Supramolecular Fullerene Materials: Dendritic Liquid-Crystalline Fulleropyrrolidines

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ABSTRACT: [60]Fullerene-containing liquid-crystalline dendrimers were synthesized from the first to the fourth generation by applying the 1,3-dipolar cycloaddition reaction from a mesomorphic dendritic-type aldehyde derivative, sarcosine (*N*-methylglycine) or glycine and C_{60}. The cyanobiphenyl unit was used as a liquid-crystalline promoter. With the exception of the first-generation fullerene dendrimer, which was found to be nonmesomorphic, all fullerene-based dendrimers gave rise to a smectic A phase. The liquid-crystalline fullerenes led to two different supramolecular organizations within the smectic layers: for the second-generation dendrimers, the molecules are oriented in a head-to-tail fashion within the layers; for each molecule the cyanobiphenyl units point in the same direction. For the dendrimers of third and fourth generations, the dendritic core extends laterally, parallel to the layer planes; the mesogenic units are oriented above and below the dendritic core. For the aldehyde precursors, only one organization inside the layers was obtained, similar to the one observed for the third and fourth fullerene-based dendrimers. Cyclic voltametry investigations displayed several one-electron and multielectron reduction processes; no significant interaction in the ground state between the fullerene and the dendrimer was noticed. The title compounds showed the typical electrochemical stability of fulleropyrrolidines.

Introduction

Fullerodendrimers,[1] which combine the outstanding electrochemical[2] and photophysical[3] properties of C_{60} with the unique structural features of dendrimers,[4] generated fascinating studies in supramolecular chemistry and materials science.[5] Dendrimers play two major roles depending upon their architecture and functionalities: they increase the solubility of C_{60} in organic solvents[6] or in water[7] (solubilizing effect), and they isolate C_{60} from the external environment such as oxygen and solvent molecules (protection effect).[8] Both effects can be adjusted to specific experimental conditions by synthetic chemistry at the dendrimer level. Dendrimers prevent also the formation of aggregates resulting from strong interactions between C_{60} units; highly ordered Langmuir and Langmuir−Blodgett films were so obtained.[9]

With the view to construct supramolecular fullerene materials, whose properties could be of interest in nanotechnology (e.g., molecular switches, solar cells), we became interested in fullerene-containing thermotropic liquid crystals. We developed two concepts to design liquid-crystalline fullerenes:[10] in the first concept, C_{60} was functionalized with liquid-crystalline malonates by applying the Bingel reaction[11] (leading to mesomorphic methanofullerenes[12]), and in the second one, C_{60} was functionalized with liquid-crystalline aldehydes and *N*-methylglycine or an amino acid derivative by applying the 1,3-dipolar addition reaction[13] (leading to mesomorphic fulleropyrrolidines[14]). A great variety of liquid

crystals was obtained, such as fullerene−ferrocene dyads (smectic A phases),[12a,b,d,14b] fullerene−OPV conjugates (smectic A phases),[14a] fullerene−TTF dyads (smectic A and B phases),[12g] a hexa-adduct of C_{60} (smectic A phase),[12c] a chiral C_{60} derivative (cholesteric phase),[12f] and dendritic liquid-crystalline methanofullerenes (smectic A phases; an additional short-range nematic phase was observed for the second-generation dendrimer).[12e] A bis(methano)fullerene was also reported (mesophase not identified).[15] Two other approaches were described: in the first one, C_{60} was complexed by mesomorphic cyclotriveratrylene (CTV) derivatives (nematic and cubic phases),[16] and in the second one, five aromatic groups were attached around one pentagon of C_{60}, yielding conical molecules (columnar phases).[17]

Whereas methanofullerenes undergo retro-Bingel reaction upon chemical[18] and electrochemical[19] reduction, fulleropyrrolidines lead to stable reduced species.[13] Dendritic liquid-crystalline fulleropyrrolidines would represent an interesting family of electroactive macromolecules, as they would combine the electrochemical behavior[2] of C_{60} with the rich mesomorphism of dendrimers.[20]

We describe, herein, the synthesis, characterization, liquid-crystalline properties, and supramolecular organization of the dendritic liquid-crystalline fulleropyrrolidines **1**−**7** (Charts 1 and 2). By means of cyclic voltammetry experiments carried out on the second-generation dendrimer **2**, it is demonstrated that such materials are electrochemically stable. The cyanobiphenyl derivatives, acting as mesomorphic groups, are located at the periphery of the dendritic core. The dendrimers were prepared by applying a convergent synthetic methodology.[21] The mesomorphic properties of **2** were already reported.[10b]
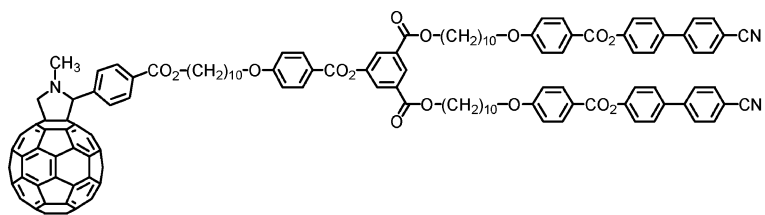
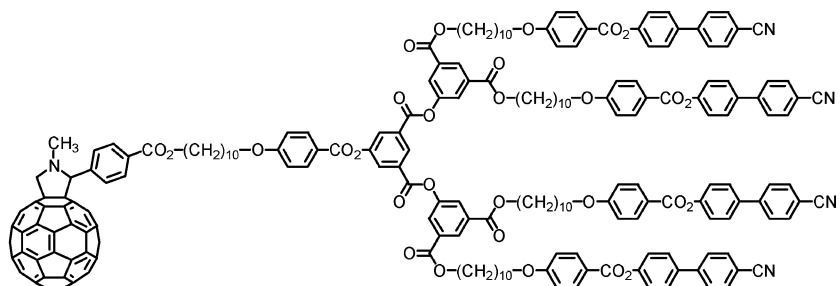* Corresponding author. E-mail: robert.deschenaux@unine.ch.
† Université de Neuchâtel.
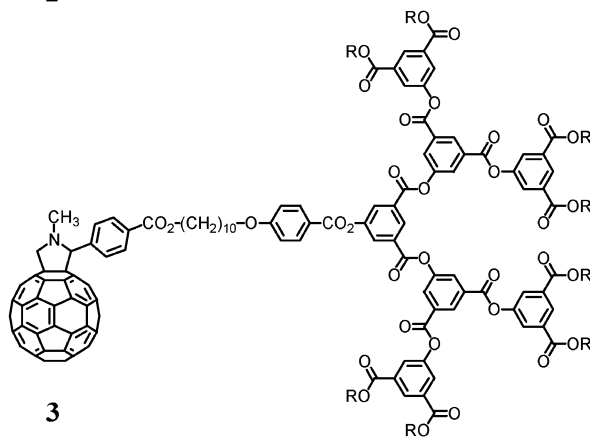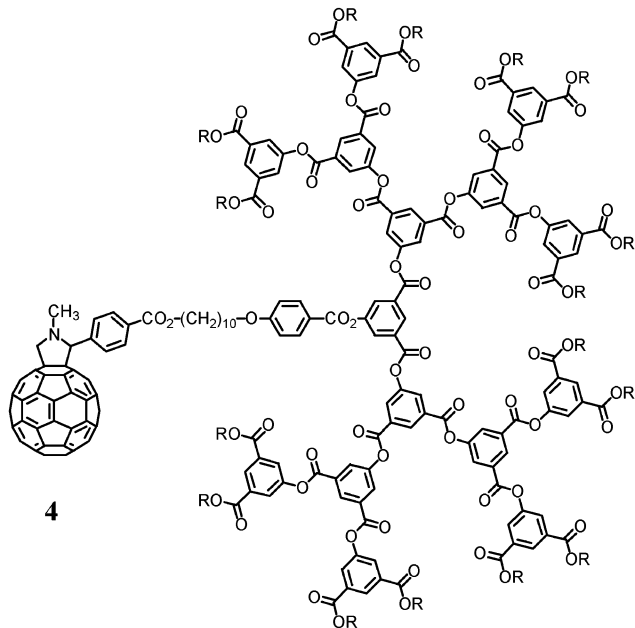‡ Universidad de Zaragoza-CSIC.
§ Università di Bologna.

