ORGANIC
LETTERS

2006
Vol. 8, No. 9
1851−1854

Liquid-Crystalline Fullerodendrimers which Display Columnar Phases

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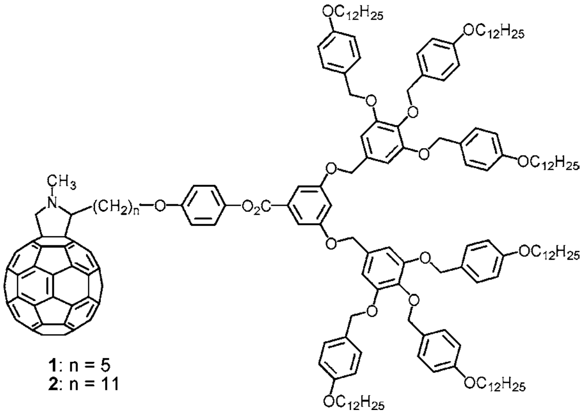
Received February 15, 2006

ABSTRACT



1: n = 5
2: n = 11

The title compounds were synthesized by applying the 1,3-dipolar cycloaddition reaction of aldehyde-based poly(benzyl ether) dendrimers and sarcosine (*N*-methylglycine) to [60]fullerene (C_{60}). The dendritic building blocks used to functionalize C_{60} displayed cubic and hexagonal columnar phases. The fullerene derivatives showed rectangular columnar phases of *c*2*mm* symmetry.

The design of supramolecular [60]fullerene (C_{60}) assemblies, in which the [60]fullerene-containing molecular units are organized in a specific and controllable manner, is an elegant and appealing way to exploit the physical properties of C_{60} in materials science (e.g., photoactive dyads and triads,[1] photovoltaic devices[2]). Grafting dendrimers onto C_{60} (fullerodendrimers) allowed this goal to be reached, as demonstrated by the formation of ordered and stable Langmuir and Langmuir−Blodgett films[3] and micelles.[4] Fullerene-containing thermotropic liquid crystals[5−10] are promising chemical components for the development of nanotechnologies by the "bottom-up" approach (e.g., photoactive supramolecular switches[5c,h] and supramolecular solar cell devices[5e]). Functionalization of C_{60} with liquid-crystalline poly(arylester) dendrimers containing mesomorphic groups at the periphery by applying either the Bingel reaction[11] (from malonate

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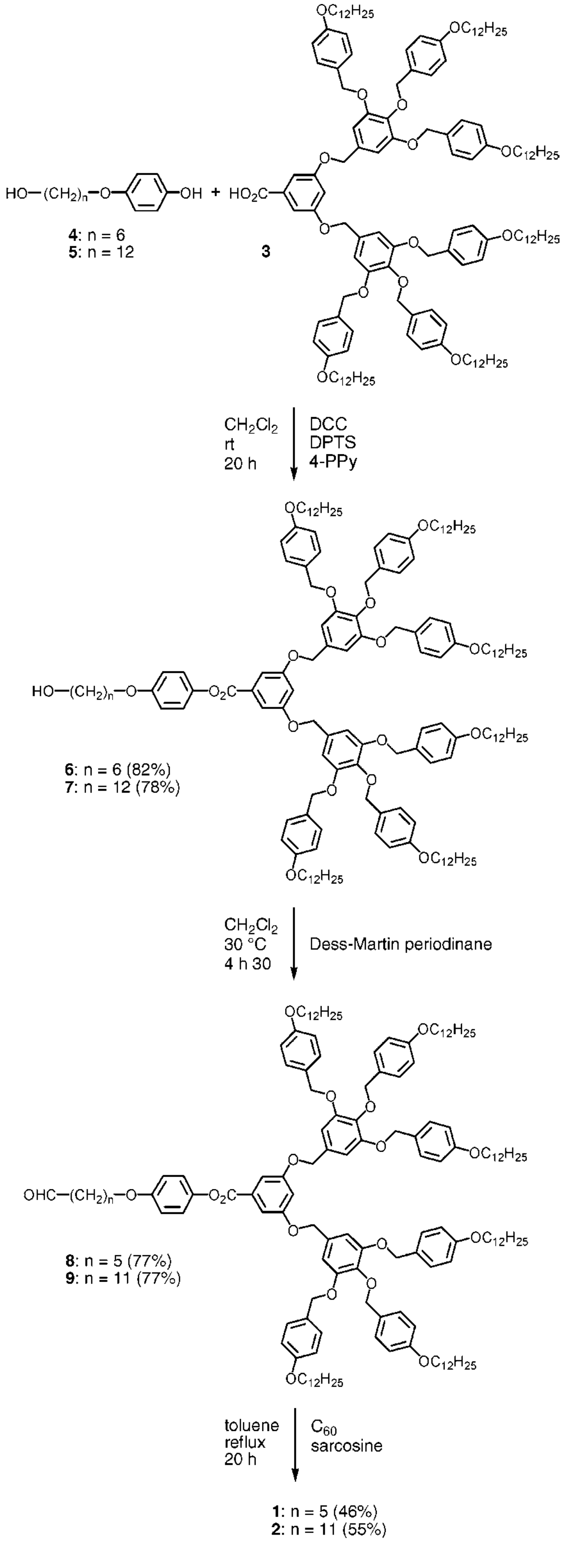
10.1021/ol0603920 CCC: $33.50

derivatives yielding methanofullerenes[5b,d,f,g,12]) or the 1,3-dipolar cycloaddition reaction[13] (from aldehyde derivatives yielding fulleropyrrolidines[5e,f,h,j]) led to a rich collection of macromolecular liquid crystals, which display smectic A, nematic, and chiral nematic (cholesteric) phases. In such systems, C_{60} is embedded in the dendrimer. As a consequence, the supramolecular organization within the liquid crystal state depends mostly on the nature of the mesomorphic units.

