Liquid-crystalline methanofullerodendrimers which display columnar mesomorphism†‡

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Liquid-crystalline methanofullerodendrimers were synthesized *via* the Bingel addition reaction of mesomorphic malonate derivatives and C_{60}. Second- and third-generation poly(benzyl ether) dendrons were selected as liquid-crystalline promoters to induce columnar mesomorphism. Based on a convergent and modular synthetic methodology, symmetrical (two identical dendrons) and non-symmetrical (two different dendrons) dendrimers were prepared, as well as hemidendrimers (only one dendron). The liquid-crystalline properties of the malonates and fullerodendrimers were investigated by polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction. All the malonates give rise to hexagonal columnar phases of *p6mm* symmetry. As for the fullerodendrimers, the second-generation hemidendrimer shows a rectangular columnar phase of *c2mm* symmetry, while the other materials give rise to hexagonal columnar phases of *p6mm* symmetry.

Introduction

[60]Fullerene-containing liquid crystals[1] displaying columnar phases are of interest for electronic and optoelectronic applications (*e.g.*, one-dimensional electron transportation). So far, only a few examples have been reported in the literature: columnar phases were obtained by (1) attaching five aromatic groups around one pentagon of [60]fullerene (C_{60}),[2] (2) complexing C_{60} with liquid-crystalline dendritic porphyrins,[3] (3) mixing two non-mesomorphic compounds, one of which is a C_{60}-triphenylene derivative,[4] and (4) functionalizing C_{60} with mesomorphic dendrimers.[5]

The use of liquid-crystalline dendrimers as mesomorphic promoters to functionalize C_{60} has two advantages: firstly, the fullerene cores are isolated from each other, and thus, C_{60}–C_{60} interactions (responsible for the formation of aggregates), which may be detrimental to the formation of mesophases, are reduced or even suppressed,[6] and secondly, the supramolecular organization within the liquid crystal state can be controlled owing to the numerous possibilities which can be used to modify the structure of the dendrimers (generation, polarity and stiffness of the core, number of branching units, nature of the end-groups).[7]

With a view to designing liquid-crystalline fullerenes which display columnar phases, we selected poly(benzyl ether) dendrons[8] as a source of mesomorphism. In a first study,[5a] C_{60} was functionalized with second-generation poly(benzyl ether) dendrons; rectangular columnar phases (*c2mm* symmetry) were obtained. Within the rectangular columnar phases, the columns were formed by a hexagonal close compact packing of C_{60}, surrounded by the dendrons, the alkyl chains forming the outer layer of the columns. In a second study,[5b] Janus-type fulleropyrrolidines bearing a poly(benzyl ether) dendron functionalized with alkyl chains and a poly(aryl ester) dendron functionalized with cyanobiphenyl units were synthesized. The generation of each dendron was varied, and, depending on the generation, smectic (C and/or A) or rectangular columnar (*c2mm* symmetry or *p2gg* symmetry) phases were obtained. We have demonstrated that the supramolecular organization of the liquid-crystalline fullero(codendrimers) within the mesophases is governed by (1) the "aliphatic terminal chains/mesogenic groups" ratio, (2) effective lateral interactions between the cyanobiphenyl mesogenic groups, (3) microsegregation of the dendrons, and (4) deformation of the dendritic core. In a third study,[9] addition of two poly(benzyl ether) dendrons onto C_{60} led to fulleropyrrolidines which were found to be non-mesomorphic. The absence of liquid-crystalline properties for those materials is the consequence of the formation of materials which lack shape specificity due to conformations induced by C_{60}.

Obviously, the formation of columnar phases for fullerene-containing liquid crystals is not yet fully understood. An important step to better our understanding of the "*structure–supramolecular organization*" relationship for liquid-crystalline fullerodendrimers could be achieved by investigating the properties of methanofullerenes and of their corresponding malonates. Such a study would emphasize the role played by C_{60} in the formation, structure, and stability of the columnar phases.

We report, herein, the synthesis, characterization, mesomorphic properties, and supramolecular organization of methanofullerodendrimers **1–5** (Charts 1 and 2) and compare their properties with those of the corresponding malonates.

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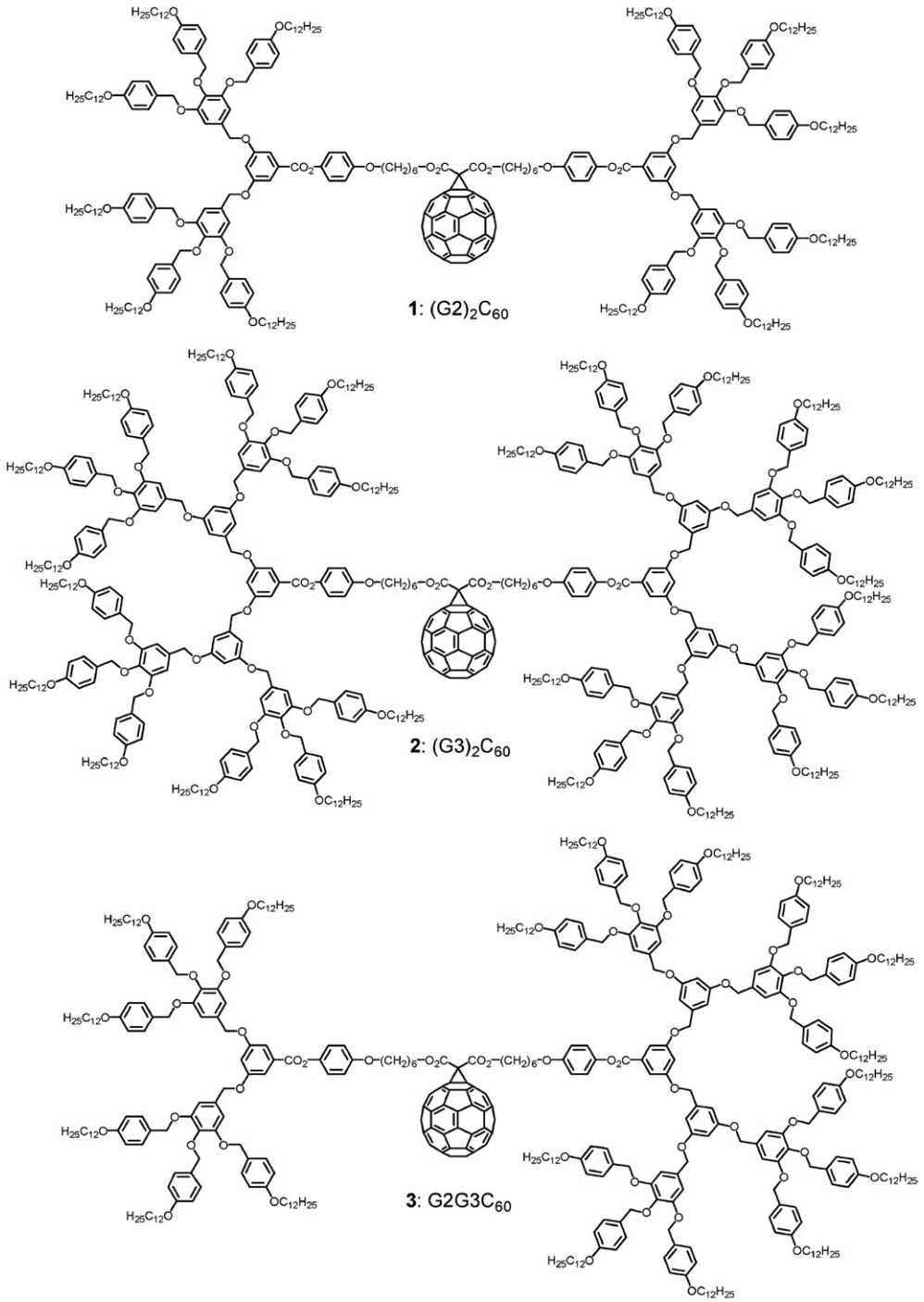