Chart 1

1

2

3

4

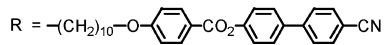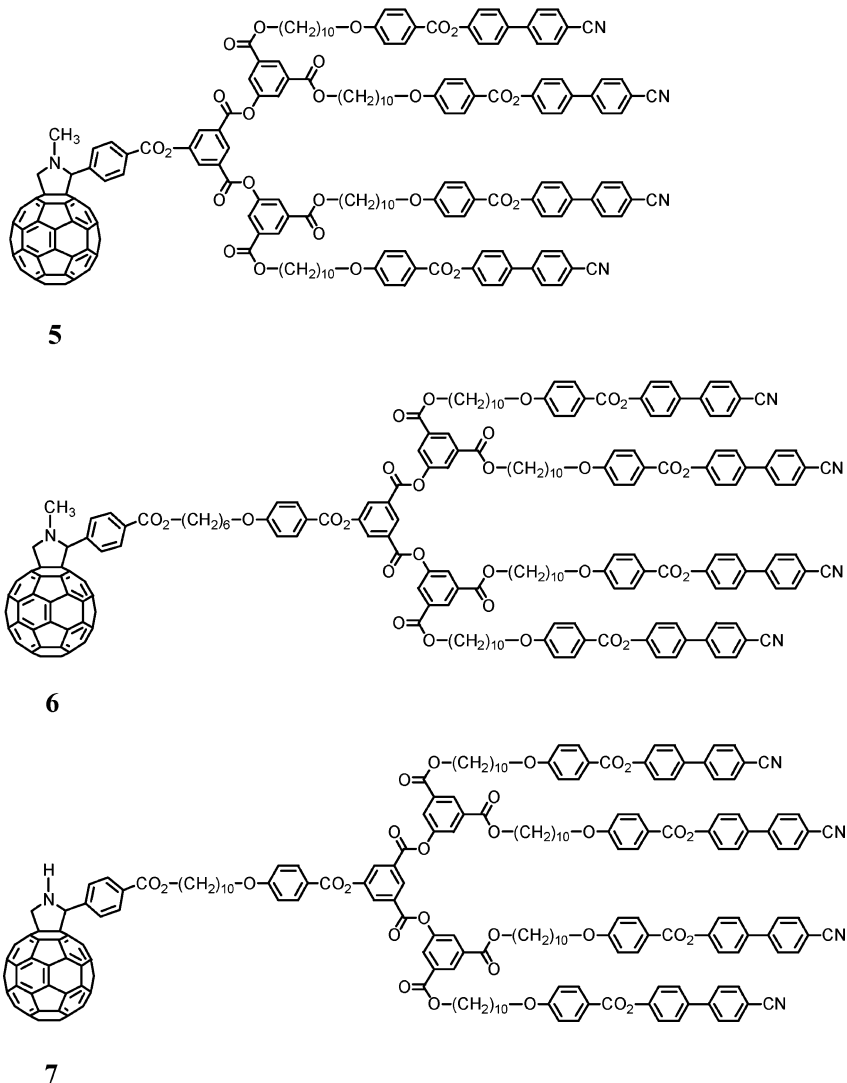R = —(CH₂)₁₀—O—⟨⟩—CO₂—⟨⟩—⟨⟩—CN

Chart 2

5

**6**

7

Results and Discussion

Design. This study is based on three different structural modifications. First, we modified the dendrimer generation (first generation, **1**; second generation, **2**; third generation, **3**; fourth generation, **4**) (Chart 1). Second, we modified the length of the flexible bridge between the second-generation dendrimer and the pyrrolidine ring (**5**, none; **6**, six carbon atoms; **2**, 10 carbon atoms) (Charts 1 and 2). Third, we modified the substituent located on the nitrogen atom of the pyrrolidine ring for the second-generation dendrimers (**2**, methyl group; **7**, hydrogen atom) (Charts 1 and 2). These compounds were designed to emphasize the role played by the dendrimer, the spacer and the pyrrolidine ring on the liquid-crystalline properties and supramolecular organization. Owing to the N−H group, **7** could be used as synthetic platform for the preparation of multifunctional liquid-crystalline fulleropyrrolidines.

Syntheses. The preparation of **1** is depicted in Scheme 1. Condensation of first-generation dendron **8** with 4-(10-hydroxydecyloxy)benzoic acid gave alcohol derivative **9**. Treatment of **9** with 4-carboxybenzaldehyde furnished aldehyde **10**. Addition of **10** and *N*-methylglycine (sarcosine) to C_{60} led to **1**. Fulleropyrrolidines **2**−**4** were prepared analogously to the synthesis of **1** from the corresponding phenol-based dendrimer,

i.e., **11** → **2** (Scheme 2), **14** → **3** (Scheme 3), and **17** → **4** (Scheme 4). The syntheses of **5** and **6** are described in Scheme 5. Second-generation phenol derivative **11** was esterified either with 4-carboxybenzaldehyde or with 4-(6-hydroxyhexyloxy)benzoic acid to give **20** and **21**, respectively. Aldehyde **20** was reacted with sarcosine and C_{60} to furnish **5**. Alcohol **21** was condensed with 4-carboxybenzaldehyde to give **22**, the addition of which with sarcosine and C_{60} led to **6**. Fulleropyrrolidine **7** was obtained by addition of **13** with glycine to C_{60} (Scheme 2).

The structure and purity of all compounds were confirmed by NMR spectroscopy, GPC (all compounds were found to be monodisperse) and elemental analysis. The vis spectra of **1**−**7** were in agreement with the fulleropyrrolidine structure; an illustrative example is shown in Figure 1. The syntheses of phenol precursors (**8**, **11**, **14**, and **17**) and 4-(10-hydroxydecyloxy)benzoic were already described;[12e] they were used for the preparation of dendritic liquid-crystalline methanofullerenes.[12e] 4-(6-Hydroxyhexyloxy)benzoic acid was prepared according to a literature procedure.[22]

Liquid-Crystalline Properties. The mesomorphic and thermal properties of alcohol (**9**, **12**, **15**, **18**, and **21**), aldehyde (**10**, **13**, **16**, **19**, **20**, and **22**) and fulleropyrrolidine (**1**−**7**) derivatives were investigated by polarized