Fullerene-containing liquid crystals, which display columnar phases, are of interest for electronic and optoelectronic applications (e.g., one-dimensional electron transportation). The synthetic approach we have developed to obtain fullerene-containing liquid crystals (see above) can be adapted to prepare such compounds. Therefore, we envisaged that functionalization of C_{60} with liquid-crystalline dendrimers, which exhibit columnar mesomorphism, should lead to fullerenes which also show columnar mesomorphism. To functionalize C_{60}, we decided to use the poly(benzyl ether) dendrimers developed by Percec[14] (prepared by a convergent synthesis[15]) since these compounds give rise to cylindrical and spherical supramolecular dendrimers that subsequently self-organize into columnar and cubic lattices, respectively. Second-generation poly(benzyl ether) dendron (4-3,4,5-3,5)-12G2-CO_2H **3** (Scheme 1), the carboxylic acid function of which allows structural modifications at the focal point, was selected as a first candidate.[14b] Compound **3** shows a cubic phase [Cr 35 Cub($Im\bar{3}m$) 196 I],[14b] the corresponding methylester derivative a hexagonal columnar phase [Cr −19

Scheme 1. Synthesis of Fulleropyrrolidines **1** and **2**



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$\mathrm{Col_h}$($p6mm$) 71 I], and the corresponding methyl alcohol derivative hexagonal columnar and cubic phases [Cr 57 $\mathrm{Col_h}$($p6mm$) 87 Cub($Pm\bar{3}n$) 101 I].[14b]

Columnar mesomorphism was already observed in two particular cases. First, attachment of five aromatic groups around one pentagon of C_{60} yielded conical molecules, the stacking of which gave rise to columnar phases.[8] Second, self-assembled columns were obtained by mixing two nonmesomorphic compounds, a fullerene derivative, and a disk-like molecule; the C_{60} units were located between the columns.[10] Our concept is a more general approach, owing to the great number of dendrimers that can be used, and should allow the design of fullerene-containing liquid crystals with tailor-made mesomorphic properties.

The synthesis of target fulleropyrrolidines **1** and **2** is presented in Scheme 1. Condensation of **3** with **4** or **5** in the presence of *N*,*N′*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridinium toluene-*p*-sulfonate (DPTS), and 4-pyrrolidinopyridine (4-PPy) led to alcohol intermediates **6** and **7**, which were oxidized to give aldehydes **8** and **9**. Addition of the latter with *N*-methylglycine (sarcosine) to C_{60} gave **1** and **2**.

Compounds **6**−**9** were purified by column chromatography. Fulleropyrrolidines **1** and **2** were purified by column chromatography and precipitated from MeOH. The structure and purity of all compounds were confirmed by NMR spectroscopy, mass spectrometry, GPC (all compounds were found to be monodisperse), and elemental analysis. The UV−vis spectra of **1** and **2** were in agreement with the fulleropyrrolidine structure.

The thermal and liquid-crystalline properties of **1**, **2**, and **6**−**9** were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The phase transition temperatures are reported in Table 1, and the XRD patterns and structural parameters of the phases are in the Supporting Information.

The columnar and cubic phases could be identified by POM from the observation of typical textures (columnar phase, pseudo-focal conic texture; cubic phase, isotropic (black) texture). On heating, compounds **7** and **9** gave, from 50 to 60 °C, a series of endothermic and exothermic peaks (DSC) revealing melting and crystallization processes. The compounds with the longer flexible spacer cleared at lower temperatures than the materials containing the shorter spacer.

The cubic nature of the phases displayed by **6**, **8**, and **9** was confirmed by XRD. For **6**, 3 orders of diffraction in the square spacing ratio $\sqrt{2}$, $\sqrt{3}$, and $\sqrt{4}$, which can be indexed as (110), (111), and (200) in a P lattice or as (200), (211), and (220) in an I lattice, were observed. As for **8** and **9**, the XRD patterns exhibited only two orders of diffraction in the cubic phase in the ratio $\sqrt{3}$ and $\sqrt{4}$, the $\sqrt{2}$ reflection being too weak to be measured. The XRD patterns of the hexagonal columnar phases shown by **7**, **8,** and **9** presented only one signal in the small angle region. On the basis of the optical textures observed for these compounds, which are typical for columnar phases (an illustrative example is given in Figure 1), this reflection was indexed as the (10) reflection of a two-dimensional hexagonal lattice. As already found for similar dendrons, the cores of the columns or of the micelles for the cubic phases result from interactions between the polar central parts of the dendrons, the alkyl chains

