolecular organization of **8** within the rectangular columnar phase.

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References

V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **2001**, *123*, 1302.
C. Bingel, *Chem. Ber.* **1993**, *126*, 1957.
M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519.
J. Lenoble, S. Campidelli, N. Maringa, B. Donnio, D. Guillon, N. Yevlampieva, R. Deschenaux, *J. Am. Chem. Soc.* **2007**, *129*, 9941.
J. Lenoble, Thesis, 2007, University of Neuchâtel.