Scheme 1[a]
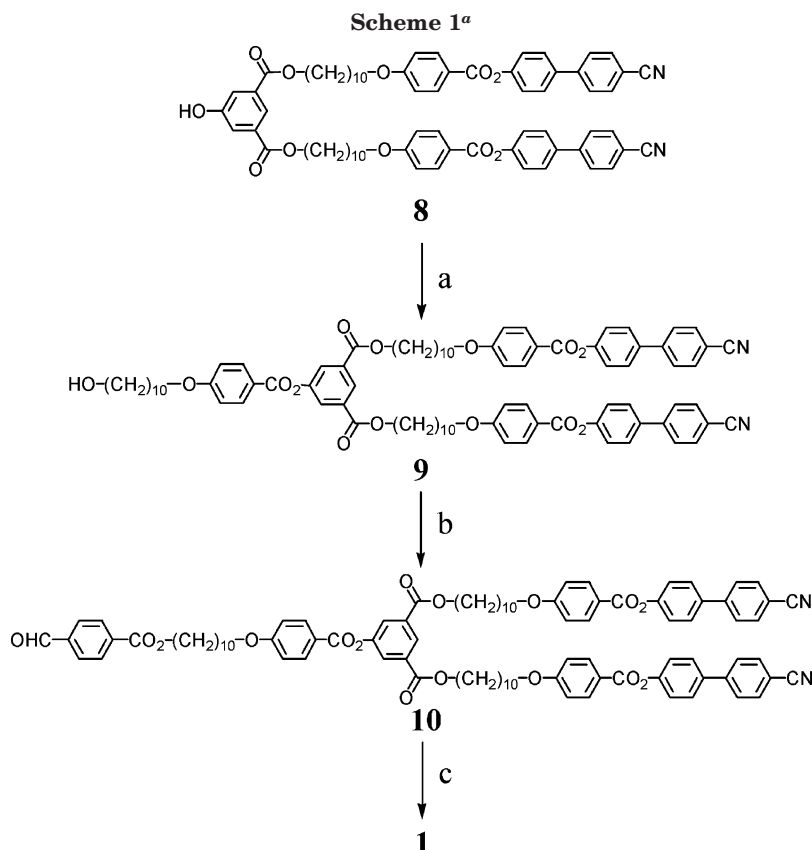
a Key: (a) 4-(10-hydroxydecyloxy)benzoic acid, *N,N*′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridinium toluene-*p*-sulfonate (DPTS), 4-pyrrolidinopyridine (4-PPy), CH$_2$Cl$_2$, room temperature, 15 h, 78%; (b) 4-carboxybenzaldehyde, DCC, DPTS, 4-PPy, CH$_2$Cl$_2$, room temperature, 17 h, 80%; (c) C$_{60}$, sarcosine, toluene, reflux, 17 h, 28%.

optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transition temperatures and enthalpy changes are reported in Table 1.

With the exception of **1**, which was found to be nonmesomorphic, all compounds displayed liquid-crystalline properties. First generation alcohol **9** and aldehyde **10** gave rise to a nematic phase. From the second generation, all materials displayed a smectic A phase. The liquid-crystalline phases were identified by POM from their textures (smectic A phase: focal-conic and homeotropic textures; nematic phase: schlieren and homeotropic textures). The texture of the smectic A phase developed by **2** is shown in Figure 2 as an illustrative example.

The fact that **1** did not show mesomorphism was unexpected taking into account that a methano-fullerene[12e] carrying also two mesogenic units (the same as those used in **1**) exhibited a smectic A phase. Two structural factors could have prevented **1** to be meso-morphic: (1) the bent structure induced by the fullero-pyrrolidine moiety and (2) the benzene nucleus located next to the nitrogen atom of the pyrrolidine ring, the presence of which increases the bulkiness around the fullerene. As a consequence, the mesomorphic part in **1** is not large enough to thwart the steric effects generated by the fulleropyrrolidine framework.

The clearing temperature increased with the dendrimer generation. This trend was observed for other liquid-crystalline dendrimers[12e] and confirmed that the stability of the mesophases increases with the number of mesogenic units. The isotropization temperatures of the fulleropyrrolidines were lower than those of the corresponding aldehyde promoters. This behavior is in

agreement with results obtained for other fullerene-containing liquid crystals and is attributed to the presence of the bulky C$_{60}$ unit.[12a,b,d−f] Comparison of the clearing points of second-generation dendrimers **2** (10 carbon atoms in the flexible spacer), **6** (6 carbon atoms in the flexible spacer) and **5** (no flexible spacer) showed that the stability of the mesophase increased when the length of the spacer decreased. This result should be the consequence of reduced molecular motion when the spacer is shorter. Finally, the substituent on the nitrogen had limited influence on the stability of the meso-phase (clearing point of **2**, 168 °C; clearing point of **7**, 162 °C). This is due to the fact that the difference in size between the H atom and the methyl group is small in comparison with the size of the molecule.

Supramolecular Organization. To gain informa-tion regarding the supramolecular organization of the liquid-crystalline fulleropyrrolidines **2**−**7** and of their aldehyde precursors **13**, **16**, **19**, **20**, and **22** within the liquid-crystalline state, the smectic phases were analyzed by variable-temperature X-ray diffraction (XRD).

The XRD patterns of fulleropyrrolidines **2**−**7** showed either one or two intense reflection peaks in the low-angle region and a diffuse signal in the wide-angle region. When two peaks were detected in the low-angle region, their spacings were in a 1:2 ratio, and they corresponded to the first- and second-order reflections, respectively. Such patterns are characteristic of disor-dered smectic phases. The *d*-layer spacings determined by XRD were found to be nearly independent of tem-perature, which is in agreement with the nature of the smectic A phase.
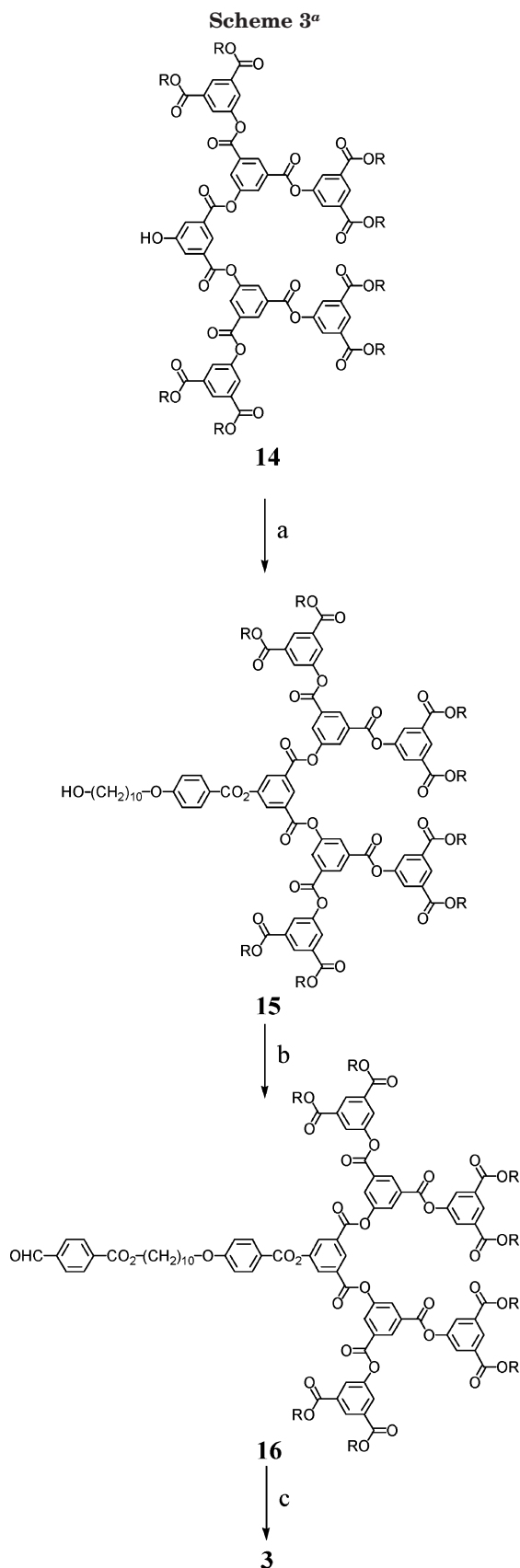
Scheme 2[a]