Chart 1

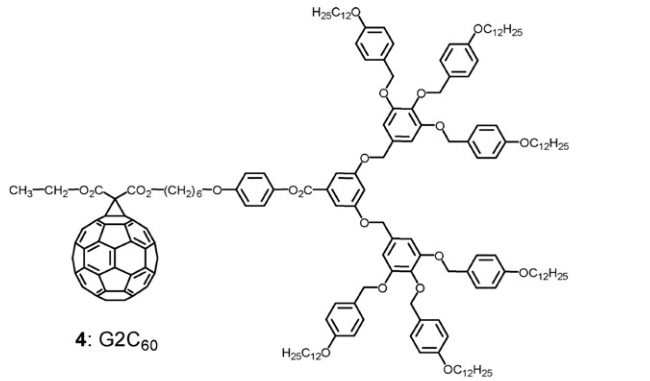
Results and discussion

Design

This study is based on symmetrical [$(G2)_2C_{60}$ (**1**): two second-generation poly(benzyl ether) dendrons; $(G3)_2C_{60}$ (**2**): two third-generation poly(benzyl ether) dendrons] and non-symmetrical [$G2G3C_{60}$ (**3**): mixed second- and third-generation poly (benzyl ether) dendrons] fullerodendrimers (Chart 1) and fullerohemidendrimers [$G2C_{60}$ (**4**): second-generation poly(benzyl ether) dendron; $G3C_{60}$ (**5**): third-generation poly(benzyl ether) dendron] (Chart 2).

Synthesis

The dendrons were synthesized *via* a convergent approach.[10] The malonates were added onto C_{60} *via* the Bingel reaction.[11] The syntheses of **6**,[5a] **8**,[12] and **9**[8b] have already been described elsewhere.



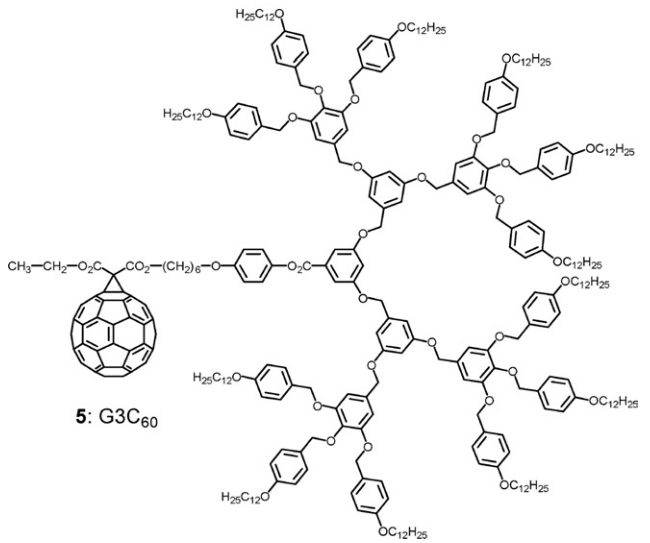


Chart 2

The synthesis of methanofullerene $(G2)_2C_{60}$ (**1**) is presented in Scheme 1. Condensation of **6** with malonyl chloride gave malonate derivative $(G2)_2$Mal (**7**), which was added to C_{60} to give $(G2)_2C_{60}$ (**1**).

The synthesis of fullerodendrimer $(G3)_2C_{60}$ (**2**) is illustrated in Scheme 2. Esterification of **8** and **9** in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridinium toluene-*p*-sulfonate (DPTS), and 4-pyrrolidinopyridine (4-Ppy) led to alcohol intermediate **10**, which was reacted with Meldrum acid (2,2-dimethyl-1,3-dioxane-4,6-dione) to furnish carboxylic acid **11**. Esterification of the latter with **10** gave malonate $(G3)_2$Mal (**12**), which was used in the addition reaction with C_{60} [→ $(G3)_2C_{60}$ (**2**)].

The synthesis of methanofullerene $G2G3C_{60}$ (**3**) is reported in Scheme 3. Condensation of **6** with Meldrum acid gave **13**, which was esterified with **10** to yield malonate G2G3Mal (**14**). Addition of G2G3Mal (**14**) with C_{60} furnished $G2G3C_{60}$ (**3**).

The synthesis of fullerohemidendrimers $G2C_{60}$ (**4**) (Scheme 4) and $G3C_{60}$ (**5**) (Scheme 5) required the preparation of G2Mal (**15**) and G3Mal (**16**), respectively, which were obtained by condensation of ethyl malonyl chloride with the appropriate alcohol derivative [**6** → G2Mal (**15**), and **10** → G3Mal (**16**)]. Addition of G2Mal (**15**) or G3Mal (**16**) to C_{60} led to $G2C_{60}$ (**4**) or $G3C_{60}$ (**5**), respectively.

The structure and purity of all compounds were confirmed by ^{1}H NMR spectroscopy, GPC (all compounds were found to be monodisperse), UV-vis spectroscopy, and elemental analysis.

Liquid-crystalline properties

The liquid-crystalline and thermal properties of the malonate and fullerene derivatives were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The liquid-crystalline and thermal properties of the intermediates were investigated by POM and DSC. The phase transition temperatures and enthalpies are reported in Table 1. The XRD data are collected in Table 2.

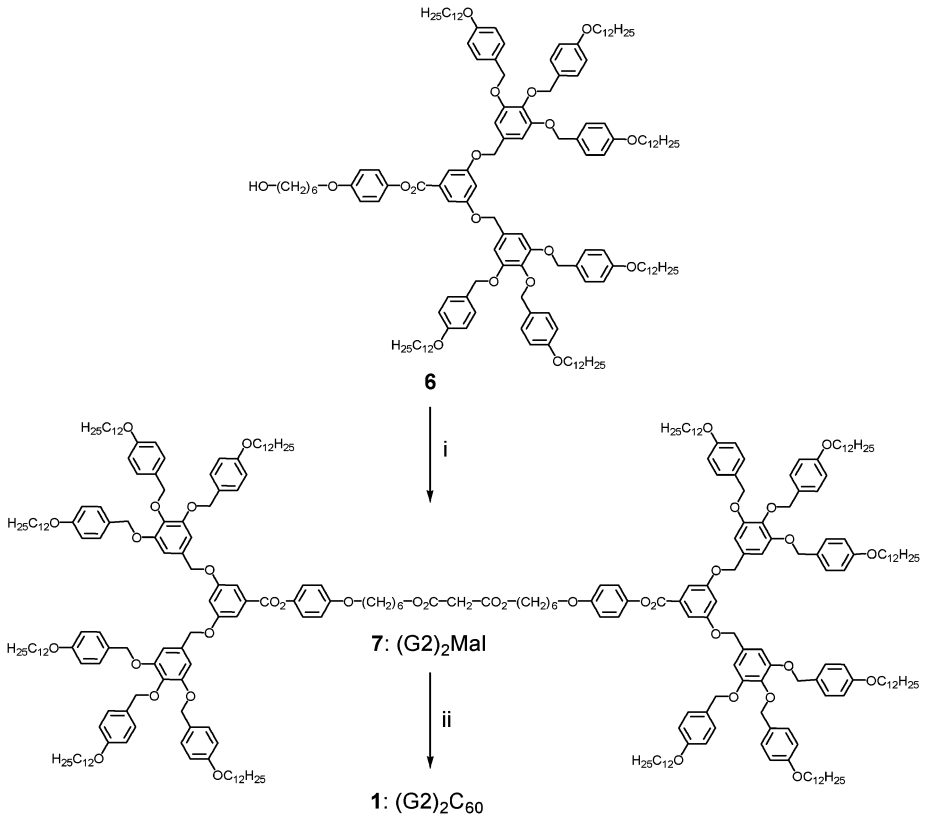
With the exception of $(G2)_2C_{60}$ (**1**), which is non-mesomorphic, all methanofullerenes display columnar mesomorphism. For $(G3)_2C_{60}$ (**2**), $G2G3C_{60}$ (**3**), and $G3C_{60}$ (**5**), hexagonal columnar phases (*p6mm* symmetry) were obtained, while for $G2C_{60}$ (**4**) a rectangular columnar phase (*c2mm* symmetry) was detected. A typical texture was observed by POM only for $G3C_{60}$ (**5**) (Fig. 1). The clearing points indicate that the stability of the mesophase increases with the dendrimer generation [*e.g.* 68 °C for $G2C_{60}$ (**4**), 85 °C for $G3C_{60}$ (**5**)] in agreement with previous results.[14]