Table 1. Phase Transition Temperatures and Enthalpy Changes of **1**, **2**, and **6**−**9**

compound	T_g[a] (°C)	transition[b]	T[c] (°C)	ΔH (kJ/mol)
6		(I → Cub)[d]	(∼64)[e]	
		Cr → I	66	2.8
7		Cr → $\mathrm{Col_h}$	57	6.1
		$\mathrm{Col_h}$ → I	88	7.6
8	37	Cub → $\mathrm{Col_h}$	84	6.3
		$\mathrm{Col_h}$ → I	98	6.8
9		Cr → $\mathrm{Col_h}$	55	6.8
		($\mathrm{Col_h}$ → Cub)[d]	(44)[f]	3.8
		$\mathrm{Col_h}$ → I	88	7.7
1	[g]	$\mathrm{Col_r}$ → I	80	3.9
2	46	$\mathrm{Col_r}$ → I	74	7.2

[a] T_g = glass transition temperature determined during the second heating. [b] Cr = semicrystalline solid, $\mathrm{Col_h}$ = hexagonal columnar phase of $p6mm$ symmetry, $\mathrm{Col_r}$ = rectangular columnar phase of $c2mm$ symmetry, Cub = cubic phase, I = isotropic liquid. [c] Temperatures are given as the onset values taken from the second heating run. [d] Monotropic transition. [e] Determined by POM. [f] Temperature is given as the onset value taken from the first cooling run. [g] Not detected.

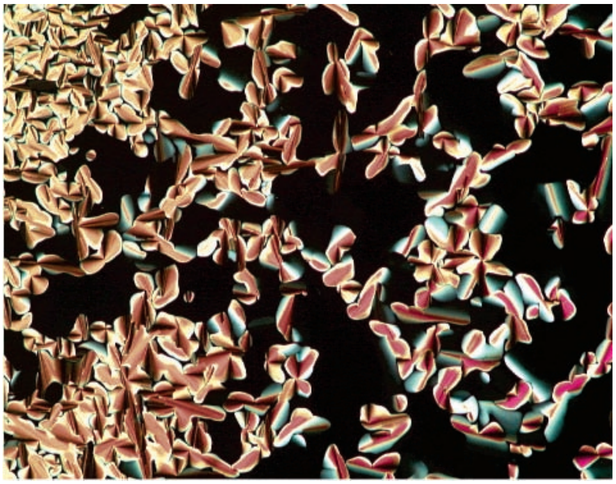

Figure 1. Thermal polarized optical micrograph of the hexagonal columnar texture (pseudo-focal conic and homeotropic textures) displayed by **9** at 87 °C.

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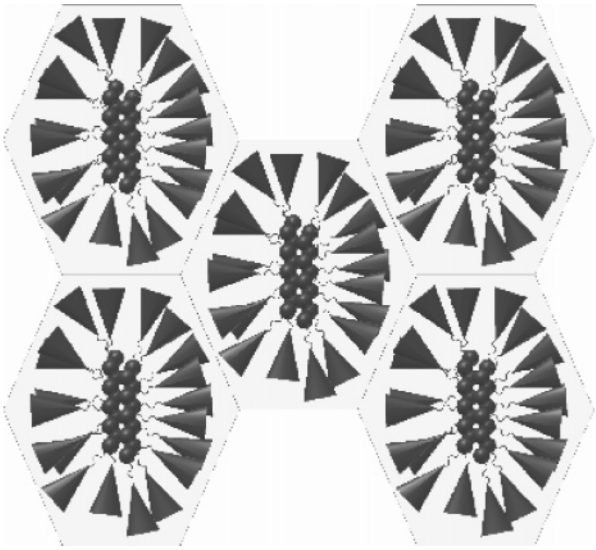

Figure 2. Postulated supramolecular organization of **1** and **2** within the rectangular columnar phases.

constituting the aliphatic medium between the columns or the micelles.

For fullerodendrimers **1** and **2**, 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 **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 $h_{ful} \sim 8.7$ 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 ($h_{ful} = (\sqrt{3}/2) \times \phi$, 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. A close hexagonal packing of the C_{60} units was then simulated (Figure 2): bundles of 10 dendrons are 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. The supramolecular organization of **1** and **2** within the columns and the texture of the columnar phase displayed by **1** are shown in the Supporting Information.

The results reported here (columnar phases) and those we have already published (smectic A, nematic, and chiral nematic phases) prove that covalent functionalization of C_{60} with liquid-crystalline dendrimers is a valuable concept for the design of fullerene-containing liquid crystals which display tailor-made mesomorphic properties.

Acknowledgment. R.D. thanks The Swiss National Science Foundation (Grant 200020-103424) for financial support. B.D. and D.G. thank Mr. N. Beyer for his help with some of the illustrations.

Supporting Information Available: Synthetic procedures and analytical data of all new compounds and copies of ^{1}H NMR spectra for **1** and **2**; XRD data of the mesophases, organization of **1** and **2** within the columns, and texture displayed by **1** in the columnar phase. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0603920