11

↓ a

12

↓ b

13

c ↓   d ↓

2   **7**
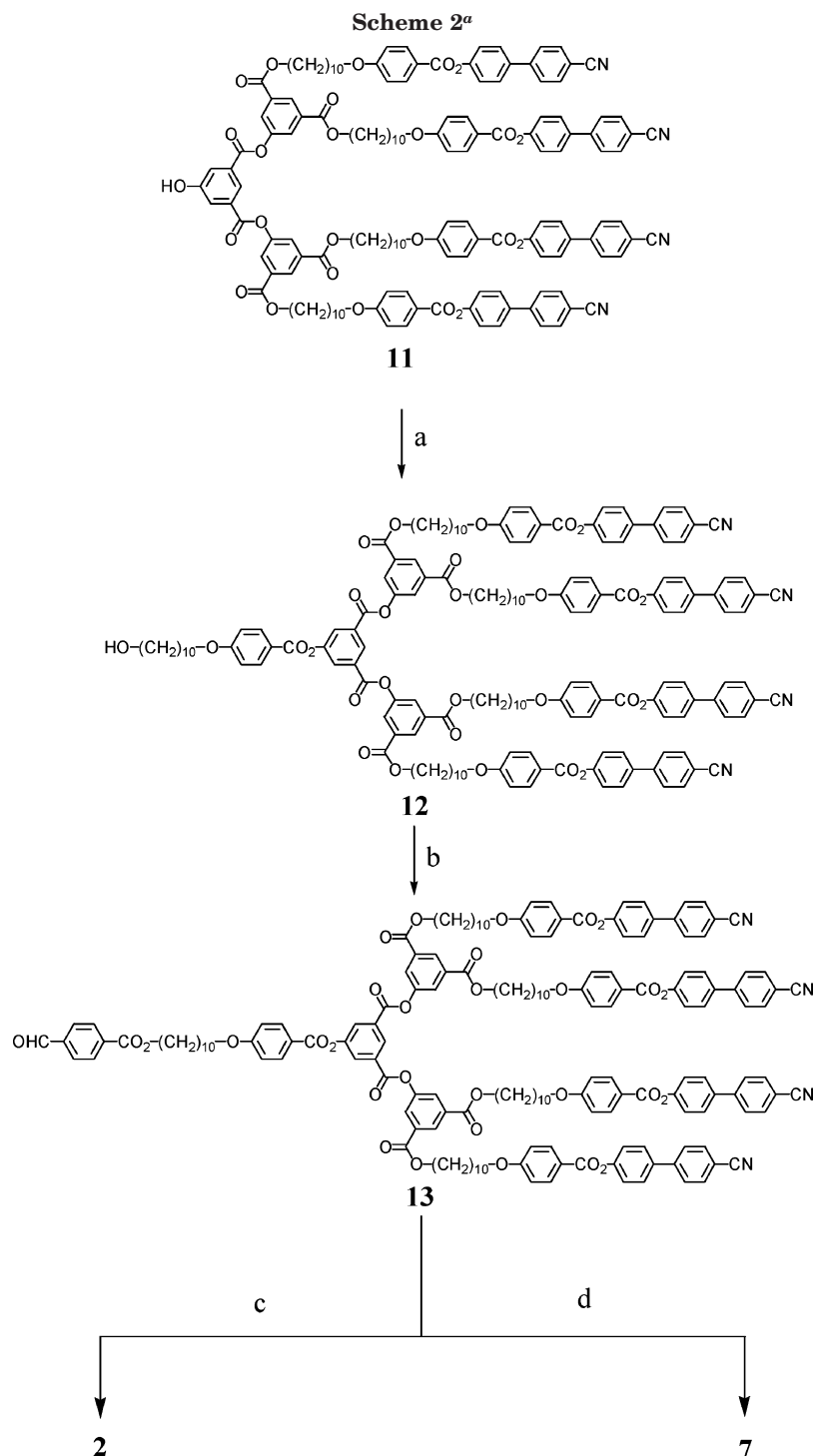
a Key: (a) 4-(10-hydroxydecyloxy)benzoic acid, DCC, DPTS, 4-PPy, CH$_2$Cl$_2$, room temperature, 24 h, 83%; (b) 4-carboxy-benzaldehyde, DCC, DPTS, 4-PPy, CH$_2$Cl$_2$, room temperature, 15 h, 91%; (c) C$_{60}$, sarcosine, toluene, reflux, 20 h, 53%; (d) C$_{60}$, glycine, toluene, reflux, 40 h, 47%. For abbreviations, see footnote *a* of Scheme 1.

The *d*-layer spacings were compared to the molecular lengths in the extended molecular conformation (Table 2). The dendrimers of second generation (**2** and **5**−**7**) gave *d*/*L* ratios of 1.3, whereas the dendrimers of third (**3**) and fourth (**4**) generations gave *d*/*L* values of 0.7. These data indicated that two different supramolecular organizations are obtained depending upon the dendrimer generation, i.e., generation 2, on one hand, and generations 3 and 4, on the other hand. Furthermore, for the second-generation dendrimers (**2** and **5**−**7**), the supramolecular organization is independent of the

length of the spacer and of the substituent located on the nitrogen atom of the fulleropyrrolidine.

For the dendrimers of second generation (**2** and **5**−**7**), for which the *d*-layer spacings are larger than their molecular lengths, the organization within the smectic layers requires the adequacy between the cross-sectional area of C$_{60}$ (90−100 Å^2) and that of four mesogens (22−25 Å^2 per mesogenic unit). For efficient space filling, the molecules are oriented in a head-to-tail fashion within the layers, and for each molecule the cyanobiphenyl units point in the same direction interdigitating with

Scheme 3[a]

14

↓ a

15

↓ b

16

↓ c

3

[a] Key: (a) 4-(10-hydroxydecyloxy)benzoic acid, DCC, DPTS, 4-PPy, CH_2Cl_2, room temperature, 20 h, 68%; (b) 4-carboxybenzaldehyde, DCC, DPTS, 4-PPy, CH_2Cl_2, room temperature, 48 h, 66%; (c) C_{60}, sarcosine, toluene, reflux, 15 h, 48%. For R, see Chart 1. For abbreviations, see footnote *a* of Scheme 1.

the cyanobiphenyl groups of the adjacent layer (Figure 3a). This model is consistent with the tendency of the

cyano-substituted mesogens to interdigitate in an antiparallel way promoted by dipole−dipole interactions. For dendrimers **2** and **5**−**7** the supramolecular organization is thus governed by steric constraints.

For the dendrimers of third (**3**) and fourth (**4**) generations, for which the *d*-layer spacings are significantly smaller than their molecular lengths, the dendritic core extends laterally, parallel to the layer planes. With such an orientation, the *d*-layer spacing does not increase (practically) when the size of the dendrimer increases; this result is in agreement with literature data.[20a] The mesogenic units are oriented above and below the dendritic core and, as for **2** and **5**−**7**, interdigitation occurs from one layer to the adjacent one. In this case, C_{60} is hidden in the dendritic core and has no influence on the supramolecular organization. Therefore, from the third generation, the supramolecular organization is governed by the nature and structure of the mesogenic units (parts b and c of Figure 3). This result opens avenues for the design of fullerene-containing liquid-crystalline dendrimers with tailored mesomorphic properties: fine tuning of the liquid-crystalline properties could be achieved when the adequate mesomorphic promoter (polar, apolar, chiral) is associated with the appropriate dendrimer (stiff, flexible).

The *d*-layer spacings (*d*), molecular lengths (*L*) and *d/L* ratios of the aldehyde precursors are reported in Table 3. The aldehydes of third (**16**: *d/L* = 0.8) and fourth (**19**: *d/L* = 0.7) generations give a similar supramolecular organization than their corresponding fullerene counterparts (i.e., **3** and **4**, repectively); this result strenghtens the model proposed for **3** and **4** (parts b and c of Figure 3). The aldehydes of second generation yielded *d*-layer spacings similar to those of third and fourth generations. This result suggests that the packing model is the same for all aldehydes (the higher *d/L* value observed for **20** reflects a slightly different orientation of the dendritic core for this chemical, most likely, because of lack of flexible bridge between the dendrimer and the aromatic ring carrying the aldehyde group). This is not unexpected taking into account that, in the absence of C_{60}, there are no steric constraints leading to the model proposed in Figure 3a and, therefore, the organization is similar to the ones shown in parts b and c of Figure 3. It is interesting to note that the intensity of the Bragg signals for the aldehydes is low. This is, most likely, related to the interdigitation which makes the interface between the layers diffuse. Although in the fullerene-containing dendrimers interdigitation is also present, the layered structure is better defined due to the sublayer of C_{60} moieties.