All the malonates give rise to hexagonal columnar phases (*p6mm* symmetry). Typical textures were observed by POM (Fig. 2 and 3). As expected, the stability of the mesophases increases with the dendrimer generation [clearing points: 88 °C for $(G2)_2$Mal (**7**), 105 °C for G2G3Mal (**14**), and 109 °C for $(G3)_2$Mal (**12**); 86 °C for G2Mal (**15**) and 114 °C for G3Mal (**16**)]. As already observed for other compounds,[14] grafting of C_{60} onto malonates lowered the isotropization temperature, or even suppressed the liquid-crystalline properties [*i.e.* for $(G2)_2C_{60}$ (**1**)].

X-Ray investigations

Compounds $(G2)_2C_{60}$ (1) and $(G2)_2$Mal (7). Whereas compound $(G2)_2C_{60}$ (**1**) is not mesomorphic, its malonate precursor $(G2)_2$Mal (**7**) shows complicated thermal behavior. The sample melts into an amorphous solid, which then crystallizes, and finally melts into the mesophase which was identified as a hexagonal columnar phase. X-Ray diffraction patterns recorded every 5 °C from 40 to 90 °C correspond systematically to a mixture of amorphous, crystalline, columnar and isotropic phases depending upon temperature. This behavior highlights some kinetic and thermodynamic features associated with the phases transformation. This mesophase is thermodynamically unstable.

Compounds $(G3)_2C_{60}$ (2) and $(G3)_2$Mal (12). Above *ca.* 40 °C, both compounds exhibit a hexagonal columnar phase characterized by a series of three sharp and intense diffraction peaks in the small-angle region, in the ratio $1 : \sqrt{3} : \sqrt{4}$. The X-ray diffraction patterns contain also two diffuse signals at *ca.* 8.5 and 4.6 Å, which are attributed to an intracolumnar periodicity along the columnar axis and to the liquid-like arrangement of the terminal aliphatic chains of the dendrons, respectively. The hexagonal cell parameters of both compounds are almost the same, and do not vary significantly as a function of temperature. Therefore, the lateral and stacking arrangements of $(G3)_2C_{60}$ (**2**) and $(G3)_2$Mal (**12**) are essentially governed by the dendritic parts.



Scheme 1 (i) Malonyl chloride, Et_3N, CH_2Cl_2, r.t., overnight, 27%; (ii) C_{60}, DBU, I_2, toluene, r.t., overnight, 26%. For abbreviations, see ref. 13.

The C_{60} unit is encapsulated in the dendritic matrix and has no significant influence on the supramolecular organization.

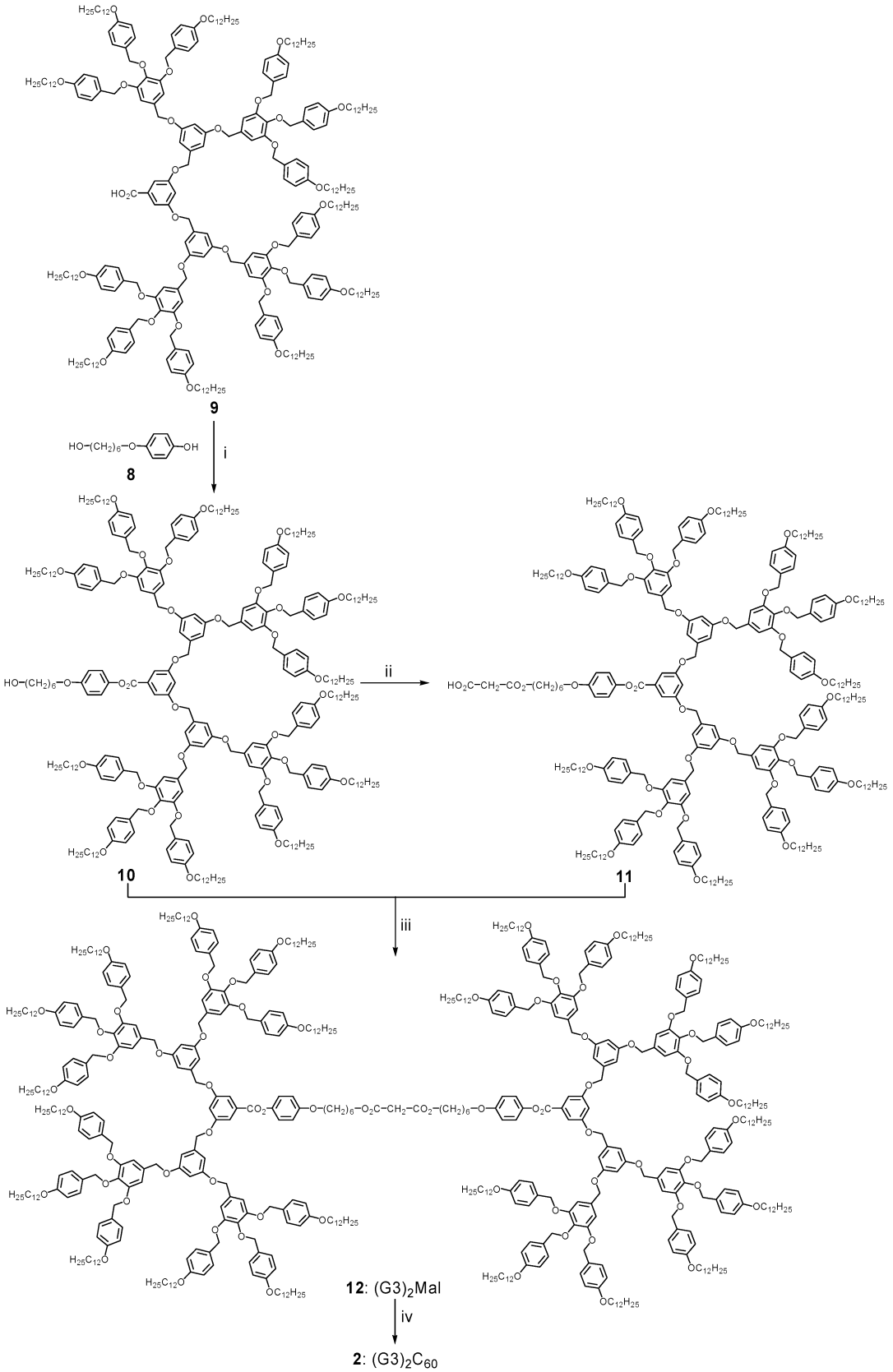
Compounds G2G3C$_{60}$ (3) and G2G3Mal (14). Both compounds display an amorphous structure at room temperature. A hexagonal columnar phase is obtained above 55 °C. The latter mesophase is characterized by two [for G2G3C$_{60}$ (**3**)] or three [for G2G3Mal (**14**)] sharp diffraction signals in the small-angle region in the ratio 1 : $\sqrt{3}$: $\sqrt{4}$; two diffuse signals at *ca.* 8–8.5 and 4.6 Å are also detected. The hexagonal cell parameters of G2G3C$_{60}$ (**3**) and G2G3Mal (**14**) are similar and do not vary with temperature, confirming that C_{60} does not influence the molecular organization of the mesophase.