The above-mentioned results are in agreement with the data we have obtained for dendritic liquid-crystalline methanofullerenes, for which we have also found that steric contraints are responsible for the supramolecular organization when C_{60} is functionalized with small addends, whereas the mesogenic groups govern the supramolecular organization when C_{60} is functionalized with dendrimers.[12e] The harmony of the *structure−supramolecular organization* relationship between both series of materials is due to the fact that in both cases the same type of dendritic core and mesomorphic units were used.

Electrochemistry. The cyclic voltammetric (CV) behavior of **2** and of reference compound **13** (Figure 4) was investigated in THF solution under strictly aprotic conditions.[23,24] The CV curve (Figure 4a) relative to a

Scheme 4[a]
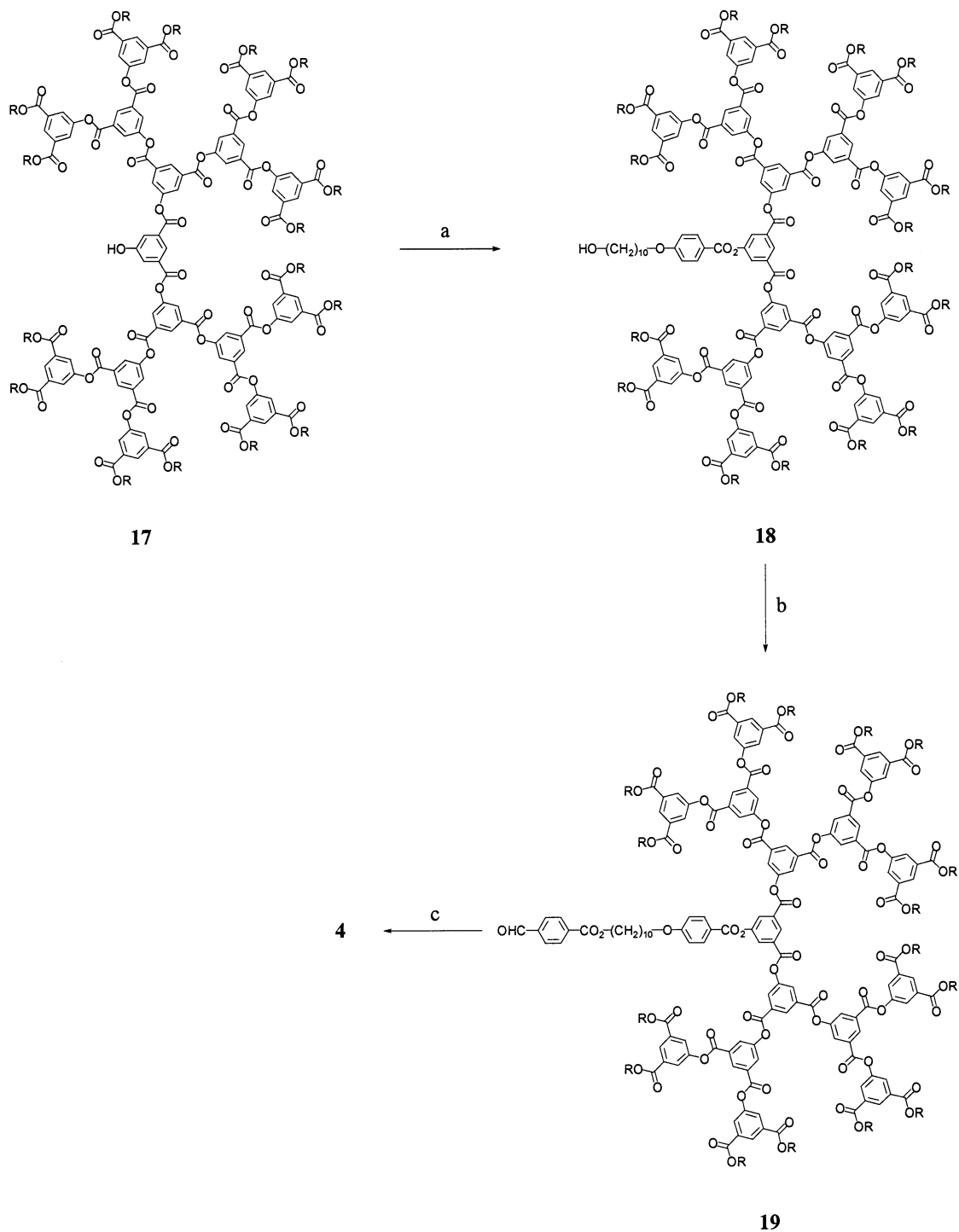
17

18

4　　　**19**

0.5 mM **2** THF solution, at 25 °C and at a scan rate of 1.0 V/s, displays a series of subsequent reduction peaks which were, in part, attributable to the fulleropyrroli-dine moiety and, for the remaining ones, to the den-drimer. In particular, peaks I, II, and III ($E_{1/2}$ = −0.47, −1.04, and −1.65 V) are located at potentials that are typical of fulleropyrrolidines studied under similar conditions,[25,26] and they were therefore attributed to the reversible subsequent reductions of the fullerene unit in **2**. At variance with fulleropyrrolidines, peak III comprises two electrons, thus suggesting the occurrence

of two one electron reduction processes, accidentally located at very close potentials, one centered in the fullerene moiety, the other one in the dendritic part. This was confirmed by comparison with the CV curve of **13** (Figure 4b), in which a one electron peak (I) is located at the same potential as peak III in the CV curve of **2**. At more negative potentials, the CV curves of both species were characterized by intense (and only partly irreversible) reduction peaks (II−IV in **13** and IV and V in **2**) that were attributed to the dendrimer. In fact, this moiety contains various functional groups that are