Compounds G2C$_{60}$ (4) and G2Mal (15). For hemidendrimer G2C$_{60}$ (**4**), a rectangular columnar phase forms above 55 °C. A series of nine sharp diffraction signals in the small-angle region has been indexed according to a two-dimensional centered rectangular lattice of *c2mm* symmetry. For precursor G2Mal (**15**), no clear organization is revealed at room temperature (only diffuse signals are observed). However, above 40 °C, a sharp and intense reflection in the small-angle region is detected, reminiscent of some of the thermal events observed for other compounds described above, and consisting of a crystallization process with slow kinetics, resulting in a mixture of amorphous and crystalline solids. Above 80 °C, the X-ray patterns exhibit three small-angle reflections which can be indexed according to a two-dimensional lattice of a hexagonal columnar phase. The difference of behavior between G2C$_{60}$ (**4**) (rectangular columnar phase) and G2Mal (**15**) (hexagonal columnar phase) is due to the presence or not of C_{60}, the attachment of which onto the spacer strongly limits the possibility for the dendritic part to self-organize into a hexagonal symmetry.

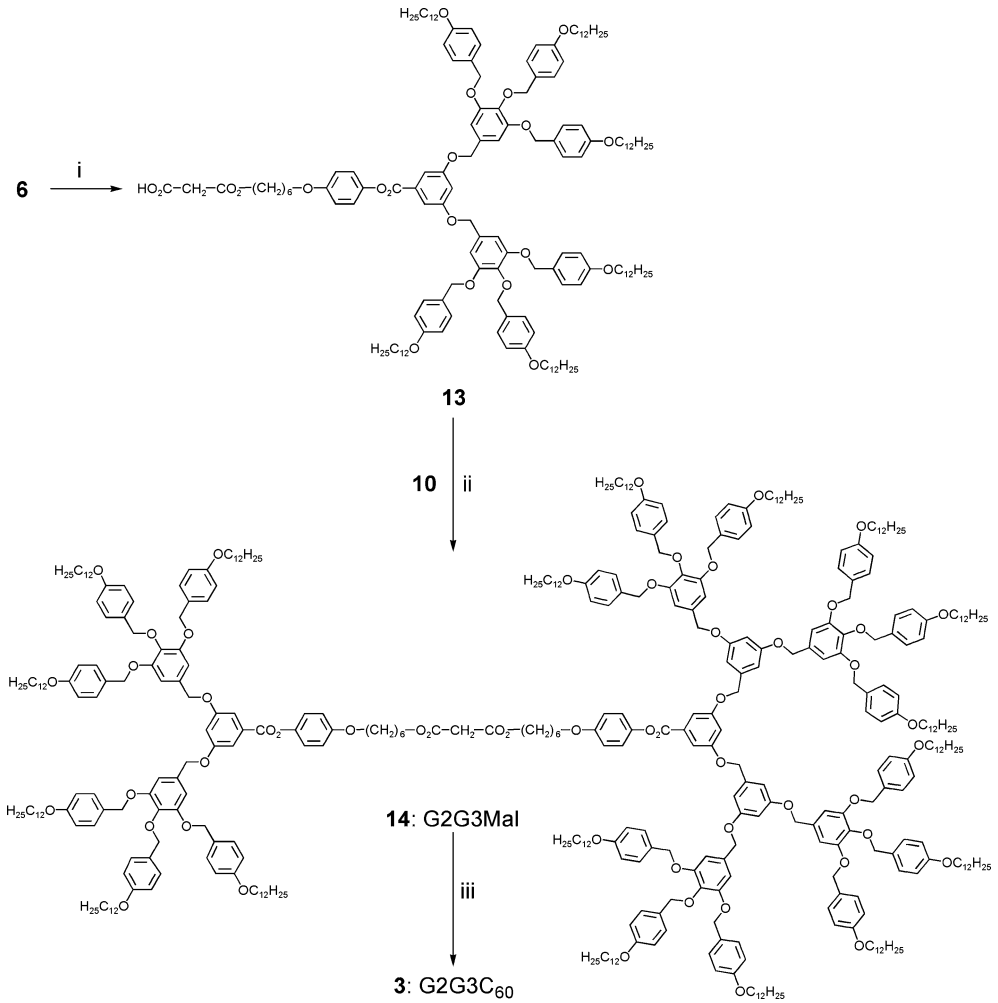
Compounds G3C$_{60}$ (5) and G3Mal (16). Hemidendrimer G3C$_{60}$ (**5**) exhibits a hexagonal columnar phase above 70 °C deduced from the presence of two sharp reflections in the small-angle region of the X-ray diffraction patterns. These signals can be indexed as the (10) and (11) reflections of a two-dimensional hexagonal lattice. In addition, a diffuse band at 8.5 Å indicates the presence of an average periodicity along the columnar axis. For the corresponding malonate G3Mal (**16**), the presence of a hexagonal columnar phase from room temperature up to 110 °C is characterized by three reflections indexed as (10), (11) and (20) of a two-dimensional arrangement. The hexagonal cell parameters are similar for both compounds, indicating the primary role of the dendrimer in the supramolecular organization. The C_{60} unit is effectively encapsulated in G3C$_{60}$ (**5**) as it is for (G3)$_2$C$_{60}$ (**2**) and G2G3C$_{60}$ (**3**).

Supramolecular organization

Liquid-crystalline malonates. Overall, the self-organization behavior of dendritic (**7**, **12**, **14**) and hemidendritic (**15**, **16**) malonates and fullerodendrimers (**2–5**) within the columnar phases retains the general characteristics of the methyl ester dendrons of second (derived from **6**) and third (derived from **9**) generation[8b] used here as building blocks. In particular,



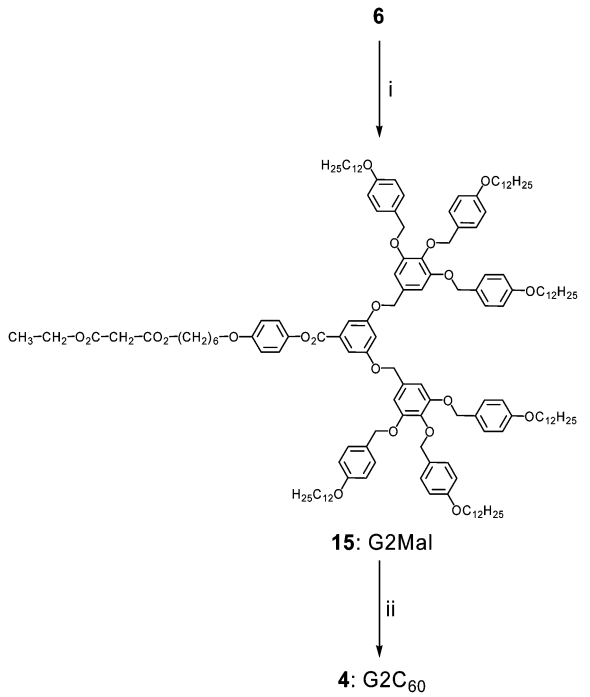
Scheme 2 (i) DCC, DPTS, 4-Ppy, CH_2Cl_2, r.t., overnight, 48%; (ii) Meldrum acid, toluene, 65 °C, 24 h, 89%; (iii) DCC, DPTS, 4-Ppy, CH_2Cl_2, r.t., overnight, 80%; (iv) C_{60}, DBU, I_2, toluene, r.t., overnight, 14%. For abbreviations, see ref. 13.



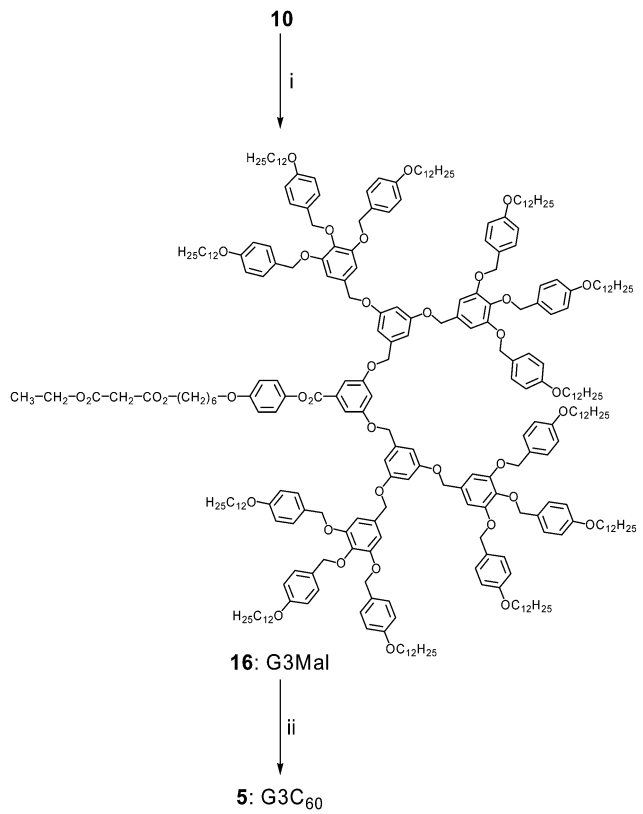
Scheme 3 (i) Meldrum acid, toluene, 65 °C, 24 h, 92%; (ii) DCC, DPTS, 4-Ppy, CH_2Cl_2, r.t., overnight, 76%; (iii) C_{60}, DBU, I_2, toluene, r.t., overnight, 28%. For abbreviations, see ref. 13.

hemidendrimers G2Mal (**15**) and G3Mal (**16**) exhibit comparable mesomorphism (mesophase stability and mesophase parameters) to that of the related esters derived from **6** and **9**, respectively, indicative that a similar packing mode within the hexagonal columnar phases is reproduced. In the flat conformation, G2Mal (**15**) approximates an open fan-shape with a planar angle α at the focal point of *ca.* 120°, whereas G3Mal (**16**) resembles more a semi-disc ($\alpha \sim 180°$), as shown in Scheme 6. Using a straightforward geometrical approach, which takes into account the relationships between the planar angle α, that represents the projection of the tapered dendrons solid angle ω ($\alpha = \omega/2$) and N_D (number of monodendrons or dendritic branches covering the columnar cross-section area, thus per repeat unit) linked through the equation $\alpha = 2\pi/N_D$,[8b] it was found that 3 molecules of G2Mal (**15**) and 2 molecules of G3Mal (**16**), respectively (here $Z = N_D$), self-associate into an elementary slice of cylindrical column, with calculated thicknesses h'' of 8.6 and 7.9 Å, respectively. The latter values are in good agreement with h', *i.e.* the average periodicities of the broad halos measured on the diffractograms. In other words, the repeating distance along the columnar axis is defined by the thickness of the disc formed by the dendritic branches. The hard part of the column is filled with the poly(benzyl ether) dendron, and the inner part accommodates the aliphatic malonate moiety; the columns are surrounded by the molten aliphatic chains.

The connection of two dendrons by a long spacer (leading to dendritic dimers) does not modify the nature of the mesophase, and hexagonal columnar phases are observed for $(G2)_2$Mal (**7**), $(G3)_2$Mal (**12**) and G2G3Mal (**14**). However, the mesophase stability, and to some extent the thermal behavior, can be affected upon dimerization as shown by $(G2)_2$Mal (**7**), for which an unstable thermal phase sequence is observed. In contrast, the behavior of $(G3)_2$Mal (**12**) is comparable to that of the third-generation methyl ester precursor.[8b] The mixed derivative G2G3Mal (**14**) also behaves like $(G3)_2$Mal (**12**) suggesting that the self-organization properties of G2G3Mal (**14**) are dominated by its large side. In both cases, intercolumnar distances are close to each other and to that of G3Mal (**16**) (and also to the monomeric methyl ester precursor[8b]); similarly, the dimensions of the hexagonal cell of $(G2)_2$Mal (**7**) and G2Mal (**15**) are identical. As a consequence, the same type of aggregation found for G2Mal (**15**) and G3Mal (**16**) can be deduced for their symmetrical and mixed dimeric structures. Applying the retrostructural analysis[8] used above, although with $N_D = 2 \times Z$, 1.5 molecular equivalents of $(G2)_2$Mal (**7**) [equivalent to three (N_D) dendritic parts as in G2Mal (**15**), $\alpha = 120°$ for each dendritic branch],



Scheme 4 (i) Ethyl malonyl chloride, Et_3N, CH_2Cl_2, r.t., overnight, 52%; (ii) C_{60}, DBU, I_2, toluene, r.t., overnight, 23%. For abbreviations, see ref. 13.



Scheme 5 (i) Ethyl malonyl chloride, Et_3N, CH_2Cl_2, r.t., overnight, 91%; (ii) C_{60}, DBU, I_2, toluene, r.t., overnight, 16%. For abbreviations, see ref. 13.