Scheme 5[a]
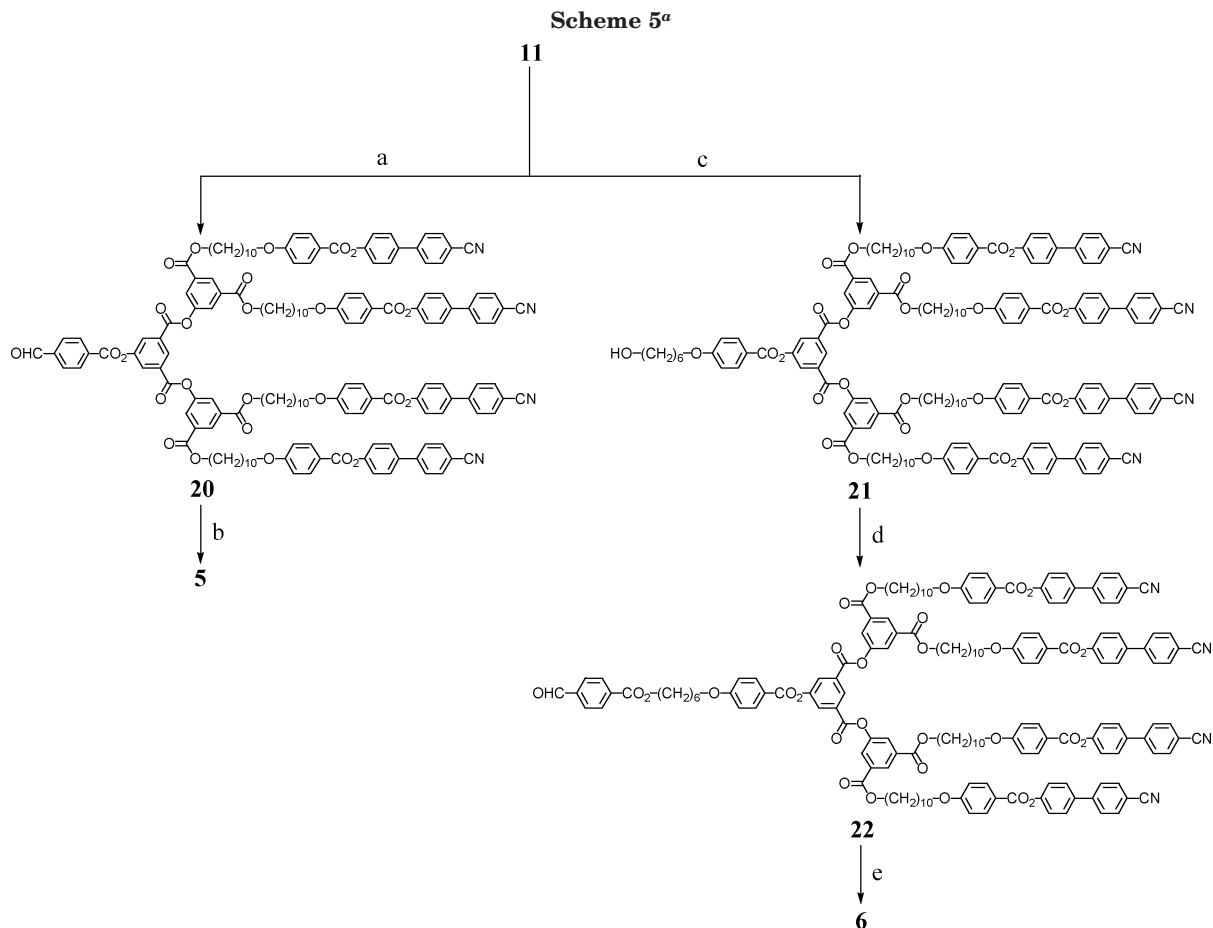
[a] Key: (a) 4-carboxybenzaldehyde, DCC, DPTS, 4-PPy, CH_2Cl_2, room temperature, 6 h, 57%; (b) C_{60}, sarcosine, toluene, reflux, 20 h, 52%; (c) 4-(6-hydroxyhexyloxy)benzoic acid, DCC, DPTS, 4-PPy, CH_2Cl_2, rt, 20 h, 90%; (d) 4-carboxybenzaldehyde, DCC, DPTS, 4-PPy, CH_2Cl_2, room temperature, 48 h, 72%; (e) C_{60}, sarcosine, toluene, reflux, 20 h, 53%. For abbreviations, see footnote *a* of Scheme 1.
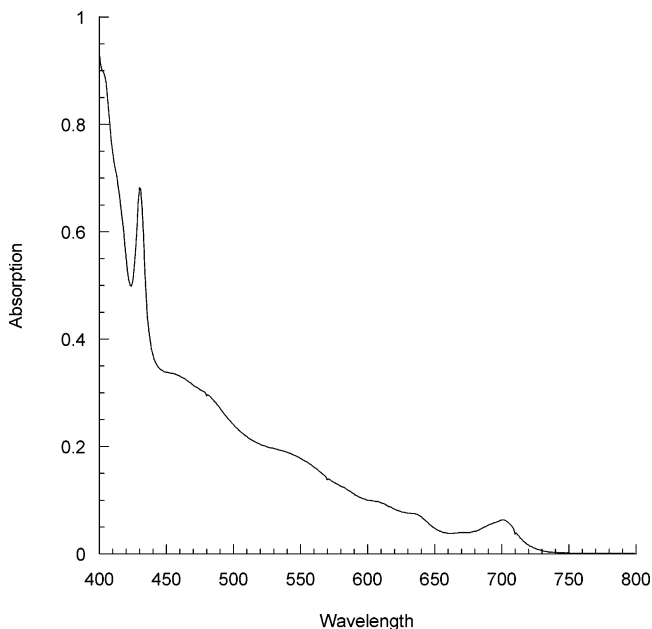

Figure 1. Visible spectrum of fulleropyrrolidine **2**.

capable to undergo reduction processes at such negative potentials, e.g., the four equivalent cyanobiphenyl groups and the three equivalent isophthaloyl ester groups.

An attribution of the various multielectron reduction peaks to the corresponding electroactive groups in the dendrimer was attempted on the basis of the cor-

Table 1. Phase Transition Temperatures[a] and Enthalpies of Alcohol, Aldehyde, and Fulleropyrrolidine Derivatives

compound	T_g (°C)	transition	temp (°C)	ΔH (kJ·mol^{-1})
9		Cr → N	123[b]	67.2
		N → I	190	3.0
10		Cr → N	102[b]	43.5
		N → I	179	3.7
1		Cr → I	178	23.0
12	38	S_A → I	185[c]	10.9
13	35	S_A → I	185	12.8
2	44	S_A → I	168	13.5
15	41	S_A → I	231[d]	42.7
16	47	S_A → I	223	43.8
3	51	S_A → I	196	22.8
18	45	S_A → I	256[d]	97.1
19	36	S_A → I	250[e]	97.6
4	36	S_A → I	231[e]	81.5
20	45	S_A → I	219	16.6
5	*f*	S_A → I	189	16.3
21	44	S_A → I	203	14.7
22	37	S_A → I	195	13.8
6	*f*	S_A → I	171	13.7
7	*f*	S_A → I	162	10.7

[a] Cr = semicrystalline solid, T_g = glass transition temperature, S_A = smectic A phase, N = nematic phase, I = isotropic liquid. Temperatures are given as the onset of the peak obtained during the second heating run except where stated otherwise. T_g's are determined during the first cooling run. [b] Observed only during the first heating run. [c] Large transition. [d] Large transition with some decomposition; determined as the maximum of the peak obtained during the first heating run. [e] Determined as the onset of the peak obtained during the first heating run. [f] Too small to be determined.
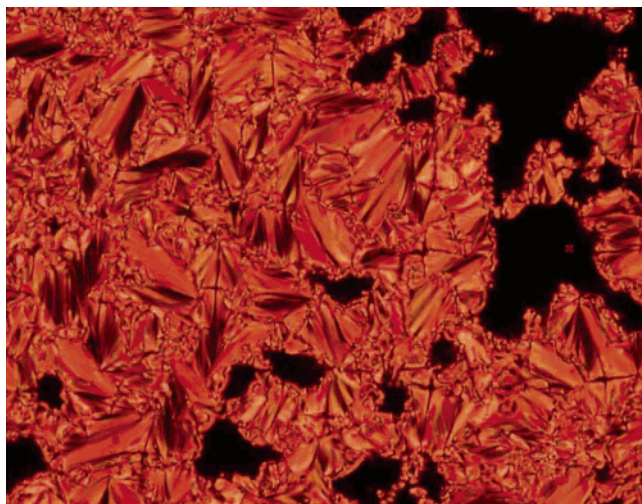
Figure 2. Thermal optical micrograph of the focal-conic fan texture displayed by **2** in the smectic A phase upon cooling the sample from the isotropic liquid to 167 °C.

Table 2. Layer Spacings d_{001}, Molecular Lengths L, and d/L Ratios of Liquid-Crystalline Fulleropyrrolidines

compound	$d_{001}{}^a$ (Å)	L^b (Å)	d/L
2	88	68	1.3
3	50	73	0.7
4	54	76	0.7
5	67	50	1.3
6	84	64	1.3
7	88	68	1.3

^{a} Determined by X-ray diffraction at 150 °C. ^{b} The molecular length was estimated for the fully extended conformation obtained by means of HyperChem software with the branching part and the mesogenic units pointing in the same direction.