Table 1 Phase transition[a] temperatures and enthalpies of dendrons **10**, **11**, and **13**, malonates **7**, **12**, and **14–16**, and methanofullerenes **1–5**

Compound	T_g/°C	Transition	Temperature/°C	ΔH/kJ mol^{-1}
10	63	Col → I	115	11.3
11	65	Col → I	112	11.6
13		Cr → I	72[b]	1.9
$(G2)_2$Mal (**7**)		Cr → Col_h-*p6mm*	73	7.8
		Col_h-*p6mm* → I	88[c]	—
$(G2)_2C_{60}$ (**1**)		Cr → I	52[b]	18.8
$(G3)_2$Mal (**12**)	[d]	Col_h-*p6mm* → I	109	20.7
$(G3)_2C_{60}$ (**2**)	44	Col_h-*p6mm* → I	93	15.8
G2G3Mal (**14**)	45	Col_h-*p6mm* → I	105	18.2
$G2G3C_{60}$ (**3**)	64	Col_h-*p6mm* → I	74	10.9
G2Mal (**15**)	40	Cr → Col_h-*p6mm*	56	5.1
		Col_h-*p6mm* → I	86	8.1
$G2C_{60}$ (**4**)	36	Col_r-*c2mm* → I	68	6.8
G3Mal (**16**)	51	Col_h-*p6mm* → I	114	11.1
$G3C_{60}$ (**5**)	35	Col_h-*p6mm* → I	85	7.9

[a] Cr = crystalline or semicrystalline solid, T_g = glass transition temperature determined during the first cooling run, Col = columnar phase, Col_h-*p6mm* = hexagonal columnar phase of *p6mm* symmetry, Col_r-*c2mm* = rectangular columnar phase of *c2mm* symmetry, I = isotropic liquid. Temperatures are given as the onset values taken from the second heating run. [b] Temperature determined during the first heating run. [c] Determined by POM and XRD. [d] Not detected.

1 molecule of $(G3)_2$Mal (**12**) [equivalent to two (N_D) dendritic parts as in G3Mal (**16**), $\alpha = 180°$ for each dendron] and 1 molecule of G2G3Mal (**14**) [as for $(G3)_2$Mal (**12**), $N_D = 2$] fitting the volume of the elemental stratum with a thickness h'' of 8.0, 8.3, and 8.3 Å, respectively. Again, a good agreement is found between h' and h'', and this periodicity is assigned to the mean stacking distance between discs. Similarly to the hemidendrimers, the column formation results from the stacking of the supramolecular discs, the hard part of the column is filled with the poly(benzyl ether) dendron, and the inner part accommodates the malonate moiety; the columns are surrounded by the molten aliphatic chains. Note that in the supramolecular organization of $(G2)_2$Mal (**7**), one of the dimer shares its dendritic branches with two consecutive slices (discs) of the columns, which is permitted due to the great flexibility of the malonate spacer.

Liquid-crystalline fullerodendrimers. The non-mesomorphic character of $(G2)_2C_{60}$ (**1**) confirms that mesophase induction in such bulky materials requires the connection of strong liquid-crystalline promoters.[1] As for fullerodendrimers $(G3)_2C_{60}$ (**2**) and $G2G3C_{60}$ (**3**), derived from malonates $(G3)_2$Mal (**12**) and G2G3Mal (**14**), respectively, they both exhibit a hexagonal columnar phase. The dimensions of the hexagonal lattices were not greatly modified upon addition of C_{60}, indicating a similar paving of the two-dimensional network of these species [$(G3)_2C_{60}$ (**2**), $G2G3C_{60}$ (**3**), $(G3)_2$Mal (**12**), and G2G3Mal (**14**)]. The same retrostructural analysis can thus be applied here for the paving of the hexagonal lattices. However, to accommodate the bulky C_{60} unit, the thickness of an elementary stratum of the column needs to increase to a minimum of 10 Å, *i.e.* the diameter of C_{60}. For $(G3)_2C_{60}$ (**2**), the planar angle of the dendritic branches is *ca.* 180°, which suggests one molecule ($Z = 1$, $N_D = 2$) to cover the hexagonal lattice and forming one

Table 2 X-Ray characterization of the mesophases

Compound	d_{exp}/Å[a]	[hk][b]	I[c]	d_{theo}/Å[ad]	Parameters[d]	N_D[e]
$(G2)_2$Mal (**7**)	35.6	10	VS (sh)	35.6	$T = 80$ °C	3
	4.6	h_{ch}	VS (br)		$a = 41.1$ Å	
					$S = 1460$ Å^2	
					$V_{mol} = 7960$ Å^3	
					$h'' \sim 8.0$ Å, $Z = 1.5$	
$(G3)_2$Mal (**12**)	40.3	10	VS (sh)	40.3	$T = 90$ °C	2
	23.25	11	M (sh)	23.27	$a = 46.5$ Å	
	20.15	20	M (sh)	20.15	$S = 1875$ Å^2	
	8.5	h'	VW (br)		$V_{mol} = 15570$ Å^3	
	4.5	h_{ch}	VS (br)		$h'' \sim 8.3$ Å, $Z = 1$	
$(G3)_2C_{60}$ (**2**)	40.75	10	VS (sh)	40.75	$T = 80$ °C	4
	23.55	11	M (sh)	23.52	$a = 47.05$ Å	
	20.35	20	M (sh)	20.37	$S = 1920$ Å^2	
	8.5	h'	VW (br)		$V_{mol} = 16160$ Å^3	
	4.6	h_{ch}	VS (br)		$h'' \sim 16.8$ Å, $Z = 2$	
G2G3Mal (**14**)	39.75	10	VS (sh)	39.8	$T = 60$ °C	2
	22.95	11	M (sh)	22.97	$a = 45.95$ Å	
	19.9	20	M (sh)	19.9	$S = 1830$ Å^2	
	8.0	h'	VW (br)		$V_{mol} = 11540$ Å^3	
	4.6	h_{ch}	VS (br)		$h'' \sim 8.3$ Å, $Z = 1$	
G2G3C$_{60}$ (**3**)	40.45	10	VS (sh)	40.4	$T = 80$ °C	4
	23.3	11	M (sh)	23.3	$a = 46.65$ Å	
	8.5	h'	W (br)		$S = 1885$ Å^2	
	4.6	h_{ch}	VS (br)		$V_{mol} = 12410$ Å^3	
					$h'' \sim 13.2$ Å, $Z = 2$	
G2Mal (**15**)	35.25	10	VS (sh)	35.25	$T = 80$ °C	3
	20.5	11	M (sh)	20.35	$a = 40.7$ Å	
	17.5	20	M (sh)	17.6	$S = 1435$ Å^2	
	8.0	h'	VW (br)		$V_{mol} = 4120$ Å^3	
	4.5	h_{ch}	VS (br)		$h'' \sim 8.6$ Å, $Z = 3$	
G2C$_{60}$ (**4**)	75.15	11	VS (sh)	75.15	$T = 60$ °C	12
	66.85	20	VS (sh)	66.85	$a = 133.7$ Å	
	45.5	02	S (sh)	45.6	$b = 91.2$ Å	
	39.9	31	VW (sh)	40.0	$S = 6100$ Å^2	
	37.5	22	S (sh)	37.7	$V_{mol} = 4760$ Å^3	
	33.35	40	M (sh)	33.4	$h'' \sim 9.4$ Å, $Z = 12$	
	29.6	13	M (sh)	29.65		
	25.1	33	M (sh)	25.1		
	22.3	60	W (sh)	22.3		
	8.8	h'	W (br)			
	4.5	h_{ch}	VS (br)			
G3Mal (**16**)	41.3	10	VS (sh)	41.3	$T = 60$ °C	2
	23.9	11	S (sh)	23.85	$a = 47.7$ Å	
	20.6	20	S (sh)	20.65	$S = 1970$ Å^2	
	8.0	h'	VW (br)		$V_{mol} = 7750$ Å^3	
	4.6	h_{ch}	VS (br)		$h'' \sim 7.9$ Å, $Z = 2$	
G3C$_{60}$ (**5**)	39.8	10	VS (sh)	39.65	$T = 80$ °C	2
	22.8	11	S (sh)	22.9	$a = 45.8$ Å	
	8.5	h'	VW (br)		$S = 1820$ Å^2	
	4.6	h_{ch}	VS (br)		$V_{mol} = 8570$ Å^3	
					$h'' \sim 9.4$ Å, $Z = 2$	

[a] d_{exp} and d_{theo} are the experimental and theoretical diffraction spacings, respectively. [b] [hk] are the indexation of the reflections; h' and h_{ch} are short range order periodicities determined by XRD corresponding to some weak liquid-like correlations (accuracy: *ca.* ±1 Å) and to the liquid-like order of the molten chains, respectively. [c] Intensity of the reflections: VS: very strong, S: strong, M: medium, W: weak, VW: very weak; br: broad, sh: sharp. [d] d_{theo} is deduced from the lattice parameters a (Col_h) or a and b (Col_r) from the following mathematical expressions: i) for Col_h, $a = 2 \times [\Sigma_{hk} d_{hk}.(h^2 + k^2 + hk)^{1/2}]/\sqrt{3}N_{hk}$ where N_{hk} is the number of hk reflections. S is the lattice area: $S = a^2\sqrt{3}/2$; ii) for Col_r, $S = a \times b/2$ and $<d_{hk}> = 1/[(h^2/a^2 + k^2/b^2)^{1/2}]$. Z is the aggregation number or the number of molecular equivalents per stratum of column. V_{mol} is the molecular volume: $V_{mol} = V_{C60} + V_{malonate}$, where $V_{C60} = 700$ Å^3, $V_{malonate} = (MW/0.6022) \times (V_{CH2}(T)/V_{CH2}(T_0))$, MW the molecular weight of the malonate and $V_{CH2} = 26.5616 + 0.02023T$. h'' is the theoretical intracolumnar repeating distance, deduced from the measured molecular volume and the columnar cross-section, $h'' = Z \times V_{mol}/S$. [e] N_D: number of dendritic branches per stratum.

stratum ($h'' = 8.4$ Å) as in $(G3)_2$Mal (**12**). However, such a height of column is not compatible with the molecular thickness imposed by C_{60}. Consequently, two molecules of $(G3)_2C_{60}$ (**2**) were considered to define one slice of column ($h'' = 2 \times h'$), with h' corresponding to the average distance between two consecutive discs (*i.e.* the thickness of the dendritic branches). Similarly, for the mixed fullerodendrimer G2G3C$_{60}$ (**3**), one molecule was first considered, by analogy to its malonate precursor, leading to a columnar slice thickness of *ca.* 6.6 Å, incompatible with the size of C_{60}. As above, two molecules were thus considered to match the structural requirements. Note that for fullerodendrimers bearing two dendritic branches, non-integer Z values are unlikely

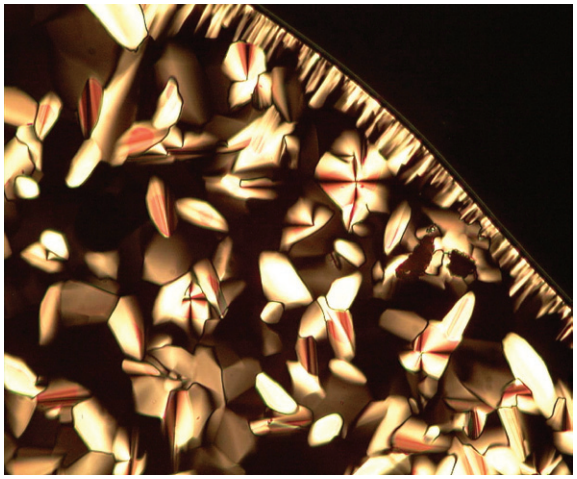


Fig. 1 Thermal polarized optical micrograph of the texture displayed by $G3C_{60}$ (**5**) in the hexagonal columnar phase at 84 °C.

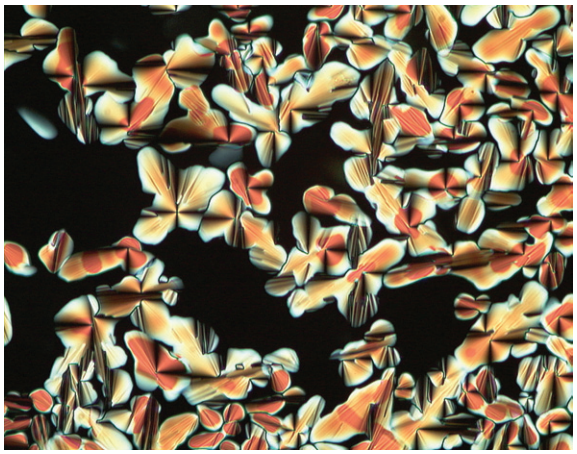


Fig. 2 Thermal polarized optical micrograph of the texture displayed by G2Mal (**15**) in the hexagonal columnar phase at 85 °C.

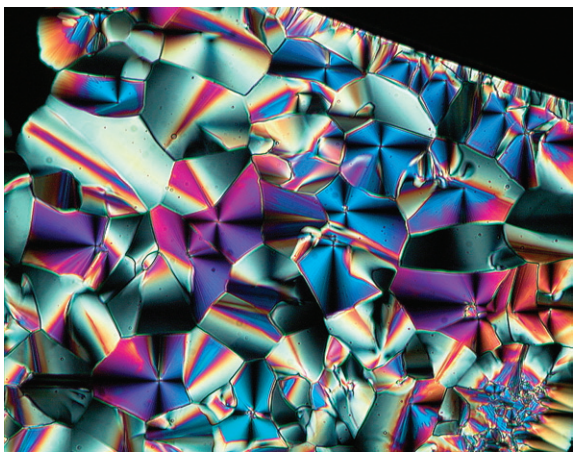
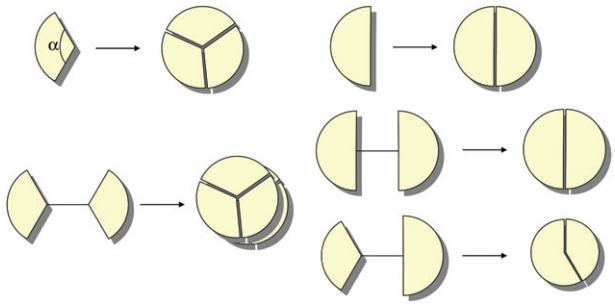


Fig. 3 Thermal polarized optical micrograph of the texture displayed by $(G2)_2$Mal (**7**) in the hexagonal columnar phase at 79 °C.



Scheme 6 Schematic representation of the formation of supramolecular discs with hemidendritic and dendritic systems. The supramolecular organization of the fullerodendrimers is derived from that of the malonate precursors. For details, see Table 2 and main text.

(the molecules are no longer dimers, C_{60} is indeed indivisible). For this compound, the discrepancy between the two periodicities is likely due to a deficit of dendritic branches, not large enough to fully embed C_{60}, with h' representing the interdisc distance over a short range correlation length. Thus, the larger hexagonal cells with a thickness h'' of 16.8 and 13.2 Å, respectively, incorporate 2 molecular equivalents of $(G3)_2C_{60}$ (**2**) and $G2G3C_{60}$ (**3**). In both arrangements, the C_{60} units are located towards the interior of the column, and loosely stacked along the columnar axis, surrounded by the dendritic part.