$n_{IV} = 3$. Peak III (at about -2.30 V in Figure 4b) is not observed for **2** and likely involves the aldehyde group in **13**. On the basis of the above n values and of the occurrence of the various electroactive groups within the dendritic structure, peak II in Figure 4b was attributed to the reduction of the four equivalent cyanobiphenyl groups, while the processes comprised in peak IV are likely to involve the three equivalent isophthaloyl ester moieties in the dendrimer core. Finally, the one electron reduction peak I might involve the (single) benzoic ester moiety which is linked to the dendritic core. On the other hand, the fulleropyrrolidine moiety in **2** is known to undergo another two subsequent reduction processes
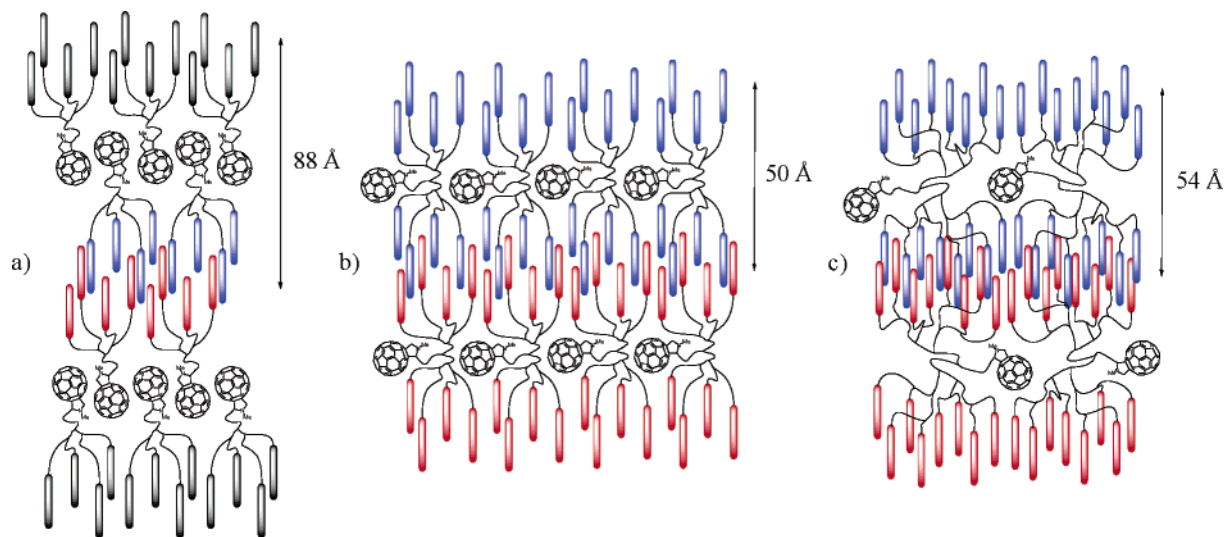
respondence between the number of electrons (n) associated with each peak and the number of equivalent electroactive groups in the structure. As far as **13** is concerned, the convolutive analysis[27] of the CV curve gave the following results: $n_I = 1$, $n_{II} = 4$, $n_{III} = 1$, and

Figure 3. Postulated supramolecular organization of fulleropyrrolidines **2** (a), **3** (b), and **4** (c) within the smectic A phases.
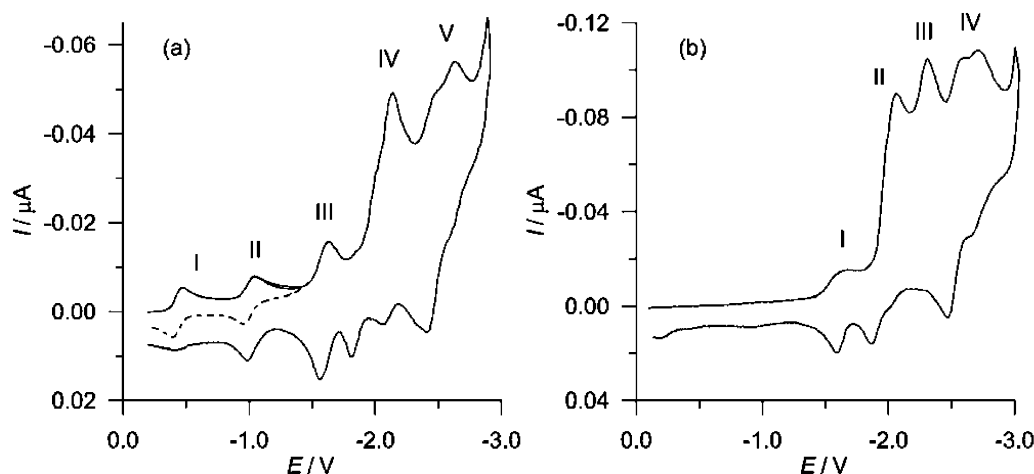

Figure 4. CV curves of (a) fulleropyrrolidine **2** (0.5 mM) and (b) aldehyde **13** (0.5 mM) in THF (0.05 M TBAH), at 25 °C and at a scan rate of 1V/s.

Table 3. Layer Spacings d_{001}, Molecular Lengths L, and d/L Ratios of Liquid-Crystalline Aldehydes

compound	$d_{001}{}^a$ (Å)	L^b (Å)	d/L
13	54.5	64	0.85
16	55	68	0.8
19	55	74	0.7
20	53	44	1.2
22	54	59	0.9

^{a} Determined by X-ray diffraction at room temperature. ^{b} The molecular length was estimated for the fully extended conformation obtained by means of HyperChem software with the branching part and the mesogenic units pointing to the same direction.

in this potential region, at -2.15 and -2.96 V, respectively.[26] While the reduction process at -2.16 V was expected to contribute to the multielectronic peak IV in the CV curve of **2**, the fifth reduction of the fulleropyrrolidine moiety is instead likely located outside the potential window investigated in the CV experiment of Figure 4a.

Conclusions

Liquid-crystalline fulleropyrrolidines were synthesized from mesomorphic aldehyde-based dendrimers of first to fourth generation, sarcosine or glycine and C_{60} by applying the 1,3-dipolar cycloaddition reaction. They gave rise to smectic A phases. The supramolecular organization of the mesomorphic fullerenes within the smectic layers could be established from X-ray diffraction data and molecular modeling. Two different organizations were found depending upon the dendrimer generation. In the first model, which was observed for the second-generation dendrimers, the molecules are oriented in a head-to-tail fashion within the layers. In the second model, observed for the third- and fourth-generation dendrimers, the mesogenic units are oriented above and below the dendritic core. In both types of structural model, there is segregation into distinct sublayers, giving rise to an alternating superstructure: one sublayer which contains the mesogenic units and the rest of the molecule (fullerene and branching part) which is located between the mesogenic sublayers. Finally, electrochemical investigations were in agreement with the redox-active nature of the subunits found in the compounds.

Supporting Information Available: Text giving techniques, instruments, synthetic procedures, and analytical data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Nierengarten, J.-F. *Chem.—Eur. J.* **2000**, *6*, 3667. (b) Nierengarten, J.-F.; Armaroli, N.; Accorsi, G.; Rio, Y.; Eckert, J.-F. *Chem.—Eur. J.* **2003**, *9*, 37.

(2) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593.

(3) (a) Guldi, D. M. *Chem. Commun.* **2000**, 321. (b) Guldi, D. M. *Chem. Soc. Rev.* **2002**, *31*, 22.

(4) (a) *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A, Eds.; John Wiley & Sons, Ltd.: Chichester, U.K., 2001. (b) *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; Newkome, G. R., Moorefield, C. N., Vögtle, F., Eds.; Wiley-VCH: Weinheim, Germany, 2001.

(5) *Fullerenes: From Synthesis to Optoelectronic Properties*; Guldi, D. M., Martín, N., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002.

(6) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J.; Wudl, F.; Srdanov, G.; Shi, S.; Li, C.; Kao, M. *J. Am. Chem. Soc.* **1993**, *115*, 9836.

(7) Brettreich, M.; Hirsch, A. *Tetrahedron Lett.* **1998**, *39*, 2731.

(8) (a) Rio, Y.; Accorsi, G.; Nierengarten, H.; Rehspringer, J.-L.; Hönerlage, B.; Kopitkovas, G.; Chugreev, A.; Van Dorsselaer, A.; Armaroli, N.; Nierengarten, J.-F. *New J. Chem.* **2002**, *26*, 1146. (b) Rio, Y.; Accorsi, G.; Nierengarten, H.; Bourgogne, C.; Strub, J.-M.; Van Dorsselaer, A.; Armaroli, N.; Nierengarten, J.-F. *Tetrahedron* **2003**, *59*, 3833.