Rectangular and hexagonal columnar phases are obtained for hemidendrimers $G2C_{60}$ (**4**) and $G3C_{60}$ (**5**), respectively. The lattice parameter of the hexagonal columnar phase on going from G3Mal (**16**) to $G3C_{60}$ (**5**) remains almost constant, so that the same packing mode is likely reproduced, and for an equivalent surface to pave, two molecules per lattice were considered leading to a cell thickness h'' of 9.4 Å. In this case, the thickness is compatible with aggregates of C_{60} if some kind of close compact-like (hexagonal or cubic) arrangement of C_{60} in the centre of the column is considered ($h'' \sim \phi\sqrt{3}/2$, $\phi \sim 10$ Å = diameter of C_{60}), which is allowed since only one dendritic branch is attached to C_{60}, encouraging C_{60}–C_{60} interactions through the "unprotected face".[5a] However, for $G2C_{60}$ (**4**), the situation is slightly more complicated since the expansion of the cell occurs in the symmetry plane as well as along the column. The section area S of the column is almost quadrupled on going from G2Mal (**15**) to $G2C_{60}$ (**4**). Considering that the dendritic parts adopt in both cases a flat conformation and that each tapered dendron paves a similar surface area, the number of fullerodrendrimers should also be quadrupled. Thus, at least twelve molecules of $G2C_{60}$ (**4**) are considered in the elementary columnar slice, with a thickness h'' of 9.4 Å, which is identical to the value found for $G3C_{60}$ (**5**). The average stacking distance, h', between consecutive disc-like [$G3C_{60}$ (**5**)] or discoid-like [$G2C_{60}$ (**4**)] assemblies remains the same. Such a non-circular arrangement was also found in related systems,[5a] and the rather low thickness value was attributed to the close packing of C_{60} into aggregates forming the centre of the column. Thus, the packing of $G2C_{60}$ (**4**) and $G3C_{60}$ (**5**) is different to that of $(G3)_2C_{60}$ (**2**) and $G2G3C_{60}$ (**3**) in the sense that for $(G3)_2C_{60}$ (**2**) and $G2G3C_{60}$ (**3**) the packing and the C_{60} interactions are rather loose whilst for $G2C_{60}$ (**4**) and $G3C_{60}$ (**5**) the C_{60} units self-assemble into aggregates, which grow along the columnar axis.

In order to confirm the above arrangements, molecular dynamics experiments on compound $G2G3C_{60}$ (**3**) were performed. Two minimized structures of $G2G3C_{60}$ (**3**) were placed in a hexagonal cell, where only the thickness was fixed ($h'' =$ 13 Å), and the molecules were only allowed to expand laterally.

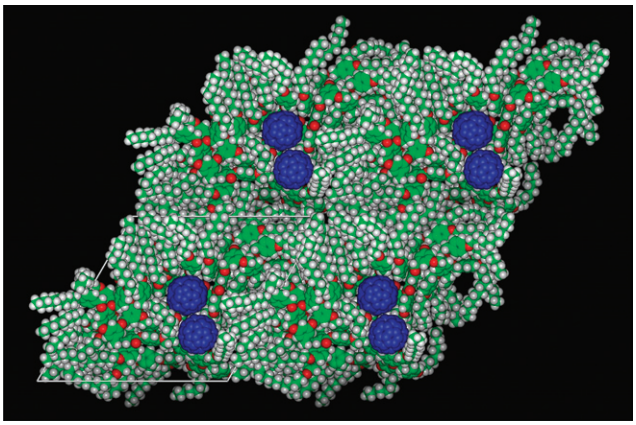


Fig. 4 Top view of the supramolecular organization of $G2G3C_{60}$ (**3**) within the hexagonal columnar phase of *p6mm* symmetry.

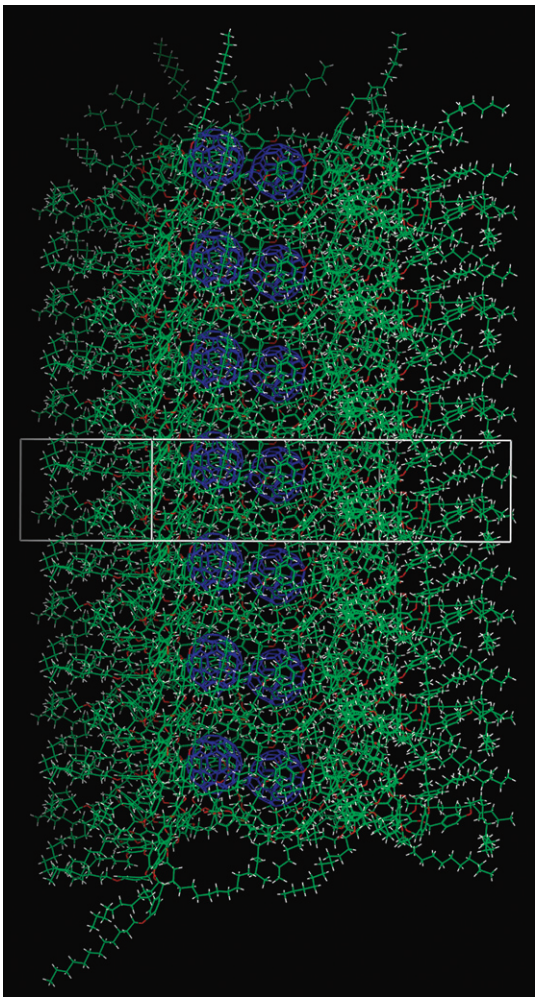


Fig. 5 Side view of the supramolecular organization of $G2G3C_{60}$ (**3**) within the hexagonal columnar phase of *p6mm* symmetry.

The results of the dynamics experiments are in agreement with the experimental data: a lattice parameter comparable to that of the X-ray experiments and a density close to unity were found. Moreover, a perfect paving of the surface and a dense occupation of the available volume were confirmed (Fig. 4 and 5).

Conclusion

In order to design fullerodendrimers which display columnar mesomorphism, C_{60} was functionalized *via* the Bingel reaction with symmetrical and non-symmetrical malonates which carry poly(benzyl ether) dendrons as liquid-crystalline promoters. The liquid-crystalline malonates were prepared by applying a modular synthetic approach. Hemidendrimers were also synthesized. All the malonate and fullerene derivatives give rise to columnar phases. The supramolecular organization of the malonate and fullerene derivatives within the columnar phases is governed by the dendrimer. Indeed, for the fullerodendrimers, C_{60} has no (or little) influence on the structure of the mesophases providing the size of the dendritic addends is large enough, *i.e.* when two third-generation dendrons [compound $(G3)_2C_{60}$ (**2**)], or one third-generation and one second-generation [compound $G2G3C_{60}$ (**3**)] dendron are associated, or for a third-generation hemidendrimer [compound $G3C_{60}$ (**5**)]. If the dendron is not large enough to encapsulate C_{60}, the latter influences the organization as observed for compound $G2C_{60}$ (**4**) (second-generation hemidendrimer) which gives rise to a rectangular columnar phase whereas its malonate precursor shows a hexagonal columnar phase. The design of fullerene-containing liquid crystals with tailor-made properties requires that the influence of C_{60} is drastically minimized and even suppressed. This work and former studies[1,5b] confirm that functionalization of C_{60} with liquid-crystalline dendrimers is an elegant strategy for the design of fullerene-containing liquid crystals for which the mesomorphism and supramolecular organization can be controlled by design.

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13 Abbreviations: r.t., room temperature; DBU, 1,8-diazabicyclo [5.4.0]undec-7-ene; DCC, *N*,*N*′-dicyclohexylcarbodiimide; DPTS, 4-(dimethylamino)pyridinium toluene-*p*-sulfonate; 4-Ppy, 4-pyrrolidinopyridine.
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