(9) (a) Cardullo, F.; Diederich, F.; Echegoyen, L.; Habicher, T.; Jayaraman, N.; Leblanc, R. M.; Stoddart, J. F.; Wang, S. *Langmuir* **1998**, *14*, 1955. (b) Felder, D.; Gallani, J.-L.; Guillon, D.; Heinrich, B.; Nicoud, J.-F.; Nierengarten, J.-F. *Angew. Chem., Int. Ed.* **2000**, *39*, 201. (c) Nierengarten, J.-F.; Eckert, J.-F.; Rio, Y.; del Pilar Carreon, M.; Gallani, J.-L.; Guillon, D. *J. Am. Chem. Soc.* **2001**, *123*, 9743. (d) Hirano, C.; Imae, T.; Fujima, S.; Yanagimoto, Y.; Takaguchi, Y. *Langmuir* **2005**, *21*, 272.

(10) (a) Chuard, T.; Deschenaux, R. *Helv. Chim. Acta* **1996**, *79*, 736. (b) Campidelli, S.; Deschenaux, R. *Helv. Chim. Acta* **2001**, *84*, 589. (c) Chuard, T.; Deschenaux, R. *J. Mater. Chem.* **2002**, *12*, 1944.

(11) (a) Bingel, C. *Chem. Ber.* **1993**, *126*, 1957. (b) Nierengarten, J.-F.; Herrmann, A.; Tykwinsky, R. R.; Rüttimann, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 293. (c) Camps, X.; Hirsch, A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1595.

(12) (a) Deschenaux, R.; Even, M.; Guillon, D. *Chem. Commun.* **1998**, 537. (b) Dardel, B.; Deschenaux, R.; Even, M.; Serrano, E. *Macromolecules* **1999**, *32*, 5193. (c) Chuard, T.; Deschenaux, R.; Hirsch, A.; Schönberger, H. *Chem. Commun.* **1999**, 2103. (d) Even, M.; Heinrich, B.; Guillon, D.; Guldi, D. M.; Prato, M.; Deschenaux, R. *Chem.—Eur. J.* **2001**, *7*, 2595. (e) Dardel, B.; Guillon, D.; Heinrich, B.; Deschenaux, R. *J. Mater. Chem.* **2001**, *11*, 2814. (f) Campidelli, S.; Eng, C.; Saez, I. M.; Goodby, J. W.; Deschenaux, R. *Chem. Commun.* **2003**, 1520. (g) Allard, E.; Oswald, F.; Donnio, B.; Guillon, D.; Delgado, J. L.; Langa, F.; Deschenaux, R. *Org. Lett.* **2005**, 7, 383.

(13) (a) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519. (b) Tagmatarchis, N.; Prato, M. *Synlett.* **2003**, 768.

(14) (a) Campidelli, S.; Deschenaux, R.; Eckert, J.-F.; Guillon, D.; Nierengarten, J.-F. *Chem. Commun.* **2002**, 656. (b) Campidelli, S.; Vázquez, E.; Milic, D.; Prato, M.; Barberá, J.; Guldi, D. M.; Marcaccio, M.; Paolucci, D.; Paolucci, F.; Deschenaux, R. *J. Mater. Chem.* **2004**, *14*, 1266.

(15) Tirelli, N.; Cardullo, F.; Habicher, T.; Suter, U. W.; Diederich, F. *J. Chem. Soc., Perkin Trans. 2* **2000**, 193.

(16) Felder, D.; Heinrich, B.; Guillon, D.; Nicoud, J.-F.; Nierengarten, J.-F. *Chem.—Eur. J.* **2000**, *6*, 3501.

(17) (a) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature (London)* **2002**, *419*, 702. (b) Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 432.

(18) Moonen, N. N. P.; Thilgen, C.; Echegoyen, L.; Diederich, F. *Chem. Commun.* **2000**, 335.

(19) (a) Kessinger, R.; Crassous, J.; Herrmann, A.; Rüttimann, M.; Echegoyen, L.; Diederich, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 1919. (b) Crassous, J.; Rivera, J.; Fender, N. S.; Shu, L.; Echegoyen, L.; Thilgen, C.; Herrmann, A.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1613. (c) Kessinger, R.; Fender, N. S.; Echegoyen, L. E.; Thilgen, C.; Echegoyen, L.; Diederich, F. *Chem.—Eur. J.* **2000**, *6*, 2184. (d) Fender, N. S.; Nuber, B.; Schuster, D. I.; Wilson, S. R.; Echegoyen, L. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1924.

(20) Selected examples of liquid-crystalline dendrimers: (a) Baars, M. W. P. L.; Söntjens, S. H. M.; Fischer, H. M.; Peerlings, H. W. I.; Meijer, E. W. *Chem.—Eur. J.* **1998**, *4*, 2456. (b) Örtegren, J.; Busson, P.; Gedde, U. W.; Hult, A.; Eriksson, A.; Lindgren, M.; Andersson, G. *Liq. Cryst.* **2001**, *28*, 861. (c) Bobrovsky, A. Yu.; Pakhomov, A. A.; Zhu, X.-M.; Boiko, N. I.; Shibaev, V. P.; Stumpe, J. *J. Phys. Chem. B* **2002**, *106*, 540. (d) Donnio, B.; Barberá, J.; Giménez, R.; Guillon, D.; Marcos, M.; Serrano, J. L. *Macromolecules* **2002**, *35*, 370. (e) Rueff, J.-M.; Barberá, J.; Donnio, B.; Guillon, D.; Marcos, M.; Serrano, J.-L. *Macromolecules* **2003**, *36*, 8368. (f) Precup-Blaga, F. S.; Schenning, A. P. H. J.; Meijer, E. W. *Macro-*

molecules **2003**, *36*, 565. (g) Gehringer, L.; Bourgogne, C.; Guillon, D.; Donnio, B. *J. Am. Chem. Soc.* **2004**, *126*, 3856. (h) Lehmann, M.; Gearba, R. I.; Koch, M. H. J.; Ivanov, D. A. *Chem. Mater.* **2004**, *16*, 374. (i) Percec, V.; Mitchell, C. M.; Cho, W.-D.; Uchida, S.; Glodde, M.; Ungar, G.; Zeng, X.; Liu, Y.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Am. Chem. Soc.* **2004**, *126*, 6078. (j) Zeng, X.; Ungar, G.; Liu, Y.; Percec, V.; Dulcey, A. E.; Hobbs, J. K. *Nature (London)* **2004**, *428*, 157. (k) Saez, I. M.; Goodby, J. W. *J. Mater. Chem.* **2005**, *15*, 26.

(21) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (c) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.

(22) Sastri, S. B.; Stupp, S. I. *Macromolecules* **1993**, *26*, 5657.

(23) Paolucci, F.; Carano, C.; Ceroni, P.; Mottier, L.; Roffia, S. *J. Electrochem. Soc.* **1999**, *146*, 3357.

(24) Cattarin, S.; Ceroni, P.; Guldi, D. M.; Maggini, M.; Menna, E.; Paolucci, F.; Roffia, S.; Scorrano, G. *J. Mater. Chem.* **1999**, *9*, 2743.

(25) Da Ros, T.; Prato, M.; Carano, M.; Ceroni, P.; Paolucci, F.; Roffia, S. *J. Am. Chem. Soc.* **1998**, *120*, 11645.

(26) Maggini, M.; Guldi, D. M.; Mondini, S.; Scorrano, G.; Paolucci, F.; Ceroni, P.; Roffia, S. *Chem.—Eur. J.* **1998**, *4*, 1992.

(27) In the case of peaks I−IV in the CV curve of Figure 4b, a four (unequal) step sigmoidal curve was obtained after convolution, where each step was proportional to n of the corresponding CV peak: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications.* Wiley: New York, 2000.